Technical studies of Renaissance bronzes

The use of neutron imaging and time-of-flight neutron diffraction in the studies of the manufacture and determination of historical copper objects and alloys

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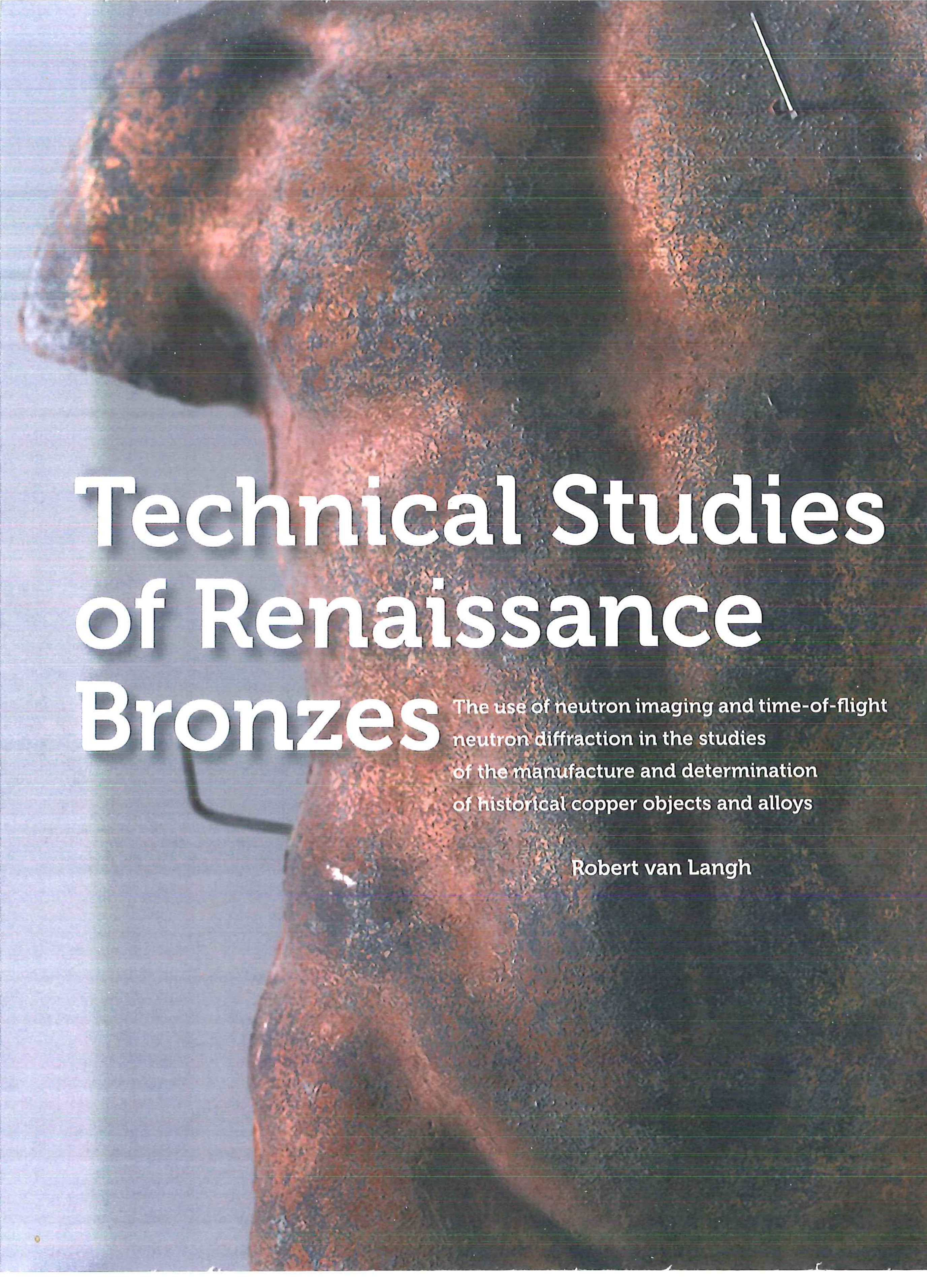

Technical Studies of Renaissance Bronzes

The use of neutron imaging and time-of-flight neutron diffraction in the studies of the manufacture and determination of historical copper objects and alloys

Robert van Langh

Robert van Langh Delft, 11 december 2012

Propositions

Supplementing the doctoral thesis of Robert van Langh

Technical Studies of Renaissance Bronzes

The use of neutron imaging and time-of-flight neutron diffraction in the studies of the manufacture and determination of historical copper objects and alloys

1. The assumption of conservators that by definition old restorations should be removed to return to the artist's original intention is an indefensible point of view when the history of the object is taken into consideration.

2. If remnants of the material for the mould remain on the surface of the bronze sculpture, it is possible to ascertain the technique used for its manufacture with stratigraphic research.

3. Up to now, neutron imaging has been used as a visualisation technique, while cold neutron imaging also makes it possible to carry out an analysis of the texture.

4. Given that industrial R&D departments barely manage to reproduce the time factor, industry is insufficiently aware that cooperation with conservation scientists with a knowledge of ageing processes results in added value.

5. If the government states that society should be innovative, it should not make cuts in the arts.

6. Both organic and inorganic research into the border areas of organic finishing layers of bronze statuettes can lead to dating these layers.

7. As a general rule, reversing the restoration ethics of the material cultural heritage is irreversible.

8. If there is no fundamental research into the degradation processes of historical art objects, succeeding generations will lose access to their cultural heritage.

9. The use of strict limits on relative humidity and temperature in loans between museums is based more on intuition than expertise.

10. A student taking a master's degree in Conservation & Restoration at the University of Amsterdam to become a restoration expert should be given the title material historian.

These propositions are regarded as opposable and defendable,
and have been approved as such by the supervisor Prof. Dr. J. Dik

Robert van Langh Delft, 11 december 2012

Stellingen

Behorende bij het proefschrift van Robert van Langh

Technical Studies of Renaissance Bronzes

The use of neutron imaging and time-of-flight neutron diffraction in the studies of the manufacture and determination of historical copper objects and alloys

1. De veronderstelling van restauratoren dat men per definitie oude restauraties moet verwijderen om terug te gaan naar de intentie van de kunstenaar is een onverdedigbaar standpunt als de geschiedenis van het object in ogenschouw wordt genomen.

2. Bij de aanwezigheid van restanten malmateriaal aan het oppervlak van een bronzen beeld kan met stratigrafisch onderzoek de vervaardigingstechniek worden herleid.

3. Neutronenimaging wordt tot nu toe als visualiseringstechniek gebruikt, terwijl koude neutronenimaging het ook mogelijk maakt om textuuranalyse uit te voeren.

4. Aangezien industriële R&D afdelingen de factor tijd nauwelijks reproduceren, realiseert de industrie onvoldoende dat een samenwerking met conserveringswetenschappers die over kennis van verouderingsprocessen beschikken tot een meerwaarde leidt.

5. Indien de overheid stelt dat de maatschappij innovatief moet zijn, moet zij niet bezuinigen op kunst.

6. Zowel organisch als anorganisch onderzoek naar het grensvlak van organische afwerklagen op bronzen statuettes, kan tot datering van deze lagen leiden.

7. Reversibiliteit in de restauratie-ethiek van roerend erfgoed is als stelregel onomkeerbaar.

8. Als er geen fundamenteel onderzoek plaatsvindt naar degradatieprocessen van historische kunstvoorwerpen, verliezen volgende generaties toegang tot cultureel erfgoed.

9. Het hanteren van strikte grenswaarden van relatieve vochtigheid en temperatuur in het bruikleenverkeer tussen museale instellingen is meer gebaseerd op gevoel dan op kennis.

10. Een masterstudent die aan de UvA opleiding Restauratiekunde afstudeert met de titel restauratiekundige, zou de titel materiaalhistoricus moeten krijgen.

Deze stellingen worden opponeerbaar en verdedigbaar geacht
en zijn als zodanig goedgekeurd door de promotor Prof. Dr. J. Dik

Technical Studies of Renaissance Bronzes

The use of neutron imaging and time-of-flight neutron diffraction in the studies of the manufacture and determination of historical copper objects and alloys

Proefschrift

ter verkrijging van de graad van doctor

aan de Technische Universiteit Delft;

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voorzitter van het College voor Promoties,

in het openbaar te verdedigen op dinsdag 11 december 2012 om 12.30 uur

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geboren te Oosterhout (N.Br.).

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Prof. Dr. B.J. Thijsse, Technische Universiteit Delft
Prof. Dr. F.T. Scholten, Vrije Universiteit Amsterdam

Samenstelling promotiecommissie:

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Table of Contents

Chapter I

Introduction

The technical and scientific study of bronze statues and statuettes began only recently. There is a remarkable lack of interest in the manufacturing process in older literature on the history of art. However, there are exceptions. For example, Johann Friedrich Christian Wuttig was surprisingly ahead of his time in 1814. His work not only contains instructions for contemporary bronze sculptors, similar to those in the *Encyclopedia* by D'Alembert and Diderot, but also contains a treatise on the casting techniques in the past related to historical objects.[1] The catalogue of the collection in the South Kensington Museum (now the Victoria & Albert Museum) in London by John Charles Robinson, dating from 1862, is another early work, which provides impressive technical descriptions of statues and does not hesitate to use chemical terms.[2] Hermann Lüer's *Technik der Bronzeplastik* dating from 1902 is another important work.[3] He analyses important bronze sculptures in Europe. At a later date similar information was provided in catalogues of collections such as that of Nettlefold about his own collection dating from 1934.[4] However, these are all exceptions. Until the late 20th century the great majority of art historians did not think about the techniques that were used at all.[5] The famous bronze specialist Wilhelm von Bode from Berlin did not say anything about this.[6] In his catalogue of the bronzes in Vienna, Julius von Schlosser admittedly went a step further by giving an indication of the materials used, but he too ignored the manufacturing techniques.[7] In all of the works he wrote about Renaissance sculpture, John Pope Hennessy did not think about the material aspects either, and only described whether a statue has a dark or light patina.[8]

It is possible that the interest in the technical study of bronze statues was stimulated by the publication of the treatise by Agricola and Biringuccio on the extraction and processing of metals, with accompanying commentaries.[9] This led to an insight into the fact that great technical efforts were required from the sculptor and his helpers to create a bronze statue during the Renaissance. During the same period the use of analytical equipment for research into the cultural heritage developed significantly, for example, microscopical techniques, equipment to examine the composition of materials, analytical equipment for corrosion products and dating techniques of core material. Obviously these were an important stimulus for the study of bronze objects.[10] The laboratory research which took place had two aspects: on the one hand, there was research which focused on visualisation techniques using microscopy, endoscopy and X-ray examination, and on the other hand, there was research into the composition of the object. A distinction was made between 2D and 3D techniques. In the past decade more attention has been devoted to analytical equipment which can be subdivided into invasive and non-invasive examinations using either portable or stationary equipment.

Technical research into bronze statues first appeared in Italian literature on the history of art with the study by Bruno Bearzi dating from 1950 on the complex casting techniques of Donatello's statues.[11] Subsequently he carried out analytical research in collaboration with Edilberto Formigli, studying the manufacture of antique and Renaissance bronze statues.[12] More historical and technical research into Donatello's *Judith and Holofernes* was carried out in 1966 and a detailed technical study with numerous analytical techniques was published following the restoration in 1988.[13] This study, which was published in book form, clearly reveals the added value of technical research into Renaissance bronzes. Analyses of the metal and metallographic research were carried out on samples of the object, as well as corrosion studies with IR spectroscopy, X-ray diffraction and electronic microscopy, resulting in a total picture of the condition of the object before it was restored.

The fact that in general more attention is devoted to bronzes from antiquity is perfectly illustrated by the study of the bronzes of Riace, two Greek statues which were discovered by a diver 300 metres from the coast of that village in southern Italy in August 1972. The research into these bronzes was another example of broad interdisciplinary cooperation. The statues were examined with X-radiography techniques, the composition of the metal with Atomic Absorption Spectrometry (AAS), the core material with petrographic research, and the corrosion issue, amongst other things, with polarisation microscopy and Back Scattered Electron Microscopy (SEM), in addition to the historical research. This research developed a hypothesis about the casting technique of the bronzes.[14] The archaeometric symposium (a branch of archaeology in which quantifiable or hard scientific data are used, amongst other things, to date archaeological discoveries), which was organised by Doeringer and Mattusch is another example of successful interdisciplinary cooperation.[15] These experts all reached the conclusion at the same time that these studies are more successful when they are based on interdisciplinary cooperation, and as a result interdisciplinary symposia were organised.[16] However, the first studies focused particularly on the acquisition of knowledge about the objects in a broad sense, rather than on a technical artistic interpretation of the data that had been obtained with regard to the object.

In the late 1970s Riederer and Werner carried out groundbreaking work with their systematic analysis of compositions of historical copper alloys, creating a reference bank for research into authenticity.[17] These studies were usually of an archaeometric or strongly scientific nature. Moreover, the data appeared in technical journals, which meant that the majority of art historians did not come across this information. Although these objects are eminently suitable for technical artistic research, the lion's share of the above-mentioned studies were not concerned with bronze statuettes but with monumental bronze statues. The technical study of small sculptures dating from the Renaissance developed in the United States only with the research by Richard Stone from the Metropolitan Museum of Art in New York.[18] Francesca Bewer from the Strauss Center for Conservation and Technical Studies, Boston, published several studies following Stone's work during her doctoral research at the University College of London, and her dissertation can be seen as a critical point with regard to involving technical research in the art historical study of Renaissance bronze sculptures.[19] Bewer systematically examined the casting process and the related alloys that were used. In the following years there was a growing awareness among art historians that studies of the oeuvre of sculptors who worked in bronze should also be studied from the technical point of view. In collaboration with the J.P. Getty Museum in Los Angeles and the National Museum in Stockholm, the Rijksmuseum published a catalogue about the work of Adriaen de Vries, also adding technical information.[20] This was followed by a study of the sculptures of Willem van Tetrode.[21] In the meantime there was a lengthy study of Renaissance and Baroque sculpture by Victoria Avery with the cooperation of Jo Dillon in the technical field.[22] The Rijksmuseum then published a similar catalogue in which Renaissance bronze statues were studied using new techniques, such as neutron imaging, to generate 3D visual material.[23] The technical insights were assimilated in the art historical descriptions of the objects. In 2007 there was an exhibition of *The Gates of Paradise* by Ghiberti with an accompanying publication, following decades of restoration, when the panels were studied by two research groups led respectively by Salvatore Siano and Francesca Bewer, who did not fully agree about the manufacture of the panels.[24] Formigli also contributed to this publication with the study of the chasing technique using hammers and punches. Other art historians who include technical studies in their research into sculptors are Denise Allen and Peta Motture with their study of Andrea Riccio.[25] Thorough research has also been carried out into the technical aspects of the bronze sculptures of Adriaen de Vries by Jane Bassett.[26] She gave a good survey of the possibilities of different analysis techniques, such as X-ray fluorescence spectrometry (XRF) in combination with the Inductive Coupled Plasma techniques (ICP) and Atomic Absorption Spectrometry (AAS). Bassett tried to forge links between the core material and the manufacturing techniques of Adriaen de Vries's sculptures with petrographic research, although promising this has not led to any clear results. In line with the attribution of art objects to particular artists using technical research, Dylan Smith has tried to demonstrate that XRF can generate significant data for bronze statues.[27] Finally, the work of Pier Jacopo Alari de Bonacolsi, also known as L'Antico, was recently examined thoroughly both at the technical and art historical level, based amongst other things on the research by Richard Stone.[28] These studies generate very valuable information about a sculptor and place the knowledge about the manufacture of Renaissance bronze statues in a broader perspective.

At the same time with this more intensive cooperation between curators and conservators, there has been increasing interest in the scientific world for the world of the arts, which was discovered as an interesting area of application for analytical technology. The reason for this lies in the broader scope and direct results which the sciences can achieve in their field of knowledge. The scientists concerned are often affiliated to technical universities or scientific institutes, and most make use of traditional research equipment which is also available in museum laboratories. In addition, there are also more advanced research techniques which are only available in a few places in the world in so-called Large Scale Facilities (LSF). These are large scientific facilities including synchrotrons (circular particle accelerators), research reactors or neutron spallation sources where new X-ray or neutron-based analytical techniques are developed.

As a result of European cooperation, this equipment is available for everyone, including technical researchers in the heritage world. Researchers can make use of this advanced research equipment free of charge with a *peer review* process of submitted research proposals. However, in general, scientists who are interested in the cultural heritage are not sufficiently aware of the literature on conservation and technical art history and mainly publish in journals on chemistry or physics, while this type of literature is frequently inaccessible to museum specialists.[29] As a result, bridges must be built between the knowledge which has developed in these different fields, and this is one of the objectives of this thesis.

A technical study of Renaissance bronze statues, whether they be large (monumental) statues or small (statuettes), gives rise to many questions. Different craftsmen played an important role in manufacturing bronze statues, including the wax cutter, moulder, bronze caster and chaser. They were all responsible for the iconography and expression which we attribute to the sculptor. In some cases the original surface has been retained in small statuettes. This is characterised by the presence of remnants of organic material such as varnishes or layers of wax on the bronze, which may have become discoloured or have a glazed appearance. Fortunately the previous owners of the objects did not all decide to replace these old layers with new layers at some point in history, so that an analysis can teach us something about the original appearance and the sculptor's intentions. But what do we really know about the manufacture of these statuettes? For many collectors and museums it remains a challenge to apply a verifiable element which can demonstrate the historical value of their collection in addition to the origin and other art historical research.

For a number of decades art historians have been aware that technical knowledge can be helpful in addition to a stylistic attribution and (conceptual) historical research. A greater insight into the production process has developed as a result of the efforts of conservators and researchers who examine objects with analytical and imaging equipment. A sculptor could never have imagined that such interesting discoveries could be made with this technical research, that X-radiography would be used one day, let alone neutron transmission radiography. These techniques are very useful to us and reveal concealed manufacturing processes. There is an even more specific question: did sculptors in the past use procedures which were characteristic of their own workplace, town or period? A great deal of technical research is carried out on the basis of this assumption, although there is currently insufficient factual knowledge available to substantiate it. It is therefore important to ask the right questions from the theoretical technical point of view and from the practical point of view, and this is clarified at the end of the thesis.

What are the important elements of research and what has a central place in this thesis? To start with, only some of the methods of current analytical research are examined. New advanced research techniques have become available recently which can probably be effectively used to study bronze statuettes, leading to a better interpretation. For example, it is now possible to study the inside of a hollow sealed metal body virtually. In this way the existing assumptions about the manufacture of (hollow cast) Renaissance bronze statuettes can be studied in more detail, leading to insights into the technological development and the above-mentioned differences in place and time. This research follows a number of stages starting with the "core" of the statue. On the basis of the core, an armature surrounded by clay adjacent to the layer of wax, it is possible to decide whether a bronze statue is unique or a copy. One of the questions related to optimising the visualisation of the interior of a hollow bronze statue is whether neutron radiography can produce more data than X-radiography. From the core we move to the metal, and the alloy that was used can be analysed in different ways. This study compares traditional techniques widely used in museums with new, advanced, non-invasive analytical techniques which are only available in a few places in the world. A comparison of the different analytical techniques exposes the limitations inherent in the traditional techniques. That is why I am presenting alternative possibilities for analysis. After analysing the alloy, we continue with the surface and the way in which the metal was finished. Here there are also two distinct stages. The first involves chasing the metal with hammers and punches, and after this the object is cleaned mechanically with stones. The second stage can involve colouring the metal either by heating it so that it turns black, or chemically, turning it green, for example, or with varnishes and layers of wax which could achieve different effects. One of the central questions was; which research technique could be used in a non-invasive way to examine the structure of the metal on the surface.

In terms of materials science, two research questions were formulated regarding the above-mentioned aspects. In the first place, are the existing methods for visualisation, such as X-radiography, adequate to answer all the possible questions related to identifying the manufacture. Secondly, are there methods to determine the composition of an alloy other than taking a sample or taking measurements only at the surface?

In the first case, the non-invasive visualisation technique of X-radiography was studied. X-radiography has existed for more than a hundred years. An unlit photographic film is placed behind the object and the rays of an X-ray tube focus on the object and are absorbed to a greater or lesser extent, showing on the film. As the metal becomes thicker, it becomes less easy to make an X-radiograph with sufficient contrast. In many bronze statues there is core material inside the hollow interior which absorbs fewer X-rays by a factor of three to four. Depending on where it is in the hollow interior, the thickness of the core material can again be thicker than the metal by a factor of three or four, resulting in an illegible X-ray.[30] Other parts, especially the limbs and extremities, are often cast as a solid piece of metal. In these cases an X-ray cannot provide any insight into the construction of the sculpture, because the metal and the related density which is characteristic of copper alloys absorbs all the radiation. In this case other visualisation techniques can be useful, particularly neutron imaging. This technique, in which the object is exposed to neutron rays rather than X-rays, also generates a radiographic image. The difference between the two techniques is that neutrons are not attenuated to the same extent by the characteristic alloy components of bronze statues. As a result, neutron imaging is in principle an interesting technique for the study of bronze sculptures. Images have been made on film with neutron radiation for more than seventy years.[31] With the introduction of cameras which can register the attenuated neutron signal more accurately, neutron imaging has become very interesting for numerous applications in the last ten years.

This research made use of neutron imaging with the NEUTRA beamline at the Paul Sherrer Institute (PSI) in Villigen, Switzerland. With the current techniques it is possible to easily film bronzes which are a few centimetres thick. Chapter II gives some examples. This chapter explains and compares the possibilities of this technique with traditional X-radiography. Using software that has been developed, it is possible to make tomographic images and even take a virtual tour through the statue. This greatly facilitates the study of bronze statues because it involves moving from a 2D X-ray film to a 3D tomographic technique. Now that it has become possible to examine the structure of a sculpture without any overlaps, it is also possible to examine the manufacture and the material composition more accurately. Chapter III explains an alternative method of using neutron imaging as a quantitative bulk analysis to determine the composition of a historical copper alloy. Although this method is still in its infancy, this chapter shows that neutron imaging presents many other possibilities in addition to visualisation. The reason that bulk analyses are necessary is to study the relevance of the composition of metals. One of the most important aspects is that this analytical technique measures different compositions from those measured by traditional methods, of which the most widely used is X-ray fluorescence spectrometry (XRF), a surface analysis technique in which the X-rays penetrate a copper alloy to a depth of approximately 30 µm. The minimal penetration of the surface is a problem, because changes can take place at this depth as a result of brazing, or because the surface has been covered with a patina or corrosion.

Any researcher who has examined a bronze statue using XRF knows that the composition can sometimes vary by a few percentage points. The history of the restoration of an object probably plays a role in this, but up to now this relationship has never been examined. In Chapter IV the extent to which the composition of the metal surface can vary is simulated in different experiments. As the characteristic surface measurement with XRF is not representative, a study was carried out into the possibility of conducting a bulk analysis at each desired place on the bronze, including under the surface. This newly developed method was made possible by linking the results of the research on NEUTRA at the Paul Sherrer Institute to the neutron diffractor Engin-X at ISIS at the Rutherford Appleton Laboratory in Oxford.[32] Chapter V looks at the results achieved with this. The analysis of alloys which contain zinc are particularly interesting. They reveal that the use of a rare-earth magnet (neodymium) can determine whether a bronze which contains zinc was produced before the beginning of the 19th century or not.

The non-invasive character is considered important for restoration and ethical reasons, because the object is spared from interventions as far as possible. This also applies when determining whether a metal surface has been traditionally chased or not. In general the surface of a bronze statue is chased with hammers and punches by a chaser after it has been cast. Since my study of the sculptures of Willem van Tetrode in 2003 I have suspected that bronze statues were also made during the Renaissance which were not chased or were hardly chased, while it seemed as if they were. This theory was based on a visual examination of *Hercules Pomarius* by Willem van Tetrode (BK-1954-43) and the bust of *Pope Gregory XIV* by Bastiano Torrigiani (BK-16937), both in the Rijksmuseum. The surface of these objects was compared with a figure representing *Paris*, which is attributed to Severo da Ravenna (BK-1959-4). There is no doubt that the *Paris* was chased. In order to examine this aspect in more detail, it would have been necessary until recently to saw a piece of metal from the bronze in order to carry out a metallographic examination of the change in the microstructure indicating that the surface had been chased. Taking a sample is not desirable because of the loss of authentic material. With the neutron diffractometer of Engin-X at the Rutherford Appleton Laboratory this is no longer necessary. Chapter VI presents the results of this study with comments, linking it to reconstruction research into similar alloys which has been used to reproduce different manufacturing techniques.

This last chapter on materials sciences was the reason to study the chasing of the bronze statues and their whole manufacturing process in more detail, and describe these processes in the second, technical-artistic section. Chapter VII reflects on the manufacturing process of bronze statues north and south of the Alps during the Renaissance. The monumental bronzes installed at the cenotaph of Maximilian I in the Hofkirche of Innsbruck also stimulated this. Work continued on these figures throughout the 16th century and they are the result of the activities of different designers and casters from South Germany. A number of the bronzes were almost perfectly cast and were hardly chased, an indication that this also occurred in monumental statues. It is striking that this casting technique took place much earlier (the first quarter of the 16th century rather that the third quarter) than in the statuettes which were examined in Chapter VI. The available source material of bronze casting for the cenotaph was compared with the methods described by Italians as in *De la Pirotechnia* by Vanoccio Biringuccio (1540), *Le Vite* by Giorgio Vasari (1550 and 1568) and *Due Trattati* by Benvenuto Cellini (1568). In addition, the casting results were compared to the bronze statues which were cast for King Francis I in accordance with the Italian method in Fontainebleau in about 1540.

The Italian sources clearly indicate that a bronze statue must be chased after it has been cast, as illustrated by the surface of Italian bronze statues. Nevertheless, there appears to be a change in the Florentine working methods in the third quarter of the 16th century, as demonstrated by the sculptures made there and by the source work by Giorgio Vasari dating from 1568. Finally, the second part of the technical-artistic section is devoted to a description of reconstructions which were made on the basis of new ideas about the manufacture of Renaissance bronzes which developed during the research for this thesis. The following questions were considered in this respect: how many casting sprues are necessary to cast bronze statuettes and how fine a bronze surface could be achieved using material that was available in the 16th century. The results of this research are presented in Chapter VIII, and in turn give rise to many new questions which can and will be studied in more detail in subsequent studies on this subject.

Literature

In the study of the manufacture of Renaissance bronzes three source categories can be distinguished: sources which can be found in archives, sources in the form of printed contemporary literature or re-publications with added transcriptions, comments and source criticisms, and finally, modern technical studies of Renaissance bronzes. The following literature was consulted: Cennino d'Andrea Cennini (1370-1440), *Il libro dell' Arte*, dating from 1437.[33] This book mainly describes the manufacture of the pigments, and in the last chapters Cennini also reflects on the moulding of humans and/or animals using plaster, resulting in moulds that could also be used to cast metal. The treatise by Pomponius Gauricus (1481/82-1530), *De Sculptura* dating from 1504.[34] Gauricus describes sculpture in two parts, making a distinction between "ductoria" and "fusoria". The "ductoria" section describes the design, dealing with perspective and symmetry, while the technical side of casting bronze statues and all the related aspects are described in "fusoria". *De la Pirotechnia* by Vanoccio Birringuccio (circa 1480-1539), published in Venice in 1540.[35] This treatise deals in depth with the extraction and processing of metals and related matters. Biringuccio gives a detailed description of the casting of sculptures, bells and cannon, as well as the different sorts of craftsmen involved in metalwork. *Le Vite* by Giorgio Vasari (1511-1574), published in Florence in 1550 (first edition) and 1568 (second edition).[36] Before writing the biographies of the artists Vasari gave a technical description of the different disciplines, including sculpture, architecture and painting. In the chapter on sculpture he dealt in detail with the casting process of bronze statues. The *Due Trattati* by Benvenuto Cellini (1500-1571) were also published in Florence in 1568. They were dedicated to Duke Cosimo de' Medici and could therefore be read by an educated layman or outsider.[37]

Cellini's autobiography *La Vita*, which was published only in the 18th century, described the manufacturing process of his bronze sculptures in more detail in a narrative style.[38]

It is clear that the sources did not describe more than one possible procedure, but it is not likely that every sculptor in the 16th century used a treatise to manufacture his sculptures. Obviously it is important whether the writer used a technique himself and thoroughly understood the problems of the craft. For example, Cennini was a painter, not a sculptor. His information was not based on his own experience, but on that of others. The same applied for Gauricus. When he wrote his work he was 22 years old and had trained as a philosopher, so he cannot have had much experience of casting bronzes, though his treatise is very useful for factual information such as names and the activities of bronze sculptors or chasers. This is quite different for Biringuccio, who was responsible for the papal forges in Rome and therefore had a great deal of experience of the processes for casting metal. His knowledge was an indication of the processes that were used. The way in which Vasari's texts have been used in this thesis particularly refer to the first descriptive chapter on the manufacture of sculptures. Vasari was not a sculptor, but he had been very well informed by fellow artists in Florence and elsewhere in Italy. It is even the case that Vasari describes the casting process in more detail than Biringuccio, as Chapter VII shows. In his second edition Vasari adds important information to his description of techniques in sculpture in 16th-century Florence. This is not done out of self-interest (except to extol Florence as the centre of arts in Europe) and therefore the information can be considered to be representative. Finally there is Benvenuto Cellini, a famous sculptor. Much has been written about him, and also about the truth of his texts. This study is not concerned with his knowledge or expertise in making bronze statues. It is actually his statements on the manufacturing process of bronze statues which I consider to be striking and characteristic in the context of this study. With the new developments which flourished in Florence in the third quarter of the 16th century, the question is whether Cellini was too old to follow the innovations in making bronze sculptures or whether this revealed a degree of conservatism.

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1 H. Wuttig, *Die Kunst aus Bronze kolossale Statuen zu Giessen*, Berlin, Carl Friedrich Amelang, 1814; M. de Felice, B. Fortunato, J. d'Alembert, D. Diderot, *Encyclopédie ou dictionaire universel raissonné des connaissances humaines*, Yverdon, 1770.

2 J.C. Robinson, *Italian sculpture of the Middle Ages and period of the revival of art.* London: Chapman and Hall, 1862.

3 H. Lüer, *Technik der Bronzeplastik*, Monographien des Kunstgewerbes, Leipzig, 1902.

4 F.J. Nettlefold, *The collection of bronzes and castings in brass and ormolu formed by Mr. F. J. Nettlefold.* London: Waterlow & Sons Limited, 1934.

5 This also applies, for example, for Richard Krautheimer, who described the work of Lorenzo Ghiberti in detail (1956), just as H.W. Janson described the works of Donatello (1957) and John Pope Hennessy, who wrote important reference works about Italian Renaissance sculpture and sculptors such as Benvenuto Cellini (1985).

6 W. von Bode, *Collection of J. Pierpont Morgan: bronzes of the Renaissance and subsequent periods*, Paris, 1910; W. Bode, "Ausstellung von Kunstwerken des Mittelalters und der Renaissance: aus Berlinier Privatbesitz veranstaltet von der Kunstgeschichtlichen Gesellschaft 20 Mai bis 3 Juli 1898, Berlin, 1899.

7 J. von Schlosser, *Album ausgewählter Gegenstände der Kunstindustriellen Sammlung des Allerhöchsten Kaisershauses*, Vienna: Anton Schroll & Co, 1901. Von Schlosser tried to demonstrate the importance of metals alloys to some extent, but does not mention this in his descriptions of the sculptures.

8 J. Pope-Hennessy, *Renaissance Bronzes*, The Phaidon Press, London, 1965; J. Pope-Hennessy, *Cellini*, Macmillan, London, 1985; J. Pope-Hennessy, *Italian Renaissance Sculpture*, 2 vols., Phaidon Press, London, 1996.

9 G. Agricola, *De Re Metallica*, Basel, 1556, translated by H.C. Hoover and L.H. Hoover, *Georgius Agricola, De Re Metallica.* New York, Dover Publications, 1950; V. Biringuccio, De La Pirotechnia, Venice, 1540, translated by C.S. Smith and M.T. Gnudi, *The Pirotechnia of Vanoccio Biringuccio: the classic sixteenth-century treatise on metals and metallurgy*, New York, Dover Publications, 1990.

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30 It is clear that this depends on the size of the statue. A large statue with metal that is 1 cm thick can easily contain core material that is 100 cm thick.

31 D. Peter, "Neutronen Radiography," *Zeitschrift für Naturforschung*,I,1946,pp.557-559;H.Kallman,"Neutron Radiography," *Research* I, 1947-48, pp. 254-260.

32 G. Burca, J.A. James, W. Kockelmann, F.E. Fitzpatrick, S.Y. Zhang, J. Hovind, R. van Langh, "A new bridge technique for neutron tomography and diffraction measurements," *Nuclear Instruments Methodologies* A, 2011.

33 The dates of Cennini's life are highly speculative. It is often incorrectly assumed that he was alive in 1437 because that date appears on one of the copies of his manuscript. This is discussed by Daniel V. Thompson in the preface to his authoritative translation of "Il libro dell'arte." Thompson himself does not speculate on Cennini's dates, a sure indication of the lack of evidence on this point. Thus, dating Cennini's book to the "early 15th century", as above, is only a guess. The techniques Cennini describes date from the late 13th and mid-14th centuries. There is no evidence in his writing of the exciting developments in oil painting taking place in the early 15th century. This suggests that his book was actually written at some time in the 14th century. The following translation was used for this study; D.V. Thompson Jnr., *Cennino d'Andrea Cennini, the craftsman's handbook: "Il Libro dell'Arte"*, New York, Dover Publications, 1933.

34 *De Sculptura* was regularly republished and the following editions are known: 1528 Antwerp, 1542 Nuremburg, 1603 Ursellis (Oberursel), 1609 Antwerp, 1622 Strasbourg, 1649 Amsterdam and 1701 Leiden. Two translations of this book are known, a German translation by F.A.

Brockhaus (*Pomponius Gauricus, De Sculptura*, translated by Heinrich Brockhaus, Leipzig, 1886), and a French translation by Chastel (A. Chastel and R. Klein, *Pomponius Gaurcius, De Sculptura 1504*, Geneva: Librarie Droz, 1969).

35 *De Pirotechnia* was published four times in the 16th century; in 1540, 1550, 1558 and 1559. This thesis made use of the 1559 edition and the intepretation by Smith (V. Biringuccio, *The Pirotechnia of Vanoccio Biringuccio: The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, translated by C.S. Smith and M.T. Gnudi, New York, Dover Publications, 1990. This translation is based on the 1540 edition.

36 G. Vasari, *Le Vite, De piu eccelenti Pittori Scultori e Architettori.* Florence, 1550/1568. In this study both editions for a comparison of the texts were used. The translation by Maclehose was also used (L.S. Maclehose, *Giorgio Vasari, Vasari on Technique*, edited by Professor G.B. Brown, New York, Dover Publications Inc., 1960).

37 In this study the original edition is used: Benvenuto Cellini, *Due trattati; vno interno alle otto principali arti dell'oreficeria : l'altro in materi dell'arte della scultura doue si veggono infiniti segreti nel lauorar le figure di marmo, & nel gettarle di bronze / composti da m. Benvevto Cellini scvultore fiorentino*, Florence, Per Valentini Panizzij e Marco Peri, 1568. This thesis also made use of the following translations: J. Brinckmann, *Benvenuto Cellini, Abhandlungen über die Goldschmiedekunst und die Sculptur.* Leipzig: E.A. Seemann, 1867, C.R. Ashbee, *The treatises of Benvenuto Cellini on goldsmithing and sculpture*, New York, Dover Publications, 1967.

38 Cellini's treatise was not published in 1568, but was only published by Antonio Cocchi, Naples, in 1728. Cocchi used the pseudonym "Seb. Artopolita" for the publication, and mentioned Colonia as the place of publication. Benvenuto Cellini, *La Vita*, Letteratura Italiana Einaudi, 1973, Einaudi Torino. There are many translations of *La Vita*. This thesis made use of H. Van Dam van Isselt and C. Van Schendel, *Het leven van Benvenuto Cellini*, Amsterdam, 1982.

Fig. 1

Chapter II

The study of bronze statuettes with the help of neutron imaging techniques

Based on R. van Langh, E. Lehmann, S. Hartmann, A. Kaestner, and F. Scholten, "The study of bronze statuettes with the help of neutron imaging techniques," *Analytical and Bioanalytical Chemistry*, 2009, 395, pp. 1949-1959.

Abstract

Until recently the manufacturing techniques used for Renaissance bronzes were studied only with the naked eye, microscopically, videoscopically and with X-radiography. These techniques provide information on production techniques, but much important detail remains unclear. As part of an interdisciplinary study of bronzes undertaken by the Rijksmuseum Amsterdam, neutron imaging techniques were applied with the aim of obtaining a better understanding of bronze workmanship during the Renaissance period. Therefore an explanation of the techniques that were used is given here to provide a better understanding of the data collected by these neutron imaging techniques. The data were used for tomography studies which reveal the hidden aspects that could not or scarcely be visualized using X-radiography. This specific study examined the representative bronze, *Hercules Pomarius* by Willem van Tetrode (circa 1520-1588), along with twenty other Renaissance bronzes from the Rijksmuseum collection.

Introduction

The Rijksmuseum possesses a collection of bronze sculptures that have an important place in the collection of the museum. As a result of interdisciplinary studies between art history, the conservation of artworks and materials science, the interest in the manufacturing techniques of these bronze statuettes has grown immensely over the years. Various technical studies have taken place resulting in catalogues and exhibitions on this interesting subject.[1] The study of bronze statuettes has to be undertaken in a non-destructive way, as sampling is not preferred because of the value of the surface of these bronzes. Therefore, the research used to be limited to visual observations using the naked eye and the microscope, videoscopy (which is possible only if there is a hole in the sculpture of a minimum of 2 mm) and with the use of X-radiography. Neutron imaging has proved to be an alternative tool for non-destructive investigation, and one that is complementary to common X-ray techniques.[2] This is of particular importance for metals, where the penetration of neutrons is generally higher than X-rays can provide. In cases where there are thicker layers of lead, bismuth, gold or silver, neutron imaging is usually a better tool for transmission investigations. Unlike X-radiographs, neutron imaging clearly shows hydrogenous materials like resins, core materials used for bronze casting, adhesives, wax and lacquer. Therefore it is possible to visualize such kinds of materials through the thick metallic layers.

In the past, advanced neutron imaging techniques, which are all based on digital detection systems, were used. Neutron tomography can be used in addition to X-ray tomography to examine three-dimensional objects. For this study twenty Renaissance bronze statuettes from the Rijksmuseum were examined using this technique but a comparative study using neutron tomographs and X-radiographs to evaluate the manufacturing technique has not been carried out yet.[3] In this paper we present the results of such an examination of Willem van Tetrode's *Hercules Pomarius* (Fig. 1). The research is a comparative study of various parts of the sculpture, using X-radiography, neutron radiography and tomography, resulting in remarkable visual differences. In addition to the good qualitative visualization possibilities of neutron tomography, it also shows that more research is needed to interpret the specific attenuation coefficients for various materials used to make sculptures, using neutron transmission as a quantitative method of analysis.

X-radiography versus neutron radiography

Two different methods using X-radiography were used in this study. The first is with film-based equipment using an X-ray tube with an energy of 320 kV/10 mA, frequently used in museums. The drawback of this technique is that one cannot be certain that the picture is the best that can be achieved, since no beam-hardening correction can take place. The second method is with a customised GE SEIFERT DP435 digital X-ray system using a 280 kV /8mA, equipped with a metal-ceramic intensifier with an integrated high resolution CCD camera. This set-up is preferable to the film-based method, as a live image of the sculpture can be adjusted and images can be recorded with both a continuous variable amperage and kV. However, both methods have the same drawback: more than one image is required to obtain a complete overview of a sculpture in which the metal walls have different thicknesses.

It is well known that X-rays interact with the electrons in the atomic shell, while neutrons only "see" the nuclei, ignoring the electrons completely. Therefore, the probability of interaction – and therefore the attenuation of X-rays – increases with increasing densities. This does not apply for neutron interactions in the same way. In most cases neutrons penetrate metals used in bronzes better than X-rays. On the other hand, materials which contain hydrogen such as resin, wax, and sometimes also the casting core, show high attenuation values and are therefore more clearly visible in a neutron radiograph.[4]

The transmission through an object with transmission thickness d can be described by the general attenuation law between the beam intensities in front of and behind the object, I_0 and I, respectively

$$I_0 = I \cdot e^{\Sigma \cdot d} \tag{1}$$

I_0 : Beam intensity in front of the object
I : Beam intensity behind the object
Σ : Macroscopic cross section [cm-1] or attenuation coefficient
d : Transmission thickness [cm]

The so-called macroscopic cross-section Σ is a material property and gives a value for the strength of interaction for the particular radiation and the beam attenuation respectively. Table 1 depicts some relevant materials which are listed together with the attenuation coefficients for X-rays (150 keV) and thermal neutrons (25 meV). All the values for the thermal neutrons are smaller than for X-rays, resulting in higher transmission in the neutron case. Slightly better transmission can be achieved with high-energy X-rays, which are available in some labs for material research. The use of even more powerful radioactive gamma sources (e.g., Co-60) might be possible in some cases. However, the penetrable material thickness currently depends on the sensitivity, dynamic range and signal-to-noise properties of the detection system. A remaining transmission behind the object of 2% is assumed in the data provided in Table 2.

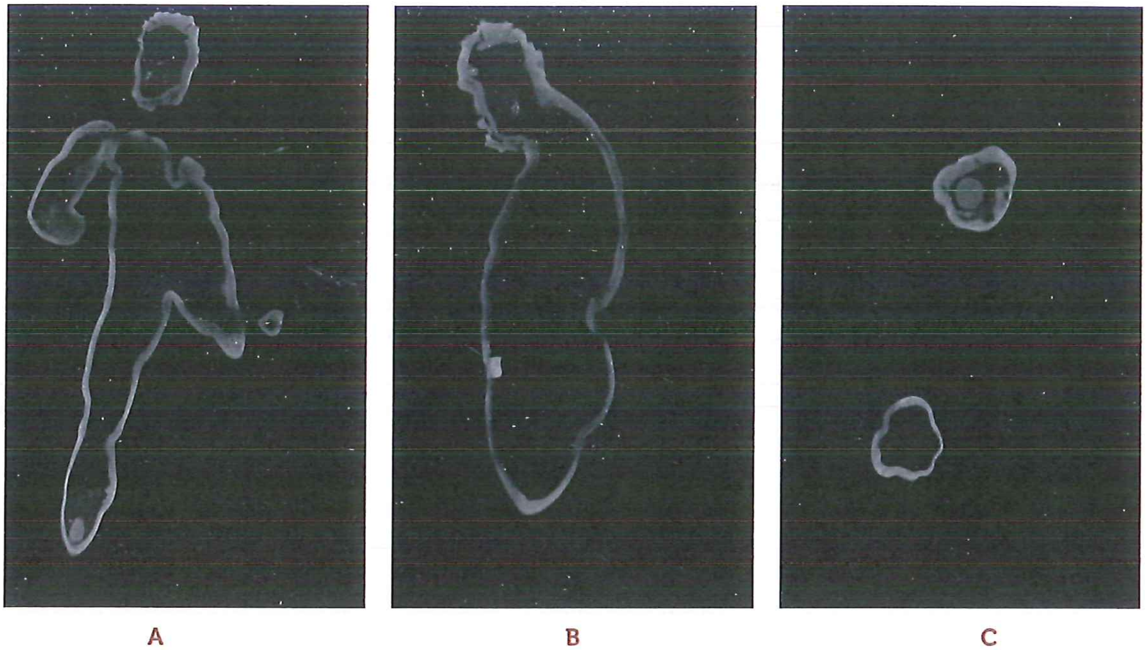
Table 1: Attenuation coefficients for X-rays and thermal neutrons for some elementary metals (unit: cm^{-1})

Material	X-ray – 150 kV	thermal neutrons
Cu	1.97	1.07
Fe	1.57	1.19
Sn	3.98	0.21
Pb	22.81	0.38
Zn	1.64	0.35
Ag	5.67	4.04
Au	35.94	6.23

Table 2: Material layer thicknesses which can be transmitted by X-rays and neutrons respectively, with a residual signal of 2% (in cm)

Material	X-ray - 150 kV	thermal neutrons
Cu	1.99	3.66
Fe	2.49	3.29
Sn	0.98	18.63
Pb	0.17	10.29
Ag	0.69	0.97
Au	0.11	0.63

Bronze is a generic term that encompasses alloys with copper as a main constituent. The alloying elements are predominantly tin, lead or zinc (found as binary, ternary and also quaternary alloys), but traces of arsenic, antimony, iron, nickel and silver are also found.[5] The binary and ternary alloys of copper/tin-lead or copper/zinc are most common in compositions of Renaissance bronzes where the amount of copper is usually at least 85%.[6] The high attenuation of copper and the average thickness of



Figs. 2: the images produced by neutron radiography are two random vertical cross sections and one horizontal cross section of *Hercules Pomarius*, showing a slice of the object. Therefore the whole object is not visible in these cross sections. The images show the variety in attenuation of the materials. A: from an X direction, B: from a Y direction and C: from a Z direction. N.b. In figure 2A different grey values are found at the position of his right calf, his right arm and his head. Figure 2B shows a different grey value in his head as well, corresponding to the different grey value in the cross section of the leg given in figure 2C. Although all of these different grey values relate to the core material, it is sometimes difficult to make a clear distinction between the core material and the bronze, as can be deduced from the top image in C.

The different transmission radiographs of the *Hercules Pomarius* can now be compared in figure 3. The neutron radiograph was obtained in two parts which were combined using the merging option with suitable image processing software tools (e.g., AnalySiS) that allow a complete image of the sculpture to be displayed. A flat field correction was made in the case of the digital neutron image, which was impossible in the X-radiography study. Therefore the neutron imaging method provides more information than single images produced by film and digital transmission X-radiography.

a bronze statuette limit the analyses using X-radiography. The attenuation of the alloying components can be much higher (Table 1): for example, if objects contain high amounts of lead or tin, the transmission of X-rays drops dramatically. Neutrons, on the other hand, lead to improved transmission when the alloy contains lead or tin and therefore larger samples can be examined. This difference in transmission cannot be overcome by any kind of X-rays (high-voltage tubes, synchrotron light or gamma radiation). A neutron transmission radiograph can be obtained from three directions (X, Y and Z), as shown in figures 2A/B/C. The different grey values are the result of the range of neutron attenuation of all the materials in the sculpture. Therefore a distinction can be made between the core materials and the bronze.

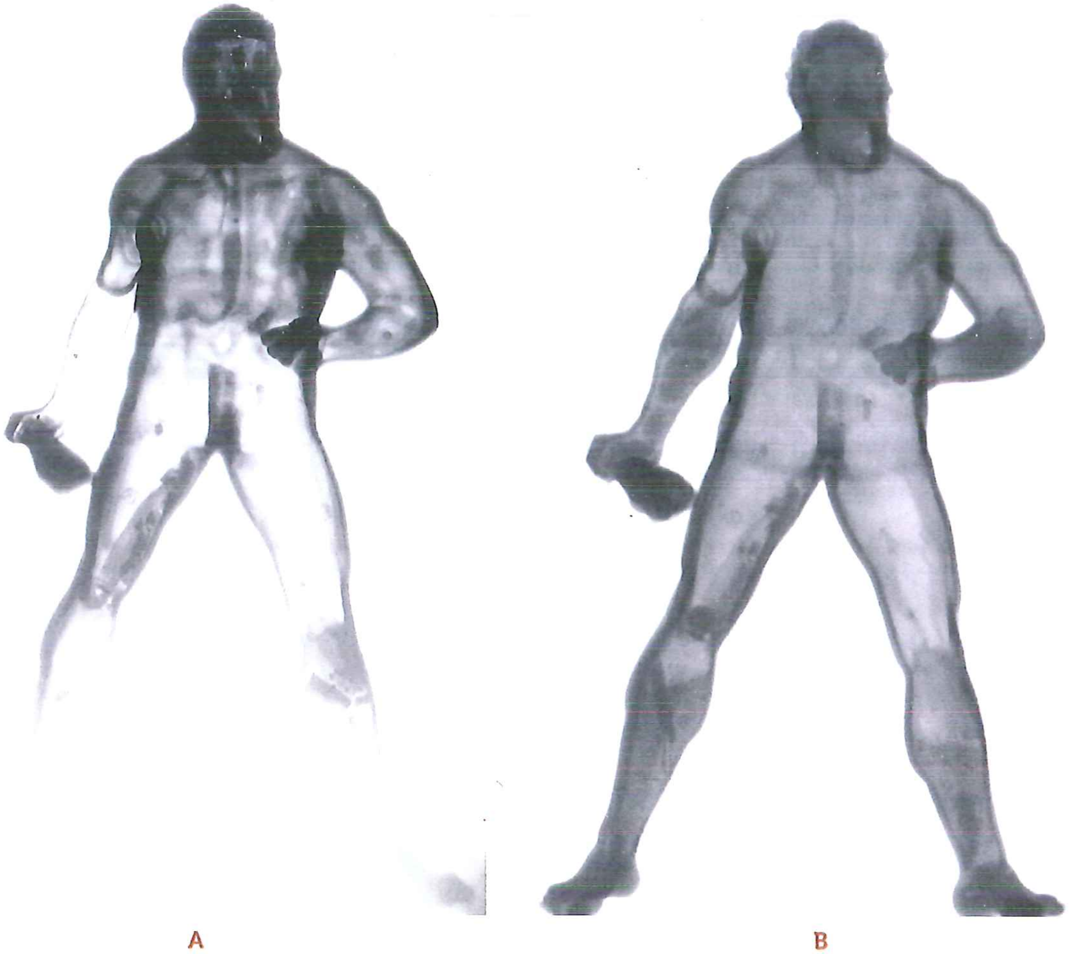


Fig. 3: Comparison of transmission radiography with X-ray and neutrons of *Hercules Pomarius* by Willem van Tetrode. A: produced with X-rays from 220 kV and captured on film, B: open beam corrected neutron radiography using thermal neutrons and a digital detector system. The first image was obtained at the Rijksmuseum Amsterdam and the neutron image was obtained at the NEUTRA facility, SINQ, PSI.

Tomography versus radiography

The neutron transmission image of the object in figure 3B immediately reveals more and additional information than can be deduced from 3A. Furthermore, it is impossible to determine the thickness of the metal from a single X-radiograph, or to quantify the amount of material. These options are possible using neutron tomography, because the sample is rotated round the perpendicular axis in relation to the detector system through at least 180° in equal steps (Fig. 4). These projections can deliver complete information about the whole volume when a mathematical reconstruction algorithm is applied. The resulting three-dimensional distribution of the attenuation coefficients Σ (x,y,z)(x,y,z) is represented by numbers for each volume element (voxel). More information about the reconstruction algorithm can be obtained by referring to endnote 7 studying the work of Banhart.[7]

The detector performance determines how many voxels have to be considered. If a single projection has, e.g., 1024 * 1024 pixels, the number of voxels is 1024 * 1024 *1024. The size of the image files gathered from a complete examination of *Hercules Pomarius* is approximately one gigabyte. Advanced visualization tools and powerful computers are needed to process the image data further. For example, *Hercules Pomarius* was examined along with twenty other Renaissance sculptures using the VG Studio Max 2.0 software tool.[8] Detailed cross-section images showing the different attenuations were gathered for all the sculptures, providing information for further research. It should be noted that a preliminary examination of the images shows that it is difficult to determine where small repairs were made using this technique. More research is needed on this topic.

Tomography offers various possibilities: researchers can examine the sculpture from any point of view by means of virtual slicing at points of interest throughout the sculpture. The following options are possible:

- enhancement of surfaces with the same attenuation level;
- segmentation of volume areas with the same voxel value;
- modification of the transparency to see inner structures better;
- measurement of distances within the object;
- determination of local densities, virtual "destruction" by removal of segmented regions;
- virtual movements around the object to provide a complete overview, including changes in illumination and reflection properties.

Neutron tomography facilities at PSI

The Swiss Spallation Neutron Source (SINQ) for research purposes at the Paul Scherrer Institut (PSI) is based on the principle of spallation, where high energy protons (energy about 590 MeV, current around 1.3 mA) strike a lead target. The spallation reaction delivers about 10 fast neutrons per spallation act, which are slowed down to the thermal energy (approximately 25 meV) in a D2O moderator or to cold energy (around 3 meV) in a liquid D2 moderator.

Two individual facilities, which complement each other, are available for neutron imaging purposes: NEUTRA provides a well-collimated and homogenous beam of thermal neutrons and ICON was built for imaging with cold neutrons. In addition, NEUTRA is equipped with a 320 kV X-ray tube (X-TRA option).[9][10] A stationary digital neutron imaging detection system has to be used for neutron tomography applications. Although some options, such as amorphous silicon arrays or semi-conductor devices using direct exposure in the beam are possible for tomography purposes, a cooled, highly-sensitive CCD camera focusing via a light-reflecting mirror on a neutron-sensitive scintillation screen is currently considered to be the best detection system[11]. This set-up is shown in figure 4, with a rotation table used to turn the object on its axis. It has to be aligned perpendicular to the detector axis. Projections are recorded with the camera detector in regular steps from 0° to 180° (or even 360°, depending on the divergence of the beam and the object size).

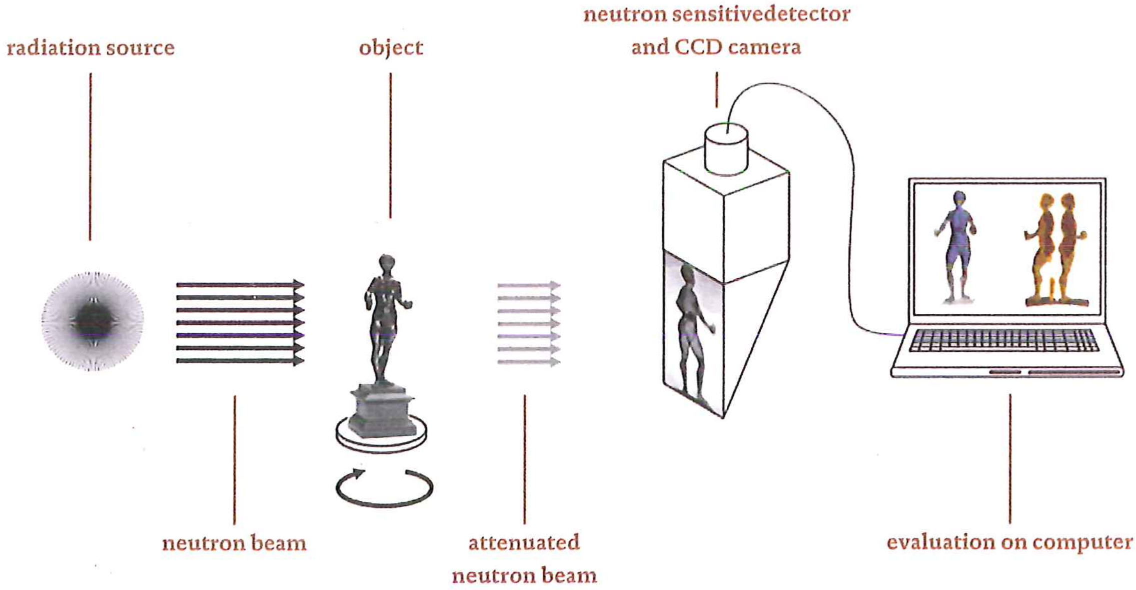


Fig. 4: Sketch of the tomography set-up at PSI, based on a cooled CCD detector focusing on a neutron-sensitive scintillation screen; the object is rotated on its vertical axis.

The neutron imaging stations at PSI (also see endnote 4) can cover a visual range between 2.7 and 40 cm, resulting in pixel sizes of between 15 to 350μm. The set-up for micro-tomography[12] is unique in its application for highest spatial resolution.

Depending on the measurement station, measurement position, the detector system, the number of projections and the current beam intensity, a full tomography run takes between about one and ten hours. The optimization depends on the final image quality needed. As neutrons can also activate materials by capture, there is the potential risk for radioactivity. Table 3 shows the captured cross sections and the half-lives of the excited isotopes for relevant structural metals. As a general rule, bronze objects will decay below the detection level within a few days of exposure.

Table 3: Activation data: excited nuclei, captured cross sections and half-lives of excited isotopes with relevance for metallic objects, taken from:[13]

Nuclide excited	Captured cross section [barn]	Half-life	Natural abundance of the target isotope [%]
Cu 64	4.5	12.7 h	69.17
Cu 66	2.17	5.1 min	30.83
Fe 59	1.3	44 d	0.28
Mn 56	13.3	2.58 h	100
Sn 121	0.13	27 h	32.59
Pb 209	0.00023	3.2 h	52.4
Ag 108	2.41	35 min	51.84
Ag 110	4.1	250 d	48.16
Au 198	98.7	2.69 d	100
Co 60	16.5	5.2 a	100
Zn 65	0.77	244.3 d	48.6

Furthermore, neutron imaging (transmission radiography, tomography) is not a method that can be set up in a museum, although it can complement the common methods in cases when other methods fail or are limited. The PSI's large-scale facilities (like other similar stations) are available on request for dedicated studies in collaboration with researchers from museums.

Quantification of the materials involved

IIn the ideal case, ignoring all reconstruction artefacts and uncertainties induced by scattering effects of neutrons or beam-hardening effects of X-rays, the reconstructed volume consists of the attenuation coefficient in each voxel $\Sigma(x, y, z)$. In the case of a material mixture, the total value of Σ is the superposition according to (2):

$$\Sigma_{tot} = \sum_i \sigma_i \cdot N_i = \sum_i \sigma_i \cdot \frac{\rho_i \cdot N_A}{M_i} \tag{2}$$

Σ : Macroscopic cross section [cm-1]
σ : Microscopic cross section [cm2]
N : Core density [cm-3]
ϱ : Density [g/cm3]
N_A : Avogadro constant = 6.022 · 1023 [mol-1]
M : Molar mass [g/mol]

While the microscopic cross sections are tabulated values, the material density ϱ and the molar mass M are often known in advance. On the other hand, it might be useful to determine these densities when (2) is rearranged correspondingly. In the case of *Hercules Pomarius* we know that the outer structure is bronze, as this was analysed using a XRF Bruker Artax 800, resulting in an approximate value of 80% copper and 20% zinc. The attenuation coefficients (macroscopic cross sections) derived from this can then be compared to the numbers in Table 1, right column. The bronze part consists of Cu and Zn, and the resulting Σ value is dominated by Cu. The contribution of Zn to the total attenuation is significantly less. As shown in figure 5 with the histogram of the whole object, two peaks can be distinguished and attributed to bronze (in this case Cu/Zn) and the core material, respectively. However, the absolute numbers for the determined attenuation coefficients are too small for both materials. The reasons for this could be the so-called secondary scattering in this sample, as well as back-scattering effects of the neutrons, which result in smaller numbers. In the future more efforts will have to be made to improve the quantitative accuracy in neutron tomography, probably by applying a scattering correction algorithm (e.g., QNI [see endnote 13]). The volume of the different zones of the object can also be quantified. As the voxel size is well defined by the imaging detector system set-up before the tomography run, the volume of the segmented part can be calculated as number of the voxels multiplied by the voxel volume. The segmentation becomes uncertain when the different attenuation coefficients overlap too much. In the case of bronze and the core material for the current object (Fig. 2C), different segmentation approaches and interpretations must be considered for the segmentation between middle attenuations (core material) and high attenuation (bronze) therefore needed some effort when comprehending. The materials could be distinguished more easily, based on the grey values visible in the neutron radiograph cross sections.

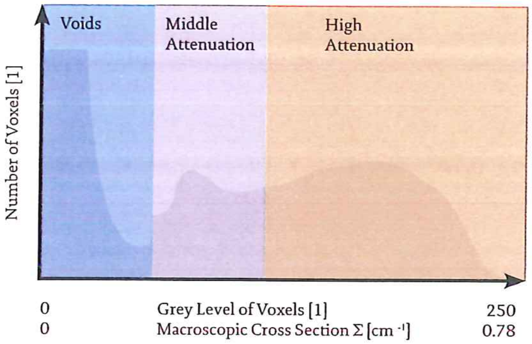


Fig. 5: The histogram of the tomography data describes the number of voxels (volume elements in the three-dimensional data set, unit integer values) with a particular grey level. The macroscopic cross-sections can be obtained by a linear scaling factor. Note the difficulty separating the middle and high attenuation when they overlap at small sections (core material and bronze).

Description of the object and the casting technique

Willem van Tetrode's *Hercules Pomarius* was selected for neutron tomographic investigation as a representative Renaissance bronze, since X-radiography could not reveal the hidden parts of the sculpture and videoscopy was not possible. *Hercules Pomarius* is a sculpture depicting a defiant naked Hercules with club, holding the three golden apples of the Hesperides (Fig. 1), a reference to one of the twelve labours he was assigned by King Eurystheus. The sculpture is sealed on all sides including the bottom, so videoscopy was excluded as a research technique. Because of the limitations of X-radiography described above, neutron tomography was undertaken in the hope that it would provide evidence of manufacturing techniques.

The bronze mainly consists of copper and zinc, according to an analysis using X-ray fluorescence spectrometry. In addition, the bronze has a worn black patina consisting of various beeswax components and a complex distribution pattern containing organic material, as indicated by direct temperature-resolved mass spectrometry on two samples (DTMS).

During the Renaissance one technique was predominantly used for casting hollow bronzes: lost wax casting, which is based on the principle that all the wax is replaced by bronze. Lost wax casting can be divided into two techniques: a direct method, when an object is made of an original model which is lost, and an indirect method, when the original model survives the process. It is important to understand the difference, because neutron tomography offers the opportunity to study which technique was used.

The direct method

This method starts with a wire skeleton covered with a core of fireproof material, such as clay or plaster, that forms the rough shape of the final sculpture. This fireproof rough model, also called the "inner core," is covered with a thin and even layer of wax with a thickness of between 3-6 mm, depending on the size of the object, which is finished according to what the sculptor wants. The resulting wax model filled with core material gives an impression of what the final sculpture will look like when the wax is replaced by bronze. Iron pins are inserted through the wax into the core material, visibly protruding. A wax ingot is mounted and, depending on the size of the sculpture, wax rods are applied to function as vents that will distribute the metal to all the openings in the mould, or free any trapped gas (Fig. 6A). The wax is then covered with a mixture of powdered fireproof material similar to the inner core material and is spread all over it. A second layer of the same material with coarser grains is applied on top of this first layer, almost covering the iron pins (Fig. 6B). Finally, everything is covered with a thick layer of the same fireproof material. The combined layers on top of the wax are known as the "outer mould". The complete mould is heated in an oven, and all the wax melts out through the rods and the ingot. At that point the inner and outer core are held in place by the iron pins. The structure is inverted and molten metal is poured into the open space between the inner and outer core through the open space left by the wax ingot. Once the empty space between the inner and outer core has been filled with molten metal, it will rise up and eventually begin to flow out of the space left by the rods.

The indirect method

This method is different from the direct method because no metal skeleton is preformed to the shape of the sculpture;

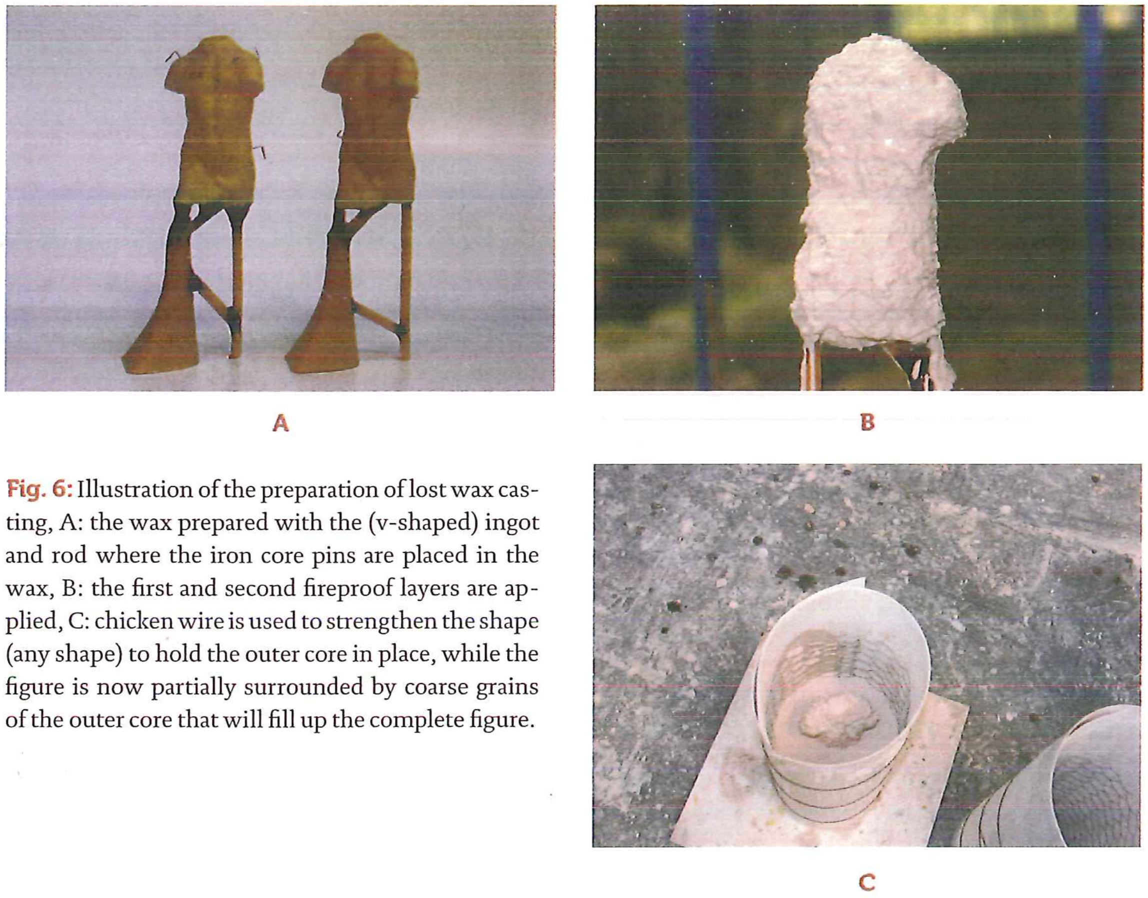


Fig. 6: Illustration of the preparation of lost wax casting, A: the wax prepared with the (v-shaped) ingot and rod where the iron core pins are placed in the wax, B: the first and second fireproof layers are applied, C: chicken wire is used to strengthen the shape (any shape) to hold the outer core in place, while the figure is now partially surrounded by coarse grains of the outer core that will fill up the complete figure.

instead an existing model is used and an imprint is made. The original material can be bronze, terracotta, wood or any other material. The imprint was usually made of plaster, and depending on how many undercuts there are in the sculpture, separate pieces would have to make up the mould. After the mould has been made the pieces of plaster are soaked in water and are put together. These create a negative form. There are various methods for applying the layer of wax. Hot wax could be poured into this mould, which was then shaken and decanted, leaving a thin layer of wax behind. By doing this repeatedly, a build-up of layers could be formed to any desired thickness, usually between 3-6 mm. The wax model was removed from the (pieces of the) mould and filled and covered with fireproof material, as in the direct method. Subsequently, the whole casting procedure followed the direct method.

Finishing

Both methods result in a rough sculpture with sprues and vents still attached; in addition, the wire skeleton and inner core are left inside the direct method, while only the inner core material remains in the indirect method. The excess metal is cut off, the sculpture is usually finished by chasing, and the core material is chipped away where accessible, through openings in the sculpture. The important difference between the two casting techniques is that the wire skeleton and a remnant of the inner core material are usually left behind inside the finished direct sculpture. For both methods, if a small chip of core material shifts or breaks off in the mould when or after the wax melts out, this results in a casting failure. In these cases repairs can be carried out using the technique called "casting on" or "after casting".[14] The technique is fairly simple: the part that failed to come out of the cast is modelled in wax again directly on the sculpture. Then the piece is cast in place following the direct casting method. However, it should be emphasized that a "casting on" technique should be considered as an early repairing technique when a bronze failed to come out of the mould perfectly.

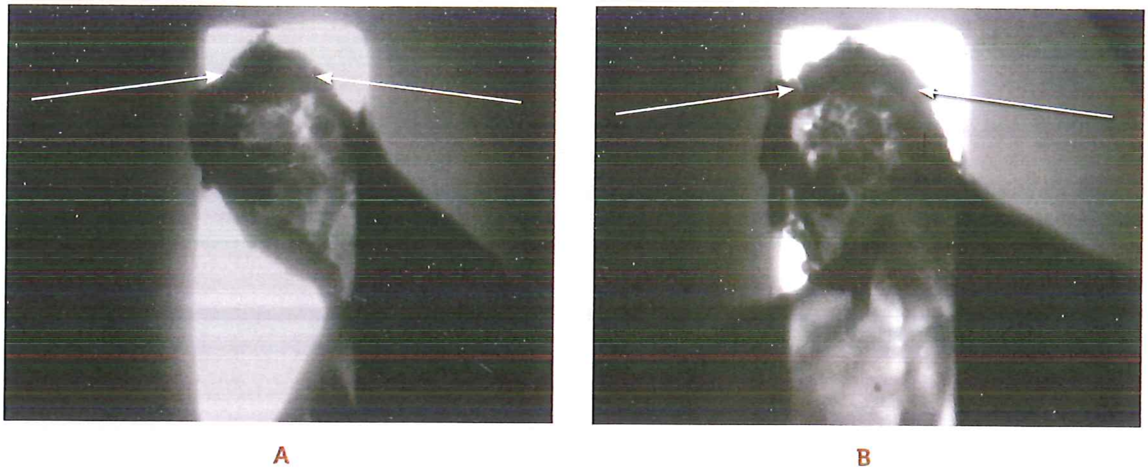


Fig. 7: Captured images of *Hercules Pomarius* from a live view. The cracks in his hair which do not appear to go right through are indicated in red. The sculpture was examined at 198 kV/1.1mA.

Results of the X-radiography

The film-based X-radiograph of *Hercules Pomarius* in figure 3A appears to show that there are various thicknesses of metal in the torso and the legs, because they do not show the same attenuation on the film. However, it is impossible to see whether variations in the grey scale are caused by the presence of a thick layer of core material or simply by thicker metal. The legs of the sculpture are overexposed and do not show anything of the manufacturing technique, and the statuette's right forearm appears to be hollow. As new methods of X-radiography are now also available, the sculpture was later examined using the digital X-radiography set-up at the Rijksmuseum, which provided more useful information. This technique showed the sculpture's head with peculiar cracks – partly through the hair – as can be seen in figure 7. Although the cracks do not appear to go right through, their presence suggests that the crown of the head could be a separate piece, meaning that the complete sculpture was not cast in one go.

Results of the neutron transmission and tomography investigation

The neutron transmission radiograph clarifies the information provided by the X-radiographs. Figure 8 shows the results of the neutron tomography images of the sculpture based on the attenuation values provided by the X, Y and Z direction, as shown in figure 3. The reconstructed pictures clearly show the absence of core material in the torso. However, core material is visible in both arms and legs, as well as in the head.

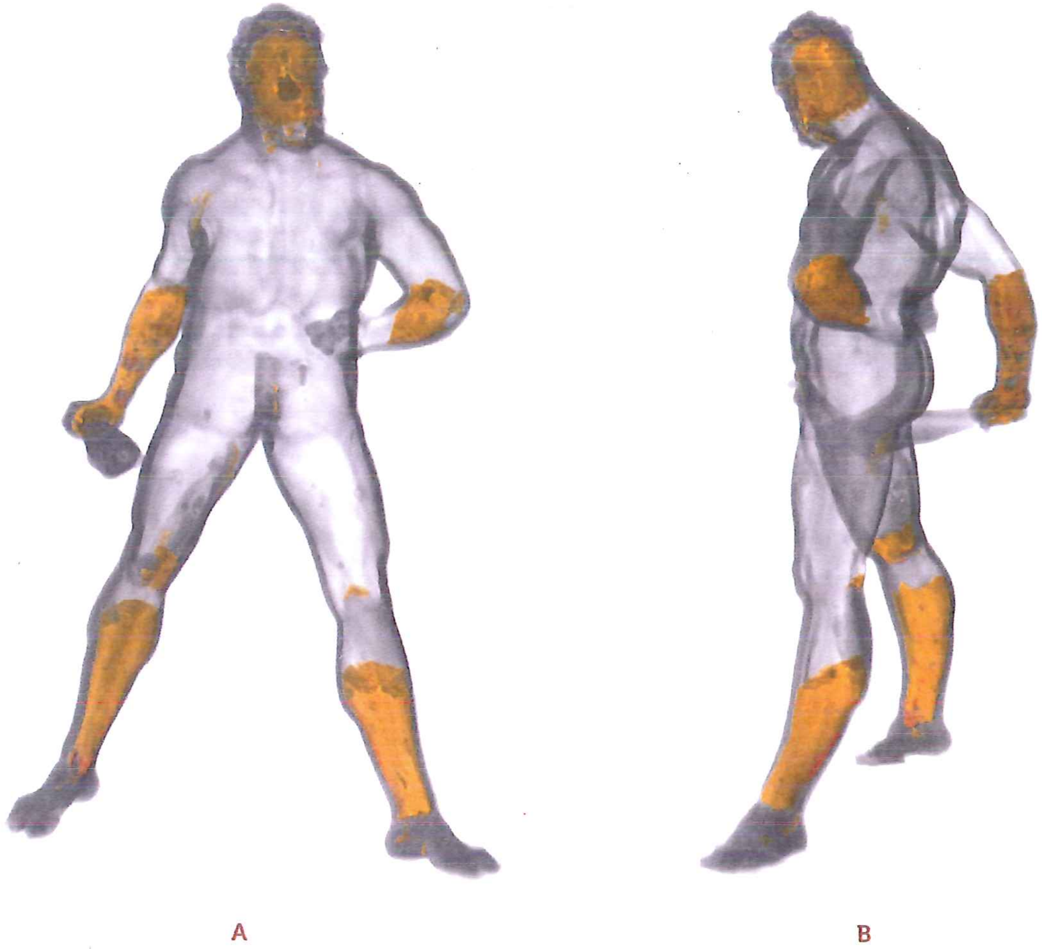


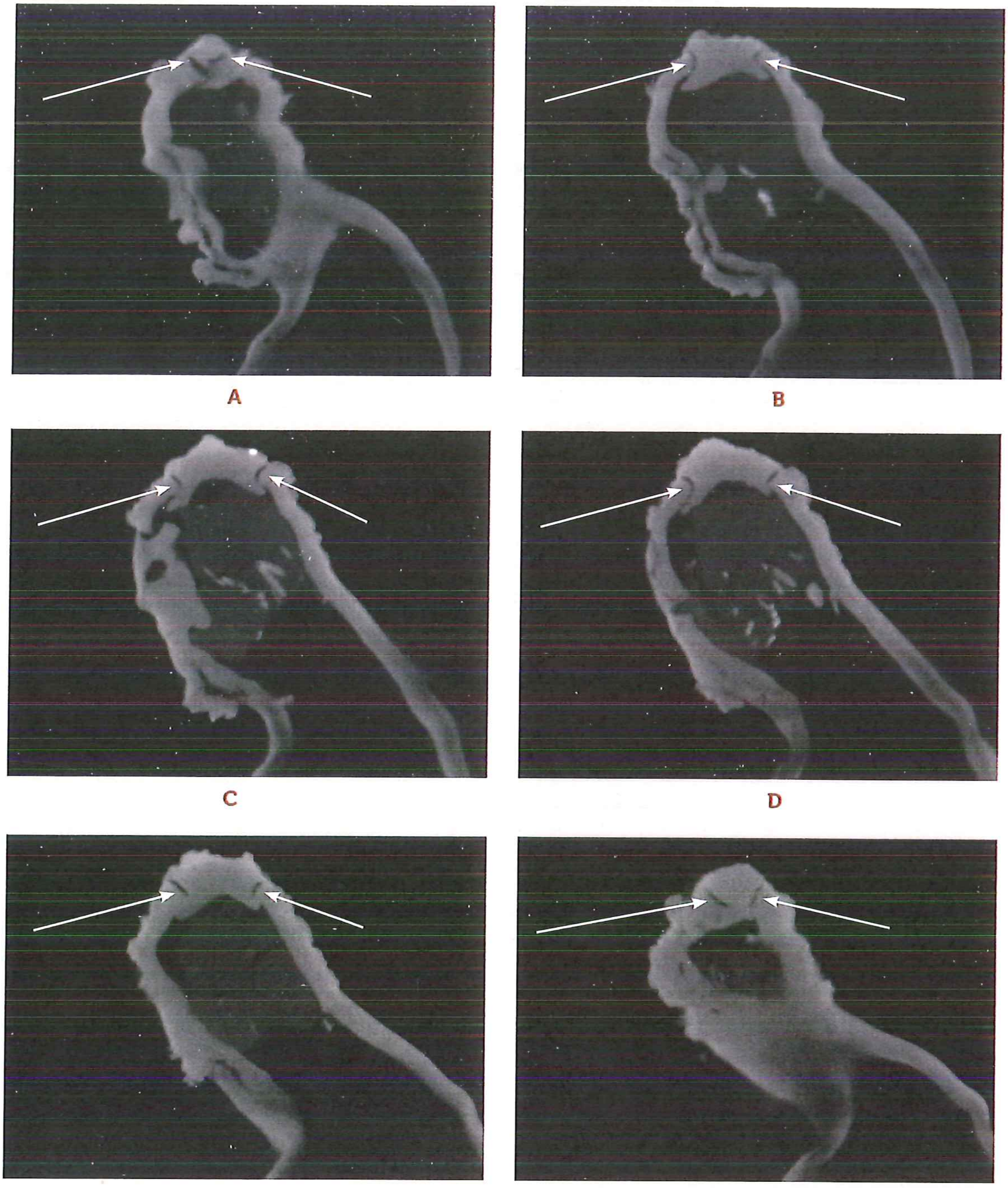
Fig. 8: Reconstructed neutron tomography of *Hercules Pomarius*. The grey colour in this image represents the bronze, the yellow colour represents the core material. Both colours are drawn with the use of software.

Regarding the casting technique: if a direct method had been used, a wire skeleton would have been present in the feet. Since this is not present, we can now safely conclude that this sculpture was indirectly cast. The neutron radiographs show that most of the core material was removed. We now need to consider how remains of the core material could have been retrieved from the sculpture, bearing in mind the absence of openings.

Figs. 9: Both the images from the X and Y direction indicate that there is a clear cut through the bronze at the top of the head. A represents the X direction, and B the Y direction. Also note the same distinct attenuation at the height of the nose in image C.

The crack that was first seen in the digital X-radiograph (Fig. 7) is more clearly revealed as a complete crack separating part of the head from the rest of the sculpture (Figs. 9A/B, Figs. 10A-F). The suggestion of the X-radiograph is confirmed here: part of the sculpture was "cast on". Furthermore, figure 9B shows that the space next to the nose is filled with additional bronze.

A plausible explanation of this could be that during the casting process the inner mould was damaged at the height of the nose. This broken piece of the inner core behind the nose fell into the space where the top of the head should be. The piece therefore blocked the flow of the metal to this area, resulting in a gap at the crown of the head. Conversely, the space from which it fell (behind the nose) was filled with excess bronze. Therefore the crown of the head had to be remodelled in wax and cast on to the finished sculpture. Furthermore, this explains how it was possible to remove most of the core material from the otherwise completely closed-off sculpture, leaving only remnants in the legs, arms and head. The core material from the body was removed through the (unintentional) opening in the head. During the casting-on of the crown of the head, additional core material was then placed inside the head as a support for the wax.



A

B

C

D

E

F

Fig. 10: The sequence of pictures A-F from a Y direction of a magnification of the head. The images show that the crown of the head is completely separate (and therefore cast on) and an excess of bronze formed in the space where a piece from the inner mould fell off, behind the nose. These images represent the centre part of the head covering approximately 10 mm of the sculpture from A to F.

Conclusions

As the attenuation of neutrons is so different from that of X-rays, neutron radiography effectively complements conventional X-radiography for studying bronzes, especially when there are core materials, or heavier elements that cannot easily be penetrated by X-rays, present in an alloy. In the case of Hercules Pomarius the manufacturing techniques could only be revealed with the use of neutron tomography. Neutron tomography is potentially a very powerful tool for the study of bronzes, as it provides a "real insight" into these objects. When fine art objects are chosen as a subject of scientific study, it is imperative to include the manufacturing techniques in these kinds of studies, because they provide the necessary information for understanding the results of scientific analyses of these objects of art.

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Chapter III

Quantification of the material composition of historical copper alloys with neutron transmission measurements

Based on S. Peetermans, R. van Langh, E. Lehmann and A. Pappot, “Quantification of the material composition of historical copper alloys by means of neutron transmission measurements,” Journal of Analytical Atomic Spectrometry, 2012, DOI: 10.1039/ C2JA30141E.

Abstract

Neutron transmission measurements using polychromatic and energy-selective neutron imaging methods were taken of plates of different reconstructed historic copper alloys containing Cu/Sn, Cu/Pb and Cu/Zn. By comparing tabulated cross section values, the alloy component weight fraction could be retrieved in an accurate quantitative and non-destructive way. The results show a good agreement for most of the compositions that were investigated, while the discussion about the remaining discrepancies suggests a lack of material homogeneity.

This study paves the way for a quantitative determination of the composition of unknown historical bronze alloy objects in a non-invasive way.

Introduction

The Rijksmuseum Amsterdam has an important collection of Renaissance bronze statuettes which are being studied both from the art historical and the scientific point of view.

Until about forty years ago this collection, as well as other similar collections, were studied only from a stylistic point of view. That approach changed in the last quarter of the 20th century when interdisciplinary studies were carried out from both with a scientific and art historical perspective. Numerous studies led to new attributions, which were subsequently published in museum catalogues or scholarly papers.[1 2 3] In the vast majority of these studies researchers made use of traditional analytical equipment. The stylistic features and interior parts of sculptures were studied with the naked eye, microscopy, videoscopy or X-radiography. Atomic Absorption Spectroscopy (AAS), Inductive Coupled Plasma (ICP) and X-ray Fluorescence (XRF) measurements were mainly used to determine the composition of the alloys. In addition to these techniques, recent studies on Renaissance bronzes have revealed the advantages of using the research possibilities at Large-Scale Facilities where, for example, neutron imaging has proved to be more valuable than traditional X-radiography for the study of the hidden parts of sculptures.[4] A relevant side effect of this technique is a slight sample activation by the neutrons, although this disappears within a few days after exposure, depending on the composition of the bronze and the exposure time. Some elements, such as cobalt, silver and gold, have a much longer half-life, which could mean that the sculpture has to stay in storage longer. Therefore XRF analyses should be carried out before neutron imaging to obtain a qualitative indication of the elements that are present. The neutron imaging data obtained in this way can lead to a better understanding of the production techniques used for the object, where the composition of the alloy is an important parameter which needs to be taken into account.

Werner and Riederer carried out various studies on alloy composition, leading to results which can reveal a correlation between an alloy to a place of manufacture or date.[5] However, for these types of studies using Atomic Absorption Spectrometry (AAS), sample taking is unavoidable.[6] Renaissance bronzes are very precious objects and museum curators prefer non-destructive testing (NDT) research to sample taking. A new technique developed by Agresti *et al.* shows that the term NDT is relative, as the sample spot is no larger than 120µm with the new developed laser induced plasma spectroscopy system (LIPS) which they developed.[7] However, for the past twenty years non-destructive techniques such as XRF have been applied by various researchers to determine composition of bronzes. This technique can be used in museums more easily as it requires a simple set-up and relatively little cost, because many museums nowadays operate handheld XRF devices. However, XRF is only a surface analysis technique and penetrates the copper alloy up to a maximum of approximately 20-30µm.[8]

Thus there seem to be several drawbacks to this method. First, the surface has to be completely clean before a measurement can be taken, taking the segregation effects of an alloy into account.[9] Secondly, the data obtained from XRF research has proved to be inconsistent, following an inter-laboratory research of XRF users in museums.[10]

In the search for different NDT methods, it was found that neutron tomography could provide a lot of information on alloy heterogeneity without any prior sample preparation. Earlier studies had proved that neutron imaging could be used to detect different metals in a Renaissance bronze sculpture (Fig. 1). However, the results were limited to a qualitative indexing of macroscopically separated regions of different materials (bronze approximated as copper and a core material).[11] Neutron imaging was combined with neutron diffraction for the quantification.[12]

As a result, this new study was carried out to quantitatively distinguish different copper alloys directly in neutron imaging based on the attenuation. Samples were cast in accordance with traditional casting techniques and the copper alloys were selected following contemporary treatises.

Experimental set-up

For the purposes of this study, 19 copper binary alloys were reconstructed with a metal alloy consisting of copper with either tin, lead or zinc, as shown in table 1. All the samples with an average size of 4.5 x 8 x 50 mm were cast and cooled down to ambient temperature and were sub-

Fig. 1: Photograph (a) and neutron tomography (b) view of a Renaissance bronze from the Rijksmuseum depicting a Striding Nobleman (reference BK-16083, about 35cm tall), showing different attenuation of the neutrons as a result of different composition at the ankles, knees and shoulders.

sequently cut down to the same dimensions (4.1 x 7.0 x 45 mm). The alloys were composed to correspond with historical alloys based on the contemporary literature. Neutron imaging of these specific copper alloys was carried out with the NEUTRA and ICON beamlines at the SINQ spallation source at the Paul Scherrer Institut, Switzerland. Neutrons are generated by spallation reactions upon impact of a 590MeV, 1.5mA proton beam on a heavy metal target (lead) and are thermalized in a surrounding heavy water tank which the NEUTRA beam port looks onto. NEUTRA provides a well-collimated and homogenous beam of thermal neutrons.[13] It is also equipped with a 320 kV X-ray tube (X-TRA option). A cooled, highly-sensitive 2048 x 2048 pixel CCD camera focusing via a light-reflecting mirror on a neutron-sensitive 100μm Li scintillation screen was used for neutron detection, with exposure times of 20s.

A smaller tank of liquid D2 at 25K was also positioned near the spallation target to slow down neutrons further to the cold energy range (i.e., wavelengths generally above 2.5Å). This is what the beam port of a second neutron imaging station, ICON, looks onto.[14] The energy spectra for these two neutron-imaging beamlines are given in figure 2, with mean wavelengths of 1.8Å for NEUTRA and 3.2Å for ICON. Based on the experiments conducted at NEUTRA and the beam time constraints, a number of alloys were selected for further energy-selective neutron-imaging measurements at ICON: Cu/Sn alloys 5, 6, 7, 8 and Cu/Zn alloys 15, 16, 17, 18. Experiments were conducted with a 1024 x 1024 pixel^2 CCD camera and a 100μm ^{6}Li scintillator. A velocity selector type of monochromator was used for the energy selection. It consists of a drum with curved lamellae coated with a strong neutron absorber (^{10}B). Depending on its rotation frequency, only neutrons with the right velocity or wavelength can pass through without hitting one of the lamellae and being removed from the beam. Therefore a less intense but monochromatic beam with a $\Delta\lambda/\lambda=15\%$ wavelength spread is obtained.

Table 1: Copper alloy compositions examined with thermal neutrons.

Alloy no.	Composition (%)			
	Cu	Sn	Zn	Pb
1	99	1	0	0
2	97	3	0	0
3	95	5	0	0
4	93	7	0	0
5	90	10	0	0
6	85	15	0	0
7	80	20	0	0
8	75	25	0	0
9	70	30	0	0
10	99	0	0	1
11	97	0	0	3
12	95	0	0	5
13	93	0	0	7
14	95	0	5	0
15	90	0	10	0
16	85	0	15	0
17	80	0	20	0
18	75	0	25	0
19	70	0	30	0

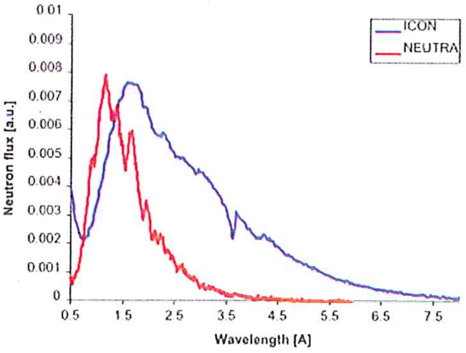

Fig. 2: Beam spectra for the NEUTRA (thermal) and ICON (cold) neutron imaging beamlines.

Theory

Neutron transmission follows the Lambert-Beer law, which gives the transmitted intensity through a sample I, of an incident beam with wavelength λ and intensity I_0, passing through a sample of thickness d and with a wavelength-dependent macroscopic cross section $\Sigma(\lambda)$.

$$I(\lambda) = I_0(\lambda)e^{-\Sigma(\lambda)d} \tag{1}$$

The macroscopic cross section is often rewritten in terms of the component i's atomic density N_i and the microscopic cross section σ_i:

$$\Sigma(\lambda) = \sum_i N_i \sigma_i(\lambda) \tag{2}$$

As neutrons have no charge, they do not interact with the electron cloud as X-rays do, but with the atomic nucleus. As a result, cross-section values can differ significantly and for materials in archaeometallurgy much higher sample thicknesses can generally be traversed with neutrons.

Neutrons are both scattered and absorbed in the sample, and in the thermal wavelength region (i.e., for wavelengths around 1.5Å), the wavelength-dependent microscopic cross section can be approximated with a tabulated mean scattering cross section term $_i^{scatt}$ and an absorption cross section term proportional to the neutron wavelength, typically determined from a tabulation of $^{abs}_{i,2200m}$ (the microscopic absorption cross section of a thermal neutron, i.e., with a velocity of 2200m/s);[15]

$$\sigma_i(\lambda) = \sigma_i^{scatt} + \frac{\sigma_{i,2200m/s}^{abs}}{1.798\text{Å}}\lambda \tag{3}$$

The atomic densities for an alloy can be calculated a

$$N_i = \frac{x_i \rho N_A}{M_i} \quad \text{with} \quad \rho = \frac{1}{\sum_i x_i / \rho_{i,0}} \tag{4}$$

where x_i is the alloy component's weight fraction, M_i is its molar mass, N_A is Avogadro's constant, ϱ is the density of the alloy calculated on the basis of the natural densities $\varrho_{i,0}$ of the components brought together in the alloy.

In standard radiography, all the wavelengths present in the neutron beam spectrum that is used contribute to an effective recorded intensity with the sample in place, I_{eff}, and without it, $I_{0,eff}$.

$$I_{eff} = \int_{\substack{beam\\spectrum}} I_0(\lambda)e^{-\Sigma(\lambda)d}\,d\lambda \quad \text{and} \quad I_{0,eff} = \int_{\substack{beam\\spectrum}} I_0(\lambda)\,d\lambda \tag{5}$$

An effective macroscopic cross section can be calculated from this as

$$\Sigma_{eff} = -\frac{1}{d}\ln\left(\frac{I_{eff}}{I_{0,eff}}\right) \tag{6}$$

a quantity that allows us to distinguish between alloys.

Results and discussion

Thermal white beam measurements at NEUTRA

Figure 3 depicts the theoretical and experimental values of Σ_{eff} for the measured alloys listed in table I. The theoretical values were calculated in accordance with the section theory: calculating the microscopic cross section using equation (3) based on the data library and atomic density obtained from equation (4). The recorded effective transmitted intensity can be found (equation (5)), as well as the effective macroscopic cross section (equation (6)). The experimental values were determined as the mean Σ_{eff} value in its distribution over the entire sample image (after open-beam corrections and background removal). Error bars indicate the 1σ uncertainty limits.

The measured effective cross section neatly corresponds to the theoretical behaviour, although there is a systematic offset. In terms of quality, this has little influence on the relative discrimination between different copper alloys, which can be present, for example, in historical bronzes when they have been repaired. The underestimation of the effective cross section is due to neutron scattering in the radiographies: part of the neutrons scattered in the sample and around it still reach the detector, and more neutrons are detected than expected from theoretical attenuation on a straight path through the sample. A clear deviation from the expected trend is found for the lead-rich alloys 11, 12 and 13. This can be explained by the assumed theoretical calculation that these alloys consisted

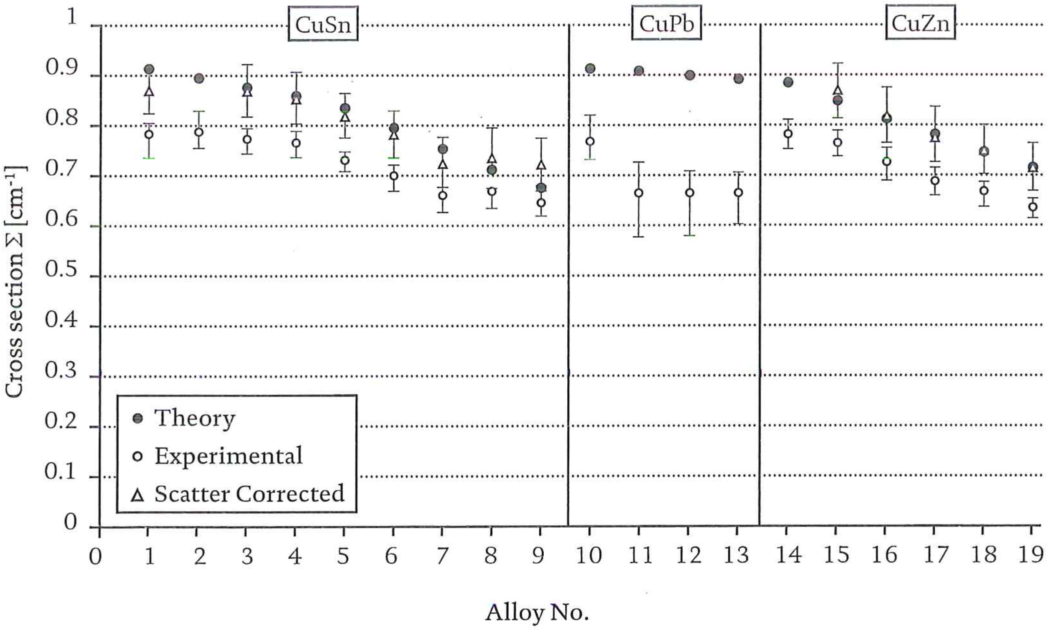

Fig. 3: Overview of the effective cross section theoretically expected (filled circles), from measurements (empty circles) and measured data corrected for scattering contributions (empty triangles) for the different copper alloys – except for alloys 2 and 14 which were used as calibration samples for the scatter correction and porous lead alloys.

completely of copper and lead, while in fact there are air pockets, i.e., bronze materials with such high lead concentrations become porous (Fig. 4). Though hardly visible on the surface of the sample, they can be clearly seen in the bulk-sensitive neutron radiographies. A maximum of 0.4% lead can be present in the solid copper.[16] This increased sample heterogeneity also leads to increased uncertainty with regard to these alloys. In this case, a computed tomography would be necessary to separate both the material thickness and the cross section in the reconstructed slices, as the outer sample thickness no longer corresponds with the true thickness of the material.

For a more quantitative evaluation, a scattering correction was made to the available measurement data. With the approximation that the scattering contribution ΔΣ to the radiography for a specific alloy (of component weight fraction x) is proportional to its macroscopic scattering cross section Σ_{scatt}, we can correct for this once we determine this proportionality factor α:

$$\Delta\Sigma(x) = \Sigma_{eff}^{theory}(x) - \Sigma_{eff}^{exp.} = \alpha\Sigma_{scatt}(x) \tag{7}$$

One alloy was selected as a calibration sample with an assumed *a priori* composition based on production values in Table 1. $_{eff}^{theory}(x)$ was then calculated using equation (3) and $\Sigma_{scatt}(x)$ taken from tabulated data. Equation 7 then made it possible to calculate α. For the Cu/Sn alloys, alloy no. 2 was selected for calibration and alloy no. 14 for the Cu/Zn series. The corrected macroscopic cross sections and quantitative alloy compositions could now be calculated. The calculated relationship between the actual recorded macroscopic cross section and the binary alloy component weight fraction was used to trace the unknown weight fraction in an experimentally recorded macroscopic cross section. That weight fraction was then used to determine the scattering contribution based on equation (7) and to correct for it. The corrected weight fraction was obtained using the calculated relationship between the cross section and the weight fraction again. After a few attempts,

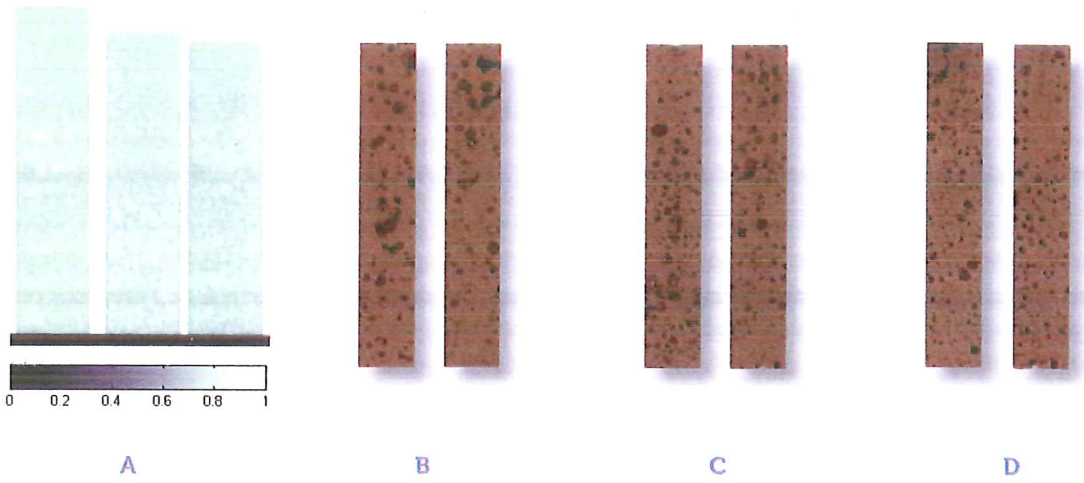

Fig. 4: Impression of porosity in historically cast copper/lead alloys: neutron transmission measurement of alloys 11, 12 and 13 (a, right to left), as well as photographs of the alloys embedded in resin and subsequently cut open – alloy 11 (b), alloy 12 (c) and alloy 13 (d) – to demonstrate the presence of porosities.

convergence values were reached for the macroscopic cross section and the unknown alloy component weight fraction. These are shown in figure 3 and figure 6 respectively.

There is a reasonable correspondence between alloy composition from production and from scatter-corrected radiographies. Uncertainty about the weight fractions of components of alloys was around 6.5%, where the calculation method and scatter correction led to an increase in the relative transmission measurement uncertainty, which was only approximately 1%.

Hassanein's extension of the scatter correction method to metallic materials provided a post-processing alternative that does not require a calibration alloy (although there is still an assumption regarding the initial sample material) and can be more easily extended to tomography, although it is currently only available for isotropic scattering in hydrogenous materials.[17] Further study is necessary in this respect. A promising alternative is to perform energy-selective neutron imaging in the absorption range, as investigated in the following section.

Energy-selective measurements with cold neutrons at ICON

In the cold energy range, the cross sections for polycrystalline materials are dominated by so-called Bragg edges. These should be viewed in the context of the Bragg law $2d_{hkl}sin(\theta_{hkl})=\lambda$, where coherent elastic scattering on the *(hkl)* lattice plane is possible up to $2d_{hkl}=\lambda$, after which there is a sharp decrease in the cross section as a result of a reduction in the neutrons removed from the direct beam.

Beyond the Bragg cut-off, i.e., for higher wavelengths where no lattice plane spacing d_{hkl} is large enough to allow for coherent elastic scattering, the cross section is largely dominated by absorption. In that absorption range, equation (3) can again be applied to describe the cross section, though σ_i^{scatt} is now limited to $^{scatt}_{i,inc}$, the incoherent scattering component (also tabulated). The scattering contribution to the transmission radiograph is negligible in the absorption range for most materials, including Cu, Sn, Zn and Pb. Therefore no scatter correction is necessary, making it ideal for quantitative studies such as ours.

Figure 5 shows beam spectra using a velocity selector type monochromator measured with time-of-flight as well as an illustration of the recorded wavelength-dependent cross- section evolution for alloy number 7. The wavelength spread is too large to separate the (111) and (200) Bragg edges, and they are seen as a single edge ranging from 3.5Å to 4.5Å. A better wavelength resolution would be required to resolve these edges, e.g. by using a crystal-based monochromator.[18] [19] However, in the absorption range, the broad wavelength spread is an advantage, as it means a higher neutron flux on the sample in wavelength regions of limited source flux and simple linear cross-section behaviour. Image exposure times

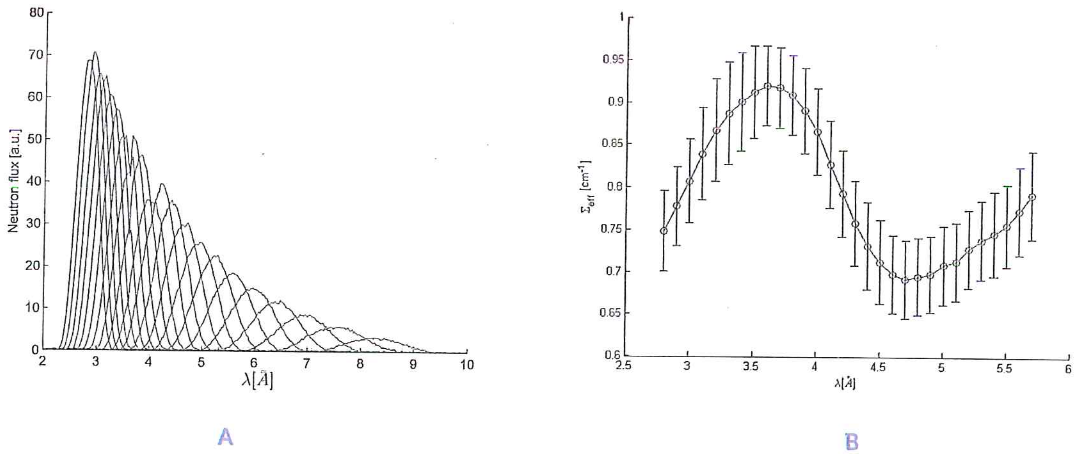

Fig. 5: Beam spectra when using a velocity selector type monochromator (a) and a wavelength-dependent cross-section example, as measured for the $Cu_{0.8}Sn_{0.2}$ alloy number 7 (b).

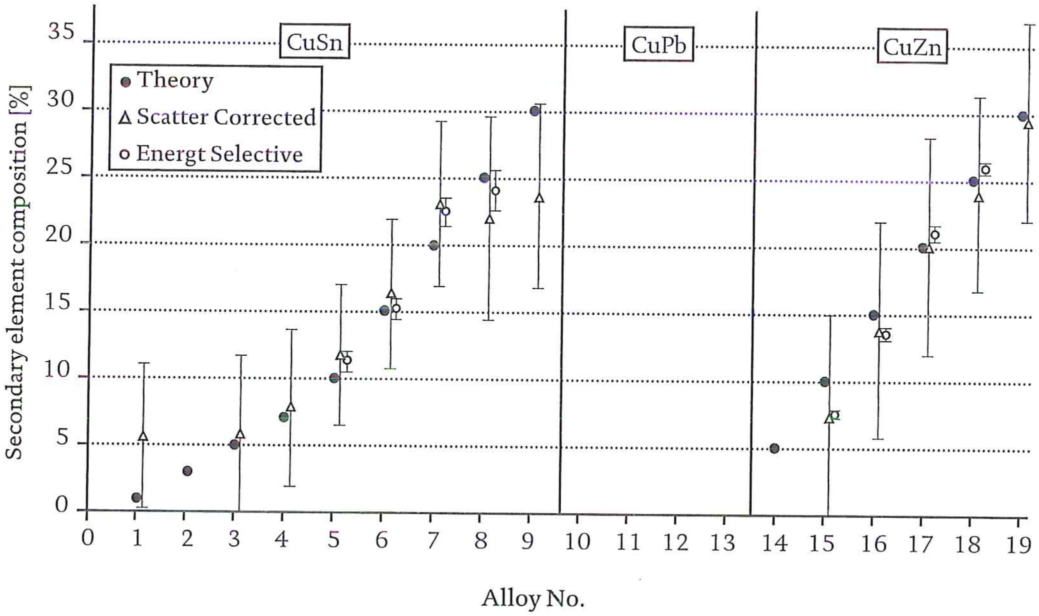

Fig. 6: Theoretical alloy component weight fractions, scatter-corrected white beam measurements and energy-selective imaging in the absorption range. A small horizontal offset has been used for clarity.

increased only to 60 seconds. The alloy composition was again determined by comparing measured and theoretical cross-section values in the absorption range. All data points above 5Å were used for the increased statistics, and no scattering correction was made. The results are summarized in figure 6. There is a very good correspondence with (scatter-corrected) values from polychromatic measurements and production values exists. The uncertainty as regards the composition was approximately 1%.

It was not possible to distinguish between Sn and Zn as secondary alloy components through energy-selective imaging, as they are both taken up in the copper FCC phase and as such do not form any new and distinctive

Bragg edges. Nevertheless, it would be possible to work with an "Sn equivalent" alloy component as proposed by E. Sidot *et al.*[20] Moreover, the reconstruction of the composition of binary alloys where the present secondary alloy element is known in advance (e.g., through XRF) does not pose any problem. Historical objects are often analysed first to exclude any metal that could negatively influence the half-life of the objects after being exposed to neutrons.

Conclusion

Neutron imaging was used to quantitatively determine historically relevant binary copper alloy composition. Radiographies using the full polychromatic beam spectrum revealed a clear need to correct for neutron-scattering contributions to draw quantitative rather than qualitative conclusions. A calibration-based scatter correction was applied to correct for the effect. Radiographies in the absorption range allowed for the successfully retrieval of information on the composition without the need for any scatter correction at the cost of a limited increase in exposure time. As a result, the way has been paved for quantitative tomography in the absorption range for 3D information on localized composition in historical bronze sculptures.

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Chapter IV

The effect of surface changes in heat-treated historic copper alloy samples analysed using X-ray fluorescence spectrometry (XRF)

Based on R. van Langh, A. Pappot, S. Creange, L. Megens, and I. Joosten, "The effect of surface changes in heat-treated bronze samples analysed by X-ray fluorescence spectrometry," in *Metal 2010*, ICOM-CC metal working group, Charleston, 2010, pp. 204-209.

Abstract

X-ray fluorescence spectrometry (XRF) is often used in museums to determine the composition of Renaissance bronze sculptures, both in qualitative and quantitative terms. The limitations of XRF are well known: patinas, platings or other surface treatments can potentially interfere with the accuracy of results. However, there has been no study of the influence that previous restorations involving the use of heat may have on surface analysis. In this study, XRF was used to examine the surface effects of heat treatment on 37 historic copper alloys following a simulated restoration treatment using heat. Cross sections were studied using reflective microscopy and SEM-EDS. The results indicate that restoration treatment using heat changes the surface composition of alloys. Alloys containing lead are particularly influenced by heat treatment; alloys containing both zinc and tin change to a lesser extent, and acid pickling also plays an important role.

Introduction

The composition of a Renaissance bronze is directly related to its appearance and this has been the subject of increasing interest in technical studies during the last few decades.[1] XRF spectrometry is frequently used to analyse the composition of bronze objects.[2] One major advantage of XRF is that it is non-destructive and provides results quickly. XRF has been shown to provide information to a depth of 20-30 μm on bronze alloys.[3] The careful choice of sample locations on exposed metal surfaces, multiple analyses and large spot size can be used to obtain the most representative results. Recent studies have tried to connect alloy composition analyses using XRF to a sculptor's workshop, yet not all parameters have been thoroughly covered.[4] A factor that appears to be significant has not yet been studied: the changes due to restoration treatments involving applied heat. As changes are often visible on the surface of bronze objects when and after heat is applied, it is obvious that changes also occur in the composition. Therefore an XRF result obtained from a sculpture that has been heat treated may not be representative of the original alloy of the sculpture.

The aim of this research is to provide greater insight into the surface changes that take place on 37 different copper alloys after a simulated restoration using heat. The simulated heat treatment employed is the common historical restoration technique of brazing, including the application of flux and its subsequent removal with an acid pickle. The alloys were chosen on the basis of the information found in different recipes, both in old treatises and in modern studies of these treatises.[5] The research focused on binary, tertiary and quaternary copper alloys, with varying and increasing amounts of the alloying metals tin, lead and/or zinc. It investigates whether treatment involving the application of heat, flux and pickle influences the surface composition measured by XRF.

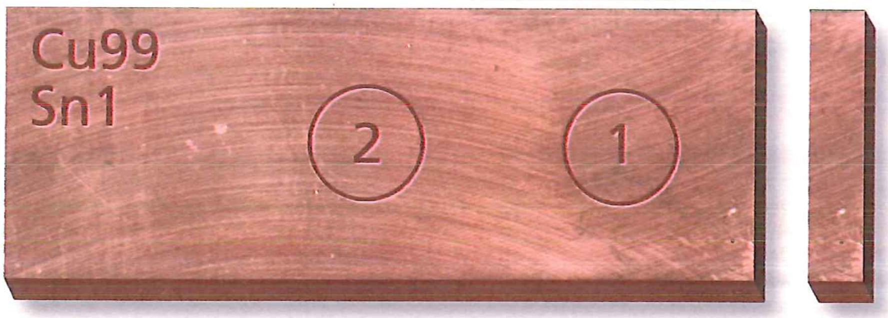

Fig. 1: Schematic overview of a copper 99% and tin 1% sample with both circular spots where XRF measurements will take place. At the end of the sample a cross section was made for possible reference. Spot 1 and 2 will be referred to in the tables as 'before brazingspot 1', 'before brazingspot 2'.

Experimental studies

A Bruker Artax X-ray fluorescence spectrometer with a tungsten tube with a 2 x 3 mm spot size and a silicon drift detector with a resolution < 145 eV for Mn-Kα was used. Analyses were performed with a tube voltage of 50 kV and a tube current of 300 µA for 120 seconds. A 25 µm nickel filter was inserted in the primary beam. The results were quantified using the Artax software (version 5.3) with a quantification method based on standards. To study the process of compositional surface changes, polished cross sections of the samples (embedded in Epo Fix) were examined with reflective microscopy (Leica D8 with a 420 Digital camera using Leica LM1000 software) and energy dispersive X-ray spectroscopy (EDS, Ultra dry silicon drift detector, Noran System 7 software, Thermo Fisher Scientific), linked to a scanning electron microscope (SEM, JSM5910LV). The X-ray micro-diffraction instrument used to identify the dark layer on the metal after treatment was a Bruker D8 DISCOVER with GADDS (Bruker, Karlsruhe, Germany). The instrument was equipped with a two-dimensional detector (HI-STAR, Bruker, Karlsruhe, Germany) and operated with Cu-Kα radiation working at 40 kV and 30 mA.

Sample preparation

Pure metals (technical grade up to 99.9%) were obtained and analysed using XRF, weighed and melted together. One rectangular plate measuring 60 x 20 x 5 mm was cast from each alloy. The plates were cast in sand moulds using traditional casting methods.[6] Each plate was subjected to the following procedure: the plate was air cooled and then sanded with 220 grit sandpaper. Two spots were stamped with circular marks so that analyses could be done in the same locations throughout the process (Fig. 1). A cross section was taken after casting sanding for reference purposes.

XRF measurements were taken on spot 1 and spot 2 to quantify the components of the alloy before heat treatment. The metal plate was sawn into two pieces and borax flux (sodium tetraborate) was applied to the cut edges and to a portion of the surrounding surfaces, covering parts of spot 2 so that they could be brazed (Fig. 2).

The cut pieces were then brazed back together following standard restoration techniques, which involve a torch and silver solder (680 °C melting point) in a reducing atmosphere caused by the flux. The heating time varied from 60 to 90 seconds, depending on the length of time required for brazing.

After brazing, the plate was air cooled and spot 1, which was not covered with a flux, was analysed with XRF before the plate was dipped in a 5%, heated (50°C) sulphuric acid solution (pickle) to remove oxides and borax. The plate remained in the pickle until the flux was removed. Spots 1 and 2 were analysed again with XRF. The results are recorded in tables 1-4. A cross section was taken after pickling, in the middle of the sample, including the brazing seam, overlapping the former borax-protected and unprotected areas.

Results and discussion

Binary copper/lead alloys

A visual examination of alloys containing less than 3% lead revealed that the copper colour of the surface does not change after heat treatment and pickling. Alloys containing more than 3% lead have a black surface that remains black after the pickle treatment in areas that

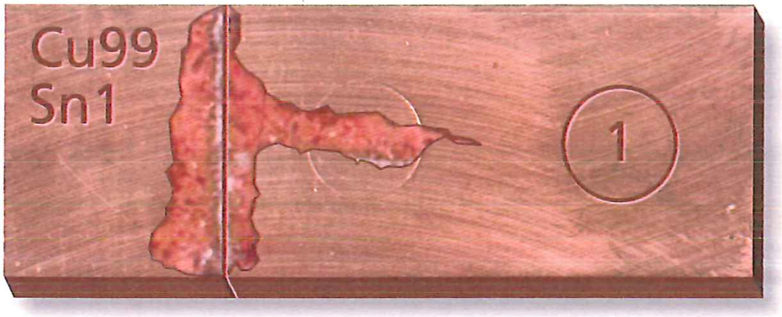

Fig. 2: Schematic overview of a copper 99% and tin 1% sample with both circular spots where spot 2 is partially covered with borax. Spot 1 will be analysed and referred to in the tables as 'after brazing spot 1 no borax'.

Cu99 Sn1 Cu99 Sn3 Cu99 Sn5 Cu99 Sn7

Fig. 3: An example of a copper/tin alloy after brazing, showing the brazing spot and partial covered borax around the seam.

were not covered by borax. Areas that were covered by borax are still copper coloured after the pickle treatment. The black surface that remained on the sample was analysed using XRD, and consists of a mixture of lead(II)oxide (PbO) and lead sulphate.

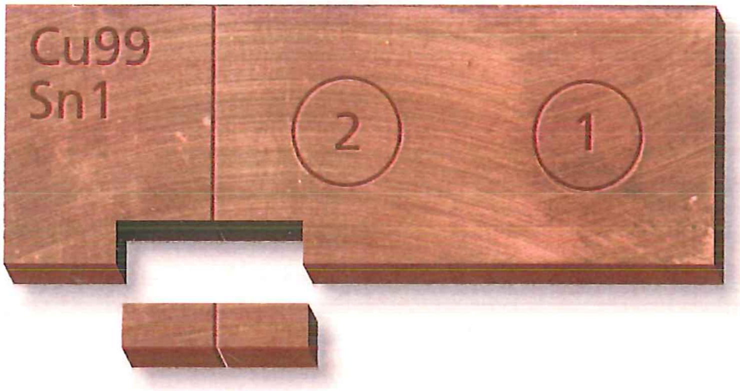

Fig. 4: Schematic overview of a copper 99% and tin 1% sample with both circular spots where after brazing a cross section was made of the seam.

XRF measurements (Table 1) show two major results: the first result indicates that before pickling, the lead concentration increases following heat treatment. After pickling the concentrations of lead below 3% are lower than the original composition. The second result shows that after pickling, the lead concentration in alloys above 3% is still much higher than the original lead concentration.

The difference in measured lead concentrations can be explained as follows. Lead is only slightly soluble in copper alloys, and therefore unalloyed lead segregates and migrates towards the surface during heat treatment.[7] However, in alloys which contain more than 3% lead, not all the corrosion products are dissolved from the surface by the pickle. The lead(II) oxide (PbO) and lead sulphate most probably account for the higher lead concentrations detected with XRF.

Binary copper/tin alloys

A visual examination revealed that after the restoration treatment using heat and pickling, the alloy turns red; however, when the tin composition approaches 30%, this no longer occurs.

XRF measurements (Table 2) show two major results: the first result indicates that there is almost no change in the concentration of tin after heating. The second result shows that after the pickle treatment, all the measurements of concentrations of tin show a decrease in comparison to the original concentration. There is no influence of borax on these analyses, as can be seen in table 2.

The tin in the alloy is clearly not affected by the heat treatment; however, the pickle depletes the tin from the surface and seems to have a considerable effect on the composition of the alloy.

Binary copper/zinc alloys

A visual examination revealed that after the restoration treatment using heat and pickling, the alloy turns red; however, as the zinc composition approaches 25-30% this effect is less noticeable.

XRF measurements (Table 3) show two major results: the first result indicates a pattern similar to that for the copper/tin alloys: heat treatment has no effect on the XRF results. The second result shows that a pickle treatment substantially removes zinc from the alloy, but the effect is not as strong as that observed with tin. There seems to be no influence of borax on the measured spots.

Tertiary copper/tin/lead alloys

A visual examination revealed that after the restoration treatment using heat and pickling, all the alloys changed to a predominantly red colour, whilst a black layer formed on the alloys with a lead content above 10%.

XRF measurements (Table 4) show three major results: the first result shows the tin concentration is hardly influenced by the heat treatment. The second result shows the lead concentration is influenced by the heat treatment. The third result shows that after pickling, both the tin and lead concentrations in all the alloys are lower than in the original tin and lead concentrations. However, when the lead content is higher than 10%, the results in the table indicate that the pickle treatment has a clear effect on the measured lead concentration. The lead concentration is in spot 1 higher (Cu81Sn8Pb10) than the original alloy,

Table 1: XRF measured composition of copper lead alloys before and after brazing (normalised to 100%).

Alloys	Cu99.5	Pb0.5	Cu99	Pb1	Cu97	Pb3	Cu95	Pb5	Cu93	Pb7	Cu90	Pb10	Cu85	Pb15
	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
before brazingspot 1	99.5	0.5	99.1	0.9	97.1	2.9	95.1	4.9	92.7	7.3	89.8	10.2	86.5	13.5
before brazingspot 2	99.5	0.5	99.0	1.0	97.0	3.0	95.3	4.7	92.7	7.3	90.7	9.3	85.3	14.7
after brazingspot 1 no borax	98.4	1.6	97.5	2.5	74.0	26.0	40.0	60.0	29.1	70.9	12.2	87.8	3.3	96.7
after picklingspot 1 no borax	99.7	0.3	99.6	0.4	93.1	6.9	60.6	39.4	38.6	61.4	12.0	88.0	3.1	96.9
after picklingspot 2 borax	99.8	0.2	99.7	0.3	94.3	5.7	98.7	1.3	75.6	24.4	72.8	27.2	22.7	77.3

Table 2: XRF measured composition of copper tin alloys before and after brazing (normalised to 100%).

Alloys	Cu99Sn1		Cu97Sn3		Cu95Sn5		Cu93Sn7		Cu90Sn10		Cu85Sn15		Cu80Sn20	
	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn
before brazing spot 1	99.1	0.9	96.8	3.2	94.5	5.5	92.4	7.6	88.7	11.3	82.7	17.3	76.4	23.6
before brazing spot 2	99.1	0.9	96.8	3.2	94.3	5.7	92.5	7.5	89.3	10.7	82.7	17.3	76.3	23.7
after brazing spot 1 no borax	99.1	0.9	96.8	3.2	94.5	5.5	92.4	7.6	88.6	11.4	82.6	17.4	76.3	23.7
after pickling spot 1 no borax	99.8	0.2	99.3	0.7	98.7	1.3	98.2	1.8	97.4	2.6	83.9	16.1	95.0	5.0
after pickling spot 2 borax	99.8	0.2	99.3	0.7	98.7	1.3	98.4	1.6	97.6	2.4	83.2	16.8	94.9	5.1

Alloys	Cu75Sn25		Cu70Sn30	
	Cu	Sn	Cu	Sn
before brazing spot 1	69.9	30.1	63.9	36.1
before brazing spot 2	70.0	30.0	63.9	36.1
after brazing spot 1 no borax	69.8	30.2	63.7	36.3
after pickling spot 1 no borax	93.5	6.5	90.7	9.3
after pickling spot 2 borax	94.5	5.5	90.6	9.4

Table 3: XRF measured composition of copper zinc alloys before and after brazing (normalised to 100%).

Alloys	Cu95Zn5		Cu90Zn10		Cu85Zn15		Cu80Zn20		Cu75Zn25		Cu70Zn30	
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
before brazingspot 1	96.4	3.6	91.7	8.3	87.9	12.1	82.1	17.9	76.8	23.2	71.8	28.2
before brazingspot 2	96.4	3.6	91.7	8.3	87.9	12.1	82.1	17.9	77.0	23.0	71.9	28.1
after brazingspot 1 no borax	96.2	3.8	91.6	8.4	87.8	12.2	81.6	18.4	76.3	23.7	71.6	28.4
after picklingspot 1 no borax	97.4	2.6	94.0	6.0	91.9	8.1	89.0	11.0	82.6	17.4	78.3	21.7
after picklingspot 2 borax	97.5	2.5	93.9	6.1	91.5	8.5	90.1	9.9	83.6	16.4	80.6	19.4

Table 4: XRF measured composition of copper tin lead alloys before and after brazing (normalised to 100%).

Alloys	Cu95Sn4Pb1			Cu93Sn4Pb3			Cu91Sn4Pb5			Cu86Sn4Pb10			Cu91Sn8Pb1		
	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb
before brazing spot 1	95.4	3.7	0.9	93.3	3.7	2.9	90.5	4.0	5.5	86.1	3.7	10.1	90.0	8.7	1.3
before brazing spot 2	95.2	3.8	1.0	92.9	3.8	3.2	90.6	3.9	5.5	85.7	3.7	10.5	89.8	8.8	1.4
after brazing spot 1 no borax	95.1	3.7	1.2	90.4	3.7	5.9	79.7	3.9	16.3	29.3	2.4	68.3	89.6	8.8	1.7
after pickling spot 1 no borax	98.7	0.9	0.4	98.4	0.9	0.7	98.4	0.9	0.7	24.5	0.9	74.6	97.9	1.8	0.3
after pickling spot 2 borax	98.9	0.9	0.2	98.4	0.9	0.7	98.3	0.9	0.8	91.6	1.0	7.4	97.8	1.9	0.3

Alloys	Cu89Sn8Pb3			Cu87Sn8Pb5			Cu82Sn8Pb10			Cu77Sn8Pb15		
	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb
before brazing spot 1	88.1	8.3	3.6	85.2	8.5	6.3	79.6	8.0	12.4	75.1	7.5	17.4
before brazing spot 2	87.9	8.3	3.7	85.1	8.4	6.5	78.8	7.9	13.4	74.6	7.5	17.9
after brazing spot 1 no borax	83.7	8.2	8.0	79.3	8.4	12.3	56.4	7.3	36.4	63.3	7.0	29.8
after pickling spot 1 no borax	97.5	1.6	0.9	94.9	1.5	3.7	82.9	2.0	15.1	88.4	1.8	9.9
after pickling spot 2 borax	97.4	1.8	0.8	96.5	1.7	1.8	89.4	1.9	8.7	85.7	1.8	12.5

Table 5: XRF measured composition of copper zinc tin lead alloys before and after brazing (normalised to 100%).

Alloys	Cu89Zn5Sn3Pb3				Cu85Zn5Sn5Pb5				Cu80Zn10Sn5Pb5				Cu75Zn15Sn5Pb5			
	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb
before brazing spot 1	90.9	2.8	3.0	3.2	86.2	2.9	5.2	5.6	79.3	9.0	5.5	6.2	79.5	9.0	5.6	5.9
before brazing spot 2	90.4	2.7	3.2	3.6	86.2	2.9	5.1	5.7	79.3	9.0	5.6	6.1	79.6	9.0	5.7	5.7
after brazing spot 1 no borax	87.8	2.8	3.0	6.4	79.6	2.8	5.1	12.5	70.6	5.6	5.2	18.6	77.3	8.9	5.6	8.1
after pickling spot 1 no borax	96.9	1.8	0.7	0.6	95.1	2.2	1.2	1.6	93.4	4.0	1.2	1.5	87.6	8.9	1.3	2.2
after pickling spot 2 borax	97.0	1.9	0.7	0.4	95.8	2.1	1.1	1.0	95.1	2.9	1.1	1.0	88.9	7.4	1.3	2.4

Alloys	Cu82Zn10Sn3Pb5				Cu77Zn15Sn3Pb5			
	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb
before brazing spot 1	85.8	5.7	3.0	5.6	82.7	8.8	3.0	5.4
before brazing spot 2	85.3	5.7	3.2	5.8	82.5	8.9	3.0	5.5
after brazing spot 1 no borax	77.8	5.2	3.0	14.1	74.4	8.3	3.0	14.4
after pickling spot 1 no borax	93.4	4.5	0.7	1.4	92.2	5.7	0.6	1.5
after pickling spot 2 borax	95.1	3.7	0.7	0.6	93.3	5.6	0.6	0.5

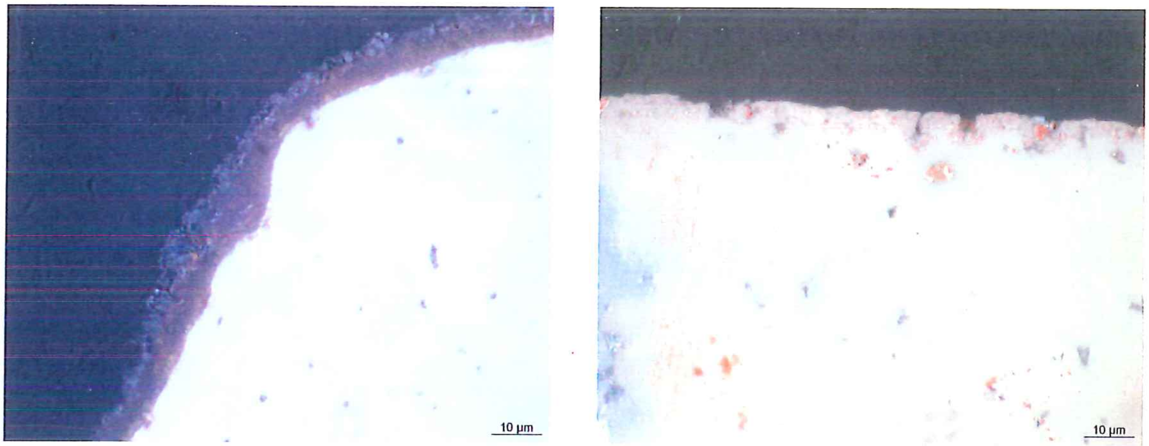

Fig. 5: Cross section of Cu91Sn4Pb5, after heat treatment (left), and after pickling (right).

while in the other alloy (Cu77Sn8Pb15) spot 1 has a lower concentration measured. The difference between both spots 1 from the different alloys could not be identified. The borax has an equal effect as with the copper/lead alloys except for (Cu77Sn8Pb15).
Cross sections of samples obtained before brazing, after brazing and after pickling, were prepared from one of the tertiary copper/tin/lead alloys, Cu91Sn4Pb5, a composition frequently measured in sculptures. These samples were analysed using reflective microscopy and SEM-EDS (Figs. 5 and 6). Figure 5 shows a layered structure on the surface of the sample after the heat treatment (left), which has disappeared in the cross section after the pickling (right).

Figure 6 shows the distribution of different phases in the alloy, marked as copper (Cu, rich in copper), lead (Pb, rich in lead) and tin (CuSn, rich in tin), represented in the X-ray mappings of cross sections of the samples before brazing, after brazing and finally, after pickling. The metal shows the presence of copper and tin-rich phases and undissolved lead globules. There is a layer of tin oxide followed by a layer of copper oxide. Finally, a layer containing lead is visible on the surface. After the pickling, the lead and copper oxide layers disappear and the upper 10µm of the metal is depleted of lead. The reason for the disappearance of both lead and tin is due predominantly to the fact that the alloy consists of various lead, tin-rich and less tin-rich phases, as can be seen in figure 6. Lead and tin from the richer phases dissolve more rapidly in the pickle, causing the values to fall sharply.

Quaternary copper/zinc/tin/lead alloys

A visual examination revealed that all the alloys turned red after the restoration treatment using heat and pickling, except for the last alloy which is slightly more yellow.
XRF measurements (Table 5) show three results. The first result shows that the zinc content is hardly influenced by the heat treatment and only slightly by the pickle treatment. The second result shows that the tin follows the

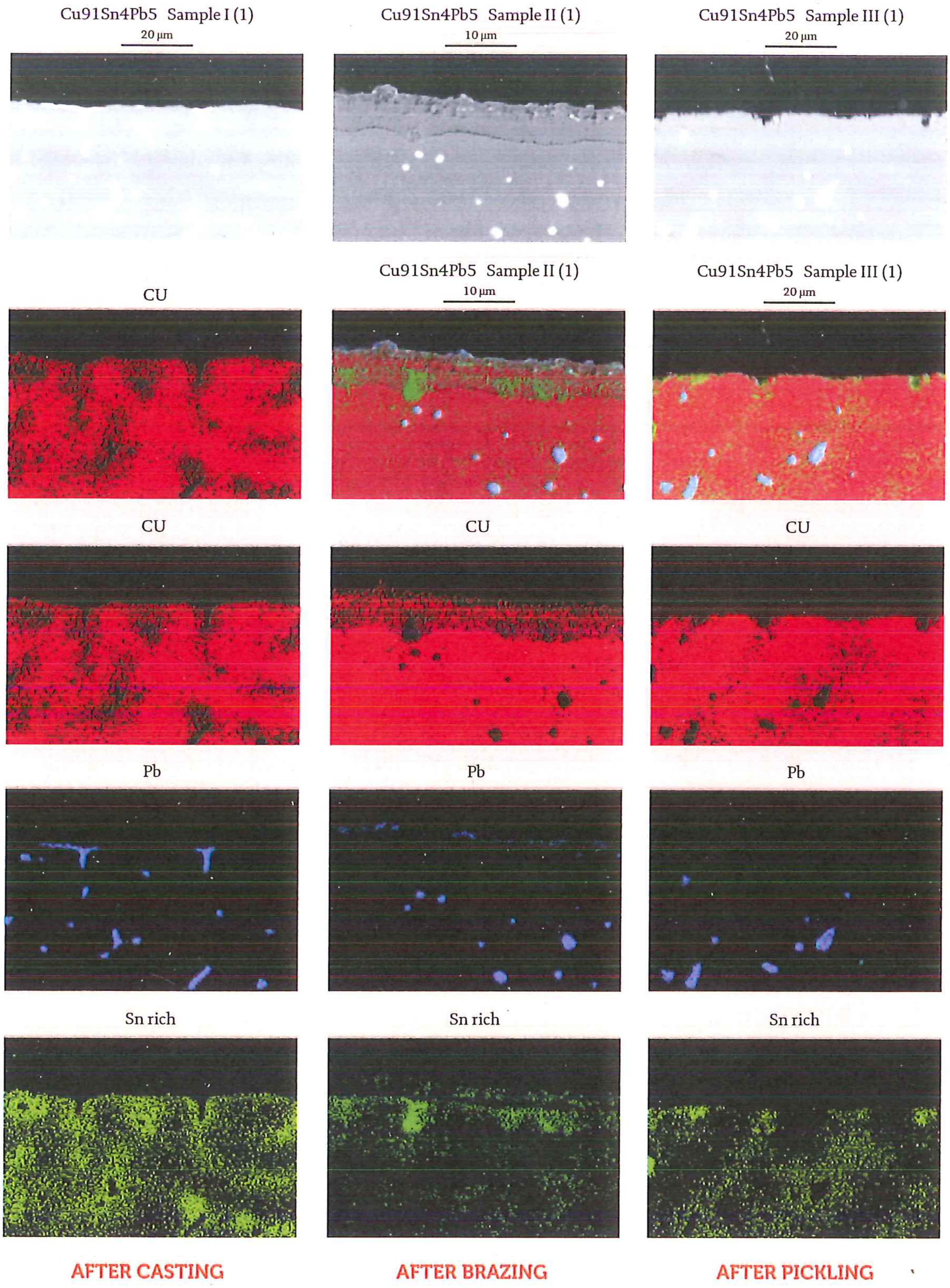

Fig. 6: Backscatter electron image X-ray mappings of the sample Cu91Sn4Pb5.

same pattern as the other alloys containing tin. The third result reveals that lead also follows the pattern of an increase in quantity after heating and a decrease after the pickle treatment. After pickling, the lead and tin concentrations are in all cases lower than the original values. The zinc concentration is in some cases lower after pickling, but to a lesser degree than lead and tin. Areas protected by borax seem to have a slightly lower lead value than areas not covered with borax.

Conclusions

This research focused on the effects of a heat treatment with temperatures above 680° C on 37 bronze test plates using XRF analyses. The heat treatment corresponds to brazing, a traditional restoration technique which is often used on historical copper alloys. The impact of heat treatment is clearly demonstrated when lead is present in the alloy, more clearly in alloys with 3% or more lead. Copper with a composition containing both zinc and tin is strongly affected by the restoration treatment when heated to 50° C pickle (5%) sulphuric acid is used for the removal of oxides and when borax is applied. Based on these findings, it indicates that XRF analyses should be carefully interpreted for alloys containing copper, lead, tin and zinc in binary, tertiary or quaternary compositions. A careful examination of the object by a conservator is necessary to choose sample spots which are likely to be representative of an alloy.

Further Research

Further research is needed into the extent of changes in the alloy which are commensurate with the size and location of the restored area. In some cases the entire sculpture may be heated during the course of a restoration treatment. The effects of pickle, the influence of patinas on alloys and the investigation of corrosion products produced during restoration treatments involving heat, also deserve to be studied in more detail.

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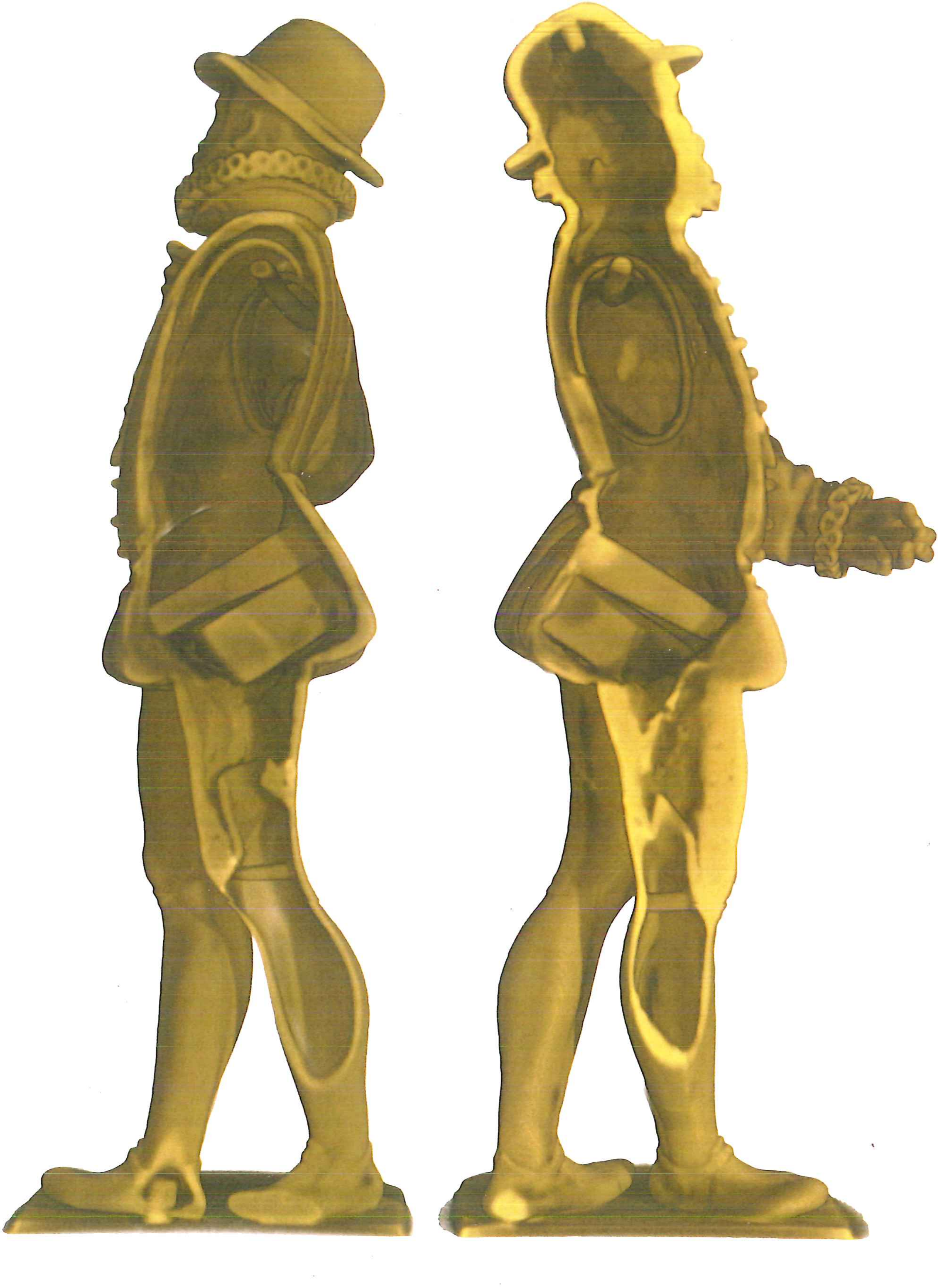

Chapter V

New insights into alloy compositions: The study of Renaissance bronze statuettes using combined neutron imaging and neutron diffraction techniques

Based on R. van Langh, J. James, G. Burca, W. Kockelmann, S.Y. Zhang, E. Lehmann, M. Estermann, and A. Pappot, “New insights into alloy compositions: studying Renaissance bronze statuettes using combined neutron imaging and neutron diffraction techniques,” in *Journal of Analytical Atomic Spectrometry*, 2011, 26, pp. 949–958.

Abstract

Until recently, the inside parts of hollow-cast Renaissance bronze statuettes were concealed, yet they hold important information on the production techniques used in the manufacture of these fine works of art. For that reason the inside of the sculptures has been made visible using a neutron imaging technique (tomography) at the Paul Scherrer Institute, Villigen, Switzerland. This method allowed us to study the internal structure of a bronze sculpture and provided an indication of different material compositions. As it is not advisable to take samples from these precious works of art, different non-destructive methods had to be investigated to obtain more specific information about the composition of the inner parts. This research focuses on analysing pre-determined small volumes selected from neutron tomographies. With this approach it has become possible to study the material compositions and crystalline structures of these statuettes with a millimetre-sized gauge volume placed at any selected point within the object, using time-of-flight neutron diffraction in the ENGIN-X set up at the ISIS facility at the Rutherford Appleton Laboratory, UK. Analysis of a Renaissance statuette from the Rijksmuseum, a *Striding Nobleman*, (BK-16083) provided evidence of the different copper alloy compositions of surface and internal parts, but also revealed the presence of small amounts of ferrite which had not been reported for Renaissance bronzes up to that time. The alloy is magnetic due to the ferrite, and strong rare-earth magnets were used to establish whether or not other Renaissance bronzes contain ferrite. The application of different neutron techniques lead to a better understanding of the production techniques and will, in general, help to advance the analytical studies of these marvellous objects.

Introduction

Hollow bronze statuettes (sculptures up to approximately 40 cm in height) from the Renaissance period are highly appreciated in the fine arts. The craftsmanship dates back to early Greek and Roman periods when beautiful sculptures were made. During the Renaissance this technique was revived in Italy and throughout Europe. Nowadays we can still read contemporary treatises that describe the production processes of these kinds of – in most cases – hollow sculptures.[1] These treatises have proved to be important for providing a better understanding of the production techniques of these sculptures, and the kinds of materials used by the sculptors. Although many details of the production techniques are still being studied, the basic techniques of sand casting and lost wax casting Renaissance bronzes are the most well known. Bewer, Stone and Bassett *et al.* have published many relevant insights on this subject.[2] In this study the generic term "bronze" is used for copper alloys the exact composition of which is not always known or does not contain zinc as a major alloying component, and refers to the type of Renaissance statuettes which are its subject. As a result of a study preceding the publication of a catalogue of Renaissance bronzes at the Rijksmuseum, strong rare-earth based magnet (Neodymium) were used to locate hidden parts of iron core pins which were used in the construction process of these statuettes. During this study it was accidently discovered that large parts of a Renaissance sculpture in the Rijksmuseum, a *Striding Nobleman*, were magnetic. This phenomenon had never been described in the literature and was poorly understood.

In the study of the production techniques of Renaissance statuettes there are two main aspects which are of interest: first, the structure of the sculpture, and, secondly, the alloys that were used. In the study of art objects researchers are usually confronted with the problem that the objects have often been altered during their lifetime. It is worth noting that this does not apply so much for Renaissance statuettes, as their appreciation is defined by the alteration of the surface over time, in addition to their form and the execution of the sculpture. This surface alteration includes a mineralization, oxidation and possible decay of organic substances that were believed to have been applied by the artist just after the statuette was made. The apparent surface alteration has always been highly appreciated and if removed, the value of the statuette diminishes significantly, both economically and aesthetically. The only time when the composition of the material on the outer surface of the statuette would have been altered is during repairs that could have taken place on these objects during their lifetime. Thus it can be safely assumed, from both an art historical and conservation point of view, that these sculptures have not been altered intentionally and that they are representative objects of study.

Until recently the study of sculptures such as these used relatively traditional methods such as X-radiography or videoscopy. However, X-radiography provides only partial information about the production technique of a sculpture. The use of neutron imaging techniques at the Paul Scherrer Institute in Villigen has proved to be necessary for more detailed studies of the construction of these sculptures, as indicated by Van Langh *et al.* and Lehmann *et al.*[3] Regarding the compositional analysis, various techniques have been used for the past twenty years. Thes include Atomic Absorption Spectrometry (AAS), X-ra Fluorescence Spectrometry (XRF), Inductive Couple Plasma (ICP) or Scanning Electron Microscopy-Energ Dispersive Spectroscopy (SEM-EDS). However, XRF wa predominantly used as it is a non-destructive techniqu even though it is only a surface analysis technique.[4] In addition to XRF, Laser Induced Plasma Spectroscopy (LIPS has recently been used successfully by Agresti *et al.* t study the composition of Renaissance copper alloys However, LIPS leaves a very small visible impact (laser impact is 120 µm) on the metal and while this is not considered a problem for life-size statues, it is not advisable fo statuettes. For this reason it is important to develop non destructive techniques, especially if the technique involves bulk and not just surface analysis. Recently Siano *e al.* demonstrated that neutron diffraction can be use quantitatively to study historic copper alloys.[6] However many researchers continue to use traditional technique such as XRF. Some of these studies have produced interesting patterns, as Smith has indicated.[7] However, thi surface analysis technique will only penetrate the alloy t a certain depth of several tens of microns, providing onl partial information of the composition. In addition to th limitations of the technique, Heginbotham *et al.* carrie out inter-laboratory research on the use of historic coppe alloys and showed that that this technique is not completely reliable for the study of historic copper alloys.[8] With XRF studies of copper alloys containing lead, zinc tin or a combination of these metals, Van Langh *et al* showed that these alloys are highly influenced by the heat treatments that these kinds of historic objects could have been subjected to.[9]

Neutrons are complementary to X-ray in terms of atomic contrasts (by reason of their different scattering cross sections) and by their deeper penetration into materials. In this research, neutron tomography was used to reveal the structure of the *Striding Nobleman* and neutron diffraction was used to detect alloy compositions of the sculpture. Based on neutron measurement results, this type of study became possible and relevant for understanding the production technique of Renaissance bronzes. Until recently it was impossible to study the composition of the alloy in the inside of a sculpture at a pre-determined point. However, this research uses the recently developed method of tomography-driven diffraction (described below), in which the results of neutron imaging techniques are used to both design and execute neutron diffraction measurements.

Casting procedures and typical alloy compositions of Renaissance bronzes

There are two main different techniques used to produce hollow statuettes: sand casting and lost wax casting. Sand casting could have been used for larger bronze statues, while lost wax casting was typically used to create hollow bronze statuettes. Over the centuries there have been many different techniques using the same basic method of lost wax casting. However, I make a distinction between the direct and the indirect method, and refer to Basset *et al.* for a more detailed description of the variations in these techniques.[2] In general the process is as follows: a clay core that functions as the body of the sculpture is covered with a wax layer that forms the shape and final appearance of the future sculpture. Iron "core pins" are inserted into the clay body through the wax, and are left protruding. Around this wax layer, and attached to the pins, a second clay core is mounted to act as a supporting outer mould. The wax is still in contact with the open air through a connected wax funnel system. The whole construction is heated in a kiln and the wax melts and flows out from between the two clay cores which remain connected and held in position by the iron core pins. As soon the wax has completely disappeared, molten metal is poured through the same opening from which the wax flowed out. When the metal has solidified the outer mould can be removed. In most cases the iron core pins remain in the bronze when it has been cast and finished. However, they can be concealed using finishing techniques.

Renaissance bronzes that have been analysed in the past twenty years using the above-mentioned analytical techniques predominantly contain Cu, Sn, Zn and Pb, with Fe, As, Ag, Sb, and Ni. Sometimes Bi is found in small quantities.[10] The alloys occur as binary, tertiary or quaternary alloys of the major elements. Current research in museum laboratories focuses on the hypothesis that sculptors understood what kind of alloys they should be using to cast their sculptures. The search for a fingerprint alloy remains understandably alive.[7] The contemporary treatises describe alloy composition, but without including the minor elements. In general, the research on alloy composition is limited to surface analytical techniques, such as XRF.[11] However, depending on the alloy and the treatment after manufacturing, segregation effects are insufficiently taken into account. Using a Secondary Target X-ray Fluorescence Spectrometer (STXRF), Basset *et al.* have also identified correlations in the work of Adriaen de Vries.[12] She showed that De Vries used copper/tin bronzes with low levels of lead and zinc and other traces of metals as consistent alloying components. The measured compositions are still difficult to understand from the point of view of production, as they can contain from 6-21% tin per object.

The historical background of the 'Striding Nobleman' (BK-16083)[13]

The sculpture is shown in figure 1a, while figure 1b and figure 1c show details of the face, torso, and back, respectively. The statuette represents a man with a beard and drooping moustache, dressed in the full baggy breeches known as trunk hose, with stockings, and a doublet with a lace ruff and cuffs. He is wearing a small, round-brimmed hat. His clothing accurately reflects the fashion of the Spanish Court in about 1575. For a long time it was thought that the statue might be a portrait of William of Orange, but there are no satisfactory grounds for this assumption; the face is too different from the known portraits of the prince. X-ray radiographies taken at the Rijksmuseum with a 280 kV Eresco tube using film methods, (Fig. 1d), show that there is a bar inside at the

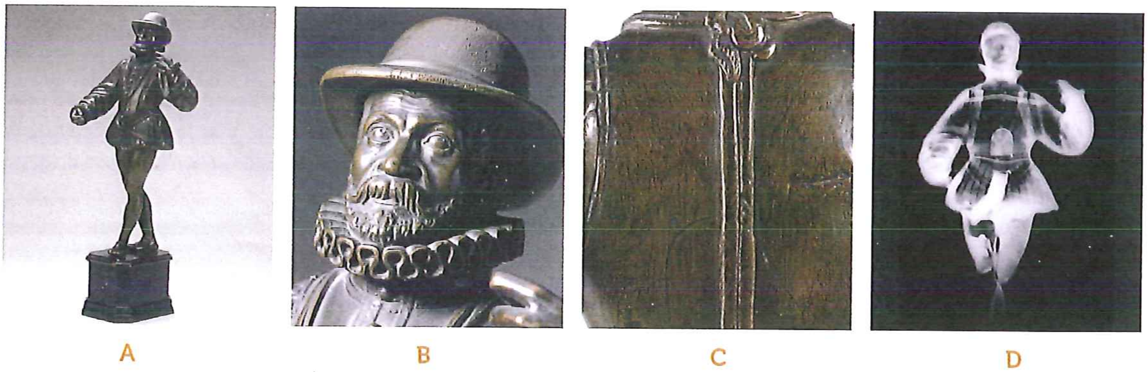

Fig. 1: (a) The *Striding Nobleman*, Rijksmuseum, Amsterdam Inv. BK-16083. The statuette is about 35 cm high. (b) Expanded view; head and part of torso. (c) Expanded view: back side of torso. (d) X-radiography.

Table 1: X-ray fluorescence spectrometry results on various parts of the *Striding Nobleman*.

Analysis points	Fe K12 (wt %)	Ni K12 (wt %)	Cu K12 (wt %)	Zn K12 (wt %)	As K12 (wt %)	Ag K12 (wt %)	Sn K12 (wt %)	Sb K12 (wt %)	Pb L1 (wt %)
Backside elbow right proper arm	0.9	0.4	83.9	10.7	0.4	0.1	0.5	0.3	2.8
Insert on proper left leg at calf	0.2	0.3	78.4	18.9	0.1	0.1	0.3	0.0	1.9
Small oval part proper right backside leg	0.1	0.6	84.8	13.2	1.0	0.1	0.1	0.0	0.1
Left proper upper leg	1.0	0.4	86.1	10.3	0.6	0.1	0.5	0.2	0.7
Left proper sleeve	1.0	0.4	85.8	10.4	0.5	0.1	0.5	0.3	1.0
Hatch on the back	0.4	0.4	91.3	1.3	0.5	0.1	2.3	0.7	3.1
Medaillon on his belly	1.1	0.4	85.4	10.8	0.4	0.1	0.4	0.2	1.3
Trunk hose	1.1	0.4	83.8	10.6	0.4	0.1	0.5	0.3	3.0

back of the statue that appears to be of different composition. The X-ray images show typical contrast variations, but the interior details are difficult to interpret.

Experimental methods

XRF neutron tomography and neutron diffraction techniques were used to study the object. Tomography data create a three-dimensional picture of the *Striding Nobleman* and were used to reveal the internal features of the sample. This information was then used to provide a virtual model of the sample to import into the SScanSS simulation and control software. This process automates the experimental set-up for diffraction measurement and allows the sample to be accurately positioned for measurements to be made on features identified from the tomography.
A Bruker Artax X-ray fluorescence spectrometer with a tungsten tube with a 2 x 3 mm spot size and a silicon drift detector with a resolution < 145 eV for a Mn-Kα was used to determine the surface composition of the *Striding Nobleman*. Analyses were performed with a tube voltage of 50 kV and a tube current of 300 µA for 120 seconds. A 25 µm nickel filter was inserted in the primary beam. Results were quantified using the ArTax software (version 5.3) with a standards-based quantification method. Data were collected from eight points, from over all the sculpture, as shown in table 1.

The attenuation of copper, and in particular tin, is much lower with neutrons compared to X-rays at a typical photon energy of approximately 150 keV. The transmission of typical bronze materials is better for thermal and cold neutrons than for X-rays by at least a factor of two. No significant beam- hardening effects occur with neutrons when the wall thickness is in the mm range. For the same reasons it is more effective to collect neutron tomography data than X-ray tomography data of bronze statuettes, in order to interpret the features in the X-radiograph (Fig. 1d).

It was therefore decided to perform a full neutron tomography study at the NEUTRA facility at the spallation neutron source SINQ in the Paul Scherrer Institute, Switzerland. Several statuettes were analysed, but here I refer only to the sculpture of the *Striding Nobleman*. With a field-of-view of 27.2 cm the whole object was covered in two acquisitions of data by adjusting the height of the sculpture. The two individual data sets were carefully combined and there was no gap between the individual data sets. Only 300 single projections were taken over the 180° rotation range for each of the two acquisitions of data. Using a cooled CCD camera-based detection system with 1024 * 1024 pixels, the resulting pixel size of the image was 0.26 mm. The exposure time per projection was approximately 15 seconds, resulting in less than two hours to acquire the data per run. Only a short-term activation from the neutron exposure was registered, which decayed within several days, to activation levels below the natural environmental levels. The acquired projection data were cleaned of "white spots", and flat-field as well as dark-field (background) corrections were applied in order to calculate the volume of the object using the common filtered back projection algorithm which is included in the OCTOPUS software tool.[14] As the L/D ratio at the sample position (position 3) on NEUTRA was greater than 550, the beam could be considered to be quasi-parallel, an assumption

Fig. 2: Neutron tomography data of the *Striding Nobleman.* (a) Alloy/metal distribution. (b) Distribution of soldered joints (left) and hollow parts (right).

which meant that it could be used in the much less demanding parallel beam analysis option within OCTOPUS, as opposed to the full cone-beam option. The whole sample volume of 1024 * 1024 * 2048 voxels (corresponding to 4.2 GBytes) was transferred to the visualization software tool VG Studio, which allowed the data to be segmented and the outer and inner surfaces of the cast material to be revealed in detail. The wall thickness could now be determined at any point and indications could be obtained regarding the homogeneity of all the materials involved. Some of the results of this demanding analysis are shown in figures 2a/b.

The time-of-flight (TOF) neutron diffraction measurements for this study were taken using the ENGIN-X strain scanner which is based at the ISIS-pulsed neutron and muon source at the Rutherford Appleton Laboratory in the UK. ENGIN-X is optimized to measure lattice parameters/strainsat precise locations in bulky specimens. ENGIN-X was placed on a methane moderator, which provided narrow pulses (in time) and high neutron fluxes over a wavelength range of 0.5 – 6 Å. A neutron guide was used to transport the neutrons from the moderator to the sample position. ENGINX was designed primarily for measuring the strain in engineering components. However, the instrument has a number of attributes which make it suitable for the examination of archaeological and art-historical objects. Zhang *et al.* described the state-of-the-art stress measurement using ENGIN-X for engineering and cultural heritage materials.[15] A diagram of the instrument set-up is shown in figure 3. ENGIN-X has a tuneable spatial resolution and can take samples over a three-dimensional space known as the gauge volume. The size of the gauge volume is adjusted by jaws, composed of neutron-absorbing boron carbide containing blades, which alter the cross section of the neutron beam, and by a pair of radial collimators in front of the neutron scintillation detectors. A gauge volume of 4 x 5 x 2 mm^3 was used for all the measurements, with a beam cross section of 4 x 5 mm^2 (width x height), and a diffracting length of 2 mm along the beam direction, as determined by the secondary collimators (Fig. 3). A full diffraction spectrum is obtained from a single measurement by applying the time-of-flight (TOF) principle. Scattered neutrons are recorded in the two 90° detector banks on either side of the sample position and at a distance of 1.5 m from the sample. Each detector bank is composed of 1200 ZnS/6Li scintillator elements. The detectors measure the TOF of each detected neutron, i.e. the time between the generation of the neutron and its capture in the detector. The positions and intensities of diffraction peaks in the spectra are used to obtain information about the presence and quantities of crystallographic phases, such as copper alloys, lead, ferrite, and corrosion phases. In addition, information about the microstructure and the material treatment can be obtained from the shape and

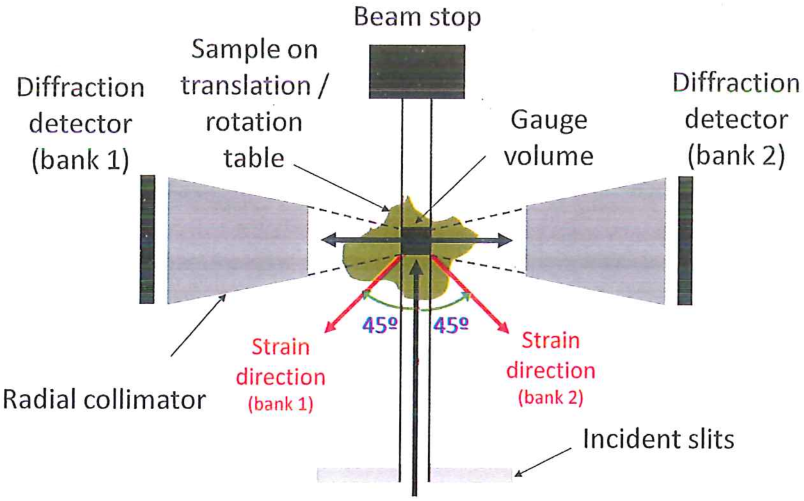

Fig. 3: Schematic neutron diffraction set-up. ENGIN-X at ISIS. The "incident slits" define the beam height and width of the incoming beam. The radial collimator defines the outgoing, scattered neutrons, thus the third dimension of the gauge volume.

intensities of the diffraction peaks, for example, whether or not the alloy was left as cast or homogenized.[16]

The statuette was mounted on the positioning table, which was used to access different analysis points. The alignment of the object and the pinpointing of particular parts with the beam were made possible with the "SScanSS" software, as outlined in the following chapter. Diffraction patterns were collected from 34 points on the wall of the sculpture and its internal parts; the collection time per analysis point was about 30 minutes. The activation of the statuette in the neutron beam was low, due to the small beam size and the short acquisition times. The activation was below measurable levels within hours of the diffraction measurements. The TOF data were normalised by the flux distribution of the incoming neutron beam. Two diffraction patterns, one for each 90° detector bank, were generated using the TOF data, and simultaneously analysed by the Rietveld method with the General Structure Analysis System (GSAS).[17] This analysis provided the lattice parameter of the copper alloy, and weight fractions for the crystal structure models which were set up in the GSAS software. The following crystal structures were included in the Rietveld model to fit the data, where u is the Debey-Waller parameter: (1) alpha-phase (space group Fm-3m) with a lattice parameter in a range from a = 3.6145 to a = 3.67 Å; u = 0.01 Å^2; (2) a Pb-phase (space group Fm-3m), u = 0.34 Å^2; Pb does not dissolve into the copper lattice, and can therefore be observed as a separate phase with a characteristic Bragg peak at 2.86 Å; (3) ferritic Fe phase (space group Im-3m), u = 0.0041 Å^2; (4) cuprite Cu_2O (space group Pn-3m), u=0.019 Å^2; (5) Fe-Ni-Cu Cu-type phase (space group Fm-3m) with a lattice parameter of 3.588 Å and a composition of 1/3 Fe, 1/3 Ni, 1/3 Cu, respectively, and u=0.01 Å^2. The Debye-Waller parameters used were empirical values determined from pure materials. The results of the Rietveld analysis are summarised in table 2.

It is important to mention that the diffraction techniques provide information only about the crystalline portion in the diffracting/gauge volume. It is also worth noting that any diffraction method provides information about the phases, and not about the constituent elements. However, information on the content of elements can be indirectly determined from structure data. The lattice constant of the copper alloy depends on the addition of alloying elements such as Sn, Zn, Sb, and As. The contents of the alloying elements can be obtained according to Vegard's rule from the lattice parameters of the alpha-phase, for example, using a calibration curve for binary Cu-Sn alloys.[18] Partitioning of the copper alloy into Cu and Zn in table 2 was achieved in a similar way, using an experimental calibration curve for the Cu-Zn system.[19]

Method of Tomography-Driven Diffraction

The task was to identify features in the tomography data that required further investigation, and pinpoint these features for diffraction analysis with the neutron beam. For example, it was not understood why the object was magnetic, and it was suspected that the material composition differs in the cast walls of the statue and in the various internal constructional elements revealed by the tomography data. Furthermore, it was worthwhile identifying and investigating the spatial variation of magnetic phase components. However, the difficulty with this seemingly simple task was how to position the sample so that the diffraction instrument focused accurately on the features of interest, when these features could be very small, hidden inside the sample, in an environment with different characteristics. This problem was partially solved by the SScanSS software simulation tool.[20] This software tool was developed to resolve sample positioning issues for engineering measurements on ENGIN-X. The method is based on virtual reality techniques in that it combines virtual sample and instrument models in an accurate virtual laboratory, so that the positioning problem can be solved with a computer. Typically a virtual sample model is generated by scanning the sample with a precision laser scanner. This approach produces an accurate model of the surface of the sample. However, no information is recorded about the interior of the sample. In a recent development the method was extended with the use of a virtual sample model generated using the neutron tomography data rather than a laser scan.[21] In this way the internal as well as external sample geometry is made accessible. Essentially this is a straightforward process, as most commercial tomography packages allow the output of segmented tomography data in the form of polygon surface models. Using this facility a greyscale value is selected that identifies the surface of the structures of interest, the data is segmented using this greyscale value and the corresponding surface is shown as a polygon surface model (typically an .STL model). The surface model is entered into the SScanSS software, the required internal structures are identified on computer-generated sections through the model and measurement points are identified and marked. This last step is shown in figure 4a. The next step is to combine the virtual sample with the virtual instrument model (Fig. 4b) prior to generating the instrument control scripts. To this end, the position of the sample on the real instrument must be measured accurately which, for engineering samples, is typically done by measuring fiducial markers which were attached to the sample beforehand (usually in the form of steel balls). Unfortunately this strategy was not suitable for the *Striding Nobleman* and the alternative strategy of employing prominent features of the statue itself was used. Specifically the fingers were measured to determine the initial position of the statue and to correctly reproduce it in the virtual instrument. Once this was done, the SScanSS software was used to automatically generate the required instrument control scripts. The experiment reported here describes the first use of this technique on a cultural heritage object. It provides a general method for positioning art objects for multi-modal measurements. A positioning accuracy of < 0.1mm is routinely achieved for engineering measurements using the combination of laser scan and fiducial spheres. The effect of a changing to the use of tomography- generated models and structural features of the object as fiducial

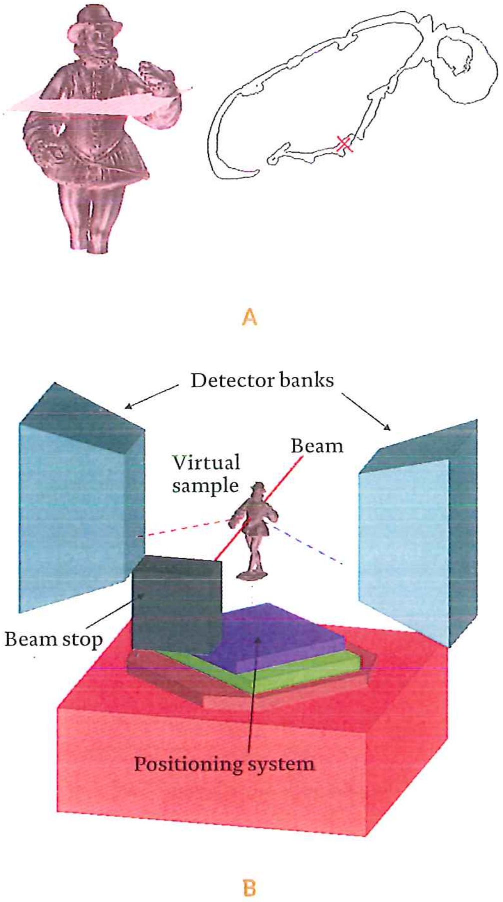

Fig. 4: Tomography data in the Virtual Laboratory program SScanSS. (a) Slicing (left) and selection of measurement points (right). (b) Virtual object from tomography, displayed in the virtual diffractometer.

markers on the final positioning accuracy is still under investigation, but it is anticipated that similar accuracy can be achieved.

Results - Neutron imaging techniques

The *Striding Nobleman* statuette is hollow, indirectly cast with separately cast arms and lower legs which are attached to the body by brazing and reinforced with copper alloy rods in the shoulders and knees (Figs. 2a/b). The sculpture is the product of careful detailing in the wax (brimmed hat, decoration of baldric), combined with some afterwork. Tomographic images also reveal two heavy, wedge-shaped copper alloy plugs in the interior of the lower body and an arched insertion soldered in the back. The results from the tomographic analysis indicate that this statuette was therefore derived from sculptures that were found in the collection of the Herzog Anton Ulrich Museum in Braunschweig, and probably functioned as sculptures for an automation.[22] The soldering of the metal is clearly visible in figure 2b and is indicated by the red colour resulting from the different attenuation of the neutrons. On the outside these repairs have been very well finished; they are barely discernable with the naked eye. With regard to the attenuation of the different copper alloys of the sculpture and the iron it was not possible to identify the variety of metals used, as they result in a similar attenuation of neutrons. Consequently no iron core pins are visible in the neutron tomography data. In principle, measurements and dimensions can be assigned to all the features and parts of the statuette, such as wall thicknesses, with an accuracy of 0.25 mm.

Results - XRF

Data taken at various points on the *Striding Nobleman* indicate that the alloy is heterogeneous, as was to be expected for a Renaissance bronze statuette. This is consistent with the theory that heat treatments, such as those that have taken place on this sculpture, influence the surface composition. The concentrations of elements for eight analysis points are given in weight percentage in table 1. The values merely indicate whether or not an element is present as major, minor, or trace element. The overall composition comes close to a tertiary composition with copper (78-86 %), zinc (10-19%) and lead (0-3%), and small amounts of tin (0.1-0.5%), iron (0.1-1.1%), nickel (0.3-0.6%) and arsenic (0.1-0.6%). Small amounts of silicon (0-0.5%), silver (~0.1%), and antimony (0.2-0.3%) were detected, except in one analysis point, the hatch on the back of the sculpture (Table 1), which exhibits unusual contents. The results indicated nothing unusual with regard to Renaissance compositions as these amounts are frequently found in these kinds of objects. In the past this sculpture has been heat treated as shown with neutron tomography in figures 2a/b. This finding is confirmed by the diffraction data.

Results – Neutron Diffraction

Figure 5 shows the measurement points on the neutron tomography data of the statuette for which diffraction data were collected. Figure 6 shows portions of the diffraction patterns for two analysis points. The results of the Rietveld refinements are compiled in table 2. The lattice parameter of the copper-type phase is a strong indication of a change in alloy composition. A phase fraction entry in brackets, e.g. (<2.0), indicates an "upper limit" of a phase not actually observed in the data, based on the statistics. Basically only three different copper alloy compositions were found in the *Striding Nobleman*.

The main alloy of the sculpture, i.e., inside the wall, is a copper alloy characterized by an average lattice parameter of 3.6506 Å, which varies only slightly in the wall scan. Further crystallographic phases are observed inside the wall of the statuette: a Pb phase with an average content of 3.5wt%, and a ferritic Fe phase with an average content of 0.8wt%. Rather surprisingly, the amounts of Pb and Fe from neutron diffraction correspond closely to the XRF data from the surface. Considering that the XRF measurements predominantly identify Zn as the alloying element, the Zn contents in the copper alloy phase can be estimated to 16.8 wt% (Table 2). However, this calculation ignores the effects of other alloying elements on the copper alloy lattice. It should be noted that at various points on the front of the statuette, small amounts (0.8 wt%) of a secondary fcc phase with a lattice parameter of 3.588 Å are found (Table 2). The lattice constant of this phase is characteristically lower than the lattice constant of pure copper.

Table 2 (right page): Neutron diffraction results from the *Striding Nobleman* statuette. Position of analysis points (run numbers) are visualized in figure 5. Lattice parameter of the copper alloy; the estimated standard deviation for the lattice parameter is 0.0001 Å. Refined, relative phase fractions of copper-type alloy phase, Pb, ferrite, cuprite, and Fe-Ni-Cu. The standard deviation for the weight fraction values for the given phases is of the order of 0.2wt%. Values in parentheses indicate upper limits for phases for which no Bragg peaks are observed, i.e. are not present. The copper alloy is partitioned into Cu and Zn fractions using the lattice parameter and Vegard's rule.

Analysis points	Rietveld refinement results						Calculated	
	Lattice parameter (Å)	Copper Alloy (wt %)	Pb (wt %)	Alpha Fe (wt %)	Cu2O (wt %)	Fe-Ni-Cu (wt %)	Cu (wt %)	Zn (wt %)
Wall scan along front (Fig.5b)								
140891	3.6506	96.8	2.5	0.7	(<0.3)	-	83.4	16.6
140892	3.6514	96.4	3.1	0.5	(<0.1)	-	83.1	16.9
140893	3.6500	96.2	2.8	0.2	(<0.2)	0.8	83.7	16.3
140894	3.6496	99.0	(<3.5)	1.0	(<0.1)	-	83.0	17.0
140895	3.6501	98.9	(<2.3)	1.1	(<0.6)	-	82.8	17.2
140896	3.6506	95.6	3.3	1.1	(<0.3)	-	82.9	17.1
140897	3.6494	98.4	(<5.3)	1.6	(<0.9)	-	83.2	16.8
140898	3.6507	100	(<2.0)	(<0.2)	(<0.1)	-	83.4	16.6
140899	3.6511	96.2	3.5	0.3	(<0.2)	-	83.2	16.8
140900	3.6517	95.4	3.5	1.1	(<0.2)	-	82.9	17.1
140901	3.6508	96.2	3.3	0.5	(<0.2)	-	83.3	16.7
140902	3.6509	95.0	3.9	1.1	(<0.4)	-	83.0	17.0
140903	3.6510	95.8	3.1	1.1	(<0.1)	-	83.0	17.0
140904	3.6512	96.0	3.2	0.8	(<0.1)	-	83.2	16.8
140905	3.6502	95.5	3.6	0.1	(<0.2)	0.8	83.6	16.4
140906	3.6504	96.6	2.5	0.9	(<0.5)	-	83.2	16.8
140907	3.6507	95.2	3.7	1.1	(<0.1)	-	83.1	16.9
140908	3.6501	95.2	3.7	0.4	(<0.1)	0.7	83.6	16.4
140909	3.6511	95.9	3.0	0.5	(<0.1)	0.6	83.2	16.8
140910	3.6513	95.9	3.7	0.4	(<0.1)	-	83.1	16.9
Support at back (Fig. 5f)								
140918	3.6654	100	(<3.3)	(<0.1)	(<1.0)	-	77.0	23.0
Internal wedge-shaped plugs (Fig.5e, Fig.5g)								
140888	3.6524	94.5	5.5	(<0.1)	(<0.5)	-	82.7	17.3
140920	3.6499	100	(<5.3)	(<0.5)	(<1.1)	-	83.7	16.3
140921	3.6494	97.2	2.8	(<0.1)	(<0.1)	-	84.0	16.0
Internal collar bar (Fig.5d)								
140889	3.6160	97.0	(<1.4)	(<0.2)	3.0	-	98.6	1.4
140890	3.6159	97.0	(<0.3)	(<0.3)	3.0	-	98.6	1.4
140911	3.6162	97.9	(<1.4)	(<0.1)	2.1	-	98.5	1.5
140919	3.6513	95.4	3.6	1.0	(<0.3)	-	83.2	16.8
Proper right Leg (Fig.5c)								
140912	3.6626	100	(<4.2)	(<0.1)	(<0.3)	-	77.6	22.4
140913	3.6623	100	(<6.4)	(<0.1)	(<0.8)	-	77.6	21.7
140914	3.6606	100	(<6.4)	(<0.6)	(<1.1)	-	77.9	22.1
140915	3.6534	97.4	2.6	(<0.1)	(<0.1)	-	82.4	17.6
140916	3.6537	97.9	2.1	(<0.1)	(<0.1)	-	82.3	17.7
140917	3.6528	97.5	2.5	(<0.2)	(<0.3)	-	82.5	17.5

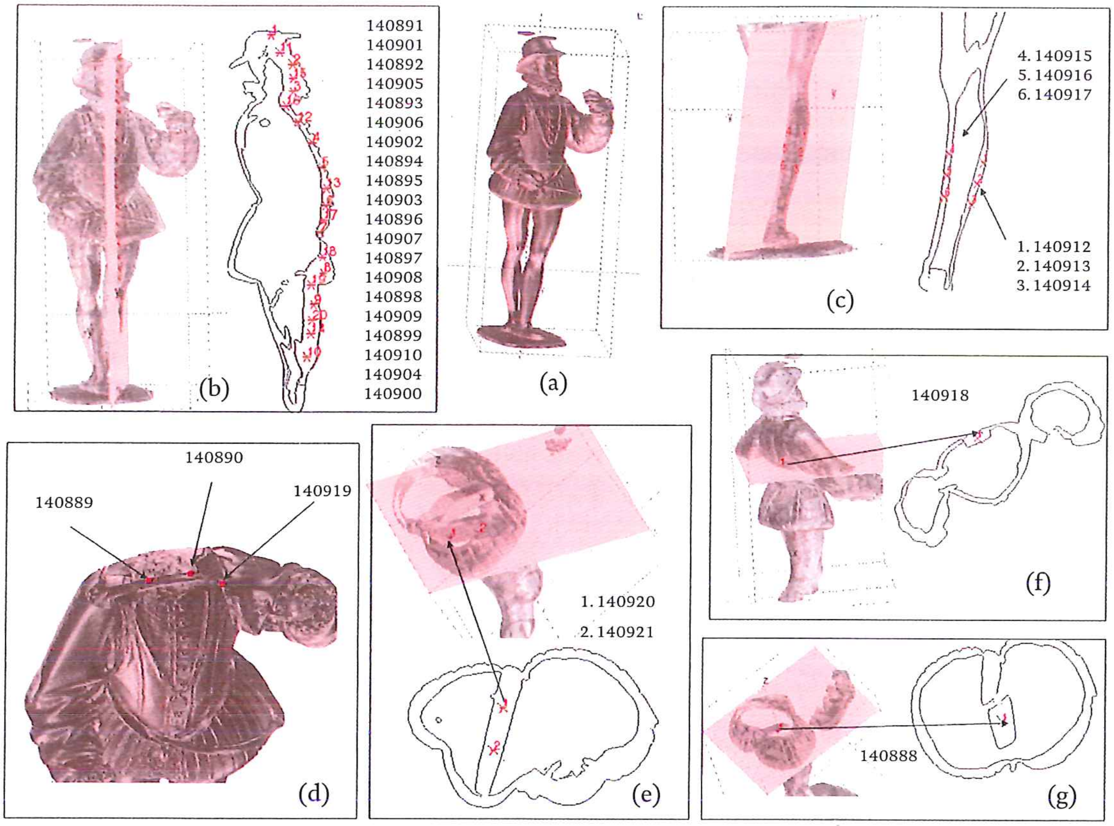

Fig. 5: Neutron analysis points, selected on the tomography data by SScanSS. The run numbers, e.g. 140891, refer to table 2. The shaded planes facilitate the selection of analysis points on the virtual model.

While different interpretations of the elemental compositions are possible for the observed lattice parameter, e.g., as Ni-Cu phase or as Fe-Ni-Cu phase, the latter is adopted as the more likely composition because of the good match with a Fe-Ni-Cu database entry.[23]

An internal support bar in the back of the sculpture reveals a slightly larger lattice parameter, and a corresponding Zn content (Fig. 5f). Furthermore, the lattice parameter of the alloy on one side of the right leg is slightly increased (Fig. 5c; points 140912, 140913 and 140914), indicating a different alloy composition. The data for these points contain significantly lower statistics, mainly because the path lengths of the neutrons through the material are longer. We have also considered a partially filled gauge volume to explain the reduced counts for these points, but came to the conclusion that this cannot account for the observed increase of the lattice parameter. The alloy compositions of internal wedge-shaped plugs in the lower part of the sculpture (Figs. 5e/g) are comparable to the composition of the wall. In contrast, a bent collar bar at the height of the shoulders reveals a completely different alloy composition, as indicated by a lattice parameter of 3.6160 Å, which is close to the lattice parameter of pure copper. The calculated Zn content of 1.5% is barely significant. In addition, the collar bar exhibits a small amount of Cu_2O (which could have been caused by re-heating the sculpture and where no flux could protect the Cu from oxidizing).

More information can be obtained from a shape analysis of the Bragg peaks. Figure 7 compares the (200) Bragg peak for the wall, internal collar bar, and the internal support plugs. First, the peak positions are indicative of the lattice parameter, i.e., Zn content, which is the same for the wall and the plug but different for the wall and the collar bar. Secondly,

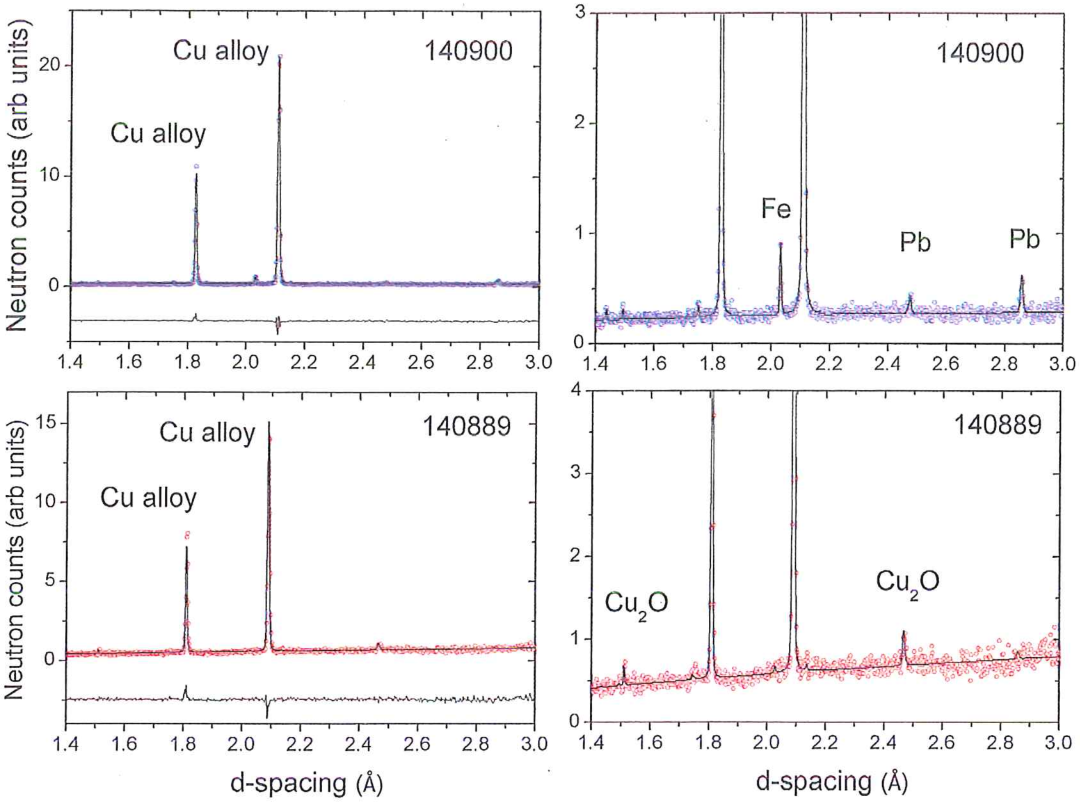

Fig. 6: Sections of neutron diffraction patterns.

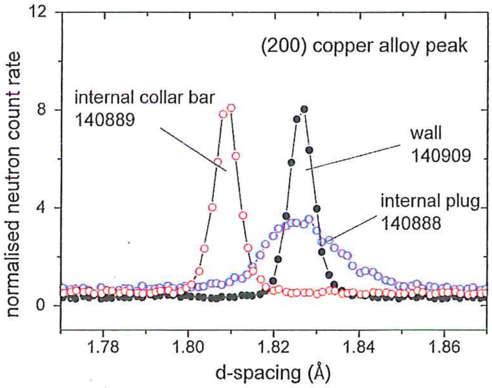

Fig. 7: Comparison of neutron diffraction peak profiles, (200) Bragg peak, for different analysis points.

the profiles of the wall peaks are narrow, almost matching the instrument resolution, indicating a homogenized copper alloy (which could indicate heat treatment). The very broad peak profiles of the internal plugs tend to indicate as-cast alloys, exhibiting segregated, dendritic microstructures, although they have the same composition as the wall.

Discussion – Methodology

The combination of imaging and diffraction data allowed us to characterise external and internal parts of the *Striding Nobleman*. The approach allowed for the efficient combination of high-resolution tomography (~0.2 mm) with spatially-resolved, compositional or microstructure data from diffraction (few mm^3). The SScanSS program significantly simplified the alignment procedures for the neutron diffractometer measurements, a task which could not have been mastered without such software and control tools. The diffraction experiment is mainly set up and optimised on the computer before the objects are even placed on the instrument. Moreover, the diffraction data could be collected in a reliable way only with the help of the tomography data. A diffraction analysis is meaningless unless the internal features are revisualised. On the other hand, the features in the tomography data can only be identified and further characterized using neutron diffraction data in combination with the XRF data.

It should be mentioned that the presented combination of imaging and diffraction techniques can be easily extrapolated to other procedures using software like SScanSS. For instance, neutron tomography data could be used to control an instrument for neutron resonance capture analysis, a large-scale elemental analysis method which was recently established in archaeological sciences.[24] Furthermore, X-ray imaging data could be used to control diffraction experiments.

Discussion

The *Striding Nobleman* has been analysed using neutron tomography where the attenuation of the neutrons indicated that different metals were used in the manufacture of the sculpture. In order to understand the production technique in more detail, a standard empirical test was done using a strong neodymium-based magnet to determine if core pins were still present. Core pins were more difficult to find as the sculpture appeared to be completely magnetic. Consequently XRF measurements were taken. The results showed a composition which corresponds with measurements taken in the past on Renaissance bronzes according to Basset *et al*, Bewer and Smith (Ref. 2 and 7). The magnetism was clearly an unknown effect that has now become apparent. It is theoretically possible that the iron originates from re-used bronze sculptures where the core pins were still present when re-melting the alloy. It is obvious that bronze can be re-used, but these sculptures are more difficult to understand. However, it was possible for a failed cast sculpture containing iron core pins to be returned to the melting pot. As the neutron diffraction results show that the ferrite is distributed throughout the object, a study of the literature was carried out for a better understanding of this phenomenon.

According to Strathmore and Aschenbrenner, the iron could have several other origins, for example, from the copper ore, or from metallic tools that were used in the smelting process.[25] To find out whether this could have been the case with the *Striding Nobleman*, magnetic response tests were carried out on approximately thirty Renaissance copper alloy statuettes at the Rijksmuseum. These showed that Renaissance statuettes which appear to contain zinc (based on former XRF measurements) are magnetic, whereas bronzes that do not contain zinc as a major element are not magnetic. We would like to point out that these results are preliminary, but they are extremely interesting for further research. This seems to exclude the possibility of Zn compounds pointed out by Strathmore and Aschenbrenner. Although calamine (ZnO) also contains small quantities of hematite (Fe_2O_3), this cannot explain areas of ferrite in a finished alloy. The cementation process in which calamine was mixed with Cu and charcoal was used up to the 19th century. By heating the components in a closed crucible the zinc is reduced and vaporizes at 907° C, so that the copper would alloy with the zinc vapour. Thus the possibly reduced iron would be left behind in the slag in the crucible.[26] Some experimental research was done to recreate an alloy containing the elements in two different proportions, one containing 10 wt% Zn and one 16 wt% Zn, along with 0.7 wt% Fe. Both alloys proved to be magnetic, but further research clearly needs to be undertaken to fully understand the magnetic response in Renaissance copper alloys.

Conclusions

This research was limited to investigating whether combining neutron tomography and neutron diffraction with the SScanSS software program will create new insights on the production techniques of Renaissance copper alloy statuette and more specifically of the *Striding Nobleman*. The results that were obtained were very helpful in two ways. First, it proved to be possible to determine the composition of any pre-determined part combining neutron tomography and neutron diffraction with SScanSS, and secondly it was possible to gain a better insight into whether the iron was used throughout the alloy of the *Striding Nobleman*. With regard to the first question, the importance of combining neutron techniques to produce new insights into the production techniques of Renaissance copper alloys became evident. With regard to the second question, it has now been proved that Renaissance copper alloys can be magnetic because of ferrite inclusions. Finally, it is clear that combining these techniques will also prove to be valuable for any other crystalline objects, and that further research is needed to determine the exact reason for the presence of the ferritic iron in Renaissance copper alloys. The art historical meaning of the object has changed as a result of the various neutron techniques that were applied. These results will now appear in a more art historical paper that will be submitted shortly. Finally, with regard to the use of neutron imaging and diffraction techniques, a new and exciting instrument is being developed with Imat, at ISIS (Ref. 15)

This instrument combines cold neutron radiography with diffraction analysis and can also be used to study archaeometric hypotheses. Museums are aware that many objects can be researched with these methods, and a great deal of new information can be obtained in a non-destructive way to place the art object in a new context. With the development of these instruments science is really helping museums to study the oeuvre of artists.

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Chapter VI

Casting and chasing of Renaissance statuettes: The use of TOF-neutron diffraction for studying finishing techniques on bronzes

Based on R. van Langh. L. Bartoli, J. Santisteban and D. Visser, "Casting technology of Renaissance bronze statuettes: the use of TOF-neutron diffraction for studying afterwork of Renaissance casting techniques", Journal of Analytical Atomic Spectrometry, 2011, 26, pp. 892-898.

Abstract

The finishing techniques of three Renaissance bronze statuettes in the Rijksmuseum Amsterdam were examined using time-of-flight neutron diffraction (TOF neutron diffraction) at the Rutherford Appleton Laboratory (ISIS) in Chilton on the ENGIN-X diffractometer. The research tested the hypothesis that a bronze sculpture which seems meticulously finished could have been cast without any finishing work of the surface being carried out with chasing tools. The statuettes with this specific feature are Willem van Tetrode's *Hercules Pomarius* (BK-1954-43) and the bust of *Pope Gregory XIV* (BK-16937) manufactured by Bastiano Torrigiani. Both of these sculptures date from the second half of the 16th century. A study of contemporary treatises indicates that casting without chasing was possible. A bronze figure from the beginning of the 16th century representing *Paris* (BK-1959-4) by Severo da Ravenna, which was without any doubt cast and chased, was analysed in the same way by way of comparison. Reference samples reproducing the techniques involved were manufactured to compare the results with the original objects. We proved that both the bust of *Pope Gregory XIV* and *Hercules Pomarius* were cast and not chased and that *Paris* was cast and chased.

Introduction

Renaissance bronze statuettes are highly valued by museums and collectors. In the past twenty years major museums and collectors, who conserve and exhibit these kinds of art objects, have shown that the study of sculptors' works must take into account both the art-historical context and the work's technical aspects to achieve a more accurate attribution.[1] From this perspective interest has grown with regard to the study of production techniques, which play an important role in the debate on authenticity. The research on Adriaen de Vries by Scholten *et al.* is an early example which involved both types of research.[2] Scholten *et al.* continued this line of research with the exhibition catalogues on the oeuvre of Willem van Tetrode.[3] More recently an exhibition catalogue by Allen *et al.* provided both a technical description of Andrea Riccio's sculptures, as well as details of his life.[4] Previously, Stone published a thorough study on the technical aspects of bronze sculptures of the Quattrocento.[5] Finally, Basset *et al.* produced a complete technical examination of Adriaen de Vries's sculptures.[6] Almost all of these studies focused on production techniques using traditional research equipment, from the naked eye and a microscope to X-radiography, videoscopy, X-ray fluorescence spectrometry (XRF), and with regard to organic and corrosion materials covering the bronze, also X-ray diffraction, Fourier Transform Spectroscopy and Gas Chromatography-Mass Spectrometry. However, in many cases these techniques proved to be inadequate for studying production techniques, unless it was possible to take a sample of the object. As these sculptures have a high economic and cultural value, taking samples of the metal is not desirable. Currently, more advanced non-invasive techniques, such as neutron tomography, have been applied to study art objects, as recently shown by Scholten *et al.*[7] This provides many opportunities for the study of production techniques.

This paper focuses on the finishing techniques, more specifically chasing, of bronze statuettes. The technique of chasing is based on flattening the surface using a hammer and iron chasing tool and is thought to have been used on each bronze after casting and removal from the mould (Fig. 1). As a result, all the casting flaws that might have been present on the bronze were removed. Two bronzes clearly stood out in a careful study of Renaissance bronzes in the collection of the Rijksmuseum. Fins (flashes) of metal were found on the outer surface of the bronze (Figs. 4a/b) of both *Hercules Pomarius* (Figs. 2a/b) by Willem van Tetrode and Bastiano Torrigiani's sculpture bust of *Pope Gregory XIV* (Fig. 3). In the past these bronzes had always been thought to have been cast and chased.[8] Apart from the fins of metal, Bastiano Torrigiani's bronze bust was remarkably thin (approximately 3mm) and was cast with great precision. This led to the following hypothesis: a bronze statuette could have been cast in the 16th century with such precision that no chasing of the surface was required. Specialists in museums throughout the world dismissed this possibility, as they believed that all bronzes were chased to remove the remnants of metal resulting from the casting process.[9] In order to prove our hypothesis, the above-mentioned works were compared with an analysis of Severo Calzetta da Ravenna's bronze statuette depicting *Paris*, which was undoubtedly chased after casting, as imprints of the hammer and chasing punches are visible. (Figs. 5a/b) The aim of the research was to identify the characteristic "strain fingerprints" left in the bronze by the chasing process, which are absent in an "as cast" specimen. This task is impossible using the above-mentioned traditional research equipment. Therefore, in order to study these effects the statuettes were taken to a Neutron Strain Scanner, specifically the ENGIN-X instrument at the Rutherford Appleton Laboratory in Chilton, United Kingdom. To test these ideas and assess the sensitivity of the technique, two reference samples were manufactured: one cast and unfinished, the other cast and chased using the traditional techniques. As this study describes, the neutron strain scanning technique provides precise answers for this type of research, and we were able to demonstrate that our hypothesis about the production techniques is correct.

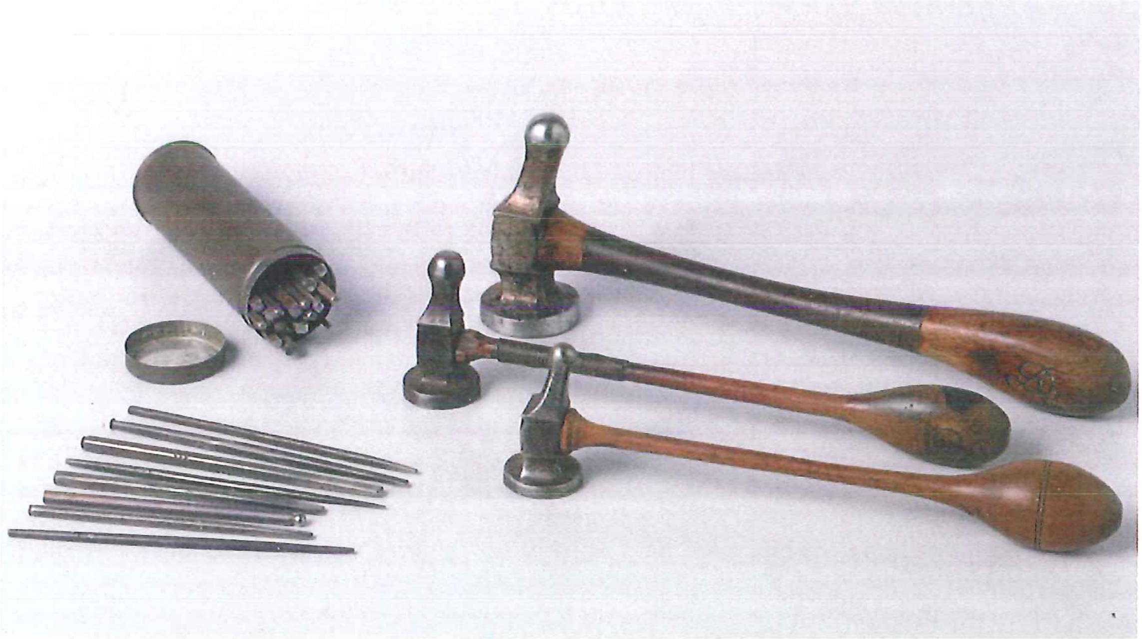

Fig. 1: Tools used in the chasing process.

Fig. 2a: *Hercules Pomarius*, overview of the sculpture.

Fig. 2b: Detail of the surface of the face illustrating the high quality of casting.

Fig. 3: Overview of bust of *Pope Gregory XIV.*

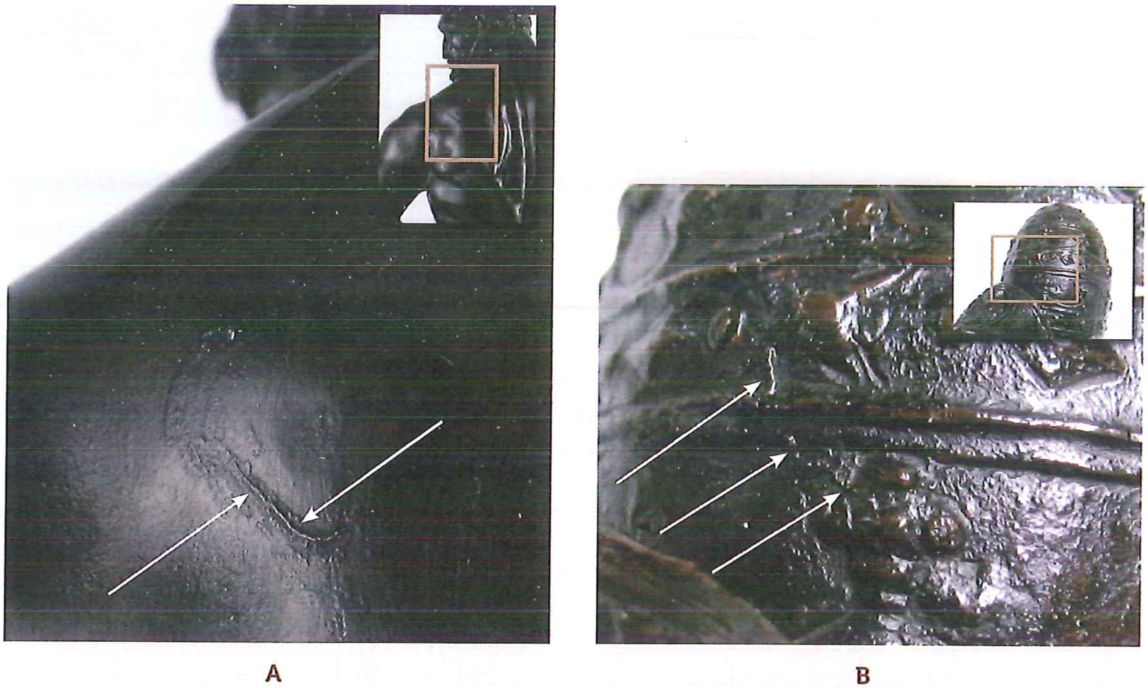

Fig. 4: Details of *Hercules Pomarius* and bust of *Pope Gregory XIV* showing the fins of metal indicated with the arrow.

Fig. 5a: Overview of *Paris*.

Fig. 5b: Detail of the torso showing the hammered surface.

The artefacts and reference samples

The *Hercules Pomarius* statuette, which was created circa 1568 by Willem van Tetrode (1525–1580), represents a defiant naked Hercules with a club, holding the three golden apples of the Hesperides. The major elements are copper, zinc and lead, as shown by an analysis using XRF. The arrow in figure 4a shows finning remaining on the left shoulder, which would have been removed if the bronze had been chased after casting.

The bust of *Pope Gregory XIV* was probably cast by Bastiano Torrigiani in 1590-1591. The steeply tapered bronze figure ends in a putto with a plinth underneath with the inscription “GRE. XIV”, referring to the name of Pope Gregory, whose short pontificate lasted from 1590-1591. The most distinctive feature of this bronze is the thin bronze layer 3-3.5mm thick, which is so perfectly finished that scholars in the past assumed it must have been meticulously chased. A fin of bronze similar to that on the *Hercules Pomarius*, was detected at the back of the tiara, where it continues over a pattern which could clearly not have been there if it had been chased (indicated on figure 4b with an arrow). The bronze is covered with a dark, presumably organic material which was not analysed. Qualitative analysis using XRF proved that the bronze consists mainly of copper and tin.

Severo da Ravenna worked as a sculptor between circa 1496-1543 in Padua. The figure depicts the Trojan prince *Paris*. The bronze was cast and heavily chased, as is evident from the rough surface of the bronze which bears clear indentations of the chasing tools, as shown in figure 5b. The bronze composition was also analysed by XRF, and the major elements are copper and lead.

The reference samples were produced to correspond with the composition of *Hercules Pomarius* and the bust of *Pope Gregory XIV*. Samples were cast and cut in two. One half was left as cast while the other was chased, using traditional production techniques.

Residual stresses in chased specimens

Depending on the quality of the wax surface and the moulding material, a certain amount of chasing would have been necessary to result in a final smooth bronze surface. Chasing tools, such as those depicted in figure 1, could have been used for this. The chasing tools would have altered the bronze surface structure in a similar manner to that resulting from shot peening, as evidenced in our own experiments.[10] Shot peening is an industrial process used in the manufacture of mechanical components. It is a mechanical surface treatment procedure which introduces beneficial residual stresses to the surface of a component and is widely used to improve fatigue performance.[11] The process involves bombarding the surface to be treated with shots of steel, ceramic or glass beads. The process is shown in the diagram in figure 6a, together with a simplified representation of the chasing tool.

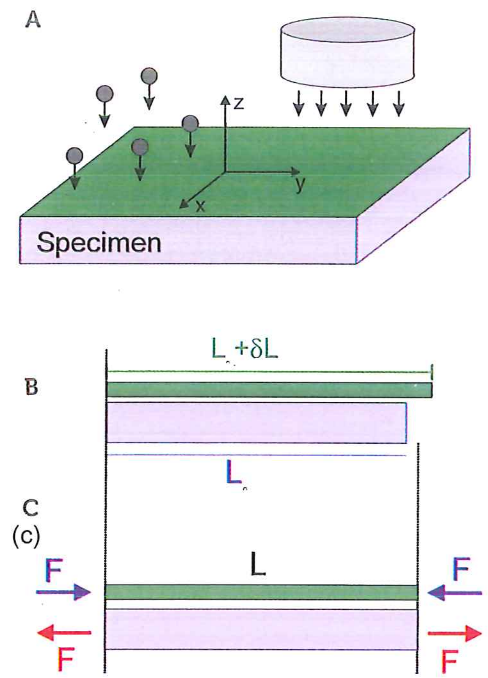

Fig. 6: Diagram showing the effect of chasing tools.

The origin of residual stresses in shot peening was discussed by Noyan and Cohen in their excellent introduction to stress measurement techniques.[12] In a simple model, it is assumed that a spherical shot will normally strike the surface layer of a flat piece of work, altering the structure of the layers. The plastic strain results from the force exerted by the shot. As the material is compressed in a particular direction, in-plane plastic deformation also occurs due to the conservation of volume. When a large number of shots impinge randomly on the surface, the plastic deformation in the surface plane is homogeneous. This in-plane plastic strain leads to a change in the length of the surface layers. This is represented in the formula in figure 6b: if the surface layer of an initial length L_0 could be separated from the rest of the specimen and shot peened (or chased in our case), the final dimension would be $L_0+\delta L$. This layer is now placed on the rest of the sample (the bulk), which still has a length of L_0. In order to match the dimensions of the surface layer and the bulk, surface traction F must be applied, as shown in the diagram in figure 6c. These forces will elastically deform both the bulk and the surface layer to a final length of L, which is between L_0 and $L_0+\delta L$. These tractions will cause macro-residual stresses in opposite directions in the surface and in the bulk volume, with blue arrows representing compression and red arrows representing tension.

Figure 7 shows another diagram representing these forces. It is more appropriate for the interpretation of the experimental results presented later in this work. The elastic strain field below the surface resulting from these in-plane forces is shown in the diagram in figure 7a. For the ideal scenario discussed above, the in-plane strain (ε_{xx} or ε_{yy}) is compressive (blue) for the surface layer and tensile (red) for the bulk. However, in practice the plastic deformation that occurs on the surface is not uniform, and there is a decline in plastic deformation from the surface into the bulk. As a result, the associated elastic strain field displays a much smoother transition between the two zones, which is represented by the broken black line in figure 7a. In any case, it seems clear that as a result of the plastic deformation of the surface, a chased specimen should contain an elastic strain field near the surface, which changes rapidly from the surface layers into the bulk.
Experimentally, it is easier for neutron strain scanning to measure the elastic strain that occurs along a direction normal to the surface rather than along an *in-plane* direction. Figure 7b is a diagram showing the elastic deformation predicted along the normal direction ε_{zz}, resulting from the in-plane stress field discussed above. The overall behaviour is similar to that expected for the in-plane strains, but the directions of the deformation have changed. As a result of the Poisson strain, i.e., the compressive strain that appears perpendicular to the direction of the tensile load, the normal strain is in compression where the in-plane strain is in tension, and vice versa. Therefore the elastic normal strain distribution depicted in figure 7b is the fingerprint of plastic deformation of the surface that we hoped to find in the experiments described here.

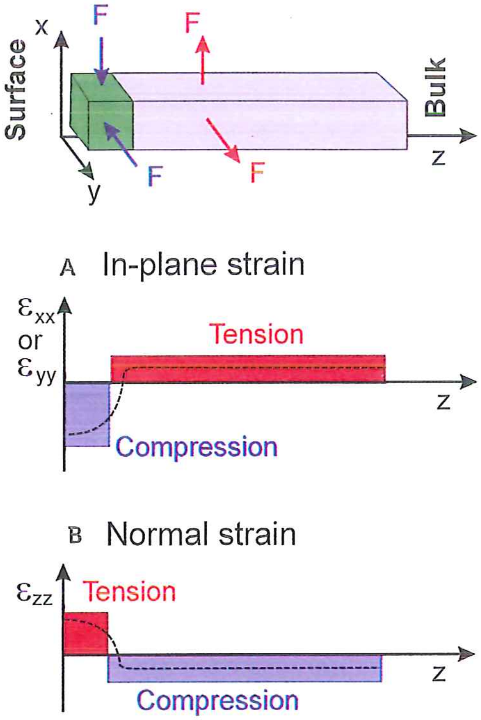

Fig. 7a/b: Diagram of strain effects representing the shot-peened effect.

Description of ENGIN-X

The residual stresses present in the specimens were assessed using ENGIN-X, the neutron strain scanner diffractometer at ISIS.[13] Siano *et al.* recently proved that ENGIN-X can be effectively used for archaeometric studies.[14] As discussed above, non-homogeneous plastic deformation introduces residual internal stresses which result in internal elastic strains. Basically, neutron strain scanning uses the planes of atoms as microscopic strain gauges, as elastic strain is demonstrated by shifts in the diffraction peaks due to very small changes in the distance between crystal planes. Thus stresses can be calculated using the strains that were measured by means of the elastic constants of the material, as shown by Lester and Aborn.[15] ENGIN-X is based on neutron diffraction, a standard technique for non-destructive strain scanning.[16] ENGIN-X uses a polychromatic neutron beam and the time-of-flight technique to perform a spectroscopic analysis of the neutrons diffracted by the sample.[17]

In particular, we analysed the spectra recorded by two detection banks placed at ±90° from the incident neutron beam, as shown in figure 8, which represents an aerial view of the experimental set-up in diagram form. In this configuration the volume measured in the experiment is a cuboid determined by the intersection of the incident and diffracted beams, as defined by the use of slits or collimators. In a typical experiment, the sample is moved across the beam using a positioning table, and the strain at each location is determined from the shift observed in the diffraction peaks recorded by the detector. In the

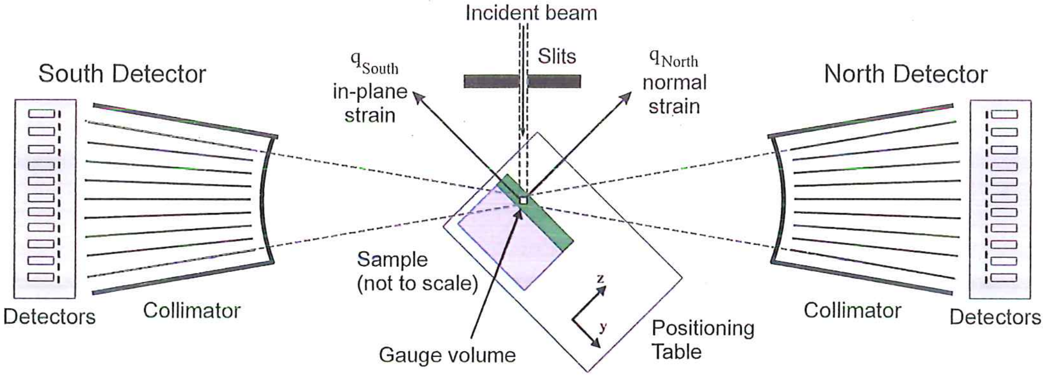

Fig. 8: Experimental set-up of ENGIN-X.

present experiments the sample was moved along a direction perpendicular to the sample surface, corresponding to the z-axis in figure 8. By moving the specimen along this line, we explored the strain within a gauge volume located at different depths from the surface of the sample. The measured strain ε corresponds to the component of the strain tensor along the direction of the momentum exchange vector **q**, located midway between the incident and diffracted beams, as indicated in the diagram. For the configuration presented in figure 8, the north detector samples the normal strain while the south detector samples the in-plane strain.

Experimental set-up

Renaissance sculptures are not industrial samples and cannot be treated as such. Therefore all the research must be carried out in a non-destructive way. The main problem in our case concerns the choice of a lattice parameter in the stress-free situation, i.e., the a_0 value. In neutron strain scanning, the elastic strain ε at each position is calculated using the change in the lattice parameter a of the cubic crystal structure (of copper in this case), $\varepsilon=(a-a_0)/a_0$. Strain is normally expressed in $\mu\varepsilon=10^{-6}$. To obtain a reliable estimation of a_0, it is necessary to release the residual stresses, which is usually done by removing a small piece from the object. This option is clearly unacceptable for valuable objects of fine art. To overcome this problem we decided to replace a_0 with an average of the lattice parameters measured from the surface to the interior of the sample. Although the absolute value may reflect a systematic error (consisting of the constant shift of the whole strain profile), the shape of the strain profile curve should still contain the fingerprint discussed in the previous section.

Another rather difficult task was the choice of a trustworthy measurement spot. The main problem that we faced was that the measurement point should be as flat as possible. This turned out to be a real challenge, given the complex three-dimensional form of the sculpture. The *Hercules Pomarius* was analysed at the point next to the flash of metal on the left shoulder, because no chasing is expected at that spot. A second measurement was taken on the left thigh. The bust of *Pope Gregory XIV* was analysed at a point on the forehead. First, because the forehead was the only spot with a reasonably flat surface, and secondly, because if there had been any chasing on this sculpture, this would be the most obvious place to look for it. The *Paris* figure was analysed at a point on the right upper leg. Furthermore, the two cast parts were both measured in a stress-free position, as well as a chased position.

The dotted area in figure 9 shows a typical diffraction spectrum measured for the *Paris* bronze. The lattice was determined using a full-pattern least squares refinement of the diffraction spectrum, which allowed the peak positions to remain unconstrained, according to Pawley.[18] A Pawley-type analysis was performed for this work using the GSAS computer code.[19] A typical refinement for the *Paris* bronze is shown by the solid red line in figure 9. The dimensions of the gauge volume used for these studies were 0.5mm x 0.5mm for the small square cross section shown in figure 5, with a height of 5mm in the direction normal to the plane of the page.

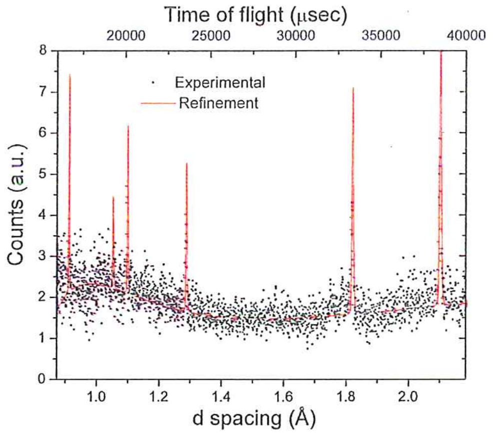

Fig. 9: Example of a diffraction spectrum. The dots are experimental data as acquired on ENGIN-X; the red line is the refinement.

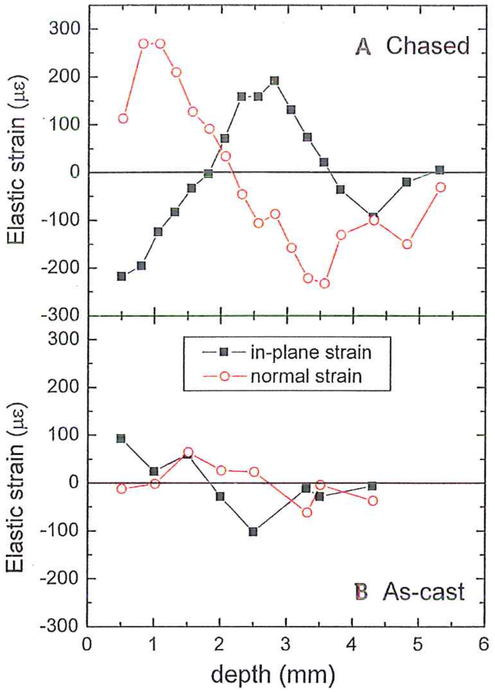

Fig. 10a/b: Behaviour of the elastic strain in the chased and as-cast (unchased) samples. The experimental uncertainty in the strain is 70 με.

Results

The results obtained for chased and as-cast (unchased) reference samples are shown in figure 10a and 10b respectively. The typical uncertainty for all points is 70 με. The reduction in elastic deformation from the surface into the bulk is clearly visible in the chased sample, for both the in-plane and the normal components of the strain. The directions of the deformation are opposite for the in-plane and normal strains, with a behaviour that undoubtedly resembles the curves discussed in figures 7a and 7b respectively. The transition between tension and compression appears to happen at a depth of about 2mm. By contrast, low strain values without a clear pattern are observed for the as-cast reference sample. The strain values for the unchased sample are very close to zero: a value of 100με that is very close to the uncertainty in the strain determination. These results prove that the neutron strain scanning technique can non-destructively assess the effect of chasing on bronze specimens.

The measurement of the actual artefacts proved to be quite difficult, mainly because of the uneven shape of the samples and their pronounced thickness, which caused a high absorption in the bulk of the material for one of the two banks, depending on the orientation of the sample itself. For example, in the case of figure 8, diffracted neutrons reach the south detector after passing through the whole thickness of the sample: absorption phenomena therefore occur, leading to an extremely active and unreliable diffraction pattern for the least-squares refinement. For this reason, only one bank (the north bank measuring the normal strain) will be considered in the following results.

Figure 11 shows the results obtained for the three artefacts: (a) the figure of *Paris*, (b) *Hercules Pomarius*, and (c) the bust of *Pope Gregory XIV*. A comparison of the behaviour of the strain for the three artefacts with that derived from the reference sample suggests that the hypotheses raised in *Paris* about the production techniques of the objects are confirmed. *Paris* shows clear evidence of chasing with a compression on the actual surface followed by a tension in the bulk. In contrast, the values of the strain for the *Hercules Pomarius* and the bust of *Pope Gregory XIV* do not show any clear fingerprint of mechanical treatment.

A final comment should be made regarding the hypothesis concerning the strain scanning technique. By showing the results in figure 11 as elastic strains, we suggest that the spatial changes measured in the lattice parameter are exclusively due to stresses within the sample, and are not caused by a local variation in the composition of the alloy. This hypothesis was confirmed in this experiment. Variations in alloy composition were ruled out by showing that different diffraction peaks, i.e., 111 and 200, produced different strain profiles, as was to be expected from the elastic and plastic anisotropy of the face-centred cubic structure of the material.

Conclusions

Two Renaissance bronzes from the collection of the Rijksmuseum, the *Hercules Pomarius* by Willem van Tetrode and the bust of *Pope Gregory XIV* by Bastiano Torrigiani, show a metal fin where it was expected to be smoothly finished. The hypothesis arose that these bronzes were cast without chasing at all. A third sculpture, a *Paris* figure from Severo da Ravenna that undoubtedly was cast and chased, was examined for the purpose of comparison. The sculptures were tested together with reconstructed samples with the same composition using neutron strain scanning on Engine-X at the Rutherford Appleton Laboratory (ISIS). The comparison of the strain patterns confirmed the hypothesis that that both *Hercules Pomarius* and *Pope Gregory XIV* were cast and not chased, while *Paris* was cast and chased. This proves the possibility that 16th-century sculptures were cast with such a high degree of precision that no further work was needed. This conclusion reveals a forgotten production technique for Renaissance bronze statuettes.

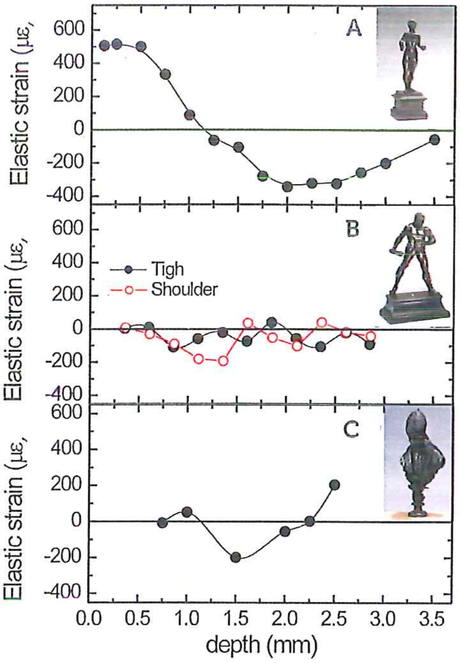

Fig. 11: Behaviour of the elastic strain on the three sculptures. The experimental uncertainty in the strain is 70 με. A distinctive "chasing" strain profile can be observed in *Paris* (a), which is clearly not present either in *Hercules Pomarius* (b) or in the bust of *Gregory XIV* (c).

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9 During the conference on Willem van Tetrode at the Frick Collection in 2003, the author suggested that the back of this sculpture could not have been finished using files or other abrasive stones. It elicited a debate in which many specialists doubted this possibility.

10 I would like to thank Marco Klijsen from Straaltechniek International BV, Bunsenstraat 1, 3316 GC, Dordrecht, The Netherlands, info@straaltechniek.net for providing the shot-peened samples.

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Chapter VII

Innovations in the casting technology of 16th-century European bronze sculptures

Introduction

As is often said, the appearance of a bronze sculpture was – and is – determined by the work carried out afterwards: the chasing, the finishing process with hammers and punches. The sculptor treats the surface of the bronze by chasing it to determine its final appearance.[1] Chapter VI showed that two sculptures in the collection of the Rijksmuseum Amsterdam were cast in such a way that they were *not* chased, although the surface would suggest otherwise. At the time I believed that casting without chasing was a southern European invention because the bronzes that were studied were of Italian origin. By examining these suspicions in a more general way I studied the finishing techniques in Renaissance bronze sculptures in a broader context. As a result I came across southern German examples dating from an earlier period than the Italian sculptures in the Rijksmuseum which did not reveal any traces either of being chased with a hammer and punch. Furthermore, in going through the contemporary treatises I came across references to casting without the need for chasing. The most important sources related to chasing and this phenomena are *Cennini's Il Libro dell'Arte* (1437)[2] Pomponius Gauricus's *De Sculptura* (1504), Biringuccio's *De La Pirotechnia* (1540) Giorgio Vasari's *Le Vite* (1550 and 1568) Cellini's *La Vita* (1568) and his *Due Trattati* (1568) and finally, Raffaello Borghini's *Il Riposo* (1584). In this chapter I have tried to find an explanation of the phenomenon of casting without chasing. Although the history of the development of Western bronze sculpture mainly took place south of the Alps after the Middle Ages and the art-historical research has therefore concentrated on the Renaissance in Italy up to now, there are strong indications that in the 16th-century casting technology was developing north of the Alps, in particular in Southern Germany, and only spread to Italy in the third quarter of the 16th century. These "Northern innovations" in the art of casting bronze have a central place here.

Fig. 1: A statue of *Hercules* by Primaticcio after an original in Rome. Chateau Fontainebleau (photograph by (C) RMN (Château de Fontainebleau) / Gérard Blot).

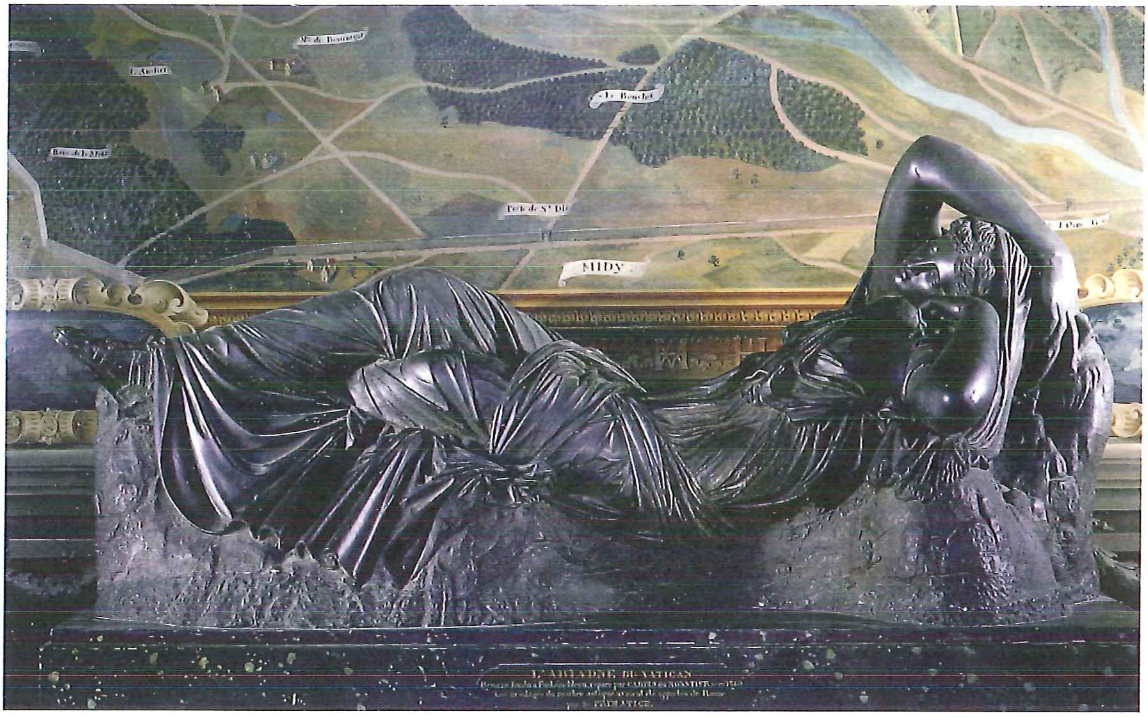

Fig. 2: The *Sleeping Nymph*, a copy executed by Francesco Primaticcio after an original in Rome. Chateau Fointaine-bleau (photograph by (C) RMN (Château de Fontainebleau) / Georges Fessy).

When we talk about the Northern Renaissance we are referring particularly to the French court and the cities of Southern Germany. The success of Italian bronze sculpture spread to France in the 16th century. King Francis I brought several prominent Italian sculptors to France, including Leonardo da Vinci (1452-1519), Francesco Primaticcio (1504-1570), Gianfrancesco Rustici (1474-1554) and Benvenuto Cellini (1500-1571). The French King hoped to introduce monumental bronze sculpture in France. Unfortunately a great deal was lost, or not achieved. However, Cellini's *Nymph van Fontainebleau* survived and Primaticcio made a series of bronze reproductions of classical statues from Rome, including a *Hercules* and the *Sleeping Nymph (Cleopatra)* (1542-1543).[3] These casts were made following the Italian method of bronze casting. Parts of the surface of the nymph are really rough, (while the Hercules has a surface that was clearly hammered). Apparently the bronzes did not come out the mould with a smooth surface and a close examination of these bronzes reveals a typical surface that requires chasing. In my opinion, this is characteristic of the Italian method of bronze casting in the 16th century.

During the period that Cellini spent in France he developed himself as a bronze sculptor next to his superb qualities as a goldsmith. Cellini's activities in France were thoroughly documented in his detailed autobiography and his two treatises. These reveal that he worked for the French court both as a sculptor and as a goldsmith. His most important work is the famous salt cellar for Francis I, which was completed in 1543. During the same period he made the bronze nymph, which crowned the monumental gateway to the king's country retreat at Fontainebleau. Cellini's autobiography was published only in the 18th century.[4] His *Due Trattati* was published in Florence in 1568. These reflect his own working practice and provide a clear picture of the materials and procedures involved in the work of a bronze caster and goldsmith.

From the 15th century, bronze casters from Southern Germany in cities such as Nuremburg had acquired a great deal of experience of casting and working copper containing zinc and lead, which they called "Rotguß". The reddish-yellow alloy was often used to make small artefacts, such as jugs and dishes. The Nuremburg family of casters, the Vischers, headed by Peter Vischer the Elder (circa 1455-1529), played a particularly important role in this respect. In fact, the influences of the Italian Renaissance style can be detected in the Vischer workplace at an early stage. From the technical point of view the Vischers could certainly compete with the Italians: the shrine of St. Sebald, the most important bronze-monument from the Vischer workplace (1507-1519), was

Fig. 3: The interior of the Hofkirche in Innsbrück, (photograph by G. Watzek, Fotoarchiv Tiroler Volkskunstmuseum).

made at a time that the sculptor Riccio was working on his monumental (and technically comparable) Paschal Candlestick in Padua. However, the climate for bronze sculpture north of the Alps was perhaps less favourable than in the south. This may have changed as the result of an ambitious imperial initiative: the cenotaph of Emperor Maximilian I for the Hofkirche in Innsbruck, for which South German bronze casters played a main role. Dozens of larger than life-size bronze figures of the ancestors of the Hapsburgs were to be placed around the Emperor's monument, a project that was unparalleled in Europe in artistic and technical terms.

The project was historically examined in detail by Vinzenz Oberhammer (1955) and Lucas Madersbacher (1996). The technical research into this important group was carried out by Otto Knitel (1987?). These authors' findings are described in this chapter, obviously supplemented with my own observations and interpretations. This project deserves further attention because it includes examples of monumental bronze sculpture which came out of the mould in such good condition that no chasing was necessary.

One of the artists was the painter and sculptor from Munich, Gilg Sesselschreiber (active from 1496 – died after 1520), who was commissioned to do this work by the Emperor in 1508.[5] He worked together with the bronze caster Peter Leiminger (Löffler).[6] Sesselschreiber had not delivered a single statue seven years later.[7] Making the first statue, which represented Ferdinand of Portugal (made partly in 1509, 1514 and 1516), got off to a difficult start. It was largely cast by Löffler, while some parts were made by Christoph Sesselschreiber, Gilg Sesselschreiber's son.[8] The emperor was dissatisfied with the slow progress, and he approached Peter Vischer the Younger (1487-1528), the Melchior brothers and Stefan Godl to speed up the work on the cenotaph and urged Sesselschreiber to become more productive. These three craftsmen from Nuremburg were responsible for the majority of the 28 statues that were made.[9] It is striking that the Hapsburg emperor did not call upon Italian bronze sculptors for the creation of his enormous cenotaph, but turned to South German bronze casters and designers, even when the project was going through a difficult stage at the start. As we shall see, the lengthy history of the creation of this imperial cenotaph was accompanied by innovations in the casting of the bronze statues. These innovations were still unknown in Italy at that time.

Bronze casting as described by Biringuccio and Vasari

It is necessary to understand how the casting processes differed in various degrees from the methods described in the contemporary literature. In this way one can understand the results of the casting surface that could be obtained after the molten metal solidified in the mould. Casting bronzes using wax models could also differ depending on the sculptor and the foundry, but broadly speaking, the casting process probably took place in the way described by Biringuccio in his treatise *De la Pirotechnia*. The sculptor started with an iron rod and kneaded clay with remnants of clothing around it in the general shape of the statue he was making. This clay core was fired in the oven, and when it had cooled down, the sculptor sculpted the final work around this with wax. According to Biringuccio, bronze pins – as thick as a finger and to a depth of the palm of a hand – were pushed through the layer of wax into the core and these protruded through the wax to a length of three or four fingers.[10] Then a mixture was made of clay, remnants of clothing, the ash from a ram's horn and iron filings. This mixture was finely ground, sieved, and mixed with water; the paste obtained in this way was applied to the layer of wax. This was repeated about six times and was applied every time when the previous layer was almost dry. Once it had dried out, the whole work was enclosed with iron bands so that it could not fall apart. Holes were made in the outside down to the wax model to serve as sprues and vents. The wax melted out through these channels into a reservoir over a copper boiler, making sure that no other materials could fall into the sprues. Biringuccio was describing the so-called direct method, which could only be used to cast unique sculptures, rather than several copies of a single model.

Biringuccio then went on to describe a method to make a cast of a model or an existing sculpture. After applying sheep fat, pig fat or oil to the model, individual moulds were placed around it with liquid plaster, and numbered. When these had dried out, they were removed and put together again. A layer of wax was pressed into the inside of this plaster mould, and then the whole thing was filled with clay. Biringuccio explained that it was a big challenge for some sculptors to cast a bronze with very thin walls, and that they therefore applied an additional thin layer of wax. Biringuccio also described several different versions of his first method. For example, he described the lengthy way in which a complete clay model was first made and then fired, only to have a layer of the clay surface scraped off and replaced by wax. In another version Biringuccio replaced the clay of the core with a mixture of organic material, such as rope, fabric and glue, which was then covered with a wax top layer in the form that it was to be cast.

Finally, the method using the "plaster technique" was also important. This type of casting is also called slush casting. The method used clay to create the model of an existing object, and then hot wax was poured into the clay. By decanting the liquid wax straightaway, a thin layer of wax which had set remained behind on the inside of the clay mould. This was then filled with a liquid mix of clay, remnants of fabric, horse dung, a small quantity of the ash of a ram's horn and plaster. This was followed by the standard process described above.[11]

Vasari followed Biringuccio's descriptions to some extent: according to Vasari, a plaster model was made of a detailed clay model. A core consisting of an iron pin surrounded by clay, horse dung and hair was then placed in the hollow shape of this mould. In the meantime this clay core was fired and then thickened with the same mixture to a thickness approaching the inner shape of the plaster mould. After this core model had been placed exactly in the middle of the plaster mould, the narrow space remaining in between was filled with liquid wax. When the wax set, the plaster model was removed and the wax model was finished. The wax model was then covered with wet ash and core pins were put in position. In this respect Vasari's method differs from Biringuccio's. A fine clay substance mixed with horse dung and hair was applied to this wax model covered with ash, layer by layer. The core pins protruding through the outer casing were connected together to create a strong outer mould. Corresponding holes were made in the mould so that the molten wax could drain away through these. Vasari then described a technique for making the sprues and vents which were placed to connect the knee and the arm in a sculpture of a human figure so that the metal could flow freely. Biringuccio did not refer to this stage, although it is very useful. Vasari specifically mentioned that the sculptor/caster had to make sure that all the wax had flowed out of the model, and had to check this by weighing the wax before and afterwards. This was very useful advice as well, because shavings of wax that remained behind cause a small explosion when the liquid bronze was poured into the mould. Vasari also gave an example of the "plaster technique" in which wax was poured in and decanted in the same way as described by Biringuccio.

After the bronze had been poured and set inside the fireproof casing, the material of the mould was completely removed until the oxidised metal became visible. Then the sprues and vents were removed with a hammer and chisel and the bronze was finished with different tools, as described in both the first and second edition of Vasari's *Vite: "These casts being finished, the workman then, with suitable tools, that is, with burins, burnishers, chasing tools, punches, chisels and files, removes material where needed, and where needed, presses inward the overflow of the metal and smoothes it down."*[12] The fact that Vasari also mentioned the delicate tools in addition to the rough tools means that he was concerned with the treatment of the whole surface. These tools were used for different purposes. It is possible to work with great precision with a hammer and punch, as in the work of a goldsmith. The finishing techniques for bronze sculptures have not been sufficiently studied up to now.

With a good technical list of terms to qualify the surface of bronze sculptures, it might be possible to compare the differences better (and more objectively).[13] This means that the different surface finishes become more important, also with regard to the attribution to (the intentions of) a particular artist.

Casting bronze by Godl and Lobsinger according to Knitel

It is striking that Emperor Maximilian I did not commission any Italian sculptors and bronze casters to work on his mausoleum, even though he and his advisors must have been aware of the Italian achievements in the field of casting bronze. Instead, he opted for German bronze casters, who had no experience of casting such large statues (except for Vischer). The detailed technical study by Knitel reveals that Stefan Godl had developed his own casting method for the cenotaph of Maximilian I, which deviated from the Italian method in significant ways.[14] Godl started his models with an iron framework to which he applied a mixture of thin loam, horse dung and plaited straw. This core was then fired at a red-hot temperature, and after it had cooled down, a layer of wax was applied to it. He did this together with the sculptor and someone who cut the wax, so that they jointly achieved the desired result as the layer of wax determined the final bronze work.

From then on Godl adopted a different technique: he applied a layer of loam without mixing it with horse dung or any other organic material, and divided his sculpture up into different sections: first the feet, then the lower legs, then part of the knees up to the groin, and then further up the whole body. He made an opening for a sprue and vent between each of the successive sections. These channels were made of wax and they were plaited together up to the opening for the bronze to be poured in. When everything was dry, a start was made on the next step: applying the coating of clay. Iron rings were placed around the coating and the whole work was heated for a number of days so that the layer of wax melted out through the channels. The casting moulds now consisted of separate sections which could be taken apart. In this way he was able to perfect the inside of the mould in which the bronze would be cast. Afterwards, the moulds were put together and the whole thing was placed in the casting pit, where the molten metal was poured into the cavities.

Smaller sections, such as the hands or chains, were cast individually. After they had been cast in bronze, they were used to create the mould. The sleeves which had to fit around the hand now had to be cast around it. The same process could be used again for other sections as is shown in figure 5a/c.[15] Godl must have been in control of every detail of the process of casting bronze. Consequently he was able to achieve an exceptionally high quality, as revealed by a detailed study of the sculptures in the Hofkirche. Both *King Arthur* (cast by Vischer in 1513) and *Sigmund der Münzreiche* (cast by Godl in 1523), the first two sculptures to be produced, reveal casting characteristics in the bronze which show that the statues overall were not finished with hammers and punches, while the details in the ornamentation are so fine that they give the impression that they were finished in that way. In comparison with Italian work, this is surprising, because during the same period Italian

Fig. 4a: *Sigmund der Münzreiche*, front view. Cenotaph Maximilian I, Innsbruck. (photograph by Georg Steinmetzer).

Fig. 4b: *Sigmund der Münzreiche*, view from back. Cenotaph Maximilian I, Innsbruck. (photograph by Georg Steinmetzer).

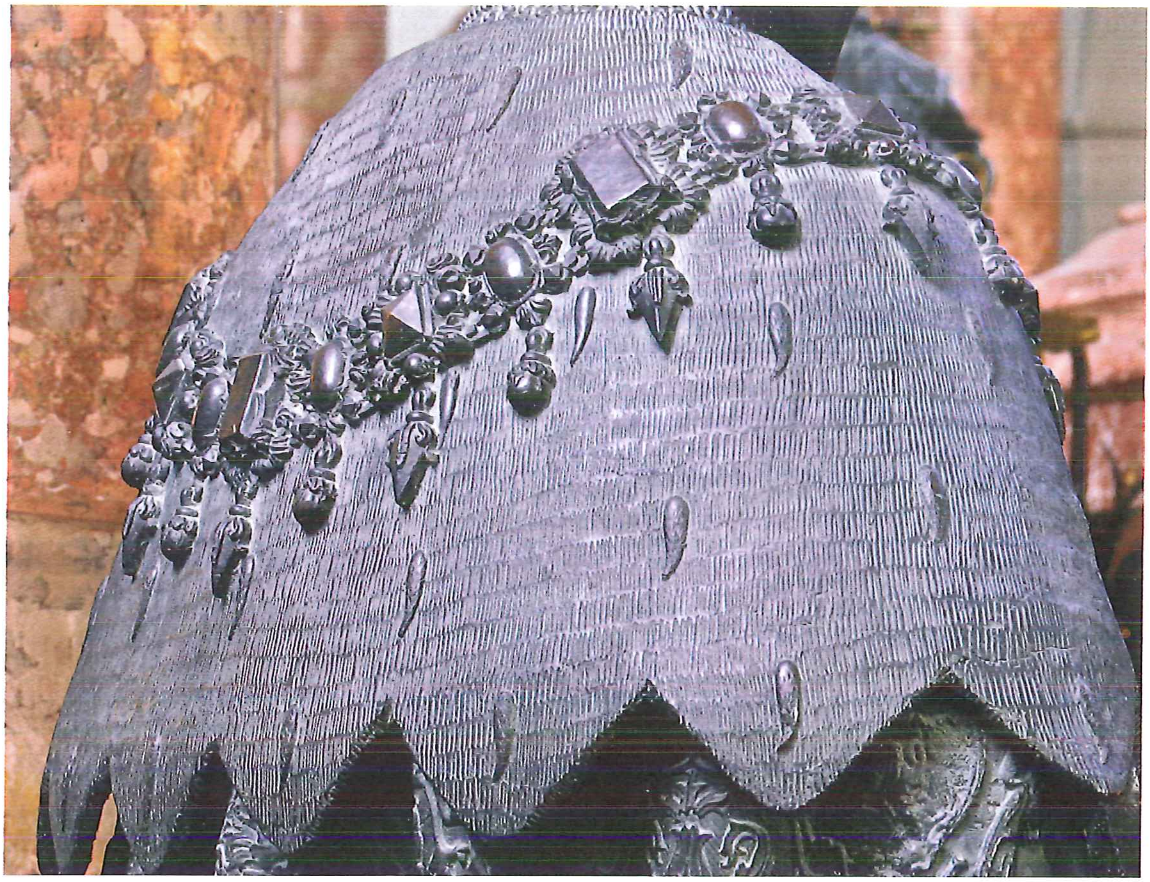

Fig. 4c: *Sigmund der Münzreiche,* A possible example of the technique described: detail of the overlapping cover with chains, where the chains were first cast in bronze. The bronze chains were re-used in the wax model of the cover. After casting of the cover with the bronze chains the same process was used where the bronze cover and bronze chains were used for the casting of the body of the sculpture. Cenotaph Maximilian I, Innsbruck. (photograph by Georg Steinmetzer).

bronzes, or bronzes cast in accordance with possible Italian methods, were chased. This was necessary in view of the casting results that were achieved using the Italian method (Fig. 7 and 18).

Chasing bronze and silver

Creating a sculpture involves several craftsmen.[16] According to Michael Cole, there were so many specialists involved that it is doubtful whether a sculpture can actually be attributed to a single artist.[17] This applies particularly for bronze sculptures, as the finish of the statue contributes to the appearance – and therefore to the end result – to a great extent. Because of this the role of the chaser must be taken into account in the assessment and attribution of bronzes on stylistic grounds. But to what level of detail? How much significance can be assigned to the technical execution of the bronze sculptures of one artist if they differ so much in the detail? For example, no one questions the attribution of a group of portrait sculptures to Antico, although the eyes of the statuettes can all significantly different.[18] A closer look at the different finishes for the eyes, could easily lead one to conclude that the different sculptures cannot be attributed to one artist whereas for less difference in apearance sculptures are not atributed to a certain sculptor. At the same time works are attributed or not attributed to an artist on the basis of the same detailed finish, for example, of the toes or hair of a sculpture. If the chaser was responsible for the finish, he was also responsible for these details, even in the works of different artists. In short, the role of the chaser in the creative process of a bronze sculpture is by no means marginal.

Fig. 5a: *Leopold*, front view. Cenotaph Maximilian I, Innsbruck. (photograph by Georg Steinmetzer).

Fig. 5b: *Leopold*, detail of head showing the enormous perfection of casting. Cenotaph Maximilian I, Innsbruck. (photograph by Georg Steinmetzer).

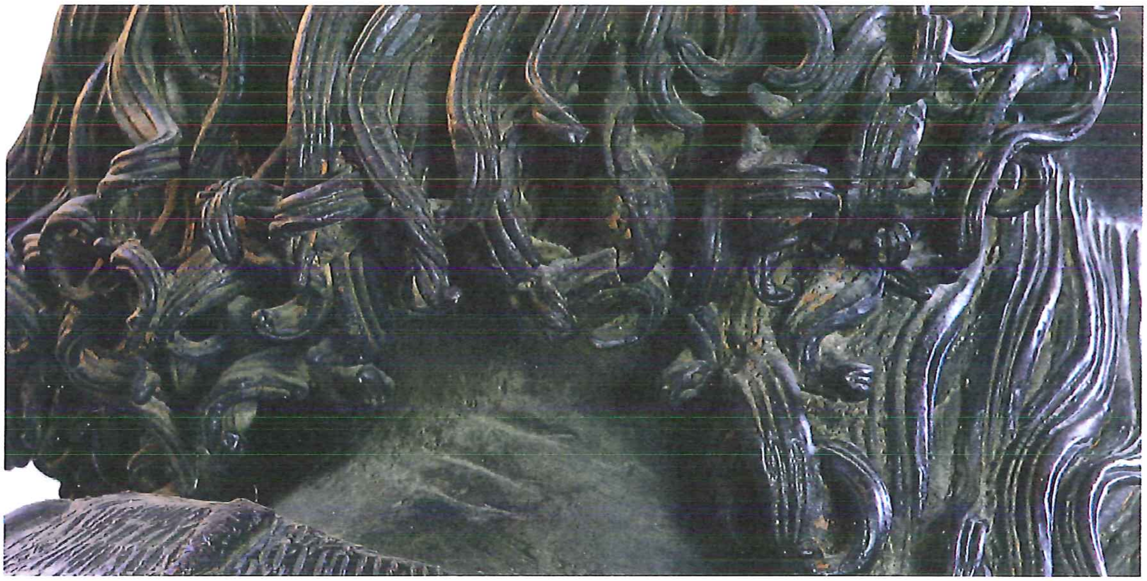

Fig. 5c: *Leopold*, detail of beard showing the enormous quality of the casting where no finishing was possible. Cenotaph Maximilian I, Innsbruck. (photograph by Georg Steinmetzer).

Chasing can refer to the details of the finish of any cast metal, which may be bronze, but also silver or other metals. In cast bronzes, it is essential that the metal is usually finished on only one side, because the inside of a sculpture is not accessible, or only poorly accessible. The cast metal is "dented" from the outside by working the surface with a hammer and punch. Chasing differs essentially in this respect from the "embossing" technique used by goldsmiths and silversmiths. In this process a thin plate of metal is worked with a punch on both sides, in copper, as well as silver and gold alloys. In the work of goldsmiths and silversmiths any distortions resulting from chasing can be corrected so that the process is more controllable and can ultimately lead to a very precise and deep level of detail. The enormous effect of depth and detail in the silver plaquettes of the Antwerp silversmith Matthias Melin (1589–1653) are good illustrations of this.

In contrast, if a hammer and punch are used to chase a bronze sculpture too forcefully, this can leave a deep impression that is irreversible. This means that for a bronze sculpture the design – and therefore the desired end result – must be formed by the sculptor as far as possible in the wax model. The task of the bronze caster (and possibly the chaser) is to reproduce the wax form in metal as accurately as possible. The goldsmith or silversmith creates a form and is responsible for the entire process from start to finish. This is an essential difference between a bronze chaser and a goldsmith. It is a common mistake to consider these two as being one and the same. The goldsmith has to think in three-dimensional terms, just like a sculptor. Many of his figures and ornaments are modelled, cast or embossed. Several 16th-century sculptors, like Cellini and De Vries, initially trained as goldsmiths and switched to making bronze sculptures later in their careers. Goldsmiths and silversmiths who do not develop a good three-dimensional insight will probably be limited to chasing metals. However, it does seem as though goldsmiths had a better understanding of the skill of chasing metal than others, as revealed by the remark of Pomponius Gauricus. He mentioned two goldsmiths – Charadoxus from Milan and Franciscus Fornius from Bologna – who allegedly excelled in chasing metals, compared to their colleagues who were not goldsmiths.[19] His comment could also explain why Cellini used chasers who were also goldsmiths for his bronze *Perseus*: Gianpaolo and Domenico Poggini, Alessandro di Pagno and Zanobi di Pagno Portigiani.[20]

Finishing a bronze

The extent to which bronzes were chased (or even the entire absence of chasing) deserves further consideration as regards the difference between the casting of bronzes in Germany and in Italy. If it has been cast well and has not (yet) been finished, the surface of a bronze is determined by the extent to which the wax layer of the cast model was finished, and by the print of that wax layer in the material of the mould. For smaller and medium-sized bronzes, some of which are intended to be seen from a short distance, or even studied close up, the following three characteristic surface finishes can be distinguished.[21]

First, the metal can be intensively finished by being chased. In that case the final form of the bronze is to a large extent

Fig. 6: Matthias Melin (BK-NM-603), embossed silver plaquette depicting the entrance of Giovanni Battista Spinola and his wife Maria Spinola into their newly acquired dukedom Borgo San Pietro in the kingdom of Naples. Rijksmuseum, Amsterdam. (27 x 64.5 cm).

determined by the chasing. This technique was used particularly when the bronze emerged from the mould with a coarse, rather than a perfect surface, for example, as a result of the use of rough or porous material for the mould. The smaller bronzes of Donatello (1386-1466) and Bertoldo di Giovanni (1420/25-1491) are good examples of this sort of intensive finish, suggesting that they – or the casters who assisted them – had not perfectly mastered every aspect of the casting process. Gauricus described how Donatello had his sculptures cast by a bell caster, and that he did not supervise this process himself.[22] The sculptures did not come out of the mould in a perfect state, and therefore needed a great deal of finishing work, as the various inserts of metal in his *David* indicate.[23] This was also the case for the sculpture of a violin player by Bertoldo, where the use of coarse material for the mould probably required an intensive finish to make the shape and details more visible. Figure 7 shows that the right side of the violinist's face is finished perfectly; while the left side of the face is heavily chased and no attempt has been made to even shape the left eye and the hair, nor the rest of the surface. The examination of this statuette indicates that there is no such thing as a finish of a bronze surface which leaves no visible traces behind. Other sculptures by Bertoldo also reveal many traces of a partial cold finish.[24]

The second, less intensive form of finishing the metal surface by chasing it or working on it with abrasive stones was used particularly when a finer material was used for the mould. Above all, this approach emphasised the details in the work more sharply. In order to determine whether tools such as chasing punches were used to work on the surface, it is useful to compare areas of the bronze which are less accessible with more "open" passages. If the appearance of the metal is the same in a place that cannot be reached with a chasing tool as a surface that can, the metal can hardly have been finished in any way. A number of bronze reliefs by Vincenzo Danti (1530-1576) fall into this second category. Danti, who was trained as a goldsmith and had been a member of the goldsmiths' guild in Perugia since 1548, made several bronzes that showed he was experimenting with the technical possibilities of working the surface. Certainly he appears to have used a material for the mould that had a very fine structure, as is clearly revealed in his plaquette of *Moses and the bronze snake* (Fig. 8a). The head in the centre of the plaquette seems to have been chased with a hammer and a punch. However, the metal around it was not finished. The difference in the detail is obvious. Admittedly more chasing was needed for the details and to emphasise the shapes, but it was precisely by contrasting these emphases with the unfinished surrounding area that Danti created his special effects. In this case the decision whether or not to chase the metal was a conscious, artistic choice.

Fig. 7: Bertoldo di Giovanno, *Violin player* with proper right part of his face chased, the rest left unchased. Museo Nazionale del Bargello, Florence (photograph Author).

As we saw above, Godl developed and introduced a third 'finishing technique', or rather a method which rendered the cold finish technique superfluous, because the desired bronze surface had already been fully achieved during the casting process and it was not necessary to finish the metal surface with hammers or punches. By using a very fine, fire-resistant material for the mould, it became possible to cast the sculpture so well that chasing was no longer necessary. The accents could be seen immediately, and the work only had to be finished with pumice stone to remove the casting skin. *King Arthur* and *Sigismund der Munzreiche* on the cenotaph of Maximilian I have straight and arbitrary fins at the back. In addition, Godl's sculpture has little balls of metal. The straight fin was caused by individual sections of the moulds in which the wax model had been made.[25]

After the bronze was cast, a fin like this was normally retouched by chasing the surface. However, in many cases the traces of the tools remain visible in the metal. This straight fin can be distinguished from a fin with an arbitrary shape, which is the result of shrinkage in the material of the mould when the wax is removed during the firing process (Fig. 9 a/b). Depending on the composition of the material for the mould, the shrinkage does not generally result in a straight break in the mould. Apart from its shape, a fin in the mould (which is straight) can be distinguished from a fin resulting from shrinkage (which is not straight) by its location. If a sculpture also has figurative motifs the sculptor will make sure that there is no fin in a section of the mould across it to ensure that the shape is not spoilt, as this would unnecessarily make it more difficult to finish.

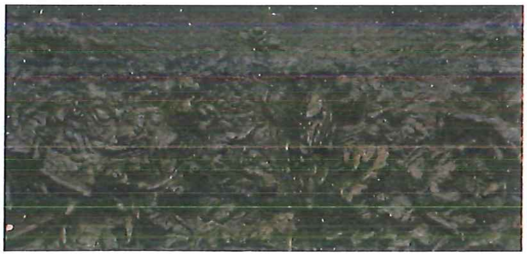

Fig. 8a: Vincenzo Danti, *Moses and the bronze snake,* overview. Museo Nazionale del Bargello, Florence (photograph by Soprintendenza Speciale per il polo museale Fiorentino, Gabinetto Fotografico).

In addition to the fins, small balls of metal are also visible on Godl's sculpture. These balls are characteristic of air being trapped under the material of the mould. This is caused by covering the apolar layer of wax with a layer of polar loam as was used at that time.[26] This caused the molten metal to run into this opening in the material of the mould, resulting in a small ball. When the bronze was finished, all three types of irregularities would normally be removed, but this does not appear to have been the case in the sculptures in the Hofkirche.[27] In short, the quality of the casting was such that no finishing was deemed to be necessary – at least on a large scale. This was a remarkable decision, as Vischer, Godl and his German colleagues were well aware of the methods used to finish the work, such as chasing as described in the Italian contemporary literature.

Another indication of the minimal amount of finish is the way in which the statue of King Arthur was beaten with a hammer. This is clearly visible on the figures of lizards at the back of the King (Figs. 10a/e).

Fig. 8b: Vincenzo Danti, *Moses and the bronze snake,* detail of the partial chasing of the head of and beard with no chasing of the background. Museo Nazionale del Bargello, Florence (photograph by Author).

Fig. 9a: *Sigmund der Münzreiche,* detail of the back of the torso showing a straight fin caused by modelling and small metallic balls in the middle of the picture, indicating that no finishing with hammers and punches of the metal took place. Cenotaph Maximilian I, Innsbruck (photograph by G. Steinmetzer).

Perhaps this specific part of the surface was beaten with a hammer to conceal the remnants of the sprues and vents, as described above.[28] It is striking that the chased bronze was not finished very finely, but it does not seem to be a coincidence that, like the shapes of fins and metal balls, this effect was not removed. The sculptors did not consider it to be necessary to continue the chasing process any further. They were obviously satisfied with this result and considered it to be successful. It illustrated the craftsmanship of the South German casters, as emphasised by Madersbacher.[29]

The quest for life casts

The emphasis on the activities of the German casters may be appropriate, but does not tell the whole story. In fact, a similar technique of casting without chasing had apparently been used in Italy a century earlier, as stated by Gramaccini and Lein.[30] These authors pointed out that casts from life had been used for bronzes in Padua in about 1500. In addition, Penny described a category of *non-finito* bronzes.[31] These were all supposedly15th or early 16th-century bronzes, including plaquettes, as well as small bronzes in the shape of animals or plants. However, the dating of these anonymous objects is tentative. It seems more logical to date these objects to the third quarter of the 16th century when life casting was an international trend.

Fig. 9b: *Sigmund der Münzreiche*, detail of the back of the torso showing an arbitrary fin in the centre of the photograph going to the right caused by the shrinkage of the mould. Small balls can be seen throughout the bronze, for example, under the leaf close to the start of the crack. Cenotaph Maximilian I, Innsbruck. (photograph by G. Steinmetzer).

Fig. 10a: *King Arthur*, overview from the back. Cenotaph Maximilian I, Innsbruck. (Photograph by Georg Steinmetzer).

Fig. 10b: *King Arthur*, head and shoulder of the sculpture indicating the high quality of casting. Cenotaph Maximilian I, Innsbruck. (Photograph by Georg Steinmetzer).

Fig. 10c: *King Arthur*, back of sculpture, below the belt some chasing is clearly visible. Cenotaph Maximilian I, Innsbruck. (Photograph by Georg Steinmetzer).

Fig. 10d: *King Arthur*, detail of the back where partial hammering is clearly visible, indicating that the rest of the sculpture was not chased. Cenotaph Maximilian I, Innsbruck. (Photograph by Georg Steinmetzer).

Fig. 10e: King Arthur, detail of the back with an arbitrary fin while the casting is of high quality. Cenotaph of Maximilian I, Innsbruck. (Photograph by Georg Steinmetzer).

A detailed study of the life casts shows that they were not finished or that very little finishing work was carried out, and that there can be no doubt that this method already existed in the late 15th century. However, the *non-finito* bronzes dating from this period are not comparable in terms of finish with the results achieved in the middle of the 16th century with casting from life.[32] The natural representations of branches with leaves on the borders by Vittorio Ghiberti framing the doors by Andrea Pisano were actually thickened with wax before they were cast. This casting method, which could result in perfect casts that required no further finish, deserves more attention. Godl's examples could be seen on their own as isolated cases, in which case it is not possible to draw any far-reaching conclusions. However, there are other things which indicate that Godl's *non-finito* method had spread as far as Nuremburg in the first half of the 16th century. The city of Nuremburg was one of the places in Europe where copper casters were united in guilds. From 1534 these so-called *Rotschmiede* were bound by strict guild regulations which prohibited them from exercising their craft outside the city limits.[33] In this way Nuremburg hoped to protect the craft of the copper craftsmen and their astonishing results. On 12 August 1550 Hans Lobsinger (1510-1584), a ring maker from Nuremburg, claimed that he had developed a special technique for the material of the mould. "*Uber das so kan er eynen kunstlichen laymen machen, darin man von kupfer und missing also scharf geust, das es kaines ausberaiten [be]darf, und is der laymen mit eynem burstlein bold von gues zu bringen und leichtlich abzuwaschen, so man ihn allein in ein wasser legt.*" He literally states that he has found a method of casting copper alloys so perfectly that no finishing is necessary.[34] The city was certainly successful in this, as it was in other fields of metalwork. It is striking that silversmiths shared the same fascination for perfecting casting techniques for silver. The Nuremburg casting technology reached its zenith at about the same time in the work of Wenzel Jamnitzer (1507/08-1585), a very important goldsmith at the time in Europe.[35] Jamnitzer was extraordinarily inventive and innovative, not only artistically but also technically, as demonstrated by his most important surviving work, the *Merkelsche Tafelaufsatz*, dating from 1549.

Fig. 11: A bronze crab. Kunsthistorisches Museum, Vienna (KK 5927).

Fig. 12a: Overview of the *Merkelsche Tafelaufsatz* by Wenzel Jamntizer, Rijksmuseum, Amsterdam. (BK-17040-A).

Fig. 12b: Detail of the base of the *Merkelsche Tafelaufsatz* by Wenzel Jamntizer, Rijksmuseum, Amsterdam (BK-17040-A).

This work was presumably intended as a gift from the city of Nuremburg to the Emperor, and obviously had to comply with the highest artistic and technical standards. In fact, it is the perfect example of technical casting ingenuity. The base, the neck and the flowers at the top of this work are cast from life in silver (Figs. 12a/b). The delicate silver could not be finished because it had been cast so thinly, but in fact it was not necessary, because it came out of the mould perfectly formed.[36] Clearly Jamnitzer had mastered a technique to cast figures exactly from life without producing any fins during the process. In fact, silver is very comparable to bronze from a technical point of view. Silver has comparable casting characteristics to the standard copper alloy (Cu90 Sn8 Pb2). Jamnitzer created several silver pieces which revealed his phenomenal mastery of the technique of casting bronze, including a silver dish in the Louvre, Paris and a silver writing box in the Kunsthistorisches Museum, Vienna. Finally, Jamnitzer showed that he had also mastered this technique for casting bronze, as illustrated by the salamander in the Rijksmuseum collection.

The innovative German casting technology appeared to have reached France in the second half of the 16th century: the ceramic artist Pallisy also experimented with casting from nature. As indicated in some passages in the work of Vasari and Cellini, the fascination for these techniques had also reached Italy by the middle of the century.[37] We will look at the situation in Italy in more detail below.

The innovations in the casting technology by Cellini and Vasari

In his autobiography Cellini discusses the cast of the head of Medusa, part of his famous *Perseus* in the Loggia dei Lanzi in Florence: "*The first cast I took in my furnace succeeded in superlative degree, and was so clean that my friends thought I should not need to retouch it. It is true that certain Germans and Frenchmen, who vaunt the possession of marvellous secrets, pretend that they can cast bronzes without retouching them, but this is really nonsense, because bronze, when it has first been cast, ought to be worked over and beaten in with hammers and chisels, according to the manner of the ancients and also of the moderns – I mean such moderns as have known how to work in bronze.*"[38] This striking comment shows that stories about perfecting casting techniques had also reached Florence. Although he rejected this as pure invention, Cellini himself was certainly focused on using the best material for the mould. At the time he was looking for improved materials for casting bronze to make his bust of Cosimo de' Medici.[39]

Fig. 13: Counterweight in the form of a lizard by Wenzel Jamnitzer, Rijksmuseum Amsterdam (BK-17006-B).

Cellini also experimented with materials for the mould to make a relief of his dog, but on the basis of his experience he explicitly doubted whether it was possible to cast a bronze which did not need retouching. In his opinion, a sculpture was not finished when it had been cast. It had to be chased to obtain a really beautiful surface. It is clear that Cellini was familiar with the latest developments in Germany, whether or not it was from first-hand experience or from reports.

Although Cellini's boastful and exaggerated tone has evoked suspicion, and sometimes even doubt about his allegations, the study of his works and treatises reveals a high standard of craftsmanship. In fact, he describes his techniques so accurately that they can be reproduced.[40] He indicates that casting bronze sculptures and then chasing them was customary in 16th-century Florence to achieve an acceptable result. Despite some minor differences with regard to the casting process of bronze sculptures, his technique corresponds virtually entirely with the casting technique described by Vasari in both his editions.[41] The second edition of Vasari's *Le Vite*, dating from 1568, suggests, without indicating their geographical origins, that the German innovations in casting bronzes had actually reached Florence in the third quarter of the 16th century.[42] More precisely, Vasari appears to refer to the work of Jamnitzer without mentioning his name:

"*Modern tour de force in small castings. But that is a truly marvellous thing which is come to pass in our times, this mode of casting figures, large as well as small, so excellently that many masters make them come out in the cast quite clear so that they have not to be chased with tools, and as thin as the back of a knife. And what is more, some clays and ashes used for this purpose are actually so fine, that tufts of rue and any other slender herb or flower can be cast in silver and in gold, quite easily and with such success, that they are as beautiful as the natural: from which it is seen that this art is more excellent now than it was in the time of the ancients.*"[43]

According to Lein, this passage should not be taken seriously and is not based on practice.[44] In his opinion it should be seen in the light of promoting the high artistic and technical standard that casting bronze had reached in Vasari's Florence. In my opinion, Vasari's statement about casting without finishing was certainly correct. In the first place it is an addition to the end of the description of the techniques, and was therefore a new insight which also deserved a mention in the second edition. Secondly, Vasari had no interest in including any inventions in his technical introduction. Thus Vasari mentioned an innovation which Cellini considered not to be credible. When Cellini started to dictate his biography in about 1560, this new technique of "casting bronze without chasing" had just been introduced in Italy. The idea that Cellini heard about this casting technique from Vasari and then acted on it is probable, but cannot be proved. The study of Italian bronze sculptures from the third quarter of the 16th century gives good reason to assume that sculptors in Florence also cast their bronzes without finishing the

Fig. 14: Bust of *Cosimo de' Medici*, Museo Nazionale del Bargello, Florence (photograph by Soprintendenza Speciale per il polo museale Fiorentino, Gabinetto Fotografico).

surface afterwards, and that Cellini was behind the times with regard to the latest developments, while Vasari's comment was more than mere propaganda, as Lein suspected.

There are various Italian bronzes dating from the second half of the 16th century which reveal that the "German casting method" which rendered chasing superfluous had also taken hold south of the Alps by 1550. With regard to the bronze group made by Vincenzo Danti for the south doors of the Baptistry in Florence in 1571, Raffaello Borghini wrote that the sculptures needed hardly any finishing work: "*With great good fortune [Danti] cast the three bronze figures that one sees above the [south] doors of San Giovanni towards the Misericordia, and they came out so well, so fine and so clean, that it was not necessary to rework them.*[45] The bust of *Pope Gregory XIV* by Bastiano Torrigiani, of which chapter VI contains a detailed technical description, also reveals clear traces of casting without retouching. This is based on the fins which are visible at the back of the tiara. It is true that Giambologna's "bronze oeuvre" appears to consist mainly of perfectly finished statues, but a careful study of a number of pieces shows that he was also able to deliver a well-cast bronze without chasing. For example, the two *putti* that he made in 1561-1562 for the Casino di San Marco show clear fingerprints (Fig. 15b). Whether or not the fingerprint was of the master himself, it confirms a casting technique without retouching.

The same can be seen in the *Turkeys* which he made in 1567.[46] Traces of the same technique can also be found in the work of two colleagues in his immediate environment: Willem van Tetrode (circa 1525-1587) and Elias Candido (Elias de Witte) (?-1574). Tetrode's *Hercules Pomarius* in the Rijksmuseum has a visible fin on the left shoulder and was described in detail in Chapter VI. De Witte's perfectly cast *Boreas* for the studiolo of Francesco de' Medici admittedly has a striking chased finish at the neck, but the rest of the sculpture has a perfectly cast surface which has hardly been retouched (Fig. 16).[47]

The method of casting without finishing was probably popular for a short time, but was used by several sculptors. As his statements reveal, Cellini did not believe in this. It is as though Cellini was born a generation too early, and therefore used the traditional method of retouching to achieve a perfect result, as he distrusted the latest developments in this field. Or perhaps Cellini was right when he wrote that this was the only method to obtain "his" desired quality for a bronze sculpture. Should his comment not be seen against the background of the materials he used for casting, and the size of his sculptures? Do the same finishing methods apply for monumental bronze statues as for bronze statuettes? To answer these questions it is necessary to compare and reconstruct the technical aspects of casting as described in the various treatises in some detail.

Models, moulds and sprues

The examination of surviving sculptures has a central place in the study of the casting technology of Renaissance bronzes, In addition, contemporary sources and the literature provide a great deal of insight into the making these objects. In the section below, the starting point is a systematic comparison of contemporary literature and bronze sculptures. The starting point is the wax model, and then discusses the role of the material used for the mould and the sprues and vents. Finally, the size of the sculpture is examined in relation to the casting process.

"In order to show how wax is modelled, let us first speak of the working of wax and not of clay. To render it softer a little animal fat and turpentine and black pitch are put in the wax. Of these ingredients the fat makes it more supple, the turpentine adds tenacity, and the pitch gives it the black colour and a certain consistency, so that after it has been worked and left to stand it becomes hard."[48]

Fig. 15a: Overview of one of the two putti for the Casino di San Marco by Giambologna, Museo Nazionale del Bargello, Florence (photograph by Soprintendenza Speciale per il polo museale Fiorentino, Gabinetto Fotografico).

In this passage Vasari shows that sculptors in Florence also knew that adding different substances to the wax made it easier to work. Although Vasari's remark may have referred more to independent wax sculptures than to models intended to be cast in bronze, the comment is also relevant for the latter category. After all, we saw above that if a layer of wax is perfectly finished and the material of the mould encases it closely, the final bronze will require very little finishing. This would save time and labour. Minuscule details in the wax, even a fingerprint, are precisely transferred to the bronze. As the wax models are always lost during the casting process, it remains unclear exactly what types of wax were used in the 16th century.[49] Up to now, most of the research into types of wax has related to 19th-century wax models.[50] These 19th-century wax models mainly consisted of beeswax, but also carnauba (Brazil) and Japanese waxes, as well as animal fats, paraffin, stearin and ozokerite. It is quite possible that pure beeswax mixed with ground, low fired clay, was used for modelling in the 16th century. This would explain the red colour of the surviving wax figures.

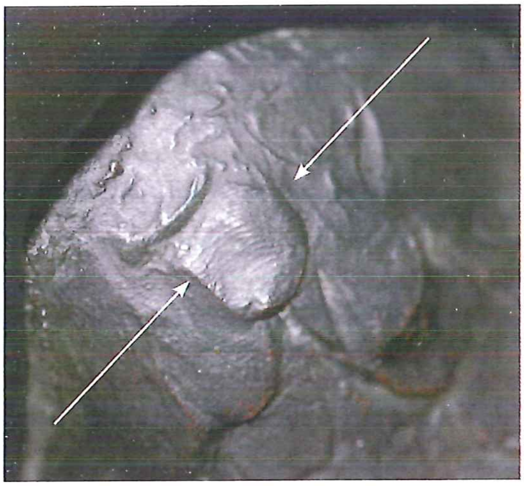

Fig. 15b: Detail of one of the two putti with a fingerprint in the bronze for the Casino di San Marco by Giambologna, Museo Nazionale del Bargello, Florence (photograph by Author).

Fig. 16: *Boreas* by Elias Candido, Palazzo Vecchio, Florence (photograph by Soprintendenza Speciale per il polo museale Fiorentino, Gabinetto Fotografico).

We know that beeswax was widely available in the 16th century, and with its plasticity which was approximately in the range of body temperature, it is ideal for working by hand. Knowing that a perfectly finished wax model can save a great deal of time (involved in chasing), it is interesting to examine Willem van Tetrode's *Hercules Pomarius* in this light. The reason for this is the surface around the fin shape on the left shoulder of the sculpture, which reveals a large number of scratches.

There is a tendency to attribute these scratches to a finishing process using files and stones. The first option, a file (in the 16th century this would have been a file cut by hand), could never have left these traces, because the scratches on the sculpture criss-cross. A file cut by hand has many teeth which are virtually all in the same direction, so that the traces left by the file will also be in the same direction.[51] An abrasive stone could have caused the scratches, because a stone can be rotated on its axis without losing its abrasive effect. However, even with this knowledge it is not possible to explain why the scratches do not continue onto the fin. One important finding is that the scratches continue up to the fin and some even appear to be interrupted only by the fin. The conclusion is that the scratches must have been present in the wax before, and not made in the bronze afterwards.[52] One possible reason is that this made it possible to attach the investment mould more closely to the wax layer, allowing for a better key for an organic layer of varnish to finish the bronze after it had been cast. In any case it indicates a high degree of control in the casting process, so that even the smallest details (scratches) in the wax are reproduced in the bronze. In this respect the material for the mould plays a key role as the material for the reproduction. With regard to the clay material used to make the bronze sculpture, Cellini wrote the following:

"You take such clay as is used by the ordnance makers for their moulds. It may be found in many places, but preferably nearby rivers, for there it has a certain sandiness, still it must not be too sandy, suffice it if it be thin, for the rich clay is delicate and soft, such as is used for small figures, cups, plates, and so forth, but not good for our purpose. When the clay and the cloth frayings are mixed and bathed with water to the consistency of a dough, you beat the mixture up well with a stout iron rod about two fingers thick; and, for this is the secret, you let it decompose for at least four months or more, the longer the better; for then the cloth frayings rot, and owing to this the clay gets to be like an unguent. To those who have not had experience of this little trade secret of mine the clay will appear too fatty, but this particular kind of fattiness in no wise hinders the accepting of the metal, indeed it accepts it infinitely better and the clay holds a hundred time more firmly than if it had not rotted."[53]

In the first part of this passage Cellini describes a material for the mould which does not contain any fired clay. When the wax melts out, there tend to be tears, because unfired clay leads to more shrinkage. Subsequently Cellini refers to the addition of cloth to the material, and then allowing it to rot. He gives another indication that he used organic material: *"After this I pounded up some ox bone, or rather the burnt core of ox horns. It is like a sponge, ignites easily, and is the best bone that one can get anywhere. With this is beat up half a quantity of gesso di Tripoli, and a fourth part of iron filings & mixed the three things well together with a moist solution of dung of horses or kine, which I first passed through a fine sieve with fresh water, till the latter took the colour of the dung."*[54]

Fig. 17: A Hirox picture of the back of *Hercules Pomarius* showing the fin, Rijksmuseum, Amsterdam (BK-1954-43).

There are two reasons why the material for the mould described by Cellini involved difficulties. In the first place, there would seem to be a problem between the apolar (fatty and therefore hydrophobe) layer of wax and the polar (non-fatty, water soluble) material for the mould. The fact that Cellini opted for this method anyway could be because, as his text indicates, his clay became a fatty substance. Whether the limited fattiness of the material for the mould is sufficient to adhere to the wax layer could be reconstructed in a future study. It is to be expected that spherical casting holes will appear between the two layers, which become visible in the final product in the form of little balls of metal as is described on the casting of *Sigmund der Münzreiche* (Fig. 8). Secondly, he uses a mixture of clay and organic material in the first layer that is applied. Irrespective of how finely the material has been ground, remnants of the organic material in the mixture – cloth or horse dung – will come into direct contact with the layer of wax when the outer casing is applied. When the wax melts out, the organic material burns up and is turned into ash, resulting in small hollows in the mould.[55] This results in a pockmarked or rough surface on the inside of the mould. As the molten bronze assumes the shape of the outer casing, it will also run into the pockmarked spaces and reproduce that surface in mirror image as can be seen in figure 7 or in figure 18 on the right and next page.

Depending on the quantity of organic material in the mixture, it is possible that there will be a fragile, fire-resistant mould.[56] This mould can crumble when the metal is poured in, because

Fig. 18a: A rough and partially hammered surface on the feet Primaticcio's *Sleeping Ariadne*, Chateau Fontainebleau (photograph by (C) RMN (Château de Fontainebleau) / Georges Fessy).

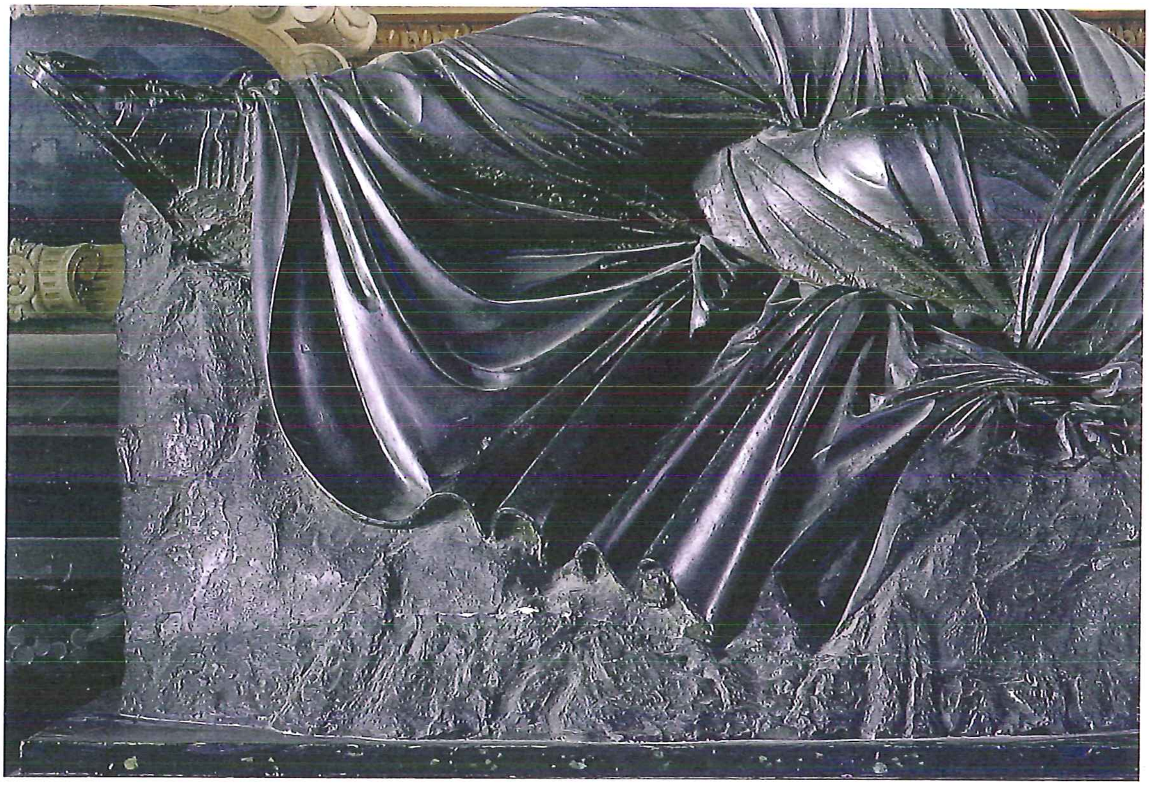

Fig. 18b: A rough surface of the bronze on *Sleeping Ariadne*, Chateau Fontainebleau (photograph by (C) RMN (Château de Fontainebleau) / Georges Fessy).

Fig. 18c: A rough surface of the bronze in the centre on *Sleeping Ariadne*, Chateau Fontainebleau (photograph by (C) RMN (Château de Fontainebleau) / Georges Fessy).

the relative density of the metal has a significant physical impact (also see the size of the sculpture). This results in more irregularities in the cast work, and it will therefore require more finishing, such as chasing and/or smoothing with stones using the traditional working methods of the time.

It is generally assumed that bronze sculptures were cast with the use of many sprues. For example, Bewer, Dillon, Sturman and Bassett all supported this view in their explanations of Renaissance casting methods.[57] They indicate that a system of sprues and vents was attached to the surface of a wax model before casting. This idea seems to be confirmed by the well-known illustration by Germain Boffrand (1743) of the statue of Louis XIV mounted on horseback cast for the Place Bellecour in Lyon by Roger Schabol 1694.[58]

Furthermore, there is also a bronze scale model of this illustrated model which is attributed to Schabol according to De La Moureyre (Fig. 20). Including the sprues, it is 52 cm tall and appears to have been intended as a model to demonstrate how the large equestrian statue should be cast in bronze. The large number of sprues is very striking. The reason for this could have been based on the fear that gas would accumulate in the mould, causing the casting to fail. However, gas probably will not accumulate in a part of a bronze where the metal flows in one direction, such as the back or legs of a figure. In this respect, Biringuccio gave the following advice: "*When it is thus reinforced, consider where you can best make your gate so that the bronze may travel unimpeded throughout the entire mould and gradually bear down onto itself so that it may be forced into the thin parts. For greater safety, make some runners in certain places so that they may convey the bronze where if it does not go by itself. Likewise, two or three vents should be made near the gate to carry off the winds and fumes that are generated by the heat in the mould, for the bronze could not go into places that are closed in, and this would make a defect in the work.*"[59]

He describes how the bronze caster should add a sprue in certain places, so that the bronze can flow easily in the casting process without accumulating. If there are too many sprues, as in Schabol's demonstration model, the opposite is likely to take place. The molten metal is poured into the mould and divides into different channels. Small grains of the material of the mould could be pressed forward and when the metal joins the flow from another sprue, this can easily result in casting errors. Good casting results could already be

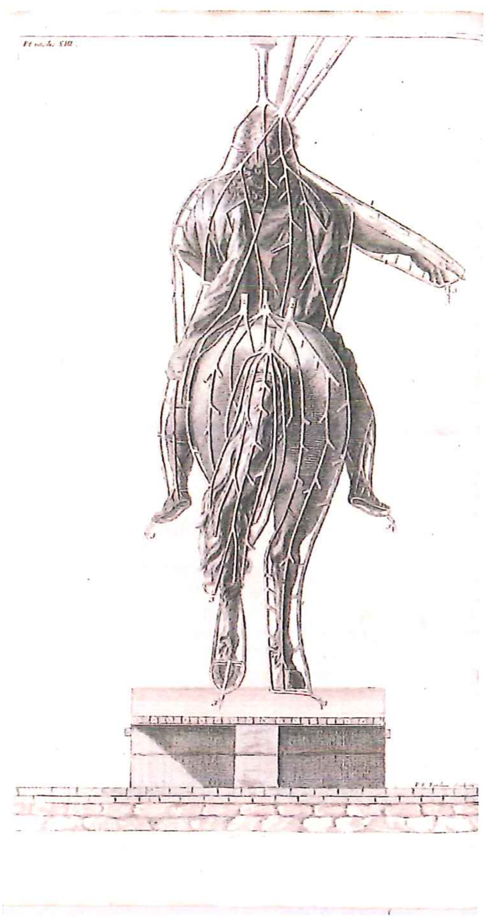

Fig. 19a: Germain Boffrand, illustration of the amount of casting sprues.

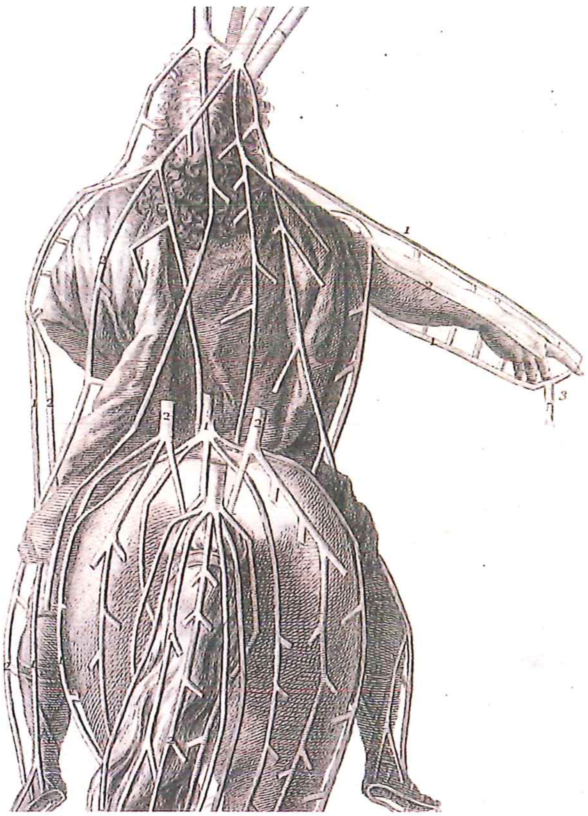

Fig. 19b: Germain Boffrand, detailed illustration of the amount of casting sprues of which some are incomprehensible such as the one below his left shoulder with a sharp twist where the metal will never be able to flow through.

achieved with fewer sprues and vents, which also saved on finishing work, because the surface required less retouching as is illustrated in figures 21a/i. Finally, using a large number of sprues has the additional disadvantage that a greater volume has to be filled with molten metal. Therefore more bronze must be heated, incurring extra energy and costs.

Monumental bronzes

During the 16th century the material used for the mould became a central concern in order to improve the quality of casting. For example, this is reflected in the terms of the contract between Pompeo Leoni (1533-1608) and Adriaen de Vries (1556-1626), when the latter came to work in Milan in 1586. "*[…] Messer Adriano referred to above undertakes to make two figures with their attributes, one of St. John and the other of St. James, in accordance with the size, dimensions and models made available to him by Signor Ponpeo [sic]. Messer Adriano must deliver these with a perfect finish and to Pompeo's satisfaction. He must make them with the maschio (the clay core in life size), and covered with fine wax evenly all over, so that the bronze will be of an even thickness everywhere. When the statues are ready, Messer Adriano is obliged to help the men apply the clay until the moulds are ready for firing. The statues must be prepared in such a way that they are completely ready to be taken to the casting pit.*"[60] This passage describes his share in the work on the prestigious high altar for the San Lorenzo de El Escorial in 1586. The formulations used here reveal a high degree of perfectionism and Leoni's strong need to strictly control the casting process. This conflicts with the notion that 16th-century sculptors were happy to let others do their casting for them. This perfectionism is all the more striking in this case because De Vries's sculptures were placed high up on the altar and could therefore be viewed close up.

However, in general it is important to take the size and original position of monumental bronzes into account in the assessment of the finish of the surface. For statuettes the finish obviously plays a more important role because a small bronze is viewed from close up. The details had to be clearly visible and the surface therefore had to be of a very high standard. The choice of a suitable material for the mould which made an elaborate finish of the bronze superfluous, was therefore an essential factor. However, a monumental statue, often intended to be seen from a distance, requires much less finishing. Therefore for larger statues there was no need for the wax model to be perfect, as stipulated in the above-mentioned contract. This makes this passage all the more remarkable.

Another significant factor regarding monumental bronze sculptures is the more complex casting process. This is because of the speed at which the molten metal falls into the mould, due to the great difference in height between the place where the metal is poured in and the distance the molten metal must cover to the bottom of the mould. Conical or funnel-shaped sprues (as shown in the engraving by Boffrand) increase the speed at which the metal falls. The molten metal runs through the mould at a speed of approximately five to six metres per second. This results in turbulence in the mould and the risk of the development of slag and an accumulation of gas, producing a poor casting. Small bronzes in which the metal does not fall so far (because the moulds are much smaller) have two advantages: on the one hand, a smaller mould penetration from lower static depth, and lower momentum impacts; on the other hand, the smaller diameter filling channels have a better chance to fill completely with metal, giving a smoother fill.[61] This explains why the choice of the material for the mould and the use of sprues and vents are important factors for the success of a casting. Therefore the role of the material for the mould and the nature of the system of channels must always be viewed in relation to the dimensions of the statue.

All the observations made above can be studied in more detail and tested by means of reconstructions. The results of this reconstruction research will be dealt with in the next chapter.

Fig. 20: Statens Museum for Kunst, Copenhagen, inv. KMS 5403 (photograph by National Gallery of Denmark, Copenhagen @ SMK Photo).

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1 For a detailed description of this Renaissance technique, see F.G. Bewer, "A study of the technology of Renaissance bronze statuettes," London, PhD dissertation, Dept. of Archaeological Conservation and Materials Science, University of London, University College, Institute of Archaeology, 1996; R.E. Stone, "Antico and the development of bronze casting in Italy at the end of the quattrocento", *Metropolitan Museum Journal* 16, 1982, pp. 87-116; R.E. Stone, "Severo Calzetta da Ravenna and the indirectly cast bronze," *The Burlington Magazine*, 148, 1245, December 2006; J. Basset, J.P. Fogelman, D.A. Scott, R. Schmidtling II, *The craftsman revealed, Adriaen de Vries sculptor in bronze*, The Getty Conservation Institute, 2008.

2 It is often falsely assumed that Cellini was alive in 1437 because that date appears on one of the copies of his manuscript. This is questioned by Daniel V. Thompson in the preface to his authoritative translation of Il libro dell'arte. Thus, dating Cennini's book to the "early 15th century" as above is only a guess. The techniques Cennini describes are

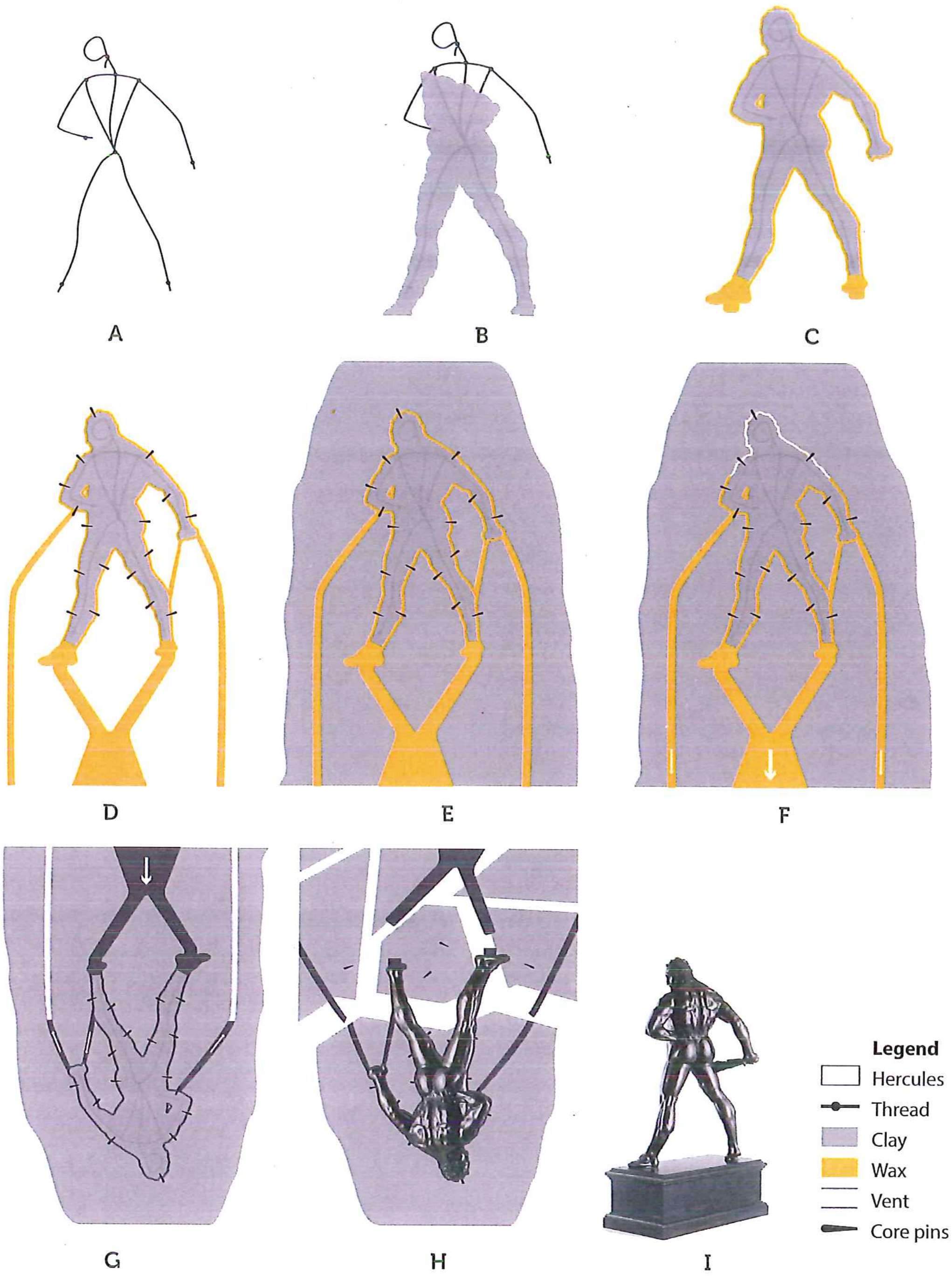


Fig. 21 a/i: A diagram showing the possible casting process of the *Hercules Pomarius* using the direct method, with fewer sprues and vents. (21a) a wire framework (21b) built up of clay around the armature (21c) wax layer forming the sculpture around the clay (21d) two sprues on his feet and two vents at the highest places (21e) pouring in the wax, with protruding core pins both in the clay core and in the covering investment mould (21f) heating the mould with wax rendering down. (21g) casting of the metal into the hollow space (21h) breaking up of the mould and retrieving the bronze (21i) the final bronze on a pedestal.

grounded in the late 13th and mid 14th centuries. There is no evidence in his writing of the exciting developments in oil painting taking place in the early 15th century. This suggests that his book was indeed written sometime in the 14th century.

3 Musée National du Chateaux de Fontainebleau, see G. Bresc-Bautier, G. Scherf, I. Wardropper, J. Draper, A. Boström, A-L. Desmas, *Cast in Bronze, French sculpture from Renaissance to Revolution*, Musée De Louvre editions, Somogy Art Publishers, Paris, 2008, pp. 64-69.

4 Benvenuto Cellini, *La Vita*, Letteratura Italiana Einaudi, 1973, Einaudi, Turin. There are many translations of *La Vita* after the first appearance in 1728.

5 O. Knitel, *Die Giesser zum Maximiliangrab, Handwerk und Technik,* Innsbruck, 1987?, The dates of birth and the years in which both Gilg and Christoph Sesselschreiber, and Peter Löffler, Melchior and Stefan Godl died are not known.

6 Knitel, op. cit., 1987?

7 L. Madersbacher in *Ruhm und Sinnlichkeit, Innsbrucker Bronzeguss 1500-1650*, Tiroler Landesmuseum, Innsbruck 1996, pp. 124-139.

8 Knitel, op. cit., 1987?, pp. 13-20.

9 Also see V. Oberhammer, *Die Bronzestatuetten am Grabmal Maximilians I*, Tyrolia A.G., 1955.

10 Biringuccio fails to explain how a core pin could be inserted in a fired clay core.

11 It is striking that Biringuccio did not describe soaking the plaster in water before the filling-in with wax. Experience shows that this was much easier to remove.

12 "Finiti guesti getti, lo artefice di poi, con ferri appropriati, ciò è bulini, ciappole, strozzi, ceselli, puntelli, scarpelli e lime, lieva dove bisogna spigne a lo indentro, e rinetta le bave." Giorgio Vasari, *Le Vite, De' più eccelenti Pittori Scultori e Architettori, Firenze 1568.* I, pp. 40. The English translation is based on L.S. Maclehose, *Vasari on Technique*, Dover Publications Inc., New York, 1960, pp. 166. Also see Chapter VI, figure 1, Tools used in the chasing process.

13 Books have been written about the materials and techniques used in sculpture, but not at this detailed level. See, *inter alia*, N. Penny, "The materials of sculpture," Yale University Press, New Haven & London, 1993.

14 Knitel, op. cit., 1987?, pp. 60-61.

15 Knitel, op. cit., 1987?, pp. 51.

16 Inter alia, M. Baxandall, "Hubert Gerhard and the altar of Christoph Fugger," *Münchner Jahrbuch der Bildenden Kunst*, 1966, pp. 127-144.

17 M.W. Cole, *Ambitious form*, Princeton University Press, 2011, pp. 19-39.

18 E. Luciano, D. Allen, C. Kryza-Gersch, S.J. Campbell, D. Gasparotto, D. Smith, R.E. Stone, and S. Sturman, *Antico, The Golden Age of Renaissance Bronzes*, National Gallery of Art, Washington, 2011, pp. 160-161.

19 Pasim quidem nunc omnes, Sed pauci propter quod commemorentur egregio aliquot opera insignes, nisi duo Arifices Charodoxus Mediolanesis, et Franciscus Furnius Bononiensis in F.A. Brockhaus, *De Sculptura von Pomponius Gauricus*, F.A. Brockhaus, Leipzig 1886, pp. 257.

20 J. Pope-Hennessy, *Cellini*, London, 1985, pp. 181.

21 There is no indication that such a division was made in the 16th century. However, the different bronze sculptures that were studied support this.

22 Brockhaus, op. cit. , 1886, pp. 224-225.

23 See the photographic report of *Donatello, Il David Restaurato* in this respect. B. Strozzi et al., *Donatello, Il David restaurato*, Museo Nazionale del Bargello, Giunti, 2008, pp. 121-153.

24 This concerns the plaquettes of Bertoldo di Giovanni which are exhibited in the Museo Nazionale del Bargello.

25 For a further explanation of this part of the casting process, also see Chapter VIII, in which visual material clarifies the formation of the fins.

26 If plaster is used for part of the process of forming the wax layer, an exothermic reaction takes place when the material hardens, so that the amount of air that is trapped can be larger, appearing as swellings in the outer casing.

27 The statues were studied during a visit to the cenotaph with a head loupe and inspection lights.

28 It is also possible for the bronze surface to be pockmarked

after it has been cast in the mould. This depends on the structure of the mould.

29 L. Madersbacher in *Ruhm und Sinnlichkeit, Innsbrucker Bronzeguss 1500-1650*, Tiroler Landesmuseum, Innsbruck, 1996, pp. 124-139.

30 For a detailed summary, see the catalogue containing, inter alia, the contributions of N. Gramaccini, *Natur und Antike in der Renaissance*, Liebighaus-Museum alter Plastik, Frankfurt am Main, 1985; E. Lein, *Ars Aeraria: Die Kunst des bronzegiessens und die Bedeutung vorn Bronze und der florentinischen Renaissance*, Mainz am Rhein: Philipp von Zabern, 2004.

31 N. Penny, "Non-finito in Italian fifteenth-century bronze sculpture", *Antologia dei belle arti, Nuova serie*, 1994, pp. 48-51.

32 The crabs were not life casts, like those made in the 16th century. This can be deduced from the hinges on the lid which were made in the wax and then cast in accordance with the casting process described before.

33 H.P. Lockner, *Die Merkzeichen der Nürnberger Rotschmiede*, Munich, Kunstverlag, 1981.

34 A. Bartelmess, "Hans Lobsinger und seine Erfindungen, Mitteilungen des Vereins," *Geschichte der Stadt Nürnberg*, 1963, Vol. 5, pp. 256-264.

35 M. Grieb, "Wenzel Jamnitzer und die Nürnberger Goldschmiedekunst 1500-1700," *Ausstellungskatalog Germanisches Nationalmuseum*, Nuremburg, 1985.

36 The leaves vary in thickness from 0.6 - 1mm.

37 In France there was an interest in working and casting from nature, as revealed by the ceramic works of Bernard Palissy (circa 1510 – circa 1589). Research by Smith & Beentjes into an anonymous treatise (Bibliothèque National de France, Paris, Ms. Fr. 640) showed that in the second half of the 16th century life casts were also made by French gold and silversmiths. According to Smith & Beentjes, the treatise was written after 1581 not by a professional who developed the technique himself, but by an amateur enthusiast. The reconstruction research by Smith and Beentjes, which focused on reproductions of the 16th-century models, came across several confusing comments in the French treatise, which meant it was not possible to make a perfect reconstruction. Nevertheless, their results come close to the life casts that were made in the 16th century, in P.H. Smith and T. Beentjes, Renaissance Quaterly, Vol. 63, No. 1, 2010, pp. 128-179.

38 "E cosi il primo getto ch'io feci in detta mia fornacina vene bene superlativo grado, ed era tanto netto ch'e' non pareva alli amici mia ik lovere che io altrimenti la dovessi rinettare; la qualcosa hanno trovato certi Todeschi e Franciosi, quali dicono e si vantano di bellissimi secreti di gettare i bronzi senza rinettare; cosa veramente da pazzi; perché il bronzo, di poi che gli è gittato, bisogna riserario con i martelli e con i ceselli, si come i maravigliosissimi antichi, e como hanno ancor fatto i moderni", Benvenuto Cellini, *La Vita*, Letteratura Italiana Einaudi, 1973, Einaudi, Turin, pp. 383 (Edizione di referimento a cura di Guido Davico Bonino, Einaudi, Turin 1973).

39 *Letteratura Italiana Einaudi*, 1973, Einaudi, Turin, pp. 382-383 (Edizione di referimento a cura di Guido Davico Bonino, Einaudi, Turin, 1973).

40 This line of research has been picked up by the University of Amsterdam in collaboration with Tonny Beentjes and Jeroen van Halder.

41 In addition to the traditional technique, Cellini describes the technique which he calls the "lasagna" technique, in which he built up his mould using a different method, although the decisive material of the mould is identical to that described by Vasari.

42 I presented this hypothesis before in F. Scholten, M. Verber, R. Van Langh, and D. Visser, *From Vulcan's forge: bronzes from the Rijksmuseum Amsterdam 1450-1800*, Daniel Katz Ltd., London, 2005, pp. 145-149.

43 "Ma quello che veramente è cosa maravigliosa, è venuto a' tempi nostri questo modo di gettar le figure così grande como piccole in tanta eccelenza, che molti maestri le fanno venire nel getto in modo pulite che non si hanno a rinettare con ferri, e tanto sottili quanto è una costola di coltello. E quello che è più, alcune terre e ceneri che a ciò s'adoperano sono venute in tanta finezza che si gettano d'argento e d'oro le ciocche della ruta e ogni altra sottile erba o fiore, ageovolmente e tanto bene che così belli riescono como il naturale. Nel chesi vede questa arte essere in maggior eccellenza che non era el tempo degli antichi." Giorgio Vasari, *Le Vite, De' più eccelenti Pittori Scultori e Architettori*, Florence 1568. Cap IIII Cap IX. The English translation by L.S. Maclehose, *Vasari on Technique*, Dover Publications Inc., New York, 1960, pp. 166.

44 E. Lein, *Ars Aeraria, Die Kunst des Bronzegiessens und die Bedeutung von Bronze in die florentinischen Renaissance*, Philip von Zabern, Mainz am Rhein, 2004, pp. 46-51.

45 "Gitto con gran felicita le tre figure del bronzo che si veggono sopra la porta di San Giovanni di verso la Miscicordia, e Veneto tanto bene, tanto sottili, e tanto pulite, che non bisogno rinettarle." R. Borghini, *Il Riposo*, IV, 1584, pp. 521. Translation by L.H. Ellis Jnr., *Il Riposo*, University of Toronto Press, Toronto, 2007, pp. 244.

46 Giambologna's sculptures are exhibited in the Bargello museum. I would like to thank both Beatrice Paolozzi Strozzi and Dimitrios Zikos for their assistance with the study of the works of art.

47 The sculpture is signed at the bottom: 1573 I.FO.ELIA D.CANDIDO FIAM.DI BRUGIA. With the current photograph of the sculpture it is not visible. At an exhibition of Pietro Candido in 2009 in Volterra the sculpture was standing free and this observation was made together with professor Scholten.

48 "Ma per mostrarvi come la sera si lavora, diremo del lavorare la cera e non la terra. Questa per renderla piú morbid, vi si mette dentr'un poco di sevo e di trementina e di pece near, della quail cose il sevo la fa piú errendevole, e la trementina tegnent in sé, e la pece le dà il colore nero e le fa una certa sodezza da poi ch'è lavorata, nello stare fat ache ella diventa dura." Giorgio Vasari, *Le Vite, De' più eccelenti Pittori Scultori e Architettori*, Florence 1568. Cap IIII, Cap IX. The English translation is by L.S. Maclehose, *Vasari on Technique*, Dover Publications Inc., New York, 1960, pp. 148.

49 At the time of writing, I am researching the composition of 16th-century wax layers. It is expected that this research will be concluded in 2013.

50 M. Regert, J. Langlois, E. Laval, A,-S. Le Hô, and S. Pagés-Camagna, "Elucidation of molecular and elementary composition of organic and inorganic substances involved in 19th century wax sculptures using an integrated analytical approach," *Analytica Chimica Acta*, 2006, pp. 140-152; M. Regert, J. Langlois, and S. Colinart, "Characterisation of wax works of art by gas chromotographic procedures," *Journal of Chromatography*, 2005, pp. 124-136.

51 In the filing itself the action is always in one direction because of the direction of the teeth of the file. Because of the enormous number of teeth in the file, there would be no change in the result, even if some teeth were pointing in a different direction. In addition, some scratches are round, and others are not. As both have the same depth, they could never have been made with a file.

52 These sorts of personal characteristics quite often remain in bronze sculptures, such as a fingerprint of Adriaen de Vries in his *Mercurius* and *Psyche*, in F. Scholten, R. Mulcahy, L.O. Larsson, G. Cavalli-Björkman, F.G. Bewer, U. Heithorn, T. DaCosta Kaufmann, and A. de Koomen, *Adriaen de Vries, 1556 – 1626*, Waanders Publishers, Zwolle, 1998, pp. 36.

53 "Piglisi di quella terra che comunemente adoperano I Maestri da fare l'Artiglieri, la quale si suuol cauare di luoghi dinersi; percioche alcuna se ne ritruona exxcre apresso de'fiumi ch'è alquanto arenosa, ma per tal effetto non vuol'essere troppo arenosa, ma basta che la si magra, essendo che la terra grassa. Ma la buona si ritruoua ne' Monti nelle Grotte, in Roma, in Forenze, in Parigi, particolarmente, se ne truova dell perfetissima, è di tal bontà che niuna dell alter ho[?] io mai ritronata approposito. La terra che si caua delle Grotte è migliori die quell ache si piglia vicino a'Fiumi. A volerla per potersene seruire bisogna la sciarla feccare, poi che fia secca staccisi con uno stastaccio alquanto radetto, accioche n'esca alcune pietruzze alter simiglianti cose. Ciò fatto si debbe mescolare con essa Cimatura di panni, la quale vuol esser per la metà manco della detta terra. E qui auuertisca l'Artefice à quello ch'io son per dire; percioche io gl'insegno un segretto da me ritrouato per mezzo dell'esperienza, il quale m'è riuscito in tutta perfezione è questo. Poi che si fara à mescolato la terra con la Cimatura, si debbe battere con una Verga di ferro grossa due dita diligentemente, in questo consiste il secreto, perchioche la si debbe mantener molle per quattro mesi almanco, quanto più sta tanto più è miglio, perche la Cimatura marcisce diuenendo cosi marcia fa esserela terra morbia com`un`unguento, la qual cosa essendo veduta da quelli che di ciò non bauno fatto sperienza sarebbe giudicata noceuole, la terrebono per terra troppo grassa, ma questa grassezza non impedisce il receuimento del metallo, anzi l'accetta più volentieri senza comparazione dell'altra terra che come questa non s'è lasciata marcire, si come in diuers'opere ho sperimentatom che qui di sotto si diranno." Benvenuto Cellini, *Due Trattati*, Florence, 1568, pp. 47, translation by C.R. Ashbee, *The treatises of Benvenuto Cellini on goldsmithing and sculpture*, Dover Publications Inc., New York, 1967, pp. 113.

54 "Cio fatto macinai del midollo arso di corna di castrato. E con esso per la meta di detto midollo, macinai Gesso di Tripoli. E altrettanto di scaglia di ferro, cosi macinate benissimo le dettre tre cose le me scolai insieme con un poco di lotodi stallatico die bue. O di canallo, passato per uno staccio

sotilissimo con acqua pura. Il quale rende solamente l'acqua tinta di detta stallatico." Benvenuto Cellini, *Due Trattati*, Florence, 1568, pp. 46, translation by C.R. Ashbee, *The treatises of Benvenuto Cellini on goldsmithing and sculpture*, Dover Publications Inc., New York, 1967, pp. 112.

55 These hollows will never be rounded because they will assume the shape of the burnt organic material.

56 After the clay has been fired it is a fire-resistant material.

57 F.G. Bewer, "A study of the technology of Renaissance bronze statuettes", London, Dissertation, Dept. of Archaeological Conservation and Materials Science, University of London, University College, Institute of Archaeology, 1996, Plate 1 and the execution in Plate 11, F.G. Bewer in V. Krahn, *Von allen seiten schön, Bronzen der Renaissance und des Barock*, Staatliche Museen zu Berlin, 1995, pp. 82-91; F.G. Bewer in F. Scholten et al., *Adriaen de Vries, 1556-1626*, Waanders Zwolle 1998, pp. 64-77; S. Sturman in D. Pincus, *Small Bronzes in the Renaissance*, National Gallery of Art, Washington 2001, pp. 121-143; J. Bassett, *The craftsman revealed, Adriaen de Vries, sculptor in bronze*, J. Paul Getty Trust, 2008, pp. 14; V. Avery and J. Dillon, *Renaissance and Baroque Bronzes from the Fitzwilliam Museum, Cambridge*, Daniel Katz Ltd., London, 2002, pp. 235, J. Bassett & P. Fogelman, *Looking at European Sculpture, a guide to technical terms*, V&A Publications, 1997, pp. 54-55.

58 G. Boffrand, "Description de ce qui a été pratiqué pour fondre en bronze d'un seul jet la figure equestre de Louis XIV," Chez Guillaume Cavelier pere, Paris, 1743; G. Bresc-Bautier, G. Scherf, I. Wardropper, J. Draper, A. Boström, A-L. Desmas, *Cast in Bronze, French sculpture from Renaissance to Revolution*, Musée De Louvre editions, Somogy Art Publishers, Paris, 2008, pp. 318-321.

59 "Cosi armata considerare dove piu potiare fare il nostro gitto, ch'il bronzo senza impedimento possi per tutta la forma caminare et caricare di mano in mano in se medesime perche si spenga nelle parte sottili et per piu sicurta, face[n]do in certi luochi alcuni condotti, che se da per se il bronzo non andasse nel portino, et cosi appresso al gitto si deve fare due, tre sfiatore che portin fuore le ventofita et li fumi che si generano il caldo nella forma, per che in quelli tuocchi ché l si rinchiudesse il bronzo non portrebbe entrarre." Vannuccio Biringuccio, *Pirotechnia*, P. Gironimo Giglio, e compagni, 1540, pp. 177. The English translation is by C.S. Smith. M. Teach Gnudi, *The Pirotechnia of Vannoccio Biringuccio, The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, Dover Publications, 1990, pp. 229.

60 Scholten, op. cit., 1998, pp. 46-51.

61 I would like to thank Professor Dr. John Campbell, Emeritus Professor of Casting Technology, The University of Birmingham, UK, for his comments and insights in the resulting working method.

Chapter VIII

Reconstructions testing 16th century casting techniques

Using the material for moulds that was available in the 16th century, how would it have been possible to produce a perfect bronze statuette that did not have to be chased without making use of a large number of vents and casting channels, also known as sprues? And how thin can a bronze be cast, as Vasari described, if it still has to be chased? To obtain answers to these and other questions about 16th-century casting technology, it is necessary to make reconstructions. The starting point in the research using the reconstructions described below is a model of a torso which was used for three different procedures.[1]

For the first procedure imperfections were deliberately incorporated into the wax layer (3.5 - 4 mm), such as a fingerprint on the right shoulder of the torso, and the seams of the individual moulds were not removed on the wax model (Figs. 1-9). This experiment tests the quality of the material used to make the mould. If the subtle imperfections in the wax are also reproduced in the bronze, the right material was used. For the second procedure the wax models – with walls varying in thickness from 3.5 - 4 millimetres – were buffed with a cotton cloth to make them shiny before they were sealed in the mould material (Fig. 10). The reconstruction should result in a bronze surface that hardly needs any finish. In the third case the models had walls of different thicknesses of respectively 1.6 mm, 2.5 mm, 3.7 mm, 5 mm and 8 mm. These thicknesses are based on measurements of 16th-century bronze sculptures (Fig. 11).[2]

Thicker walls were omitted because they were rarely used to cast bronze sculptures which needed very little finishing.

Fig. 1: The plaster mould in three parts..

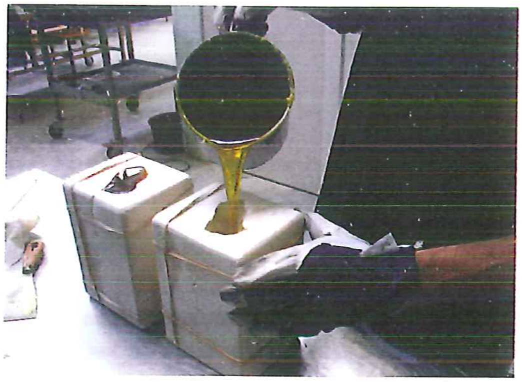


Fig. 2: Pouring the wax into the mould.

Fig. 3: Decanting the wax from the plaster mould.

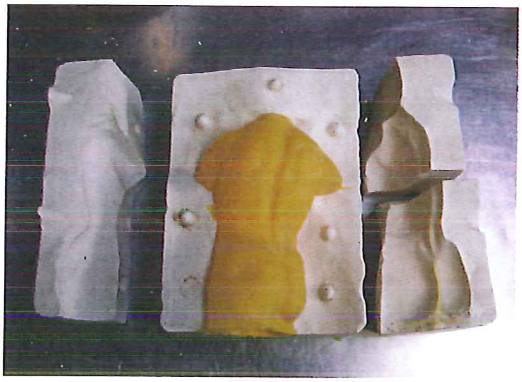


Fig. 4: The plaster model taken apart with the wax model within.

Fig. 5: The wax model placed on one conical sprue (feeder) and one vent.

Fig. 6: Applying of the first investment layer with a mixture of very fine plaster, and grog.

Fig. 7: The second coarser material of the same ingredients of the investment. Note that the sprue and vent are not covered with the fine detailed first layer of the investment.

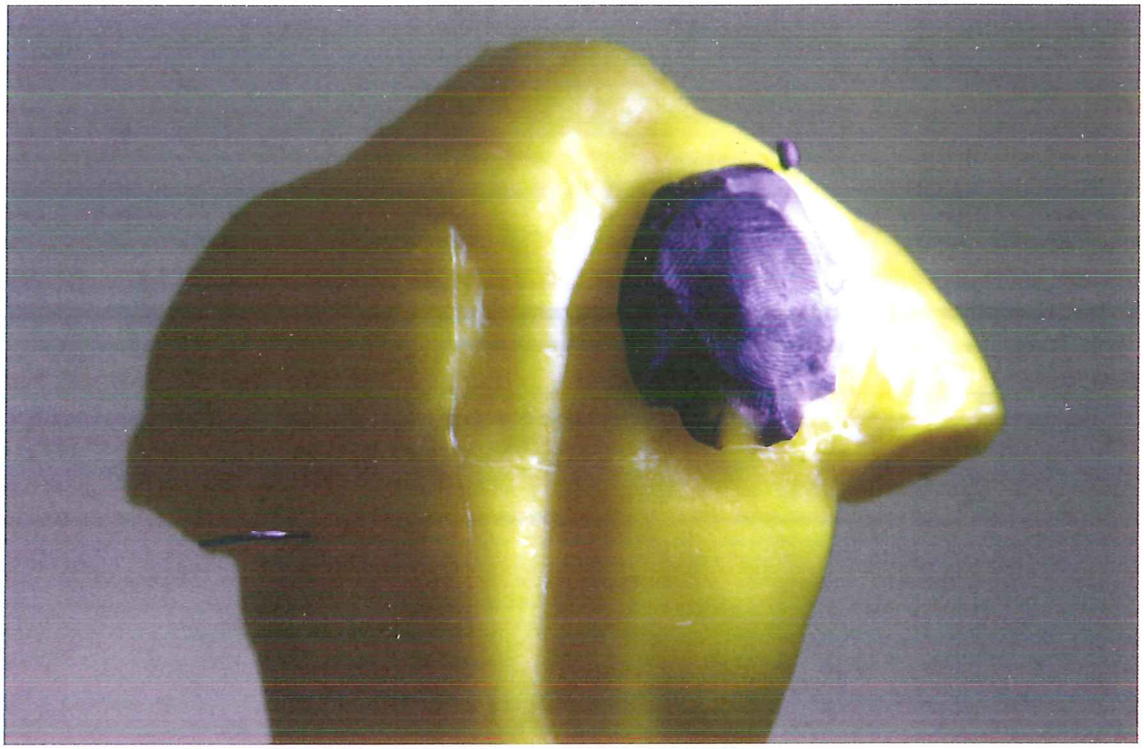


Fig. 8: Close up from the fingerprint on the back of the torso.

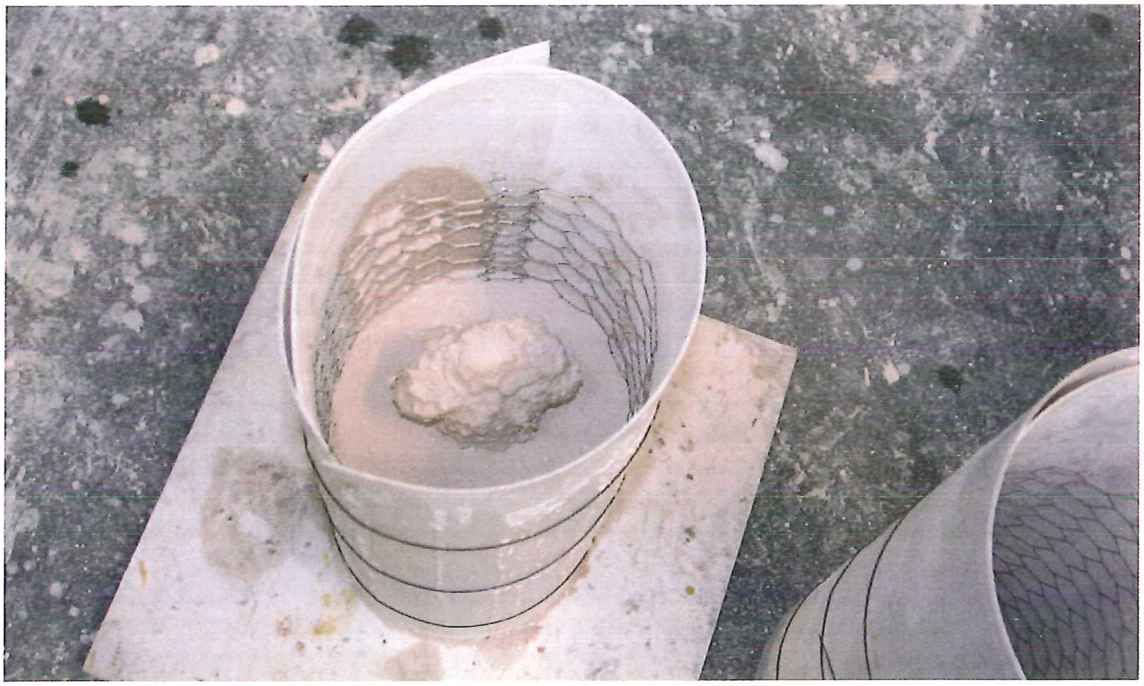


Fig. 9: The most coarse investment material is cast around the model with the two layers attached to it.

Fig. 10: An example of a buffed wax model.

In this case tests were carried out to see how thin the bronze could be cast. These models also serve for a chasing test to see whether there is any change in shape with a particular thickness of metal.

All the wax models which were used for the three different experiments were placed on one vent and one sprue. In addition, ox gall was applied to all the wax models.[3] Ox gall was already being used as a decorative material for sculptures in Pliny's time, but in this case it has a dual purpose: one of its characteristics is that it adheres to both a greasy and a watery layer.[4] It is possible to apply a very thin layer of ox gall to the wax model before the heat-resistant layers of the outer casing are applied. In contrast with the procedure used by Cellini, but using materials available in the 16th century, it was decided to use a mould material consisting of a mixture of grog and plaster ground into very small grains with the consistency of flour. While this mixture is applied to the layer of wax, air is blown onto the surface through a tube. The heat-resistant substance that is applied (with a viscosity comparable to yoghurt) becomes firmly attached to the surface of the wax as a result of the movement of the air, so that virtually no air bubbles can develop. A new layer consisting of the same ingredients is applied before the first layer of the mould material hardens (Fig. 8). The difference from the first layer is that the second layer has a slightly coarser composition. After the second layer, the whole recreation is sealed with an even coarser material consisting of the same ingredients, once again before the second layer has hardened, resulting in a mould that can be used for casting as shown in figure 9.

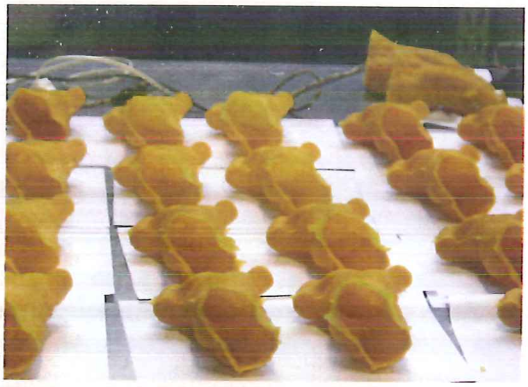


Fig. 11: Various thicknesses of wax.

The sprues are made of the same wax as the torsos, but the floury mould material is not applied (Fig. 7). The sprues are covered only with the coarser mould material. This means that it is possible to indicate any differences that have resulted because of the type of mould material that was used. All of these reconstructions were made using pure metals, cast with the following different compositions (based on the weight ratio). The composition of the first series of models is a tertiary alloy of 87% copper, 8% tin and 5% lead. The second model has a quaternary composition of 89% copper, 7% tin, 2% zinc and 2% lead. This composition was often used to cast detailed ornaments. The choice for bronze of different compositions can lead to a greater insight into the casting characteristics of these alloys. For the first series of models the casting temperatures used were 1131 C and 1180 C, both monitored with a pyrometer (Figs. 12-17).

Results

At the higher temperature the metal was significantly easier to cast, and the casting of the test of the fingerprint and with the shiny wax models resulted in an almost perfect bronze surface (Figs. 18-20).

The torsos seemingly did not require any finish and in terms of precision, corresponded to the surface of Willem van Tetrode's *Hercules Pomarius*. The result of the test, using wax models with imperfections, showed that all the details of the wax model were reproduced in the bronze. In the third test the results were different, as had

Fig. 12: The various investment moulds are placed in sand.

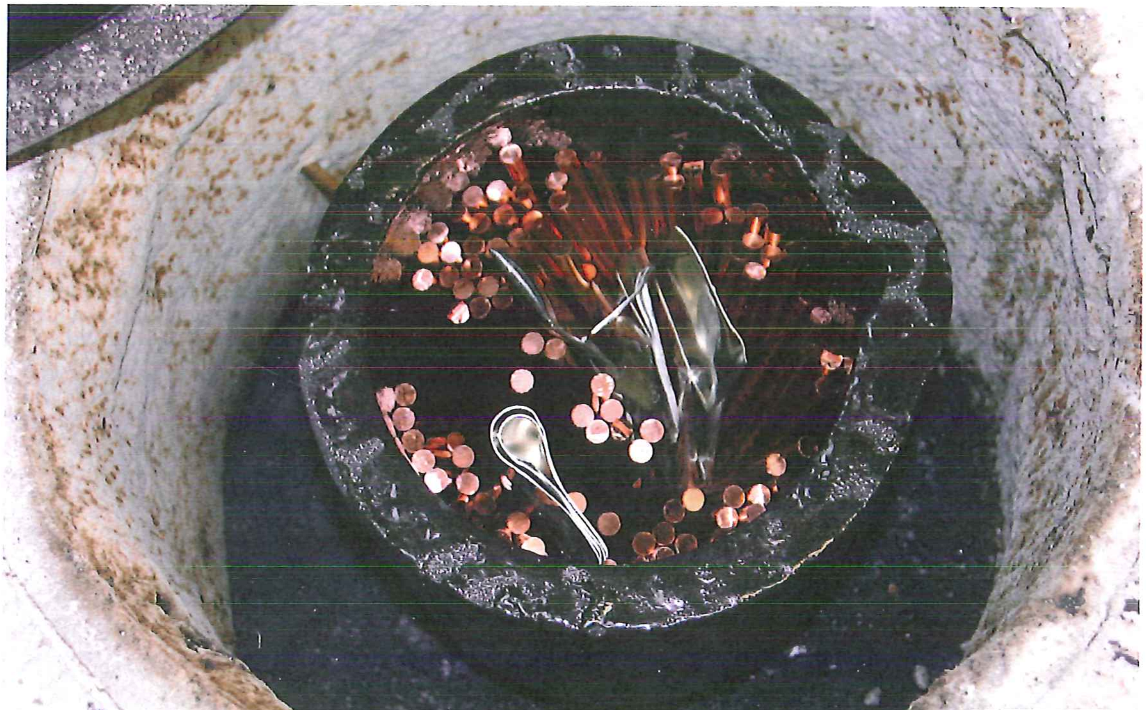


Fig. 13: Pure metals are used in the crucible.

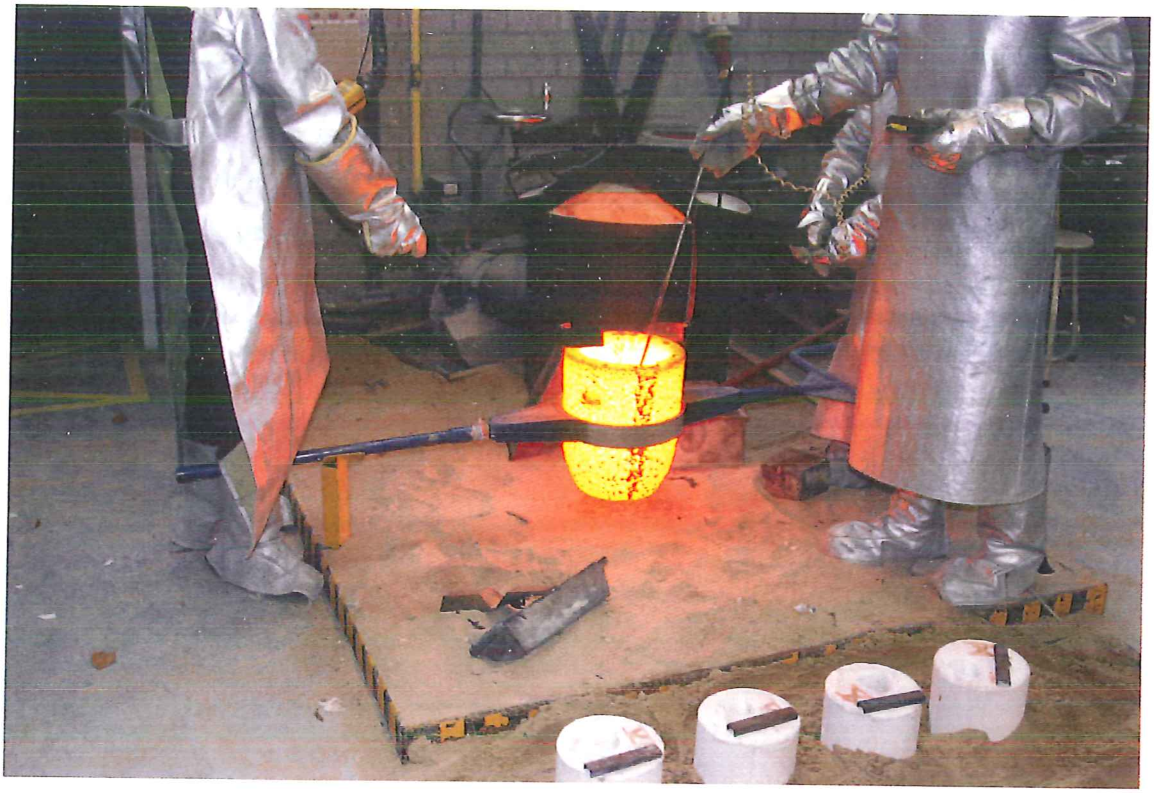


Fig. 14: The metal is heated to a temperature so it can be cast.

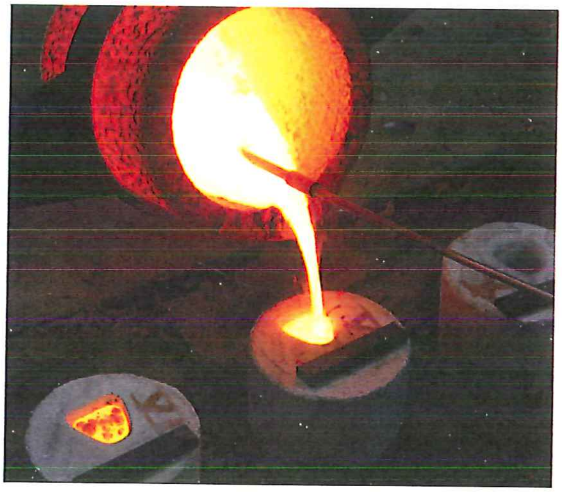


Fig. 15a: The bronze is cast in the investment mould.

Fig. 15b: A pyrometer shows the casting temperature.

Fig. 16: After sufficient cooling, the investment is removed from the cast bronze.

Fig. 17: The casting results still partially covered with the investment material. Note the colour change in the investment material closer to the cast metal.

Fig. 18: The final casting result of a fingerprint in metal.

Fig. 19: The result of a cast torso with a fingerprint and fin moulds.

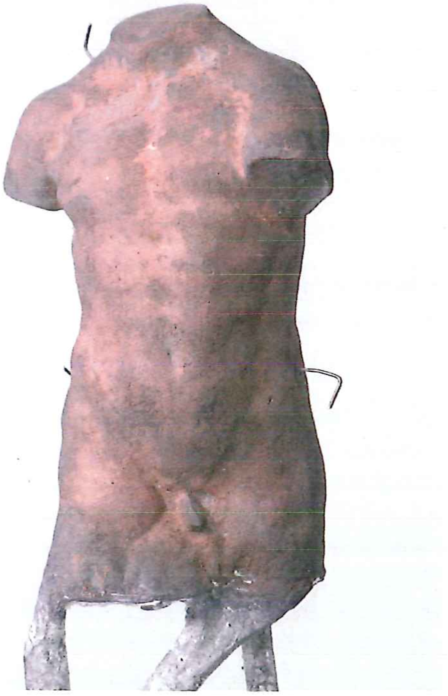
Fig. 20: The result of a cast torso started from a buffed wax model after casting.

been expected. Some of the models did not come out of the mould well: the model of 1.6 mm was not entirely successful, though a good result could have been achieved with some extra work. The subsequent models did come out of the mould perfectly (Figs. 21a/e-22).

Finally, one other striking fact emerged. The sculptures were placed on vents and sprues with a wax surface comparable to that of the torsos, but without the application of the mould material ground to flour. The resulting surface here was significantly coarser (Fig. 23). Therefore this reconstruction research demonstrates that it is possible to cast a virtually perfect bronze surface using a shiny wax surface and a refined mould material that was also available in the 16th century.[5] In addition, it showed that the same refined mould material transferred details, such as a fingerprint and lines of the individual mould, to the bronze surface. It also showed that with a wax model with walls from 2.5 mm thick, and with materials available in the 16th century, it was certainly possible to achieve a good casting result with the above-mentioned alloy and without additional vents or sprues, with the transfer of all the details present in the wax model to the bronze (the fingerprint and lines on the individual mould).

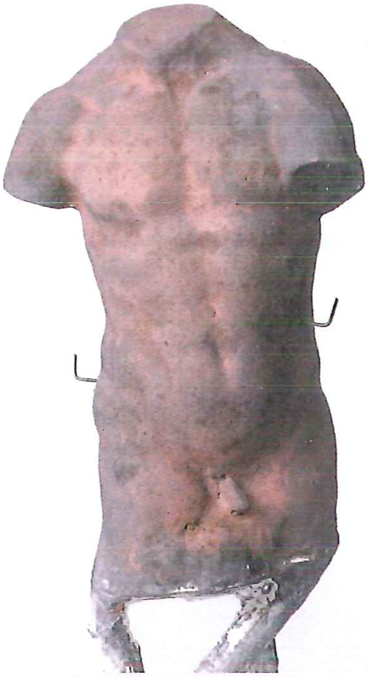
21 A1: 1.6 mm

21 A2: 1.6 mm



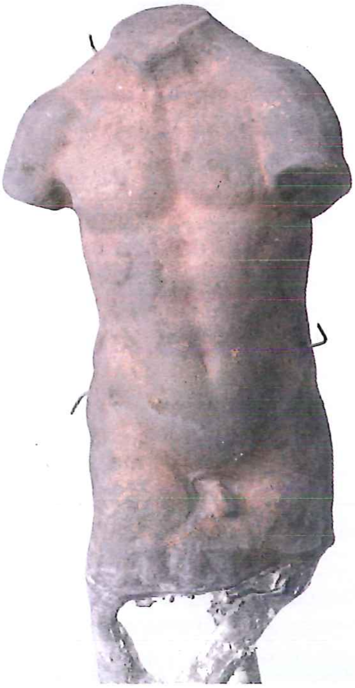
21 B1: 2.5 mm

21 B2: 2.5 mm



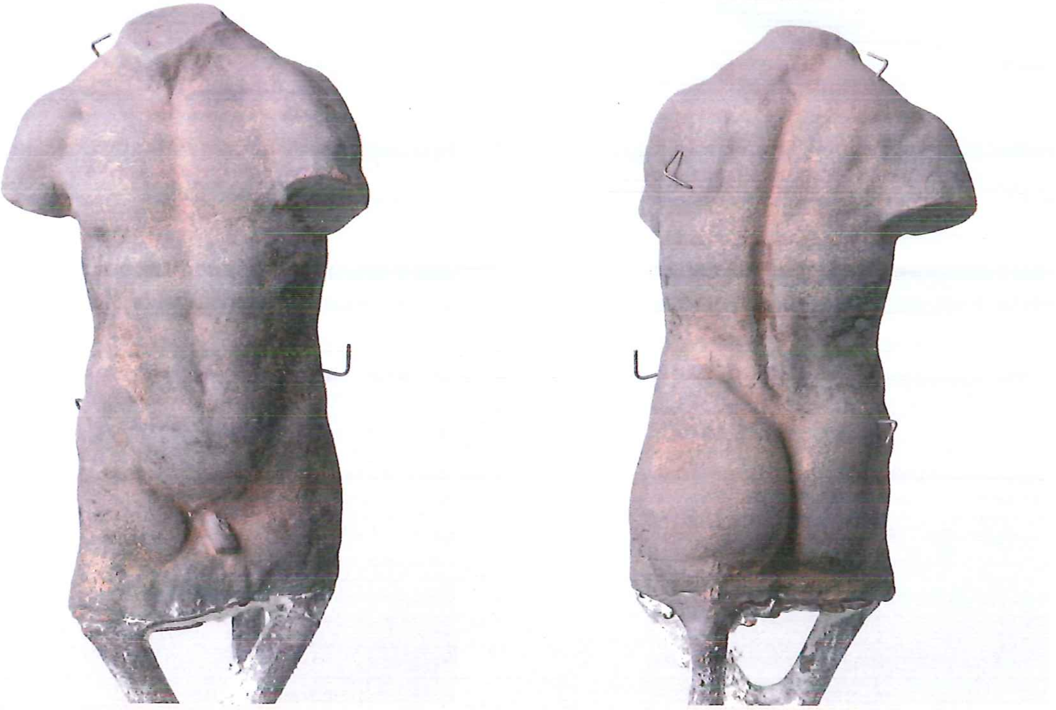
21 C1: 3.7 mm

21 C2: 3.7 mm



21 D1: 5 mm

21 D2: 5 mm



21 E1: 8 mm

21 E2: 8 mm

Fig. 21 a/b/c/d/e: Five different casting results, front (1) and back (2) from thicknesses starting from 1.6, 2.5, 3.7, 5 and 8 mm after removal of the casting skin. Note that thickness 1.6 mm did not come out of the mould completely.

A change in the shape of the metal as the result of chasing

What is the minimum thickness for the wall of a bronze sculpture that can still be chased without resulting in a change in the shape of the sculpture? The reason for this question is a bronze bust of *Pope Gregory XIV* with a maximum thickness of 3.5 mm (Chapter VI, Fig. 3). As chapter VI shows, using neutron diffraction, this bronze was not chased, but the question is whether this would even have been possible as the bronze is so thin. The bronze reconstructions in the third test with a thickness of 2.5 and 3.7 mm were scanned for the chasing treatment.[6] Subsequently the surface was chased (while the core material was still present), using a chasing hammer and punches. The surface was then scanned again to record any change in shape.

Figures 24 a/d shows that the change in shape as a result of chasing is minimal and barely visible with the naked eye. In the bronze with a thickness of 2.5 mm the blue colour indicates where the metal has been slightly depressed (in mm), creating a minimal change in shape. The front and back have been slightly depressed, while the sides are actually slightly bulging. In the bronze with a thickness of 3.7 mm there is virtually no visible change in shape as a result of the chasing. The metal is so thick that the use of the chasing punch does not cause any distortion on the surface. This shows that it is possible to chase even thin sculptures (with walls from 2.5 mm thick) without causing a perceptible change in shape. Renaissance bronze statuettes are generally thicker than 2.5 mm and therefore this research confirms that most 16th-century bronze sculptures could be chased without any problems. However, the composition of the alloy does play a role, as will be discussed below.

Casting metal with different compositions

Biringuccio wrote that some metal casters were not very precise about the composition of their alloys:

Also, many artificers, in order to avoid expense, are content with having a larger quantity of metals and do not care so much about their perfection. For this reason they willingly

Fig. 22: Detail of 3.7 model showing the superbly soft finish of the bronze after removal of the casting skin.

Fig. 23: The casting result of investment material that was not ground to flour.

accept mixtures of one metal with another, for example, of silver or copper with gold, of copper with silver, and likewise of tin or lead with copper.[7]

Obviously the requirements imposed on copper alloys were different from those for alloys containing gold or silver, because gold and silver represent(ed) a direct monetary value. Therefore it is rare for historical copper alloys to always have exactly the same composition. This also corresponds within the variations of the compositions which have been measured in bronze statuettes in various museum collections.[8] There is usually a series of compositions, in which copper is always the main component. In addition, tin, zinc, lead, arsenic, antimony, iron, silver and bismuth are found either individually or in different combinations.

In the past few decades scientific research into bronze sculptures has devoted a great deal of attention to the composition of alloys, though often without clarifying its significance.[9] The question is whether an alloy is significant for the (art)historical identification of a bronze. In other words, can the composition of the metal serve as the "fingerprint" of an artist, bronze caster or foundry?

Many techniques have been used to analyse metals up to now.[10] A number of these require a small sample to give a detailed picture of the composition of the alloy.[11] As museums prefer to work in a non-invasive way, they usually make use of the X-ray fluorescence spectrometry (XRF) technique. Inter-laboratory research by Arlen Heginbotham into XRF users in museums reveals that the XRF technique is not without its dangers: the same samples did not produce the same results in different laboratories with different XRF equipment.[12] This is caused above all by the use of different software to interpret the data. XRF analyses the surface of the metal and, with a quantification per element that is measured, it can produce a composition percentage of the place that has been measured.[13] XRF is a surface analysis technique in which only a small part is analysed.[14] The measurement can penetrate the copper alloy to a maximum depth of only 20-30μm.[15] The question therefore arises of how representative such limited measurements can actually be.

Furthermore, in historic bronzes the choice of the surface area to be measured is of essential significance. Is the metal free of oxides? Is there a patina which could interfere with the measurement? Have there been any old repairs or treatments causing a change in the composition? Chapter V shows that a Renaissance bronze sculpture does not have uniform alloy compositions. Advocates of the XRF technique maintain that it is possible to achieve representative measurements by choosing and analysing different measurement points, and then taking the average values. However, this also contains the danger that alloys do not necessarily have a balanced composition because of the possible segregation of the metals in the alloy. Furthermore, in the pre-industrial era there was a problem of divergent compositions, as is shown by that specific research.[16] A heterogeneous composition resulted if the metal was insufficiently heated during the melting process.[17] Even if these risks are avoided as far as possible, what is the value of the results of XRF research? What precise composition was the starting composition used by the bronze caster when different results were achieved? If the composition of the bronze is to be linked to objects presumed to have been made by the same artist, as Smith

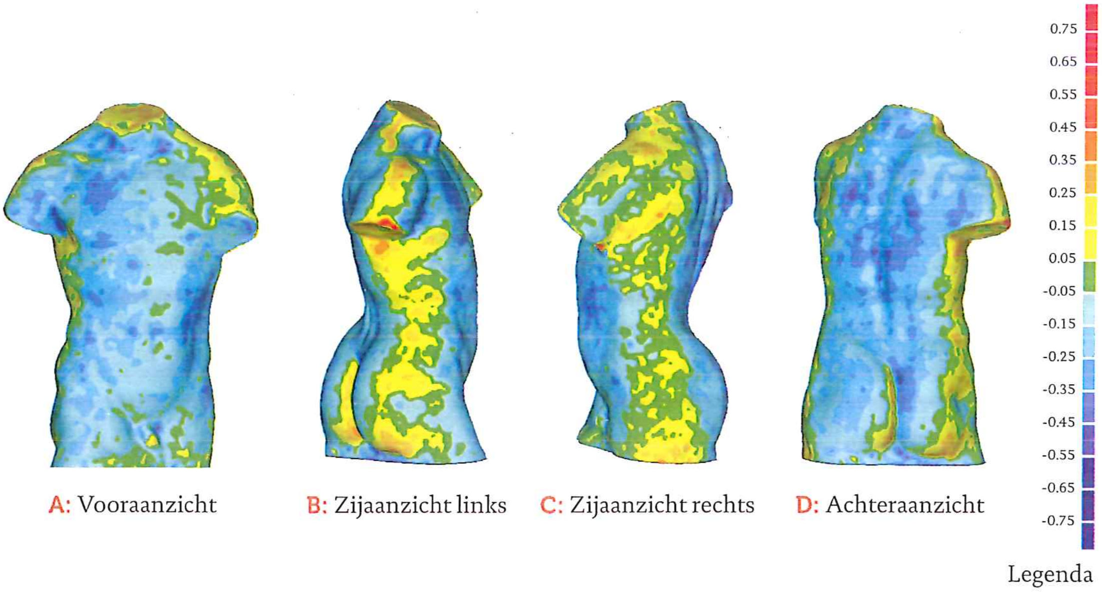


Fig. 24a/d: 3D measurements of 2.5 model from four angles showing the differences before and after chasing: Max. +/- : 0.83 / -0.67 Average +/- : 0.10 / -0.16, STDEV : 0.15 (illustrations by Gerben Botman TATA Steel).

did, this implies that artists were able to work with pure and consistently refined metals in the past.[18] The question is whether this was possible in the pre-industrial era. For example, more research must be carried out into the distribution of copper alloys and pure metals in Europe during the 16th century.[19] It is virtually impossible to determine with any certainty whether alloys were made by a bronze caster from "pure" metals, or, for example, by re-melting cannon bronze or bells. At the same time it is not very likely that a bronze cannon weighing 1500 kilos would have been melted to make a small statuette weighing 20 kilos or less. Moreover, there were certainly some rules of thumb for the choice of an alloy in the art of casting, as indicated by Biringuccio:

Now, so that you may understand well, I tell you that various kinds of this are made, all according to the proportions of the quantities and according to the kind of work. For one kind of bronze is desired by those who make statues; this is not desired by those who make artillery or by those make bells, mortars, basins, and similar cast objects. Now in order to alloy it into the species of bronze, eight, nine, ten, up to twelve pound of tin are put with every hundred pounds of copper. Those who want to make bells put twenty-three, twenty-four, twenty-five and twenty-six, depending on the tone, on whether they are large or small in form, and on whether they wish to make the tone deep or sharp and clear. From twelve upwards is used for all other works that need it, either for hardness or to give them fluidity in casting by surpassing the degree of bronze.[20]

The percentages which Biringuccio gives for bronze statues are fairly accurate, varying from 89% with two intervening stages, to 92.5 % for a copper/tin alloy. Therefore in the 16th century people were able to weigh these percentages. In addition, Biringuccio stated that in the 16th century it was possible to recognise pure metals empirically. For tin, he described this as follows:

The best of these is the one that is the purest in its kind. In the alloy of tin is the one that is the whitest and hardest, or when it is bent, or some thin end of it is held tightly by the teeth, it heard to crackle as frozen water does.[21] What Biringuccio said about this was correct: pure tin does actually have this property when it is bent. However, alloys which are measured hardly ever consist only of copper and tin. In some cases sculptors were consistent in their use of metal alloys, like Adriaen de Vries.[22] The results of measurements of samples of his sculptures reveal a reasonably consistent pattern.[23] Nevertheless, deviations were also measured, as demonstrated by Bewer.[24] The assumption that measurements of very low concentrations of elements would give clearer results should be examined in more detail.[25] However, for the time being it would be risky to attribute a bronze statue to an artist on the basis of low concentrations.

More detailed research into copper alloys containing lead would seem to be relevant in this respect. Information on the age of the lead ore, and therefore possibly its place of origin, can be obtained by determining the ratio of lead isotopes. There is a danger here because it was recently demonstrated that lead isotopes are also found in measurements of zinc ore containing lead, which can result in an imbalance in the ratio for the "normal lead" in bronze alloys.[26] Therefore research into the ratio of lead isotopes appears to be insufficiently reliable to serve as a basis for studies of authenticity. However, the information which is obtained from non-destructive measurements of the composition of an alloy is not by definition useless, though it is important to see this information in a context which applies in practice. Thus the choice for a particular type of alloy will depend on the function and the shape of the bronze object to be made. Different requirements apply for artillery than for a statue or a bell. Biringuccio warned of this:

I warn you to understand that it is the requirements of the work that determine the alloy.[27]

In the practice of casting bronze there are five factors which are important for the composition of the alloy:

- the melting temperature of the alloy;
- the viscosity of the metal in its molten condition;
- the working properties of an alloy;
- the size of the statue;
- the colour.

The melting temperature is directly related to the composition. A binary alloy of copper/tin with a composition of 93% copper and 7% tin (93/7) has a melting temperature of approximately 1050 °C. For an alloy of 90% copper and 10% tin (90/10) it is approximately 1020 °C, and finally, for an alloy of 85% copper and 15% tin (85/15) it is approximately 980 °C. The amount of energy needed for a copper alloy to be melted so that it can be cast differs enormously. It is useful to remember that in the past the ovens were fired with wood/charcoal. Biringuccio was aware of the fact that a higher tin percentage makes the alloy more watery and therefore easier to cast:

..but to corrupt it for the art of casting and to destroy a certain natural viscosity. For this result it is accompanied by tin and also, sometimes brass. But its proper and true alloy is fine tin, except, however, when you wish to make hammered works.[28]

The viscosity of a molten alloy is determined by the composition. From practical experience we know that an alloy of copper/tin 93/7 has a higher viscosity and will therefore not flow as easily into every detail as an 85/15 copper/tin alloy. Knowing this, it is interesting to look at the casting process that Cellini described for his Perseus. In his *Due Trattati* he describes how he was taken from his sickbed by his workers, and how he had a brilliant idea for the bronze which would not melt.[29] He had tin plates brought from his house and added them to the mixture. The temperature at which the metal melts is actually reduced by the addition of tin, so that the bronze becomes easier to cast. It is not quite clear why Cellini referred to this as if it were his own personal discovery. Every bronze caster knew about it and the process had been described five years earlier in *De la Pirotechnia*. It is striking that in analyses of the Perseus the tin percentages are extremely low (2.29%) while they are significantly higher for the head of Medusa (6.32%).[30] The temperature at which the alloy melts is higher because of the low percentage of tin, and this explains why the Perseus was more difficult to cast, as the metal did not become sufficiently viscous. The viscosity of the copper alloy is also determined by the surface tension of the metal, thus by the percentage of tin. Biringuccio was familiar with this phenomenon, which was influenced by the addition of metals such as lead and arsenic. In this respect Biringuccio referred to a specific passage in the chapter on arsenic:

And because of a certain subtlety and easy digestion they penetrate very easily into the fused metals. Indeed they act in such a way that they corrupt and convert almost into another nature any metal with which they find themselves.[31]

One example of this practice is illustrated by a statue of *Paris* attributed to Severo da Ravenna (chapter VI).[32] In addition to arsenic, the alloy used for the *Paris* also contained lead, which makes the metal very suitable for being worked with hammers and punches, as was the case in this statuette. The fact that lead makes chasing so easy is explained by the following physical property: lead can only penetrate the alloy to 0.4%, and the surplus remains within the grain limit.[33] This remaining lead serves as a 'lubricant' between the crystals, so that the metal is easily distorted when it is chased. If there is too much lead in an alloy, the metal becomes porous and more difficult to cast. As bronze was often melted down, the information on the exact composition was lost. The casters carried out tests in order to ascertain whether the metal could still be cast, The calculations book of the papal bronze caster Giacomo Laurenziano (who worked from 1599-1633) gives an example of this. It concerns the work for two eagles and two dragons for the column of the Virgin in the Piazza Santa Maria Maggiore in Rome (1613-1614). Laurenziano obtained the bronze from the Pigna

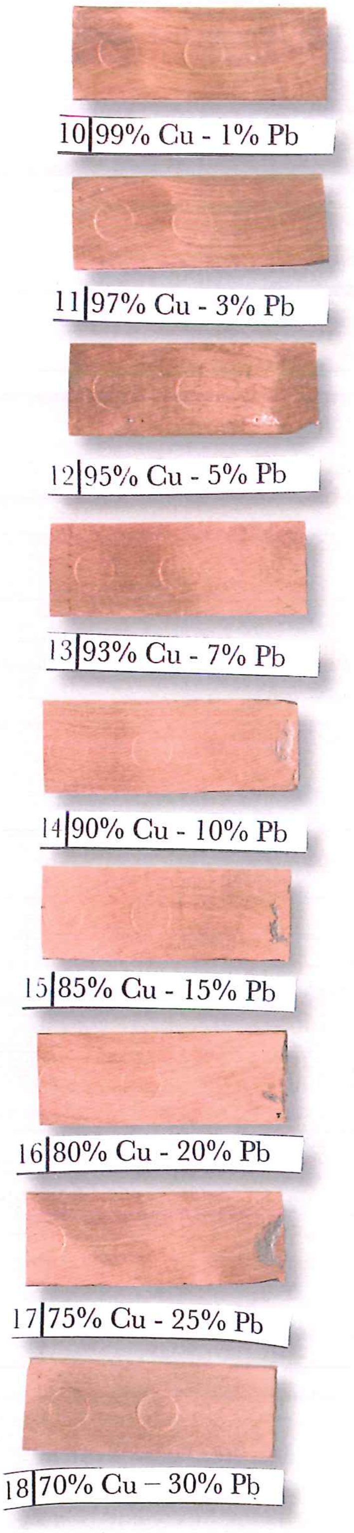


Fig. 25: Overview of various copper/lead alloys ranging from 1-30% lead added.

fountain, which was demolished by Pope Paul V. The reference to the low quality of the bronze concerns a passage about the carriers, who brought the metal to the bronze caster.

And more for the carriers for taking, bringing and weighing the bronzes from the Belvedere, which was full of lead, with casting it all went in foam (porous)? and cast badly (shrinkage) as can be tested [...].[34]

It is not clear whether there was actually a difference between alloys used for casting large and small bronze statues. The choice of an alloy for large bronze statues was probably largely determined by the casting quality of the alloy, and there was less emphasis on the working properties of the bronze. For smaller statues the aspect of working the bronze admittedly played a more important role, but it is doubtful whether this had a significant influence on the composition of the alloy. For example, a comparison of the different compositions of the *Hercules Pomarius* and the bust of *Pope Gregory XIV* suggests that it was not a decisive factor. The composition of the *Hercules Pomarius*, a tertiary copper-zinc alloy with added lead, does not have a particularly low viscosity, nor does the binary copper-tin alloy of the bust of *Pope Gregory XIV*. Therefore in both cases the viscosity of the metal is sufficiently large to produce a casting result which follows the finely detailed hollow space in the material of the mould. Biringuccio also noted, as we have seen before, that not all bronze casters were precise about the composition of the casting metal. Therefore the result depends on where a sculptor had his bronze cast. In some cases it is known that sculptors had their bronzes cast by founders of bells or artillery, but in addition, "ordinary" bronze casters also worked with statues. Founders of cannon or bells were certainly aware of the fact that the composition of the alloy determines the quality of the final product. After all, a bell which produced the wrong sound, or a cannon which exploded, would be unacceptable. With regard to the casting of bells, Biringuccio wrote the following:

See that the metal is perfectly melted but not too hot and, if you wish the bell to have a good tone, be careful not only of its shape and suitable measurements but also that its alloy of metal be made with good tin that has no lead whatever in it, for this, besides making the cast ugly, impairs its tone.[35]

It is probable that founders of cannons and bells had a greater knowledge of the influence of the addition of metals to their alloys and of the advantages and disadvantages of working with pure metals. It also goes without saying that they applied this knowledge to a greater extent than the "ordinary" bronze casters. They will also have been familiar with the metallurgical techniques of purifying metals, as described by Biringuccio and Agricola, and as they are still used in mining.[36]

The last factor which influences the choice of a particular composition for the metal may be the colour of the metal. When the metal has been cast, possibly finished and polished with abrasive stones to a high polish, the colour of the metal is perfectly visible. It is determined by the composition of the alloy. Some sculptors leave their statues untouched when the polished surface becomes visible, and consider the colour of the metal as an integral part of their design. After a while the metal oxidises, resulting in a darker colour. Pliny knew this and he advised covering the metal with bitumen.[37] According to Heithorn, this is what happened to the bronzes of Adriaen de Vries.[38] However, as Vasari noted, different sculptors had their own ideas about this:

This bronze which is red when it is worked assumes through time a natural change of colour that draws towards black. Some turn it black with oil, others with vinegar make it green, and others with varnish give it the colours of black, so that everyone makes it come as he likes best.[39]

The choice of an alloy will have been determined in close consultation between the sculptor and the bronze caster. The characteristics of the colour are dependent on the composition, but this in turn determines the casting properties. According to Biringuccio, the following facts are relevant:

When you come to this association, just as it changes nature and appearance according to the proportion of tin which you give it, so it changes name and is no longer called copper but bronze, or for a greater distinction of the quantity of tin for every hundred or more of copper, it is called by skilled workmen metal of more or less fineness as it contains more or less tin. This is recognized by the whiteness and brittleness, changing from red, which is the colour of copper, it becomes white; from soft and flexible it becomes hard and brittle as glass.[40]

This last passage once again clarifies that there was an awareness of the physical effects of the composition. A sculptor who did not want to give his sculpture a patina was aware of the composition which had to be chosen for this. The addition of lead was an exception: the colour of a copper alloy remains virtually constant, irrespective of the percentage of lead that is added (Fig. 25).

However the porosity does increase if it contains more than 0.4%, as shown in figure 4 of Chapter III. Once again this illustrates the fact the compositions of alloys can only partially be tested visually; even an experienced bronze caster could make a mistake. The physical analysis of the composition of alloys and of their optical effects provides valuable indications of the original colour of sculptures, and therefore contributes to the history of preferences in bronze statues.

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1 I would like to thank Francesca Bewer for providing the basic shape of this model, which I adapted to the current model, as well as Jeroen van Halder and Kunstenaarswerkplaats Beeldenstorm in Eindhoven for their constructive contributions to this research.

2 The *Hercules Pomarius* has a maximum thickness of 8 mm, while the bust of *Pope Gregory XIV* has an average thickness of 3.5 mm. The thinner thicknesses of the walls have been chosen to test the hypothesis of casting thin metal.

3 The ox gall used came from Talens. Royal Talens, PO Box 3, Apeldoorn, The Netherlands

4 Pliny, *Natural History, Books XXXIII-XXXV*, Loeb Classical Library, Harvard University Press, Cambridge MA, 1996, pp. 197.

5 It is impossible to determine whether this was actually applied in the 16th century, because the outer mantle was always completely removed after the bronze was cast.

6 The scans were carried out with an EXAscan 3D scanner. I would like to thank Hans van der Weijde and Gerben Botman of Tata Steel for their help with these tests. Technical specifications: Weight 1.25 kg (2.75 lbs.), Dimensions 172 x 260 x 216 mm, (6.75 x 10.2 x 8.5"). Measurement 25,000 measures/s, Laser Class II (eye-safe), Resolution in x, y, z axis 0,05 mm (0.002"), Accuracy up to 40 µm (0.0016"), ISO 20 µm + 100 µm/m, Depth of field 30 cm (12").

7 "Perche sono alcuni d'essi, che redutti alla loro finezza, e perfettione in certe opere malamente servirebbeno, molti artefici ancho per fuggire spesa lor basta l'haver della cosa piu quantità, non si curano delle molte lor perfettione. Perilche voluntariamente vengano à gli mescolamenti dell' un metallo con l'altro, come l'oro, l'argento, ò il rame, e similmente co'l rame lo stagno ò piombo; co'l stagno, non volendo guastar del tutto la sua natura." Vannuccio Biringuccio, *Pirotechnia*, Venice, P. Gironimo Giglio, e compagni, 1540, Libro II, Cap VII, pp. 160r. The translation is by C.S. Smith, M. Teach Gnudi, *The Pirotechnia of Vannoccio Biringuccio, The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, New York, Dover publications, 1990, pp. 207.

8 F.G. Bewer, "A study of the technology of Renaissance bronze statuettes," London, dissertation, Dept. of Archaeological Conservation and Materials Science, University of London, University College, Institute of Archaeology, 1996; D. Smith, "The application of alloy analysis to questions of attribution: Giovanni Francesco Susini and the workshop of Giambologna," *Conference proceedings, Metal 2010*, ICOM-CC metal working group, Charleston, South Carolina, 2010, pp. 189-197; J. Basset, J.P. Fogelman, D.A. Scott, R. Schmidtling II, *The craftsman revealed, Adriaen de Vries, sculptor in bronze*, The Getty Conservation Institute, 2008, pp. 27-33.

9 Bewer, op. cit., 1996, pp. 27-33

10 Researchers have often used Atomic Absorption Spectrometry (AAS), Inductive Coupled Plasma (ICP) and Laser Induced Plasma Spectroscopy (LIPS). In addition, X-ray Fluorescence Spectrometry (XRF) and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) are also used.

11 The results of AAS, ICP and LIPS are reliable, but these types of examination are invasive and do not indicate the content of the bulk composition.

12 A. Heginbotham, A.Bezur. M. Bouchard, J.M. Davis, K. Eremin, J.H. Frantz, L. Glinsman, L. Hayek, D. Hook, V. Kantarelou, A.G. Karydas, L. Lee, J. Mass, C. Matsen, B. McCarthy, M. McGath, A. Shugar, J. Sirois, D. Smith, R.J. Speakman, "An evaluation of inter-laboratory reproducibility of quantitative XRF of historic copper alloys," *Metal 2010, ICOM-CC Metal Working group*. Charleston: ICOM, 2010, pp. 178-188.

13 This technique is easy to apply, but also has a number of disadvantages. The equipment must be calibrated and the place where the measurement is taken is very important. XRF was developed for industrial purposes on flat polished metal. Renaissance bronze statuettes do not comply with this standard, and therefore it is recommended to interpret percentages as being indicative rather than in absolute terms. For further research and the application of this technique, also read: L.D Glinsman, "The application of X-ray fluorescence spectrometry to the study of museum objects," dissertation,

University of Amsterdam, 2004; Smith, op.cit., 2010; Heginbotham, op. cit., 2010; R. van Langh, A. Pappot, S. Creange, L. Megens, I. Joosten, "The effect of surface changes in heat treated bronze samples analyzed by X-ray fluorescence spectrometry," *Conference proceedings, Metals 2010*, pp. 204-209, ICOM-CC metal working group, Charleston, South Carolina, USA, 2010 (in this dissertation).

14 The spot measurement is dependent on the equipment. It is preferable to use a spot measurement that is as large as possible, so that lead in the alloy, which is difficult to mix, can still be included in the measurement result.

15 L.D. Glinsman, "The application of X-ray fluorescence spectometry to the study of museum objects," dissertation, Amsterdam," University of Amsterdam, 2004.

16 D. Smith and S. Sturman, "The art and innovation of Antico's bronzes. A technical investigation." In *Antico. The Golden Age of Renaissance Bronzes*, by E. Luciano, D. Allen and C. Kryza-Gersch. London: Paul Holbertson Publishing, 2011, pp. 157-177.

17 This leads to a presumption that it occurred less when a start was made with pure metals, although the opposite is actually the case. Segregation occurs less often when pure metals are cast than when alloys are reused (depending on the composition and the temperature).

18 Smith, op. cit., 2010, pp. 189-197.

19 The role of the Fugger family seems very important in this respect. Jakob Fugger the Rich (1459-1525), who owned copper mines in Hungary, Carinthia and Spain, particularly traded in metals, as did his successors. See N. Lieb, *Die Fugger und die Kunst*, Verlag Schnell & Steiner, Munich, 1958, pp. 76-90.

20 "Hor perche bene intendiate , di questo se ne fa di varie forte, tutto seco[n]do le proportioni delle quantita, et secondo le specie de lavori. Perchè di tale forte, il vogliano quelli che fanno le figure, che non il vogliano quelli che fanno l'artigliarie, ne ancho quelli che fanno le campane, mortari, laveggi, et simili altri lavori di gitto. Hor per legarlo nella spetie dell bronzo, otto nove dieci fin dodeci libre di stagno si mette in ogni cento libre di rame, e quelli che ne voglian far campane ve ne metteno vintitre, vintiquatro, XXV e XXVI , respetto al suono et secondo che le son di forma grandi, ò piccolo, ò che voglian fare il suon grave, ò acuto, et chiare, et da dodeci in su se ne fanno tutti queli altri lavori c'han di bisogno , ò per durezza, ò per far che corra il gitto per trapassare il grado del bronzo." Vannuccio Biringuccio, Pirotechnia, P. Gironimo Giglio, e compagni, 1540, Libro V, Cap III. pp. 162r-163v. The translation is by C.S. Smith, M. Teach Gnudi, *The Pirotechnia of Vannoccio Biringuccio, The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, Dover publications, 1990, pp. 210-211.

21 "Quello di questi è migliore che è nella sua specie piu puro, in quella dello stagno è quello che è piu bianco, et piu duro, ò piegandolo, col de[n]te in qualche estremita piccola stregnendolo si sente strider come ancho fa acqua ghiacciata." Vannuccio Biringuccio, *Pirotechnia*, P. Gironimo Giglio, e compagni, 1540, Libro V, Cap. IV. pp. 163r-164v. The translation is by C.S. Smith, M. Teach Gnudi, *The Pirotechnia of Vannoccio Biringuccio, The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, Dover publications, 1990, pp. 211.

22 J. Basset, J.P. Fogelman, D.A. Scott, R. Schmidtling II, *The craftsman revealed, Adriaen de Vries sculptor in bronze*, The Getty Conservation Institute, 2008, pp. 27-33.

23 Basset, op. cit., 2008, appendix II.

24 This concerns the measurements of the rearing horse. Most measurements gave a percentage of 6-7% tin, while 10-11% was measured in two other places in, Bewer, op. cit., 1996, pp. 556.

25 This concerns trace elements. For instance the presence of silver in historic copper alloys is for this reason always seen as a condition if there is a suspicion that the copper alloy is older than the 19th century.

26 D. Bourgarit, N. Thomas, "Ancient brasses, misconceptions and new insights," keynote lecture, *Archaeometallurgy* 2011, Bochum.

27 "Avertendoni che pre supponiate che il bisogno de lavori sia quello che n'ordini la legha" V. Biringuccio, *Pirotechnia*, P. Gironimo Giglio, e compagni, MDLIX, Libro V, cap III, pp. 163r. The translation is by C.S. Smith, M. Teach Gnudi, *The Pirotechnia of Vannoccio Biringuccio, The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, Dover Publications, 1990, pp. 211.

28 ".. ma per coromperli, entròcargli [?] certa viscosita naturale respetto all'arte del gitto. Donde per questo s'acompagna per tale effetto con lo stagno, e anchor alcuna volta con l'ottone, pura la propria et vera sua lega è lo stagno fino." Vannuccio Biringuccio, *Pirotechnia*, P. Gironimo Giglio, e compagni, 1540,

Libro II, cap VII. pp. 162v. De vertaling is van C.S. Smith, M. Teach Gnudi, *The Pirotechnia of Vannoccio Biringuccio, The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, Dover publications, 1990, pp. 210. In addition, Biringuccio was aware of the fact that as a result there can be a stage that is very bronze (depending on the percentage of tin that is added).

29 C.R. Ashbee, *The treatises of Benvenuto Cellini on goldsmithing and sculpture*, Dover Publications Inc., New York, 1967, pp. 122-124.

30 I would like to thank Salvatore Siano and Francesco Grazzi for the article they sent: "Notizie Storiche, Sulla Fusione del Perseo, con alcuni documenti inediti di Benvenuto Cellini, a cura di Guglielmo Somigli". The article indicates that the same method was used for the measurement. Irrespective of how correct the end results are, there is a tangible difference in the measurements.

31 "Per l'apperente qualità loro diremo esser la compositione loro una vera adusta, ben dipurata, et certa sottigliezza. E molta digestione son ne metalli fusi molto pentrabili, anzi operano di tal forte che con qual si trovino , il corrompeno, convertono quasi una altra natura." Vannuccio Biringuccio, *Pirotechnia*, P. Gironimo Giglio, e compagni, 1540, pp. 80r. The translation is by C.S. Smith, M. Teach Gnudi, *The Pirotechnia of Vannoccio Biringuccio, The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, Dover publications, 1990, pp. 105. In this respect it should be noted that if the antimony and bismuth are also measured in the alloy, the copper was probably copper ore containing arsenic.

32 This statuette was measured qualitatively using XRF and does not contain antimony or bismuth, while there was a clear peak in the measurement of arsenic and lead.

33 W. Langenkamp, *Thermospannung bei der Rastertunnelmikroskopie der metallischen Heterostruktur Blei auf Kupfer (111)*, Witten, Langenkamp, 2008.

34 "E più per portature di carrettieri homini per pigliar portare e pesare li bronzi presi in Belvedere, cosi pessimo qual è stato tutto piombo, et ghetta che è andato in schiuma et calo come se ne pol far saggio." Archivio di 'Stato di Roma (ASR), Camerale I, Giustificazioni die Tesoreria, bust 40, fascicolo 4. I would like to thank Emmanuel Lamouche for sharing this reference with me.

35 "Et fate che il metallo sia perfattamente fuso, ma non troppo caldo et avertendovi, se volete che la ca[m]pana habbi buono sono, oltre al garbo, et le grossezze convenienti, sia fatte nella sua lega di metallo con buono stagno, et che non habbi in se per alcun modo piombo, il quale oltre al far il gitto bruto li tolle di suono." V. Biringuccio, *Pirotechnia*, P. Gironimo Giglio, e compagni, 1540, pp. 209r/210v. Translatedted by C.S. Smith, M. Teach Gnudi, *The Pirotechnia of Vannoccio Biringuccio, The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, Dover publications, 1990, pp. 268.

36 I would like to thank Prof. Dr. Gregor Borg, Martin Luther University, Halle-Wittenberg, Institute for Geosciences, for this insight. See also G. Sarton, *Six wings, Men of science in the Renaissance*, Indiana University Press, Bloomington, 1957, pp. 122-127.

37 Pliny, *Natural History, Books XXXIII-XXXV*, Loeb Classical Library, Harvard University Press, Cambridge MA, 1996, pp. 201.

38 F. Scholten, R. Mulcahy, L.O. Larsson, G. Cavalli-Björkman, F.G. Bewer, U. Heithorn, T. DaCosta Kaufmann, and A. de Koomen, *Adriaen de Vries, 1556-1626*, Waanders Publishers, Zwolle, 1998, pp. 78-83.

39 "Questo bronzo piglia co ' l tempo per se medesimo un colore che trae in nero e non in rosso come quando si lavora. Alcuni con olio lo fanno venire nero, altri con l'aceto veniere verde, et altri con la vernice li danno il colore di nero, tale che ognuno lo conduce come piú gli piace." *Giorgio Vasari, Le Vite, De' più eccelenti Pittori Scultori e Architettori, Firenze 1568.* Parte I, pp. 40, the English translation is based on L.S. Maclehose, *Vasari on Technique*, Dover Publications, Inc. New York, 1960, pp. 165-166.

40 "Ma come con esso venite à tal compagnia cosi muove natura, et aspetto, secondo la proportione de lo stagno, che gli date, cosi cambia nome, et non piu rame , ma bronzo si chiama , overo per maggior distintione di certa quantita di stagno per ogni cento de rame in su da maestri è detto metallo, piu e manco fino, secondo che piu, ò manco di stagno contiene. Il che si conosce alla bianchezza, et alla frangibilità mediante il quale di rosso, che è il colore del rame vien bianco, di dolce et flessibile diventa duro, et come vetro fragile." Vannuccio Biringuccio, *Pirotechnia*, P. Gironimo Giglio, e compagni, 1540, Libro V Cap II pp. 162r. The translation is by C.S. Smith, M. Teach Gnudi, *The Pirotechnia of Vannoccio Biringuccio, The Classic Sixteenth-Century Treatise on Metals and Metallurgy*, Dover publications, 1990, pp. 210.

Samenvatting

Dit proefschrift is een materiaalkundige en kunsttechnische studie naar bronssculptuur uit de Italiaanse en Noordelijke Renaissance. De technische analyse van kunstobjecten speelt al langer een rol bij authenticiteits- en toeschrijvingsvraagstukken. Maar het verband tussen materiële eigenschappen van bronzen beelden en de historische vervaardigingscontext is tot dusver weinig onderzocht, te weinig in ieder geval om op basis van technische analyses algemeen geldende uitspraken te kunnen doen. De doelstelling van dit proefschrift is om met behulp van materiaalkunde, en technisch-historisch onderzoek een beter inzicht te verkrijgen in het maakproces van bronssculptuur in de Renaissance. Bij de materiaalkundige studie is gebruik gemaakt van zowel traditionele als geavanceerde onderzoeksapparatuur, waarbij röntgenfluorescentiespectrometrie (XRF), neutron imaging en time of flight neutronendiffractie het meest zijn toegepast. Het proefschrift is opgebouwd uit twee delen. Het eerste gedeelte is materiaalkundig van aard, het tweede gedeelte kunsttechnisch en vloeit uiteraard voort uit de inzichten van het materiaalkundig onderzoek.

Het materiaalkundig georiënteerde gedeelte beslaat vijf hoofdstukken. Hoofdstuk I is de inleiding, waarna in hoofdstuk II wordt de toepassing van neutronentransmissie, ook wel *neutron imaging* genoemd, behandeld. In mijn onderzoek heb ik gebruik kunnen maken van de NEUTRA beamline aan het Paul Sherrer Institut (PSI) in Villigen, Zwitserland. Tot voor kort werden bronzen met het blote oog, microscopisch, videoscopisch of met behulp van röntgenfotografie technisch bestudeerd. In dit hoofdstuk wordt aan de hand van een bronzen beeld van Willem van Tetrode, de *Hercules Pomarius* uit 1568, gedemonstreerd waarom het gebruik van neutronen de voorkeur verdiend boven een radiografisch onderzoek met traditionele röntgenstraling. Met neutronen imaging blijkt het mogelijk een tomografische reconstructie van een sculptuur te maken waarbij de interne structuur van een sculptuur zichtbaar wordt. Anders dan met röntgenstraling toont deze visualisatie een onderscheid tussen de verschillende metaalsamenstellingen in het beeld, waardoor veel meer informatie beschikbaar komt dan bij een röntgenfoto. Metaalsamenstellingen spelen een belangrijke rol in de bestudering van bronssculptuur. In de veronderstelling dat er referentiegegevens bestaan, worden op basis ervan zelfs toeschrijvingen gedaan. Ik plaats in dit hoofdstuk kritische kantekeningen bij zowel die veronderstelling als bij de gangbare methoden van collega-onderzoekers, en reik daarbij alternatieven aan.

In hoofdstuk III wordt beschreven hoe neutronen imaging is toegepast om historisch relevante binaire koperlegeringen kwantitatief te bepalen. Door gebruik te maken van hierme verkregen radiografieën die met een spectrum van een volledig polychromatische straal zijn verkregen is aangetoond dat de verstrooiing van neutronen die alsnog de detector bereiken moest worden gecorrigeerd. Indien men kwantitatieve in plaats van kwalitatieve conclusies wil trekken is het noodzakelijk om een - callibratie gebaseerde verstrooiings correctie - toe te passen om dit verstrooingseffect op te heffen. Daarnaast kon op succesvolle wijze neutronen imaging met een monochromatisch spectrum in het absorptiebereik (waar neutronen verstrooiing verwaarloosbaar is) worden toegepast om samenstellingsinformatie te achterhalen, met slechts een geringe toename van de belichtingstijd, zonder de noodzaak van een verstrooiingscorrectie. De getoonde resultaten stemmen grotendeels overeen met de bestudeerde samenstellingen terwijl de discussie over de resterende onderlinge afwijkingen in de richting van een heterogene samenstelling wijst. Met deze studie is het het pad geëffend voor een non-invasieve analyse van de samenstelling van een historisch brons. Een voorwaarde voor het gebruik van neutronen imaging bij Renaissance bronssculptuur is het vooronderzoek met XRF. Met XRF onderzoek kunnen elementen gedetecteerd worden die, indien geactiveerd door neutronen, langdurig radioactief blijven. Om dit te voorkomen wordt met een kwalitatieve meting uitsluitsel gegeven of het brons wel of niet met neutronen mag worden onderzocht. De XRF techniek wordt door veel musea ook kwantitatief – precieze percentages van de afzonderlijke legeringselementen – gebruikt. In dit onderzoek wordt deze specifieke toepassing van XRF bekritiseerd. Een bronzen object is vaak doorspekt met reparaties na breuk, of ander verval van het object.. Dit kan een zichtbare mechanische verbinding zijn, of een minder zichtbare techniek zoals solderen door middel van verwarming van het object. Bij verwarming van een bronzen beeld kan, afhankelijk van de samenstelling, segregatie van de legeringselementen optreden, waarbij deze elementen naar het oppervlak migreren. Omdat

XRF een techniek is die enkel het oppervlak analiseert, is het belangrijk te onderkennen in welke mate, hoe snel en ingrijpend de samenstelling van een oppervlak verandert bij een traditionele reparatie met warmte. De resultaten van dit onderzoek zijn voor historisch relevante koperlegeringen samengevat in hoofdstuk IV. Dit onderzoek bewijst dat het oppervlak na een warmtebehandeling van het metaal niet representatief is voor de samenstelling van de bulkcompositie van de legering.

In hoofdstuk V wordt een mogelijke oplossing aangedragen voor dat specifieke probleem. Daarbij is gebruik gemaakt van neutronen imaging van PSI in combinatie met time-of-flight neutronendiffractie op ENGIN-X van het Rutherford Appleton Laboratory, Chilton, Engeland. De noodzaak voor de combinatie van beide technieken diende zich aan na analyse van de neutronentransmissies van een Rijksmuseumsculptuur, de *Lopende Edelman* (BK-16083). Voorgaande XRF analyses duiden op een koperzink legering, terwijl met neutronen imaging ook een andere legering werd vermoed. Door volumeanalyses op basis van virtuele reconstructies op ieder gewenste plaats in de sculptuur uit te voeren, kan een nauwkeurige samenstelling van de legering worden verkregen. Tijdens dit onderzoek kwam een ander onverwacht resultaat aan het licht. Het neutronendiffractiespectrum vertoont een duidelijke ferriet-piek in de bulkcompositie van het metaal. Dit duidt op de aanwezigheid van ijzerhoudend zink, typerend voor de winning van zink uit calamine dat tot in de eerste helft van de 19de eeuw werd gebruikt. Tot die periode werd voor de winning van zink een cementatie proces toegepast dat resulteerde in een lage concentratie van ijzer in het zink. Afhankelijk van de wensen van de beeldhouwer kon zink aan een legering worden toegevoegd. Als gevolg van de lage ijzerconcentratie leidt dit tot magnetisme van het brons. Een zinkhoudend brons van na 1850 hoeft niet noodzakelijk magnetisch te zijn; echter, voor die periode wel. Dit resulteert in een eenvoudige test op geelkleurige Renaissance beelden (veelal zinkhoudend) met een aardmagneet (Neodymium). Deze eigenschap is niet eerder in de literatuur naar voren gebracht.

In het laatste hoofdstuk van het materiaalkundig gedeelte, hoofdstuk VI, is aangetoond dat neutronendiffractie ook voor stress- en strainanalyses kan worden toegepast. Het onderzoek toetste de hypothese dat een Renaissance brons met een zeer verfijnd uiterlijk kon worden gegoten zonder een ciseleerproces. De aanleiding tot dit onderzoek is de aanwezigheid van een normaliter verwijderd stukje metaal, een 'vin', op het linkerschouderblad van de *Hercules Pomarius* van Willem van Tetrode (BK-1954-43) en eenzelfde fenomeen op de tiara van de buste van *Paus Gregorius XIV* van Bastiano Torrigiani (BK-16937). Gesteld wordt dat deze 'metaalvinnen' opzettelijk door de kunstenaar zijn behouden. Bestudering van traktaten bevestigt dat het in het tweede kwart van de 16e eeuw in Italie technisch mogelijk is geweest brons te gieten zonder nabwerking met hamers en ponsen. Ter vergelijking is een met zekerheid geciseleerd vroeg 16e eeuws brons, een *Paris* figuur toegeschreven aan Severo da Ravenna (BK-1959-4) met neutronendiffractie geanalyseerd. Aangetoond is dat zowel de *Hercules Pomarius* als de buste van *Paus Gregorius XIV* na het gieten níet geciseleerd zijn, terwijl het bronsoppervlak oogt alsof dit wel het geval is. Aangezien tot dusverre werd aangenomen dat alle bronssculptuur met een oppervlak zoals van de *Hercules Pomarius* geciseleerd was, is dit een verrassend nieuw inzicht.

Het tweede deel is opgesplitst in twee hoofdstukken. In hoofdstuk VII worden de vervaardigingstechnieken van bronssculptuur in Noord- en Zuid-Europa diepgravend onderzocht. Hoewel de ontwikkeling van de bronssculptuur na de Middeleeuwen zich vooral bezuiden de Alpen afspeelde en het kunsthistorisch onderzoek zich daardoor tot dusver concentreerde op Italië als de bakermat van bronsgietinnovaties, wordt in dit hoofdstuk beargumenteerd dat de giettechnologie boven de Alpen in de 16de eeuw, in het bijzonder in Zuid-Duitsland, een minstens zo revolutionaire ontwikkeling doormaakte, waarvan de effecten pas in het derde kwart van de 16e eeuw tot Italië doordrongen. Deze 'noordelijke innovaties' in de bronsgietkunst staan in dit hoofdstuk centraal. Een belemmering bij de bestudering van dit fenomeen is dat uit deze periode geen kunsttechnologische traktaten uit het Noorden bekend zijn. De Italiaanse werkwijze kan wel met behulp van teksten bestudeerd worden, namelijk door zorgvuldige lezing van de traktaten van Biringuccio (1540), Vasari (1550 en 1568) en Cellini (1568). Zij beschrijven het gehele proces van de verloren was-methode als modelleer- en giettechniek tot en met het ciseleren van het metaaloppervlak met hamers en ponsen. Italiaanse gietingen die deze beschrijvingen bevestigen kunnen vervolgens vergeleken worden met Duitse gietingen. Als vertegenwoordigers van deze laatste categorie heb ik de monumentale bronzen figuren bij de cenotaaf van Maximiliaan I gekozen, alsmede de uitermate verfijnde gietingen van de Neurenbergse zilversmid Jamnitzer. Door vergelijkingen met Italiaanse gietresultaten kan de Duitse gietkunst in nieuw perspectief worden geplaatst. De ontwikkelde technieken waren veel verder ontwikkeld en resulteerden in zeer goede gietresultaten. De nauwkeurige bestudering van het gietproces gaf bovendien aanleiding om in dit hoofdstuk een verhandeling toe te voegen over op de effecten van toevoer- en ontluchtingskanalen tijdens het gietproces.

In hoofdstuk VIII wordt een aantal hypotheses die in hoofdstuk VI aan de orde zijn gekomen door reconstructie getoetst: kan men met het malmateriaal dat voorhanden was in de 16de eeuw, een perfect brons oppervlak van een statuette produceren zonder te ciseleren? Is het tevens mogelijk om daarbij een minimale hoeveelheid toevoer- en ontluchtingskanalen te gebruiken? Hoe dun kan een brons worden gegoten om nog zonder vormverandering te kunnen worden geciseleerd? In dit laatste hoofdstuk zijn de technische grenzen van 16de-eeuwse productietechnieken in kaart gebracht, waarbij de vormverandering op de monsters met 3d scanning vooraf en na het ciseleerproces is vastgelegd. Uit het reconstructieonderzoek blijkt dat met het voorhanden zijnde malmateriaal een vrijwel perfect gegoten brons kan worden geproduceerd met één enkel aangiet- en ontluchtingskanaal. Een torso met een gemiddelde dikte van 2,5 mm is zodanig gegoten dat geen afwerking van het brons noodzakelijk is. Een vingerafdruk kon eveneens worden gereproduceerd. Bovendien is aangetoond dat een brons met een dikte van 2,5 mm geen vormverandering ondergaat als een ciseleerbehandeling wordt uitgevoerd.

Summary

This thesis is a materials science and technical art historical study of bronze sculpture from the Italian and Northern Renaissance. The technical analysis of art objects has played a role in questions of authenticity and attribution for a long time. However, the relationship between the material characteristics of bronze statues and the historical context of their manufacture has not been examined very much up to now, or at least not enough to be able to pronounce any general conclusions on the basis of technical analyses. The aim of this thesis is to gain a better insight into the manufacturing process of bronze sculptures in the Renaissance with the help of materials science and technical historical research. The materials science study made use of both traditional and advanced research equipment, with X-ray fluorescence spectrometry (XRF), neutron imaging and time-of-flight neutron diffraction being the most used. The thesis consists of two parts. Part 1 is concerned with the science of materials; part 2 has an artistic technical nature and is obviously based on the insights obtained from the materials science research.

The part concerned with materials science consists of five chapters. Chapter I is the introduction and Chapter II deals with the application of neutron transmission, also known as neutron imaging. In my research I was able to use the NEUTRA beam line at the Paul Sherrer Institute (PSI) in Villigen, Switzerland. Until recently, bronzes were examined with the naked eye, a microscope, a videoscope or with the use of X-radiography. This chapter demonstrates why the use of neutrons is preferable to a radiographic examination with traditional X-rays, using a bronze statue of Willem van Tetrode, the *Hercules Pomarius*, dating from 1568. Using neutron imaging it is possible to create a tomographic reconstruction of a sculpture, revealing its internal structure. In contrast with the use of X-rays, this visualization reveals the distinction between different metal compositions in the statue, producing a great deal more information than an X-radiograph. The compositions of metals play an important role in the study of bronze sculptures. On the assumption that there are reference figures, it is even possible to attribute sculptures on this basis. In this chapter I make some critical notes both regarding this assumption and regarding the usual methods used by fellow researchers, and provide some alternatives.

Chapter III describes how neutron imaging was used to quantitatively determine historically relevant binary copper alloy compositions. Radiographies using the full polychromatic beam spectrum showed a clear need to correct for neutron scattering contributions. To draw quantitative rather than qualitative conclusions, a calibration-based scatter correction was applied to correct for the effect. Radiographies in the absorption domain made it possible to successfully retrieve composition information without the need for scatter correction, with only a limited increase in exposure time. The results show a good level of agreement for most of the investigated compositions, while the discussion about the remaining discrepancies suggests a lack of material uniformity. The results of this study show the way to a non-invasive analysis of the composition of a historic bronze. One condition of the use of neutron imaging in Renaissance bronze sculptures is the preliminary research with XRF. With XRF research, it is possible to detect elements which remain radioactive for a long time if they are activated by neutrons. To prevent this, a qualitative measurement is made to decide whether or not the bronze may be examined with neutrons. The XRF technique is used by many museums quantitatively for the exact percentages of individual elements in an alloy. This research criticizes this specific application of XRF. A bronze object has often been subject to many repairs after a break or deterioration of the object. This may involve a visible, mechanical compound or a less visible technique, such as brazing by heating the object. If a bronze statue is heated, a segregation of the elements in the alloy can take place depending on the composition and these elements can migrate to the surface. As XRF is a technique which analyses only the surface, it is important to identify to what extent, how quickly and how invasively the composition of the surface has changed with a traditional repairing technique using heat. The results of this research have been summarized for historically relevant copper alloys in Chapter IV. This research demonstrates that after the metal has been treated with heat, the surface is no longer representative of the composition of the bulk of the alloy.

Chapter V presents a possible solution for this specific problem. This was done making use of neutron imaging at PSI, Villigen Switzerland in combination with time-of-flight neutron diffraction on ENGIN X at the Rutherford Appleton Laboratory, Chilton, England. The need for the combination of these two techniques became apparent after an analysis of the neutron transmissions in the sculpture, the *Striding Nobleman* of the Rijksmuseum

(BK-16083). The preceding XRF analyses reveal a copper and zinc alloy, while the neutron imaging also led to the assumption that there was another alloy. By carrying out volume analyses on the basis of virtual reconstructions at every place of interest in the sculpture, it is possible to obtain a precise composition of the alloy. During this research another unexpected result came to light. The neutron diffraction spectrum reveals a clear ferrite peak in the bulk composition of the metal. This reveals the presence of zinc containing iron, characteristic of the extraction of zinc from calamine, which was used up to the first half of the 19th century. Up to that period, the cementation process was used for the extraction of zinc, which resulted in a low concentration of iron in the zinc. Depending on the requirements of a sculpture, zinc could be added to an alloy. As a result of the low iron concentration, this leads to the bronze becoming magnetic. A bronze containing zinc dating from after 1850 was not necessarily magnetic, but before that period it was. This results in a simple test on yellow-coloured Renaissance statues (frequently containing zinc) using a Neodymium magnet. This characteristic has not been revealed before in the literature.

The last chapter of the part of the study dealing with materials science (Chapter VI) demonstrates that neutron diffraction can also be used for stress and strain analyses. The research tested the hypothesis that a Renaissance bronze with a very fine external appearance could be cast without needing to be chased. The reason for this research was the presence of a piece of metal that is normally removed, a fin on the left shoulder blade of the *Hercules Pomarius* by Willem van Tetrode (BK-1954,43) and a similar phenomenon on the tiara on the bust of *Pope Gregory XIV* by Bastiano Torrigiani (BK-16937). A study of the treatises confirms that during the second quarter of the 16th century it was technically possible to cast bronzes in Italy without the need for chasing with hammers and punches. By way of comparison, a figure of *Paris* attributed to Severo da Ravenna (BK-1959-4), an early 16th century bronze that was certainly chased, was analysed with neutron diffraction. This demonstrated that both the *Hercules Pomarius* and the bust of *Pope Gregory XIV* were not chased after being cast, while the bronze surface suggests that they were. As it has been assumed up to now that all bronze sculptures with a surface such as the *Hercules Pomarius* had been chased, this is a surprising new insight.

Part 2 is divided into two chapters. Chapter VII examines the manufacturing techniques of bronze sculptures in northern and southern Europe in detail. Although the development of bronze sculpture predominantly took place south of the Alps after the Middle Ages and art historical research has therefore up to now concentrated on Italy as the cradle of bronze casting innovation, this chapter argues that in the 16th century, casting technology north of the Alps, particularly in southern Germany, had undergone a development that was equally revolutionary and that the effects of this spread to Italy only by the third quarter of the 16th century. These "northern innovations" in the art of bronze casting have a central place in this chapter. One obstacle to the study of this phenomenon is that no treatises on artistic technology from the north dating from this period are known. The Italian processes can be studied with the use of texts, mainly with a careful reading of the treatises of Biringuccio (1540), Vasari (1550 and 1568) and Cellini (1568). They describe the whole process of the lost wax method as a modelling and casting technique up to the chasing of the metal surface with hammers and punches. Italian casts which confirm these descriptions can then be compared with German casts. To represent this last category I opted for the monumental bronze figures on the cenotaph of Maximilian I, as well as the extremely fine casts of Jamnitzer, a silversmith from Nuremburg. By comparing these with Italian casting results, the German art of casting is seen from an entirely new perspective. The techniques that were developed were much more refined and led to very good casting results. Furthermore, a detailed study of the casting process resulted in the addition of a section to this chapter about the effect of the sprues and vents used during the casting process.

Chapter VIII tests a number of hypotheses which were presented in chapter VI with reconstructions: was it possible to produce a perfect bronze surface of a statuette without chasing it with the materials that were available in the 16th century? Is it also possible to use a minimal number of sprues and vents for this? How thin can bronze be cast and still be chased without changing the form? This last chapter examined the technical limits of 16th-century production techniques, recording the changes in form on the samples with 3D scanning before and after the chasing process. The reconstruction research reveals that it was possible to produce a virtually perfectly cast bronze with the materials for the mould that were available and with a single sprue and vent. A torso with an average thickness of 2.5 mm was cast in such a way that it was not necessary to chase the bronze. It was also possible to reproduce a fingerprint, and the reconstruction demonstrated that a bronze with a thickness of 2.5 mm does not change shape when it is chased.

Future prospects

Up to now a number of different analysis techniques have been used for the technical research on Renaissance bronze statues to examine the composition of the material and the method of manufacture. For example, X-radiography can show the interior of a sculpture as a visualization technique. The composition of an alloy can be determined with Atomic Absorption Spectrometry (AAS), Inductive Coupled Plasma Spectrometry (ICP), Laser Induced Plasma Spectroscopy (LIPS) and X-ray fluorescence spectrometry (XRF), provided they are properly used. In this thesis I have examinated the possibilities and results of new, more advanced research techniques.

During the presentations of my research I sometimes came across a degree of scepticism about the added value of the new research techniques, mainly based on the assumption that the "traditional" analysis techniques were sufficient. Obviously these can answer all sorts of research questions provided they are properly used. However, in my opinion, the advanced research techniques undeniably have great added value.

In the first place, the reliability of the results is sometimes higher than that of many of the traditional techniques, particularly with regard to research with non-invasive visualization techniques. Secondly, this research showed that neutron imaging and neutron diffraction provide many possibilities as a visualization and analysis techniques to provide new insights into the manufacturing process of bronze statuettes. Thirdly, there are research questions that cannot be answered with the traditional methods, for example, the non-invasive research into stress and strain in the surface of Willem van Tetrode's *Hercules Pormarius* (Chapter VI). One general conclusion was that the cooperation with (fundamental) scientists working at Large Scale Facilities results in a wider perspective, which means that research that was considered impossible did prove to become possible. In my experience 'conservation science' can make significant progress with new techniques and contacts.

In the past the projects on which conservators, art historians and scientists worked together sometimes showed that it was difficult to formulate research questions which are considered relevant by all the parties. Many colleagues have had this experience, but I have found that there is a great new willingness, particularly in the sciences, to use the knowledge and facilities available there for research into art objects.

I would like to mention two developments by way of illustration. First, Synchrotron Soleil in St Aubain, France, developed a dedicated beamline for the cultural heritage to study research problems on a small and large scale in museum conditions in terms of safety and climate control. These advanced research techniques (such as neutron imaging and neutron diffraction in this research, yet not at Soleil) can certainly be applied in the science of conservation, provided the research question is innovative and relevant and cannot be answered with traditional techniques. In the Netherlands it is even the case that thanks to the vision and dedication of Louis Vertegaal, the Netherlands Organisation for Scientific Research (NWO) has played an active role in making this available with the science4arts project. Secondly, cultural heritage studies have evolved in such a way that they are considered a serious science, as once again proved by a recent Gordon conference on Scientific Methods in Cultural Heritage.[1]

As a result of the research I learned a great deal and realized that for me interdisciplinary cooperation can really lead to new insights. I hope that more conservation scientists will take this step because a truly interdisciplinary approach to the study of cultural heritage will lead to a better understanding of the creation and decay of our cultural heritage.

By using advanced research techniques such as neutron imaging and neutron diffraction in this research it has become clear that these techniques not only generate an increasing amount of relevant information about art objects, but in addition they are also important for other areas of application. The combination of neutron imaging and neutron diffraction as described in chapter V is a good example of this. This is proved by the current development of the IMAT beamline (Imaging Materials Science) at ISIS of the Rutherford Appleton Laboratory.[2] This beamline will be operational from March 2015. The combined neutron imaging technique and neutron diffractor is mainly used in materials science (also with applications in the aviation and space industries, hydraulic engineering, energy, agriculture and earth sciences), but has been partly developed from research in the field of the cultural heritage, as indicated by Winfried Kockelmann, the beamline scientist at ISIS.

Using the results of this research, a number of new perspectives were examined in the technical study of bronze statues and these require further examination. A number of the resulting insights obtained in the past few years are described below:

In the past year, two meetings took place independently of each other in Amsterdam and London, between art historians, conservators and scientists. One of the aims of the meetings was to define the question with regard to the direction of the technical research into bronze. The meetings mainly led to insights about the technical and historical context of copper alloys in early modern Europe. One of the questions which was discussed in detail during the meeting in Amsterdam concerns determining the usefulness of the analysis of an alloy without a critical research question. The focus in Amsterdam was on XRF research and the historical significance of an alloy. This was partly in response to a round-robin research focusing on XRF analyses of samples, of which the composition was known in advance. The aim was to discover whether all laboratories achieved the same result using XRF. The results revealed that many museums did not produce the same analysis results for the same samples. On the one hand, it proved necessary to demonstrate the limitations of the equipment more clearly, while on the other hand it was necessary to use the correct software, of which PyMCA is an example.[3] In addition, it is recommended that any future technical studies should indicate exactly whether a bronze statue has been exposed to heat treatment or not when XRF research is carried out.

The technical analysis of art objects is an important part of questions about authenticity and attribution. Unlike utensils such as bronze pestles, mortars, cannons and bells, the manufacturing method of bronze sculptures can vary enormously, both in terms of place and time. The links between the material characteristics and the historical manufacturing context has not been sufficiently examined to draw any definite conclusions on the basis of technical analyses. The question of the historical significance of a particular metal composition concerns the considerations taken into account when the metal is cast, or how the knowledge about this method of production is spread. These questions cannot be answered by one discipline and require solid cooperation between conservators, art historians and material scientists. This sort of research follows three main lines which have historical, economic, technical and aesthetic aspects. Each of these main lines contains a component which is consciously directed by the historic user or manufacturer. This concerns for example, the ores that were used, the scarcity of metals but also how ores were purified. As regards the role of the manufacturer, some of the central questions are: what historical copper alloys (with specific pollutants) were the result of the extraction of metals. It is also important to examine the physical characteristics of metals, and what alloys can be chased. Further research into the casting qualities plays a role in this, as does the structure of the mould. Together with the historical survey, this distinction enables us to reconstruct the typical characteristics of a particular historical copper alloy and possibly even define in more detail where a bronze statue was produced.

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1 A Gordon conference is a conference in the sciences, also see http://www.grc.org/. This year the first Gordon conference took place on cultural heritage. Gordon Research Center, *Scientific Methods in Cultural Heritage Research*, July 29-August 3, 2012 at the Mount Snow Resort, West Dover, Vermont.

2 (http://www.isis.stfc.ac.uk/instruments/imat/imat8259.html

3 V.A. Solé, E. Papillona, M. Cottea, Ph. Walter, and J. Susinia, "A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra, Spectrochimica Acta Part B" *Atomic Spectroscopy*, Volume 62, Issue 1, January 2007, pp. 63–68.

About the author

Robert van Langh was born in Oosterhout (North Brabant) on 19 June 1968 and started secondary school at the Willem van Duvenvoorde MAVO (Oosterhout). He then went on to the St. Olof secondary commercial School (Breda) and went on to study to be a goldsmith at the Free Technical School "Technicum" (Antwerp, Belgium) in 1988.

In 1992 he continued his studies with the Metal Restoration and Conservation course at the National Higher Institute for Fine Arts (Antwerp, Belgium).

In 1995 he started on the training for conservators in Amsterdam, where he was responsible for setting up the course for metal conservation up to 2006. In addition he worked for two months at the Tropenmuseum in Amsterdam in 1995 and then went on to work as a metal conservator for the Rijksmuseum.

In 1998 he briefly carried out a research project on behalf of the Rijksmuseum at the Sherman Fairchild Center for Objects Conservation at the Metropolitan Museum of Art, New York.

In 2001 he became head of the metal conservation department, and since 2006 he has been head of the whole department of Conservation at the Rijksmuseum in Amsterdam. He started his doctoral research at the department of Technical Materials Sciences at the 3 ME Faculty (Hydraulic Engineering, Maritime Technology & Technical Materials Sciences) in Delft in September 2006.

In 2011 he spent three months as the museum scholar selected by the Getty Research Institute (Los Angeles, United States).

A word of thanks

At this point I am able to fulfil the wish that I have had for a long time to conclude this doctoral research.

The subject of the technical studies of Renaissance bronze statues has become increasingly clearly defined over the years and my promotor Joris Dik gave me the opportunity to carry out this research. It was extremely pleasant to work with Joris, because in addition to his enormous capacity for relative thinking, he has a clear vision of scientific research in the arts. However, doing my doctorate at the Delft University of Technology was not an obvious choice as I trained as a metal conservator at the National Higher Institute for Fine Arts in Antwerp. I am very grateful to Joris and to my promotor Barend Thijsse for the confidence they had in me to do my doctorate externally. Joris and Barend made a gesture both to me and to my whole field of study, and I would like to thank them for this.

Many years ago, Frits Scholten was present when I started my development as a (research) conservator. With his technical interest in objects, Frits was one of the few curators who believed in the scientific approach to conservation. I felt enormously stimulated by him and that is why I am so pleased that he could be a promotor for my doctoral research because he is a professor at the VU. His critical abilities have been very helpful in my scientific training and therefore for the quality of this thesis. I am extremely grateful to him for his unique combination as a supervisor and colleague.

There are still many things that are not known about the manufacture of Renaissance bronzes. This thesis fills some of the important gaps but also reveals the lack of knowledge. Using advanced research equipment, such as neutron imaging and time-of-flight neutron diffraction it was proved that new perspectives can be achieved with this sort of research.

Obviously I am very grateful to my co-authors, but several deserve a personal mention. These include Dirk Visser with his first presentation on the possibilities of neutron imaging and his mediating role at the start of the research. I would like to thank Eberhard Lehmann from the Paul Scherrer Institute in Villigen, Switzerland, for his constant support and critical approach to neutron imaging as an analysis technique of historical copper alloys and Steven Peetermans for his contribution in Chapter III in which he tackled the mathematical aquations and the idea of quantitative neutron imaging. The possibility of carrying out time-of-flight neutron diffraction with ENGIN-X, the neutron diffractor of ISIS, Science and Technologies Facilities Council at the Rutherford Appleton Laboratory in Oxfordshire, England, would not have been possible without Javier Santisteban and Winfried Kockelmann. I would like to emphasise Winfried's inspirational role as a supporting beamline scientist. I would have achieved less without his help. Similarly, I could not have done without the help of Shu Yan Zhang during the experiments on ENGIN-X, and Jon James and Genoveva Burca for the interpretation of the data generated by their software program SScanSS in Chapter V.

Javier Santisteban and Laura Bartoli played a special role in the study, interpretation and processing of the results of surface chasing described in Chapter VI. The interpretation of the data was carried out jointly during my temporary stay at the Consiglio Nazionale delle Ricerche (CNR) in Sesto Fiorentina which was made possible by Salvatore Siano. The opportunity to interpret the results at CNR together with Laura Bartoli was possible because I was able to stay at the Dutch Institute for Art History (NIKI) in Florence, for which I would like to thank the secretary Tjarda Vermeijden and the director Michel Kwakkelstein. The NIKI was not only a wonderful place to stay while I was in Italy, but was also a source of ideas on the history of art. The role played by Beatrice Paolozzi Strozzi and Dimitrios Zikos of the Museo Nazionale del Bargello for allowing me to study the collection should be emphasised and I would like to express my thanks to them.

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Before deciding on a particular line of research, I carried out a great deal of experimental research into techniques used in casting bronze. This started in 2005 at "De Remise" a bronze foundry in Nieuweschans, where Rob van der Kleij was pleased to make his knowledge and studio available. My cooperation with the artists' workplace, the "Beeldenstorm" in Eindhoven, made an even greater impression, specifically the cooperation with Jeroen van Halder. By exchanging and testing ideas, some good results were obtained which contributed to new insights into possible methods of manufacturing bronze statuettes during the Renaissance.

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Marieke Stakenburg.

Je naam te schrijven is voldoende.

List of relevant publications

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