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**DOI**

[10.1016/j.jeurceramsoc.2018.02.002](https://doi.org/10.1016/j.jeurceramsoc.2018.02.002)

**Publication date**

2018

**Document Version**

Final published version

**Published in**

Journal of the European Ceramic Society

**Citation (APA)**

Carabat, A. L., Meijerink, M. J., Brouwer, J. C., Kelder, E. M., van Ommen, J. R., van der Zwaag, S., & Sloof, W. G. (2018). Protecting the MoSi<sub>2</sub> healing particles for thermal barrier coatings using a sol-gel produced Al<sub>2</sub>O<sub>3</sub> coating. *Journal of the European Ceramic Society*, 38(7), 2728-2734. <https://doi.org/10.1016/j.jeurceramsoc.2018.02.002>

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## Original Article

# Protecting the MoSi<sub>2</sub> healing particles for thermal barrier coatings using a sol-gel produced Al<sub>2</sub>O<sub>3</sub> coating



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## ARTICLE INFO

## Keywords:

Self-healing thermal barrier coatings

MoSi<sub>2</sub>

Alumina shell

Sol-gel

## ABSTRACT

A successful sol-gel process to encapsulate molybdenum di-silicide MoSi<sub>2</sub> particles with a closed and thermally stable Al<sub>2</sub>O<sub>3</sub> layer using aluminium tri-sec-butoxide as a precursor is presented. The processing conditions such as precursor selection and temperature were optimized through analysing the interaction of the MoSi<sub>2</sub> particles with the sol. The application of the sol-gel based coating was followed by calcining the coated particles at temperatures between 900 and 1200 °C in Ar. The shell composition and the mechanical stability of the microcapsule were analysed by means of X-ray diffraction, scanning electron microscopy and thermogravimetric analysis. Upon calcining at 1200 °C in Ar, the MoSi<sub>2</sub> core remains intact as it is, covered by an  $\alpha$ -alumina shell with a thickness of about 0.6  $\mu$ m. The stability tests proved that the encapsulate particles are about five times more oxidation resistant than the uncoated MoSi<sub>2</sub> particles.

## 1. Introduction

Molybdenum di-silicide not only is an attractive monolithic high temperature material because of its excellent refractory and mechanical properties [1–6], but is also as attractive candidate for repairing crack damage in brittle ceramic coatings such as in thermal barrier coatings (TBCs) [7,8]. TBCs are often applied to metallic surfaces of combustion chambers, blades and vanes in gas turbines and jet engines to protect them from corrosion and oxidation at elevated temperatures [9,10]. Yttria stabilized zirconia (YSZ, ZrO<sub>2</sub> containing 4–5 mol% Y<sub>2</sub>O<sub>3</sub>) is the most employed TBC material due to its excellent chemical and thermo-mechanical properties, such as low thermal conductivity at elevated temperatures (2.3 W m<sup>-1</sup> K<sup>-1</sup>), low density (6.4 g/cm<sup>3</sup>), high melting point (2700 °C), high toughness (7.7 MPa m<sup>0.5</sup>) and good corrosion resistance [9–11]. However, the durability of the TBCs is negatively affected by thermal cycling due to the starts and the stops of the engine resulting in temperatures varying over more than 1000 °C. High compressive stresses develop in the coating during cooling as a result of the mismatch between the coefficients of thermal expansion of the metal substrate (14·10<sup>-6</sup> °C<sup>-1</sup>) and that of the YSZ TBC (10–11·10<sup>-6</sup> °C<sup>-1</sup>) [11,12]. As a consequence, microcracks form within the ceramic coating. They propagate and coalesce during subsequent thermal

cycling leading to coating debonding and ultimately engine failure [11,13–15].

As YSZ TBCs are thermodynamically stable and hence do not pose autonomous crack-healing capabilities, a self-repair mechanism active at the high temperature encountered in a turbine engine is highly desirable to prolong the lifetime of these coatings. The concept of autonomous high temperature crack-healing based on the presence of MoSi<sub>2</sub> sacrificial particles embedded in a YSZ matrix has been presented elsewhere [7,16]. It is based on the release of viscous silica (SiO<sub>2</sub>), that fills the crack running through the matrix and re-establish the adherence in the ceramic coating. Subsequently, the formed SiO<sub>2</sub> reacts with the matrix via a solid-state reaction, resulting in a load bearing crystalline zircon phase (ZrSiO<sub>4</sub>), which gives a better adhesion between the healing agent and the fractured surface. However, in porous yttria partially stabilized zirconia based TBC matrix the transport of oxygen ions is likely to prevail [17]. This will lead to the premature oxidation of MoSi<sub>2</sub> particles and, consequently, offsetting the healing reaction even in the absence of a crack. Thus, the presence of an inert and oxygen impenetrable shell around the actual intermetallic particles is critical to prevent the premature triggering of the healing mechanism and to keep the particles in a dormant state.  $\alpha$ -Alumina seems an ideal candidate to protect the MoSi<sub>2</sub> particles from premature oxidation since

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it has a good thermal stability [18] and a low permeability for oxygen [19,20]. Hence, the healing mechanism will become active only when a crack penetrates the alumina shell protecting the active MoSi<sub>2</sub>.

Several soft-chemical routes have been proposed to deposit alumina shell such as: precipitation [21,22], hybridization [23] and sol-gel [24]. Among them, the sol-gel method is the most economical way to develop coatings of sizeable thickness and to generate solids of high purity [25]. So far, alumina coatings have been applied successfully on silicon containing particles such as silicon carbide (SiC) grit and MoSi<sub>2</sub> to improve their oxidation and corrosion resistance [21,26,27]. However, in the case of MoSi<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> core-shell system in which the protective  $\alpha$  alumina layer was produced by a precipitation reaction, a rather thin layer of alumina – silica mixed oxides of only 0.15  $\mu$ m was obtained after annealing at 1000 °C [21].

The current paper aims to create a closed and continuous thicker shell of  $\alpha$  alumina around MoSi<sub>2</sub> intermetallic particles through a simple sol-gel approach. Experimental results proved that by tuning the processing conditions (i.e. type of precursor and calcining temperature), a robust and stable shell of  $\alpha$  alumina with a typical thickness of 0.6  $\mu$ m could be obtained.

## 2. Experimental details

### 2.1. Materials

The chemicals for the sol-gel coating of MoSi<sub>2</sub> particles were aluminium oxalate tetrahydrate (Al<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> · 4H<sub>2</sub>O, 99% purity, Alfa Aesar, Karlsruhe, Germany), aluminium tri-isopropoxide (Al(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>, 98% purity, Sigma-Aldrich Co., St. Louis, Missouri, US), aluminium-tri-sec-butoxide (Al(OC<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, 97% purity, Sigma Aldrich Co., St. Louis, Missouri, US), nitric acid (HNO<sub>3</sub> 99% purity, 65 wt% solution as a source, Sigma-Aldrich Co. St. Louis, Missouri, US), isopropanol (C<sub>3</sub>H<sub>8</sub>O, 99.8%, Sigma-Aldrich Co., St. Louis, Missouri, US), ethanol (C<sub>2</sub>H<sub>6</sub>O, 99.8%, Sigma-Aldrich Co., St. Louis, Missouri, US), molybdenum disilicide (MoSi<sub>2</sub>, 99.5% purity, particle size of 29  $\mu$ m; ChemPur GmbH, Karlsruhe, Germany) and deionized water (18.2 M $\Omega$  cm at 25 °C). All chemicals were used without any further purification.

### 2.2. MoSi<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> core-shell synthesis

To produce sol-gel encapsulated MoSi<sub>2</sub> particles, a modified Yoldas method [28,29] was employed. This method is based on a polycondensation reaction leading to the formation of a boehmite sol, which upon further annealing transforms into a dense and defect free  $\alpha$ -alumina layer.

Prior to the encapsulation process, the MoSi<sub>2</sub> powder was wind sifted to remove the fine fraction and the impurities. Wind sifting was performed using an Alpine 100 MRZ laboratory zig-zag classifier (Alpine Multi-Plex 100 MRZ, Hosokawa Micron Powder System, Summit, New Jersey, USA). Airflow was fixed at 15 m<sup>3</sup>/h and the classifier rotational speed was kept at 5000 rpm. The wind sifting resulted in a powder having an average particle diameter of 30  $\mu$ m with a D<sub>10</sub> and D<sub>90</sub> value of 10 and 60  $\mu$ m, respectively, as will be described further on.

Three precursors were selected and tested to obtain more detailed information on the reaction of MoSi<sub>2</sub> particles with the sol: aluminium oxalate (Al<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>), aluminium tri-isopropoxide (Al(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>) and aluminium tri-sec-butoxide (Al(OC<sub>4</sub>H<sub>9</sub>)<sub>3</sub>), respectively. The experiments were performed in a reactor consisting of a glass beaker (1000 mL) positioned on a magnetic stirring hot plate (IKA RET control-visc, IKA – Werke GmbH & Co, Staufen, Germany) with thermocouple to control the temperature of the sol and a magnetic stir bar with controlled speed. Nitrogen gas (5 N purity) was supplied to the reactor by a custom-made ring-shaped bubbler with a flow rate of 200 sccm, to ensure a better dispersion of the healing particles in the sol suspension by reducing the rate of oxidation.

First, aluminium oxalate tetrahydrated was dissolved in 20 mL of 1.0 M HNO<sub>3</sub> solution and 20 mL deionized water (Mili-Q ultrapure water type 1; 18.2 M $\Omega$  cm at 25 °C), to obtain a molar ratio of 1:110 of Al<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O to H<sub>2</sub>O. Then, the suspension was heated to 60 °C and stirred for 30 min at 800 rpm to dissolve the aluminium oxalate. Next, MoSi<sub>2</sub> particles (10 g) with an average size of 30  $\mu$ m were added to the solution and the temperature was increased to 80 °C to initiate the gelation of the aluminium oxalate around the particles. The as-formed mixture was kept at this temperature for 90 min while continuing stirring.

In the case of aluminium tri-isopropoxide, the precursor was dissolved in 200 mL isopropanol and 50 mL ethanol with a molar ratio of 1–70 of Al(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> to C<sub>3</sub>H<sub>8</sub>O. 10g of MoSi<sub>2</sub> powder was dispersed in 72 mL deionized water and 72 mL of isopropanol by ultrasonication, prior to the sol-gel process. After, the dispersed powder was added to the dissolved Al(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> solution, together with 3mL of 1.0 M HNO<sub>3</sub> solution. The mixture was heated to 90 °C and left to gelate for 30 min.

The sample based on aluminium tri-sec-butoxide was prepared by heating a mixture of 600 mL of deionized water and 15 ml of 1.0 M HNO<sub>3</sub> to 80 °C to obtain a molar ratio of 1 : 150 of Al(OC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> to H<sub>2</sub>O. First, 10 g of MoSi<sub>2</sub> powder was added in the solution mixture of deionized water and HNO<sub>3</sub> and 200 sccm nitrogen (5N purity) was purged through the suspension to improve the dispensability of the particles in the solution. When the temperature was stable at 80 °C again, 10 g of Al(OC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> was added with approx. 25 mL of ethanol to transfer the viscous liquid. After, the system was left to gelate for 60 min. Next, the nitrogen flow and stirring were stopped and the solution was left at 80 °C until the liquid fraction was evaporated.

All the three resulting gels were filtered using a glass - vacuum filtration system (Sartorius Stedium, Biotech, Goettingen, Germany) with a hydrophilic propylene membrane with a pore size of 0.45  $\mu$ m. To remove the unreacted precursors, the samples were washed with warm deionized water (about 60 °C). Finally, the coated particles were dried in an autoclave (WTC binder, TAMSON, Tuttlingen, Germany) at 110 °C overnight and gently ground to break up the agglomerates.

To improve the structural integrity of the coating and obtain a thicker shell, the molar ratio of the selected precursor (aluminium tri-sec-butoxide) was increased from 1:150 to 2:150 of Al(OC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> to H<sub>2</sub>O, following the same coating procedure, as described above; see Fig. 1. Next, the coated particles were subjected to a two-step annealing treatment. First, a calcination treatment was applied at 450 °C for 30 min in laboratory air and 15 h in Ar, to slowly release the molecular water, followed by a post-treatment between 900 and 1200 °C for 1 h in Ar, to consolidate and to promote the formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> shell.

### 2.3. Characterisation

The particles size distribution of the wind sifted MoSi<sub>2</sub> particles was determined with a laser diffraction instrument (Malvern Mastersizer X, Malvern Instruments Ltd, Worcestershire, UK). Prior to the measurement, the particles were dispersed in water for 20 min by applying ultrasonic vibration.

The morphology of the sol-gel MoSi<sub>2</sub> coated particles was investigated by scanning electron microscopy (SEM) using a JSM 6500F (JEOL, Tokyo, Japan) operated with an electron beam energy of 15 keV and a beam current of approx. 600 pA. Prior to the SEM observation, the particles were coated with a thin carbon film to prevent charging.

The shell and core composition was analysed with X-ray diffractometry (XRD). A Bruker D500 diffractometer equipped with a Huber incident-beam monochromator and a Braun PSD detector operated with Cu K $\alpha$ 1 (1.54060 pm wavelength) was used to record the diffractograms in the 2 $\theta$  range of 15–70° with a step size of 0.0387° 2 $\theta$ .

The shell integrity was investigated by exposure of the coated particles to a quasi-stagnant oxidizing environment at high temperatures using a thermogravimetric analysis (TGA). For this purpose, a symmetrical thermogravimetric analyser (Setaram TAG 16/18, France) was

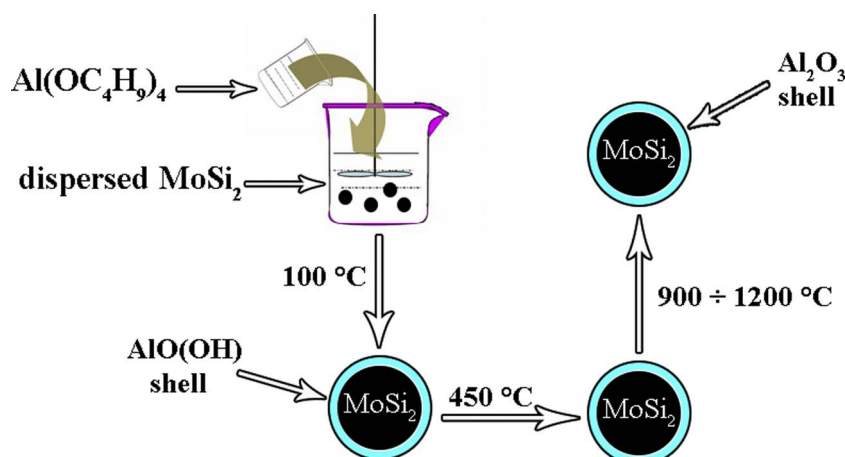


Fig. 1. Schematic of sol-gel coating of  $\text{MoSi}_2$  healing particles using aluminium tri-sec butoxide as a precursor. The set up consist of a glass beaker fixed on a heating and stirring plate. Nitrogen was supplied to the reactor by a custom made ring-shaped bubbler to ensure a good dispersion of the  $\text{MoSi}_2$  healing particles.

used. First, the decomposition kinetics of the uncoated  $\text{MoSi}_2$  particles was investigated by monitoring the weight change during isothermal hold at  $1100\text{ °C}$  for 100 h in synthetic air (20 vol.% oxygen in nitrogen). Thereafter, the core-shell system was analysed under the same conditions. The typical mass of each ‘sample’ was about 200 mg which corresponds to about  $2.12 \cdot 10^7$  particles.

### 3. Results and discussion

#### 3.1. Oxidation kinetics of the uncoated $\text{MoSi}_2$ particles

The thermal response of the uncoated  $\text{MoSi}_2$  particles was recorded by monitoring the weight change with the temperature using a symmetrical thermogravimetric analyser; see Fig. 2. Since oxygen was readily available to react with the unprotected  $\text{MoSi}_2$  core particles, a rapid weight gain was recorded between 450 and  $600\text{ °C}$ . This is associated with the concomitant formation of  $\text{MoO}_3$  whiskers and  $\text{SiO}_2$  clusters [30]. Above  $600\text{ °C}$ , the mass gain becomes almost constant due to the formation of a passive layer of  $\text{SiO}_2$  around the  $\text{MoSi}_2$  particles. However, as temperature increases ( $> 800\text{ °C}$ ), gaseous  $\text{MoO}_3$  forms due to the cracking of the passive  $\text{SiO}_2$  layer [31], resulting in a weight loss; see Fig. 2.

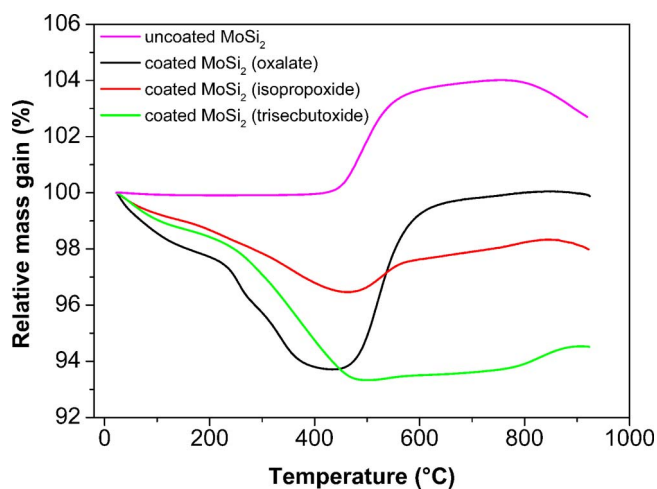


Fig. 2. Mass gain versus temperature during exposure in synthetic air (20 vol. %  $\text{O}_2$  in  $\text{N}_2$ ) with heating rate  $5\text{ °C/min}$  of uncoated and coated  $\text{MoSi}_2$  particles with a sol derived from aluminium oxalate, aluminium iso - propoxide and aluminium tri-sec-butoxide precursors.

#### 3.2. Oxidation kinetics of $\text{MoSi}_2$ particles coated with the ‘green’ sol-gel coating

The mass change of the three samples consisting of ‘green’ (i.e. uncalcined) coated particles versus the temperature is shown in Fig. 2. A large mass decrease was recorded between 100 and  $500\text{ °C}$  for the all three type of precursors. Three reaction regimes can be distinguished: (i) from room temperature to  $150\text{ °C}$ , the evaporation of physical bonded water and residual solvent occurs; (ii) the temperature region of 150 to approx.  $350\text{ °C}$ , is assigned to the desorption of chemically bonded water and the decomposition of the unreacted precursor in the gel, and (iii) from 350 to about  $500\text{ °C}$ , the dehydroxylation reaction of boehmite to  $\gamma\text{-Al}_2\text{O}_3$  takes place [32,33]. A major weight gain was observed between 600 and  $900\text{ °C}$  for the  $\text{MoSi}_2$  particles coated by the sol with either aluminium oxalate or aluminium isopropoxide, indicating a poor coverage of the healing particles, thus leading to the oxidation of the core. Furthermore as shown in Fig. 2 the precursor was not fully converted into boehmite and alumina. In the case of the sol derived from aluminium tri-sec-butoxide a smaller weight gain was recorded and the weight became constant at  $800\text{ °C}$  (see Fig. 2), indicating that the precursor fully coated the healing particles and was converted into boehmite. Hence, aluminium tri-sec-butoxide was selected as an optimum precursor for the further sol-gel encapsulation process.

#### 3.3. Shell morphology and composition after deposition and drying

A comparison of the morphology of uncoated and coated  $\text{MoSi}_2$  particles using aluminium tri-sec-butoxide as a precursor is presented in Fig. 3. The recorded images revealed that the surface of the coated  $\text{MoSi}_2$  particles is completely covered by a closed layer; see Fig. 3b.

The X-ray diffractogram of the coated particles revealed both peaks belonging to  $\text{MoSi}_2$  and smaller peaks corresponding to boehmite in a pseudo-crystalline state [34]; see Fig. 4.

#### 3.4. Shell composition after calcining

The integrity of the shell should be maintained during the phase transformation of boehmite to  $\alpha\text{-Al}_2\text{O}_3$  through the calcining process. When annealing, the boehmite shell undergoes several phase transformations which are associated with volume change [35–37]. The most critical volume change ( $\Delta V/V = -29.4\%$ ) occurs between 300 and  $500\text{ °C}$ , when the dehydroxylation of  $\text{AlO(OH)}$  takes place [21]. Thus, to avoid the fragmentation of the boehmite shell, the encapsulated particles were first exposed at  $450\text{ °C}$  to gradually release the molecular water, followed by a gradual increase of the calcining temperature from



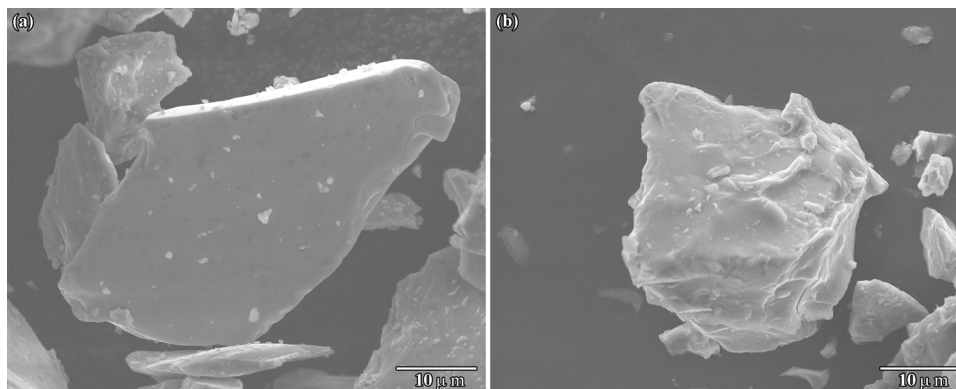


Fig. 3. Surface morphology of uncoated and sol-gel coated MoSi<sub>2</sub> particle after drying at 80 °C overnight: (a) as received and (b) boehmite-coated particles by using aluminium tri-sec-butoxide as a precursor.

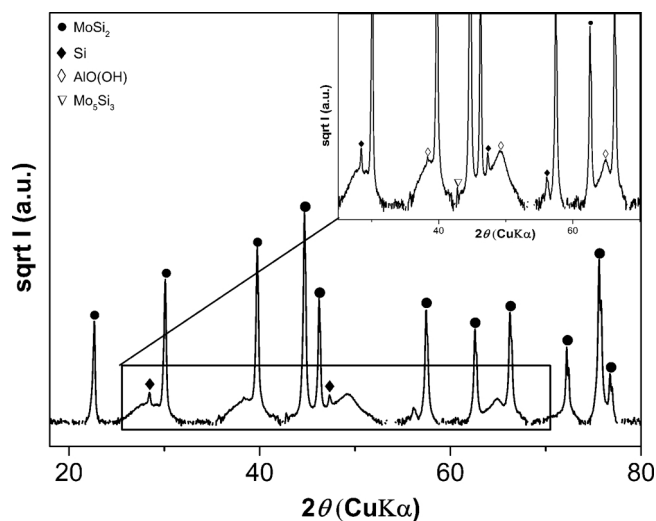


Fig. 4. X-ray diffraction pattern of sol-gel coated MoSi<sub>2</sub> particles using aluminium tri-sec-butoxide precursor after drying in air at 80 °C overnight. Peaks between 30 and 70° 2θ, display the formation of AlO(OH).

900 to 1200 °C, to identify the phase transformation after each annealing step; see Fig. 5. The XRD analysis reveal that the MoSi<sub>2</sub> core remained intact at all the annealing temperatures. Only after annealing at 1200 °C, the diffraction lines corresponding to  $\theta$ ,  $\delta$  and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> were observed in addition to those for the MoSi<sub>2</sub> tetragonal phase; see enlargement Fig. 5.

### 3.5. Alumina shell thickness

The alumina shell thickness was measured from SEM images of cross-sections of the encapsulated MoSi<sub>2</sub> core-shell particle after calcining at 1200 °C. A representative cross section is shown in Fig. 6. The shell is continuous, however, not of a constant thickness as the healing particles are of irregular shape. The layer was thinnest at the sharp edges of MoSi<sub>2</sub> particles [27]. The average layer thickness of the coated MoSi<sub>2</sub> particle was determined to be about 0.6 μm; see Fig. 6.

### 3.6. Microcapsule stability

The stability of the encapsulated particles at high temperature was investigated via thermogravimetric analysis; see Fig. 7. The weight gain of the uncoated and coated MoSi<sub>2</sub> particles calcined at 1200 °C was measured after exposure to 1100 °C in synthetic air for 100 h. The uncoated particles increase in weight due to the oxidation of MoSi<sub>2</sub> core. For the encapsulated particles, a smaller mass increase in the

initial slope is observed. This can be associated with the partial oxidation of the MoSi<sub>2</sub> core via cracks that may form in the alumina shell, during the stability test. About five times lower weight gain was observed for the alumina encapsulated MoSi<sub>2</sub> particles as compared to the uncoated MoSi<sub>2</sub>; see Fig. 7. This indicates that during the stability test, the encapsulated particles are more stable than the MoSi<sub>2</sub> in as received conditions and the alumina shell acts as a protective layer against severe oxidation. The oxygen partial pressure at the interface between the MoSi<sub>2</sub> particle and the alumina shell is governed by the dissociation partial pressure of Al<sub>2</sub>O<sub>3</sub> (i.e. about 10<sup>-33</sup> atm at 1100 °C), which is too low to form SiO<sub>2</sub> (which requires about 10<sup>-24</sup> atm at 1100 °C). However, when defects like pores or cracks are present in the alumina shell, the MoSi<sub>2</sub> may be exposed to higher oxygen partial pressures causing silica to form.

The microstructure of the uncoated and coated particles calcined at 1200 °C and subsequently exposed at 1100 °C in air for 100 h is shown in Fig. 8. In the absence of the alumina shell, all the unencapsulated particles oxidized and, as a result, a uniform and amorphous SiO<sub>2</sub> layer developed on their surface; see Fig. 8a and b. In contrast, the encapsulated MoSi<sub>2</sub> particles remained intact after isothermal exposure at 1100 °C; see Fig. 8c. However, a few of the alumina coated particles displayed fine cracks at the surface; see Fig. 8d. This may be caused by the presence of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase in the shell which has not been fully converted to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> after 1 h of calcining at 1200 °C; see enlargement in Fig. 5. During the thermal stability test, the phase transformation of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> occurs along with a volume change of about -10% [21]. This volume shrinkage generates a large strain misfit, which cannot be accommodated by the plastic deformation of the crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, thus leading to the crack formation in the shell.

Due to alumina shell cracking, the MoSi<sub>2</sub> core is exposed to the oxidizing environment and a thin layer of SiO<sub>2</sub> forms during the thermal stability test. Assuming that the total volume of the particle after the test comprises the volume of the MoSi<sub>2</sub> core and the volume of the silica shell (see Fig. 9), then the thickness of the SiO<sub>2</sub> layer formed during the 100 h of exposure can be estimated using the following relation:

$$V_{total} = V_{particle} + V_{shell} \quad (1)$$

If the MoSi<sub>2</sub> particle has a spherical shape and a diameter  $d$ , then Eq. (1) can be rewritten as:

$$\frac{1}{6}\pi \cdot (d_{particle} + \delta_{SiO_2})^3 = \frac{1}{6}\pi \cdot d^3 + \frac{m_{SiO_2}}{\rho_{SiO_2}} \quad (2)$$

where

$$m_{SiO_2} = n_{SiO_2} \cdot M_{SiO_2} \quad (3)$$

with  $n_{SiO_2}$  moles of SiO<sub>2</sub> and  $M_{SiO_2}$  the molar mass of silica.

If all the Si is depleted, then  $n_{SiO_2} = n_{Si}$  and thus Eq. (3) becomes:

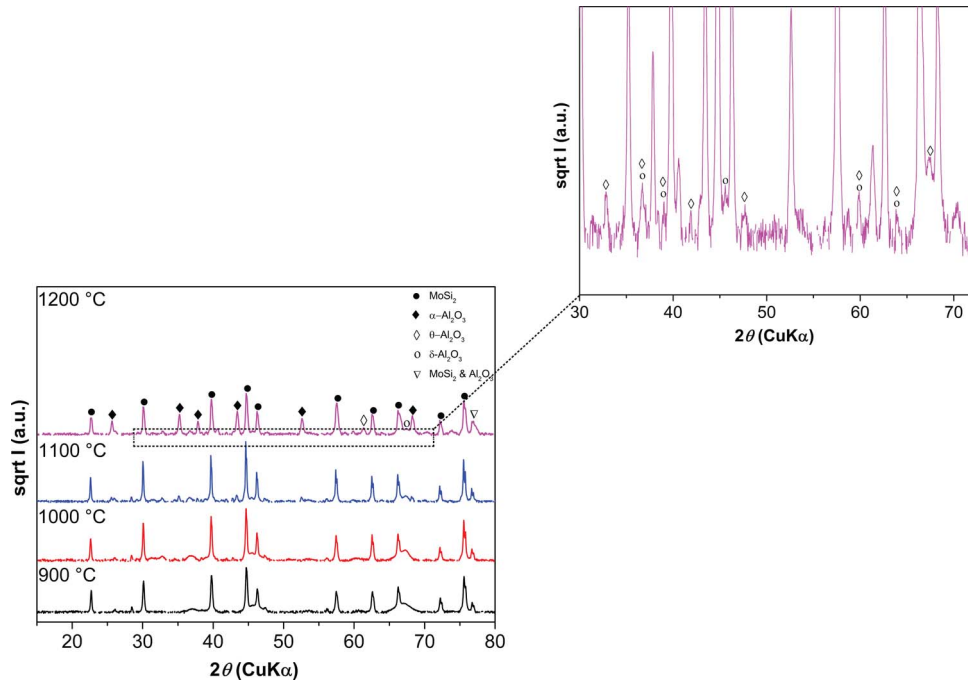


Fig. 5. X-ray diffraction pattern of encapsulated MoSi<sub>2</sub> particles pre-calcined at 450 °C for 12 h in Ar followed by calcination at different temperatures: (a) 900 °C, (b) 1000 °C, (c) 1100 °C and (d) 1200 °C for 1 h in Ar. The enlargement between 30 and 70° 2θ displays the formation of metastable alumina phases (θ- and δ-Al<sub>2</sub>O<sub>3</sub>).

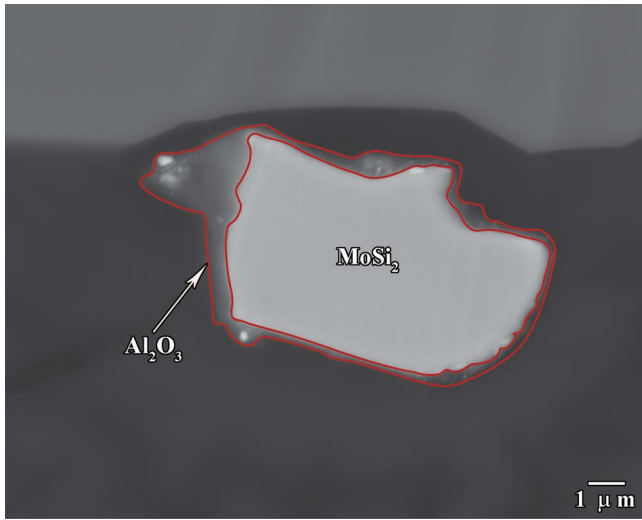


Fig. 6. Cross-section image of encapsulated MoSi<sub>2</sub> particle with a shell of Al<sub>2</sub>O<sub>3</sub> after annealing at 1200 °C for 1 h in Ar.

$$m_{SiO_2} = n_{Si} \cdot M_{SiO_2} \tag{4}$$

with  $n_{Si} = m_{Si} / M_{Si}$  and  $m_{Si}$  equals the wt % of Si in MoSi<sub>2</sub>, then Eq. (4) can be rewritten as:

$$m_{SiO_2} = x \cdot wt\%Si \cdot m_{particle} \frac{M_{SiO_2}}{M_{Si}} \tag{5}$$

And

$$m_{particle} = V_{particle} \cdot \rho_{particle} \tag{6}$$

Then, Eq. (2) can be re-arranged in terms of Eqs. (5) and (6):

$$\delta = d \left[ \left( 1 + x \cdot wt\%Si \cdot \frac{M_{SiO_2} \cdot \rho_{particle}}{\rho_{SiO_2} \cdot M_{Si}} \right)^{1/3} - 1 \right] \tag{7}$$

However, Eq. (7) holds for case when all the MoSi<sub>2</sub> is fully transformed into SiO<sub>2</sub>. Knowing the mass gain of the uncoated and

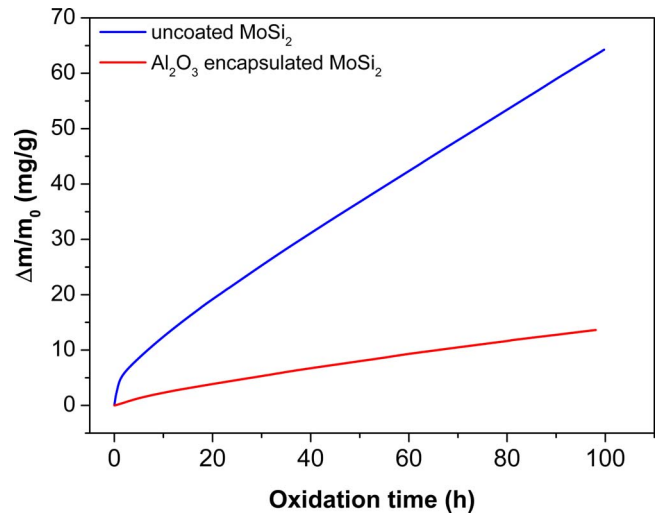


Fig. 7. Mass gain versus isothermal exposure at 1100 °C in synthetic air (20 vol.% O<sub>2</sub> in N<sub>2</sub>), for 100 h of: (a) uncoated and (b) coated MoSi<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> core-shell particles calcined at 1200 °C.

encapsulated particles after isothermal exposure at 1100 °C (see Fig. 7), Eq. (7) can be re-written as:

$$\delta = d \cdot \left[ \left( 1 + x \cdot \frac{\Delta m_{MoSi_2} \cdot \rho_{MoSi_2}}{m_{MoSi_2} \cdot \rho_{SiO_2}} \right)^{1/3} - 1 \right] \tag{8}$$

where  $x$  is the amount of Si in MoSi<sub>2</sub> (30 wt %),  $\rho_{SiO_2}$  and  $\rho_{MoSi_2}$  are the density of SiO<sub>2</sub> and MoSi<sub>2</sub> particles, respectively, while  $\Delta m_{MoSi_2}$  and  $m_{MoSi_2}$  are the mass gained after the stability test corresponding to the oxidation of MoSi<sub>2</sub> particles to SiO<sub>2</sub> and the initial mass of MoSi<sub>2</sub> particles before the stability test. For the encapsulated MoSi<sub>2</sub> particles studied here it is estimated that a layer of SiO<sub>2</sub> with a thickness of about 90 nm is formed during the stability test at 1100 °C as a result of partial exposure of the healing particle via the micro-cracks in the alumina shell. Applying the same relation for the uncoated MoSi<sub>2</sub> particles (Eq.

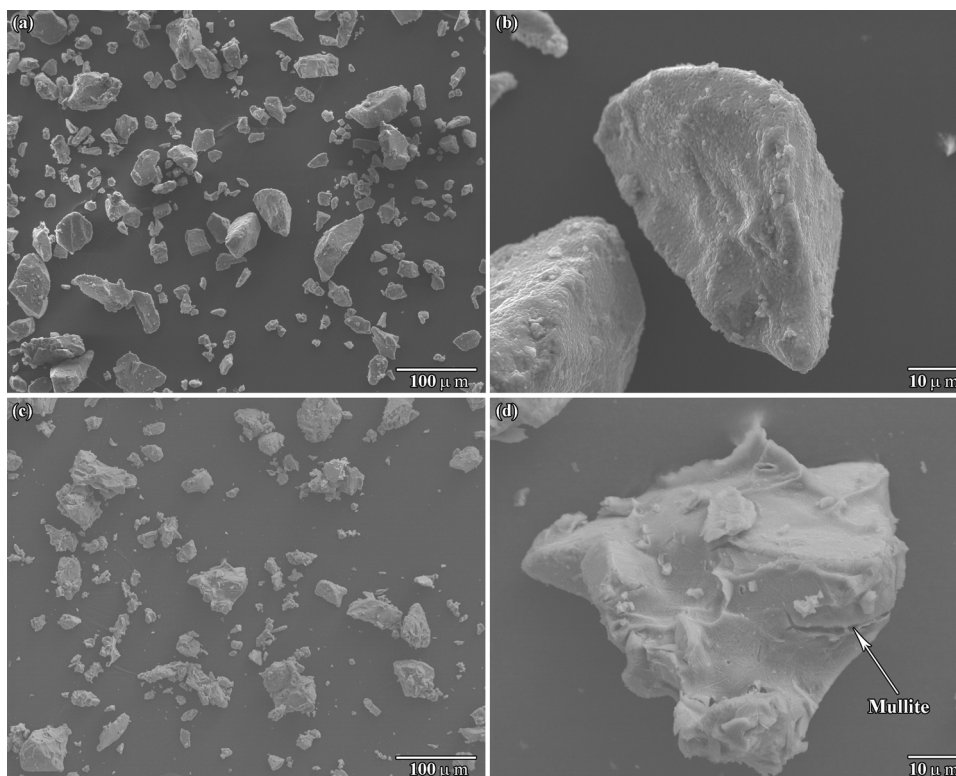


Fig. 8. Shell morphology of uncoated (a), (b) and alumina encapsulated  $\text{MoSi}_2$  particles calcined at  $1200^\circ\text{C}$  (c) and (d), after oxidation test at  $1100^\circ\text{C}$  for 100 h in synthetic air (20 vol.%  $\text{O}_2$  in  $\text{N}_2$ ).

(8)), a  $\text{SiO}_2$  layer with a thickness of about 400 nm is estimated to form during the isothermal exposure.

In addition, the resulting  $\text{SiO}_2$  inside the crack either reacts with the existing alumina shell to form mullite [38] (see Fig. 8d) or transforms to cristobalite. This is supported by the XRD analysis, where  $\text{Mo}_5\text{Si}_3$ , cristobalite (as a result of  $\text{MoSi}_2$  oxidation) and mullite were observed in addition to  $\text{MoSi}_2$  and  $\alpha\text{-Al}_2\text{O}_3$  peaks; see Fig. 10. However, the intensity of cristobalite and mullite peaks are very low, confirming that most of the alumina encapsulated particles preserved their integrity during isothermal exposure at  $1100^\circ\text{C}$ . In addition, the mass change of these encapsulated particles becomes almost monotonic during the remainder of the stability test as a result of mullite formation inside the crack; see Fig. 7. Also mullite preserves the  $\text{MoSi}_2$  core, since its diffusivity at  $1100^\circ\text{C}$  is comparable with that of alumina ( $1.2 \cdot 10^{-20}$  [39] versus  $4.6 \cdot 10^{-18} \text{ m}^2/\text{s}$  [40]).

#### 4. Conclusions

Coarse and irregular  $\text{MoSi}_2$  healing particles of about  $30 \mu\text{m}$  were successfully encapsulated via sol-gel method. Lower calcining temperatures (i.e.  $900 \div 1100^\circ\text{C}$ ) promoted the formation of a metastable  $\delta\text{-Al}_2\text{O}_3$  phases. Only after calcining at  $1200^\circ\text{C}$  in Ar, a closed  $\alpha$  alumina shell of about  $0.6 \mu\text{m}$  thickness was formed. The oxidation test confirmed that the particles remained intact after 100 h exposure in air at  $1100^\circ\text{C}$  as they had a five times lower mass gain than the uncoated  $\text{MoSi}_2$  particles. The shell morphology after the oxidation test indicated that the healing particles partially reacted with alumina shell to form mullite, providing further protection against oxidation.

#### Acknowledgements

This project has received funding from European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n°

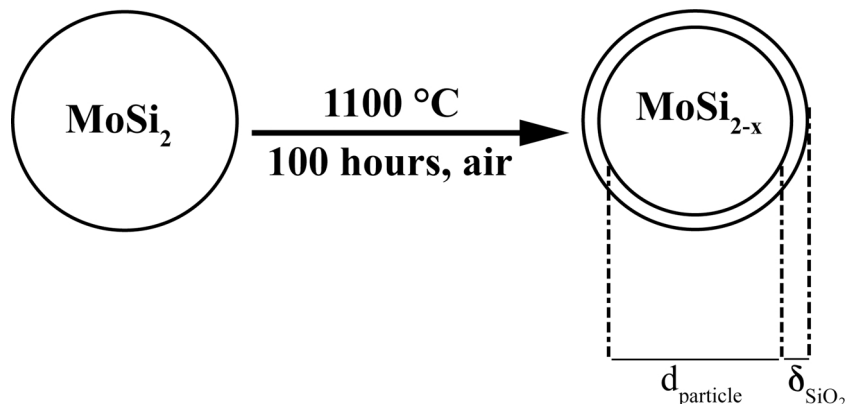


Fig. 9. Schematic of a spherical  $\text{MoSi}_2$  particle after oxidation test at  $1100^\circ\text{C}$ , 100 h in synthetic air used to calculate the thickness of the formed  $\text{SiO}_2$  layer.



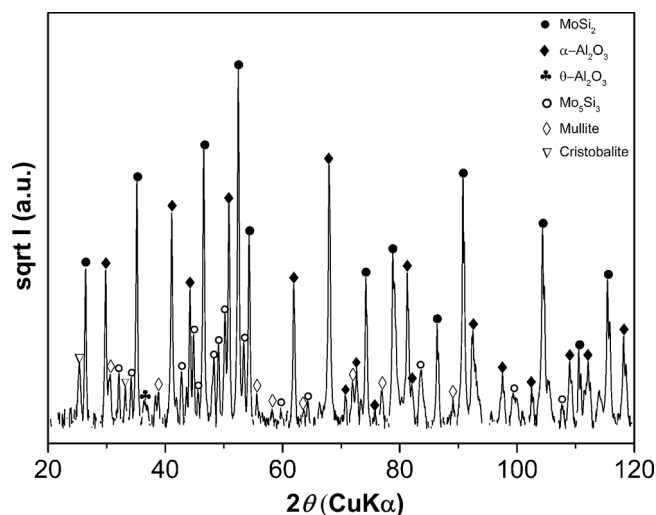


Fig. 10. X-ray diffraction pattern of alumina coated MoSi<sub>2</sub> particles calcined at 1200 °C, after shell stability test at 1100 °C, 100 h in synthetic air (20 vol.% O<sub>2</sub> in N<sub>2</sub>).

309849, SAMBA. The authors thank Ing. R. W. A. Hendriks for the XRD analysis.

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