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Full length article



Recovery of rare earths from glass polishing waste for the production of aluminium-rare earth alloys

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ABSTRACT

The circular economy demands waste utilization for the production of high-value products, and this requires the development of novel processing routes. In this study, rare earth (La and Ce) oxides were completely (>99%) recovered from polishing waste by a combined novel reductive acid leaching and alkali treatment process. About 70% of rare earths were dissolved during the first leaching step. The undissolved rare earth compounds are converted to oxides/hydroxides by alkali treatment and dissolved in the acid solution – the 2nd leaching step – for the complete recovery of rare earths. The recovered rare earth oxides were used for producing *in-situ* high-value Al-La-Ce alloys with fused salt electrolysis. Mechanical properties of our Al-La-Ce alloys are similar to the known high temperature Al-Ce alloys. This development of new alloys by our novel process helps in utilization of both overproduced primary La and Ce oxides as well as La and Ce recovered from polishing waste.

1. Introduction

Ce as ceria (CeO₂) is used in glass polishing applications due to its chemical and mechanical properties (Janoš et al., 2014). Globally, about 16,000 t of rare earth oxides (REOs) containing Ce and La are used annually for polishing applications, which is about 10% of total REO production. Glass polishing powder is accumulated with SiO₂ and other impurities during polishing and in subsequent settling processes (Ter-cero Espinoza et al., 2015). The particle size distribution (PSD) also changes during polishing (Binnemans et al., 2013). An increase in impurity content and/or change in PSD decreases its polishing ability, and eventually, the product ends its service life and will be landfilled, which leads to a loss of natural resources. Recovery of Rare earth elements (REEs) from the polishing waste and utilizing the REEs in the polishing process or high-value applications will contribute to the circular economy and closes the rare earth metal loops (Bao et al., 2020; Borra et al., 2018; Yu et al., 2019).

SiO₂ and Al₂O₃ contaminants can be removed from the polishing waste by NaOH roasting or NaOH leaching (Kato et al., 2000a, 2000b; Moon et al., 2011; Wang et al., 2020). It increases the lifespan of the

polishing powder. However, the change in PSD and accumulation of other impurities limits the number of reusing cycles (Borra et al., 2018). Therefore, the selective recovery of REEs from polishing powder is required. Several studies have been carried out to recover the REEs from polishing powder (Bao et al., 2020; Byeon et al., 2011; Henry et al., 2013; Janoš et al., 2015, 1988; Kim et al., 2011; Poscher et al., 2016, 2015, 2013; Terziev et al., 1996; Yu et al., 2019). Most of them include an acid leaching step. Ceria is a stable compound, which needs high acid concentrations, high temperatures, or costly reductants such as hydrogen peroxide used during leaching. Furthermore, the recovery of Ce and La is not complete as the polishing powder contains insoluble compounds such as rare earth fluorides and phosphates (Borra et al., 2019; Poscher et al., 2014; Tanaka et al., 2013). In a recent study, Borra et al. proposed an alkali roasting and leaching process to recover rare earths from leach residue containing rare earth fluorides and phosphates (Borra et al., 2019). However, the authors used HCl for leaching the polishing waste and alkali roasted residue, which generates hazardous chlorine gas. A detailed literature review on REEs recovery from the polishing waste can be found elsewhere (Borra et al., 2018).

In a recent study, Sims et al. proposed to use a 12 wt.% Ce containing

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Al alloy in automotive Internal Combustion (IC) engines as the alloy can withstand higher temperatures than commercial Al alloys, which enhances the fuel efficiency and decreases the pollution (Czerwinski, 2020; Sims et al., 2016). 1% replacement of commercial aluminium alloys with 12% rare earth-containing alloys in the automotive sector can consume about 2400 t of REEs (Sims et al., 2016). La and Ce oxides generated from the polishing waste can be used for the production of Al-La-Ce alloys. These alloys may have similar mechanical properties to Al-Ce alloys as the atomic radii of La and Ce are quite similar. The similar mechanical properties of Al-La-Ce and Al-Ce alloys were recently confirmed by Sims et al. in a brief study (Sims et al., 2020).

During primary production of Nd and Dy for permanent magnet production, a large volume of La and Ce are co-produced (Binnemans and Jones, 2015). Some of the overproduced La and Ce are stockpiled due to their low demand. Therefore, the development of Al-La-Ce high-value alloys can also increase the demand for primary La and Ce. An increase in demand for La and Ce can address the so-called balance problem in rare earth mining (Sims et al., 2016).

Harata et al. attempted to produce Al-Sc alloys directly from Al and Sc_2O_3 by molten $CaCl_2$ fused salt electrolysis (Harata et al., 2009). This process consumes less energy than Al-Sc alloy production from individual metals. This process route can be applied for Al-La-Ce alloy production as the stability of La and Ce oxides are similar to Sc oxide. However, the Al-Sc alloy produced was not homogenous and needed an extra processing step for homogenization. Moreover, the concentration of Sc was low (<2 wt.%) in the alloy. Furthermore, Ce and La oxides behave differently in the molten salt compared to Sc oxide (Mukherjee et al., 2017).

In this study, a complete (>99%) recovery of REEs from polishing waste was developed using a novel combined process route. The recovered REOs were used for the production of new Al-La-Ce alloys for high temperature applications. REEs were dissolved from polishing waste by acid leaching in the presence of a low-cost organic reductant. The undissolved rare earth compounds in the polishing waste were further treated with alkali roasting and acid leaching for complete recovery. The recovered REOs were converted to an *in-situ* Al-based rare earth alloy using a new fused salt electrolysis route. Finally, the temperature dependant mechanical properties of the proposed Al-La-Ce alloys were compared with the Al-Ce alloys.

2. Experimental

Two polishing waste samples, one from plate glass polishing and another from mirror polishing, were used in the current study. The polishing waste slurry was dried at 105 °C until constant mass and sieved to $-90\ \mu\text{m}$ mesh to remove the foreign particles. Analytical reagent grade nitric acid (65%) (Chem-lab), NaOH (Sigma Aldrich), Na_2CO_3 (Sigma Aldrich), sodium tetraborate decahydrate (Sigma Aldrich), and D-Glucose (Sigma Aldrich) were used in this study. Chemical analysis was performed using wavelength dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Spectro Arcos-OEP). Chemical analysis with ICP-OES was performed after the complete dissolution of polishing waste by alkali fusion followed by acid digestion in a 1:1 (v/v) HCl and water solution. The alkali fusion was carried out by mixing 0.5 g of polishing waste with 1.5 g of sodium carbonate and 1.5 g of sodium tetraborate decahydrate.

2.1. Leaching, alkali roasting, and selective precipitation studies

The leaching experiments were carried out in a vibratory shaker (VWR Thermoshake) at 600 rpm. The leach solution was filtered using a syringe filter (pore size of 0.45 μm) and diluted with distilled water for ICP-OES analysis.

The leach residue was dried in an oven at 105 °C for 12 h. For roasting, 1 g of leach residue was mixed with NaOH powder in a nickel

crucible. Then, the mixture was roasted at 500 °C in the air at atmospheric pressure in a muffle furnace. After roasting, the samples were leached with water at 60 °C for one hour to remove water soluble impurities. The residue was filtered and dried. The dried alkali treated residue was leached with 4 M nitric acid in presence of glucose with a glucose to residue ratio of 0.1 at a liquid-to-solid ratio of 5:1 at 60 °C for 1 h.

The filtrate from the first acid leach solution and the acid leach solution after alkali roasting were treated with oxalic acid at a 1:2 mole ratio of REEs to oxalic acid for the selective precipitation of REEs. After precipitation, the rare earth oxalate precipitate was filtered and thoroughly washed with demineralized water and calcined at 850 °C for 1 h to produce REOs.

2.2. Fused salt electrolysis

The rare earth oxides obtained after acid leaching and alkali treatment were converted to metals in fused salt electrolysis. $CaCl_2$ powder (40 g, charged into a graphite crucible) was used as the electrolyte. The crucible was placed in a vertical alumina tube furnace with a controlled atmosphere. The salt was melted at 850 °C under an argon (Ar) atmosphere. Rare earth oxide powder and Al were charged in the $CaCl_2$ salt. Glassy carbon was used as an anode, and Mo wire was used as the cathode. The current applied was 0.5 A, and the electrolysis was carried out for 4 h. After the electrolysis, the crucible was gradually cooled down to room temperature in the electric furnace. The Al alloy was recovered by leaching in water. The Al-RE alloy samples obtained by the electrolysis were analysed by X-ray diffraction, Scanning Electron Microscope with Energy Dispersive X-Ray analysis (SEM-EDX), and X-ray fluorescence (XRF) spectroscopic analysis.

Fig. 1 shows the flowsheet of the proposed process. This process includes acid leaching and alkali roasting of glass polishing waste for the recovery of REOs. The recovered REOs are used for the production of Al-RE alloys by fused salt electrolysis. This flowsheet also includes primary mining, where the overproduced REOs can be used in Al-RE alloys production.

2.3. Thermo-mechanical studies

Alloys were prepared with pure metals of Al, Ce, and La. Both Al-Ce alloys and Al-La-Ce alloys were prepared by arc melting of the metals under ultra-high purity argon gas. The melted alloy was subsequently sucked into a water-cooled copper mould by vacuum suction to obtain a cylindrical rod with a 6 mm diameter and 80 mm length. The schematic of arc melting and vacuum casting setup is shown in Fig. 2. Processed Al-RE alloys samples were cut into cylindrical specimens of 6 mm radius and 9 mm length using Electrical Discharge Machining (EDM), and compression tests were performed to understand the material properties of the alloys. True stress-true strain curves were obtained by conducting compression tests at various temperatures on different Al-RE alloys using Gleeble 3800®. K-type thermocouples were spot welded on to the samples before the compression test. The compression tests were conducted at a strain rate of 0.001 s^{-1} until failure.

2.4. Chemical composition of the samples

The sample from plate glass polishing is named A, and the sample from mirror polishing is named B. Images of sample A and B are shown in the Fig. 3. Table 1 shows the chemical analysis of the two samples. Sample B mainly contains polishing powder with a minimal amount of impurities. However, it contains F and P together with La and Ce. F and P are not derived from the polishing process but added during powder production to neutralize the basic La oxide. On the contrary, sample A is rich in impurities. It mainly contains Ca, Ce, La, Al, and Si together with fluorine and phosphorus. XRD analysis shows that Ca is in the form of calcium carbonate, Ce is in the form of ceria, and La is in the form of

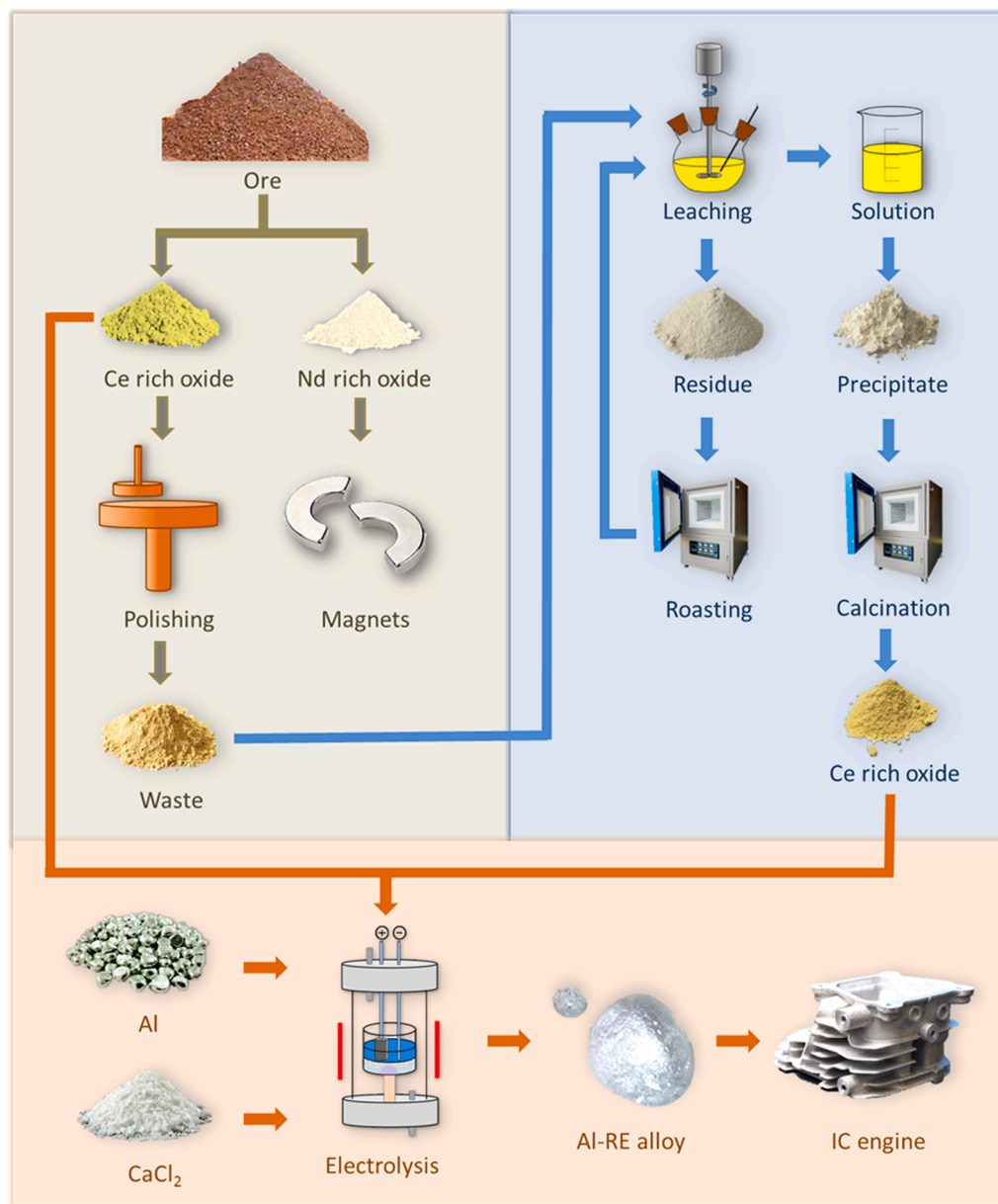


Fig. 1. Flow sheet for producing Al-RE alloys from polishing waste and primary ore. The polishing waste was first treated with reductive acid leaching. The solution after leaching was treated with oxalic acid to selectively precipitate rare earth oxalates. These rare earth oxalates are decomposed to oxides by calcination at 800 C. The residue generated after leaching is treated with NaOH to convert undissolved fluorides and phosphates to oxides/hydroxides. These oxides/hydroxides can contain impurities. Therefore, they are dissolved in acid in the presence of a reductant for purification. After rare earth dissolution, pure rare earth oxides can be recovered by oxalic precipitation followed by calcination. The purified rare earth oxides are used for producing aluminium rare earth alloys by fused salt electrolysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oxyfluoride and phosphate (Borra et al., 2019).

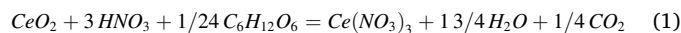
3. Results and discussion

Ca in sample A needs to be removed before the leaching of REEs (Borra et al., 2019). If Ca is present in the leach solution together with REEs, it will precipitate together with the REEs as oxalate during oxalic acid precipitation (Chi et al., 2004). Hence, calcium was removed from sample A before REEs leaching. The process for calcium removal was discussed elsewhere (Borra et al., 2019).

3.1. Leaching

For optimizing the parameters, leaching studies were carried out first on sample B as this sample is almost a pure polishing powder, except the change in particle size distribution compared to the original polishing powder (Borra et al., 2019). Leaching experiments were carried out with nitric acid in the presence of a reductant (glucose) as the dissolution of ceria (Ce^{4+}) in an acid solution is difficult (Borra et al., 2018). Ceria

dissolves in the nitric acid solution in the presence of glucose according to the following reaction.



The amount of reductant was varied to understand the effect and to optimize the reductant amount (Fig. 4A). Ce recovery is very low (~20%) without a reductant, and it increased with an increase in the reductant amount. However, no significant increase in the Ce recovery was observed above 0.08 wt ratio of reductant (Fig. 4A). On the other hand, the addition of reductant has no major role in La recovery since La is already in trivalent state and easily soluble (Borra et al., 2019). However, La recovery slightly increased with an increase in the reductant amount. It may be due to the presence of La in the CeO_2 structure (Borra et al., 2019). Based on these results, a reductant weight ratio of 0.1 was chosen for further experiments.

Fig 4B and 4C show the effect of acid concentration and temperature on the recovery of REEs from sample B. It shows that the recovery of Ce and La increases with increasing acid concentration. The maximum recovery of Ce increased with an increase in temperature up to 50 C and

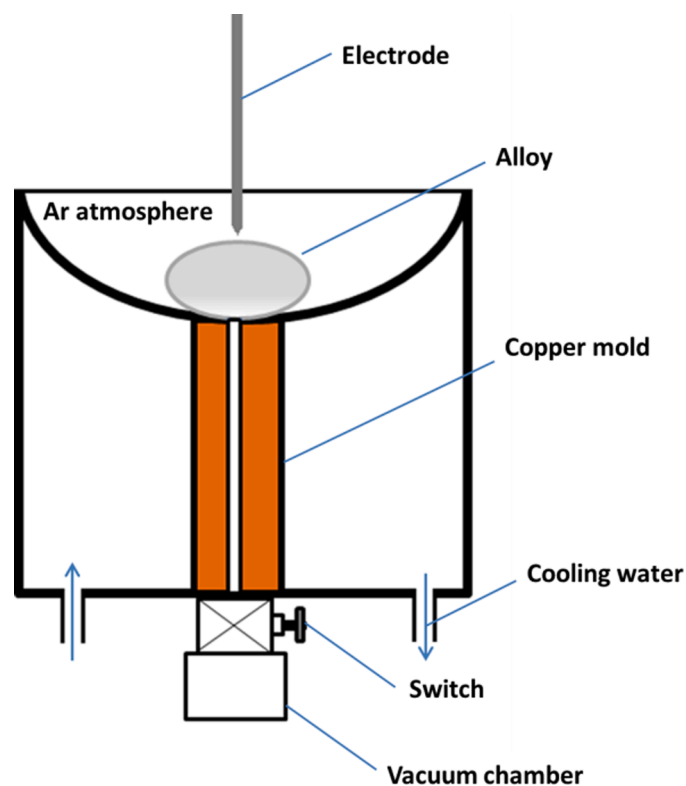


Fig. 2. Schematic of arc melting and vacuum casting setup.



Fig. 3. Images of sample A and sample B.

Table 1
Chemical analysis of the studied polishing waste samples (Borra et al., 2019).

Elements	Sample A	Sample B	Analysis
	(wt.%)		
Ce	23.3 ± 0.7	52.2 ± 1.5	ICP-OES
La	9.1 ± 0.3	18.7 ± 0.6	
F	2.3	5.9	XRF
Si	2.6	0.4	
Al	2.2	–	
Ca	20.8	0.2	
Fe	0.4	0.6	
P	0.4	0.9	
Ba	0.2	0.4	
Na	0.2	–	
Mg	0.1	–	
Ti	0.1	–	
Sn	0.1	0.4	
Ag	–	0.2	

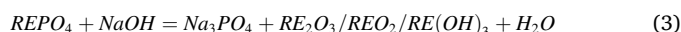
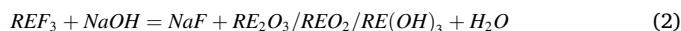
slightly decreased with a further increase in temperature. This decrease is due to the precipitation of Ce from the leach solution together with the dissolved fluorine at higher temperatures (Zhang et al., 2017). The temperature has a significant effect on the leaching of La compared to

Ce. Recovery of Ce and La is not improving above 75 °C as most of the soluble Ce and La are dissolved. About 70% of Ce and La can be dissolved during leaching. Further improvement in recovery is difficult due to the presence of Ce and La fluorides and phosphates (Fig. 4F).

Fig. 4D shows the effect of time on leaching of sample B, and it shows that about 2 h is required to dissolve the maximum amount of REEs from the sample at 75 °C. Based on the results of sample B, sample A was leached at 75 °C at different acid concentrations (1–5 M). The maximum recovery of REEs was obtained at 4 M HNO₃ concentration (Fig. 4E). The recoveries are comparable with sample B.

3.2. Alkali roasting

Based on previous studies (Borra et al., 2019), the residues generated after leaching can be treated by alkali roasting to convert fluorides and phosphates to oxides. Hence, the leach residues generated at 75 °C at 4 M acid concentration with L/S ratio of 5 were treated with NaOH to convert rare earth fluorides and phosphates to hydroxides/oxides (Reaction 2 and 3). During NaOH treatment, fluorine and phosphorous from rare earth compounds form sodium fluoride and sodium phosphate. This sodium fluoride and phosphate, together with excess NaOH, was removed from the alkali-treated residue by hot water washing. The residue after water washing contains rare earth hydroxides/oxides together with some impurities. Therefore, these oxides were dissolved in 4 M nitric acid in the presence of glucose reductant. The total recovery of rare earths from acid leaching and alkali roasting-leaching is more than 99% based on the ICP-OES analysis of both the leach solutions.



3.3. Selective precipitation of REEs

Leach solutions generated from direct leaching and alkali roasting-acid leaching were filtered, and the pH of the solution was adjusted to 5 to remove the impurities like Al, Si, and Fe in the form of hydroxides/oxides. Then oxalic acid was added to the solution to precipitate the REEs. The precipitate was calcined to form a La and Ce mixed oxide product (>99% purity).

Ce and La can be separated from the leach solution by selective oxidative precipitation of Ce by keeping La in the solution (Borra et al., 2018). However, this increases the process cost. The separated Ce(IV) oxide can be used for producing Al-Ce alloys or for other applications, and La oxide can be used in other applications.

3.4. Fused salt electrolysis

One of the main aims of this study is to convert the recovered REOs to high-value Al-RE alloys. Hence, the feasibility of producing a direct (master) alloy of Al-RE by chloride fused salt electrolysis process route developed by Harata et al. was explored (Harata et al., 2009). However, CeO₂ and La₂O₃ react with CaCl₂ and form the respective oxychlorides CeOCl and LaOCl (reactions 4 and 5), unlike scandium during electrolysis (Mukherjee et al., 2017). The formation of (Ce, La)OCl was confirmed by XRD analysis. The formation of CeOCl and LaOCl generates CaO (reactions 4 and 5). The CaCl₂ electrolyte can dissolve about 20% of CaO in the molten state. During electrolysis, the dissolved CaO is reduced instead of CaCl₂ as the decomposition voltage for CaO is lower compared to CaCl₂ decomposition (Suzuki, 2008). The Ca metal formed during electrolysis reduces REOCl to RE metal, which dissolves into Al and forms an alloy according to reaction 6. In the current study, a homogeneous Al alloy was produced containing about 5% RE and a small amount of Ca (0.2%). However, sometimes, Ca directly reacts with aluminium and forms a Ca rich alloy. Therefore, further studies are required to optimise the process conditions to prepare RE- rich and

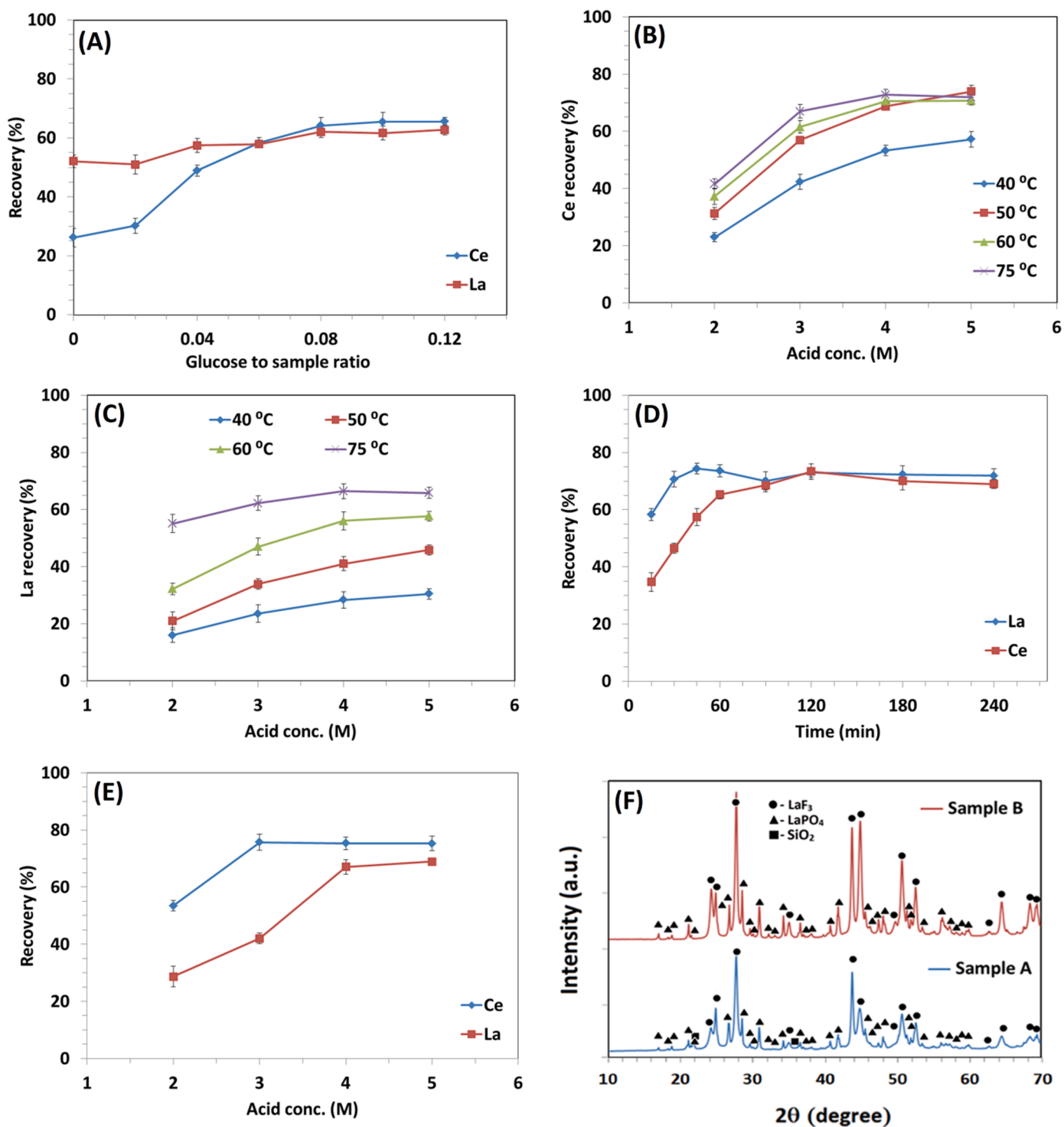
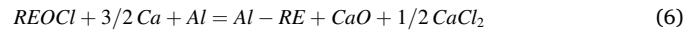


Fig. 4. Leaching of REEs from polishing waste samples. (A) effect of reductant on leaching of REEs from sample B (HNO_3 – 3 M, L/S – 5, t – 4 h, T – 75 °C); (B) effect of temperature and acid concentration on the recovery of Ce during leaching from sample B (HNO_3 , L/S – 5, t – 4 h, reductant to polishing waste ratio – 0.1); (C) effect of temperature and acid concentration on the recovery of La during leaching from sample B (HNO_3 , L/S – 5, t – 4 h, reductant to polishing waste ratio – 0.1); (D) effect of time on recovery of REEs during leaching from sample B (HNO_3 – 3 M, L/S – 5, T – 75 °C, reductant to polishing waste ratio – 0.1); (E) effect of acid concentration on the recovery of REEs during leaching from sample A (HNO_3 , L/S – 5, t – 4 h, T – 75 °C, reductant to polishing waste ratio – 0.1); (A) to (E) - Relative standard deviation is < 5%; The lines between two points in Fig 4A to 4E are provided to guide the reader; (F) XRD patterns of the leach residues of sample A and B show mainly the peaks of RE fluorides and Phosphates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Ca-lean Al alloys. Fig. 5A shows the schematic diagram of the electrolysis setup and Fig. 5B shows the alloy produced after electrolysis. XRD analysis (Fig. 5C) and SEM-EDX and XRF analysis of the alloy confirms the formation of $Al_{11}(La, Ce)_3$ phase and SEM micrograph (Fig. 5D) shows the uniform distribution of intermetallic ($Al_{11}(La, Ce)_3$) phase (Sims et al., 2020). Peak shift towards the right (from 33.749° to 34.02°) was observed in the XRD pattern of the alloy compared to the standard $Al_{11}La_3$ XRD pattern, which is due to the smaller atomic radius of Ce. SEM-EDX, XRD analysis and literature also confirms that Ca can also replaces rare earths in the intermetallic phase as $Al_{11}(Ca,La,Ce)_3$ (Akopyan et al., 2020). Calcium presence in Al-RE alloys is beneficial for the mechanical properties of Al-RE alloys (Akopyan et al., 2020). However, calcium can be removed from the alloy during refining.



The cell voltage in the process is about 3.1 Vs. It is difficult to evaluate the current efficiency and power consumption of the process due to the formation of intermediate products (REOCl), which also consumes the current. Hence, a detailed study of this process is planned to optimise the process and measure current efficiency and power consumption.

3.5. Al-RE alloys

Producing Al-RE alloys with a high concentration of REEs and in a larger quantity is difficult due to the limitations with the laboratory electrolysis setup. The alloy needs to be re-melted and refined to remove $CaCl_2$ and Ca. Hence, in this study, alloys were prepared with pure metals of Al, Ce, and La. True stress-true strain curves obtained after compression testing are shown in Fig. 6. The stress required for a given strain increases with increasing Ce content in the alloy. About 40% of

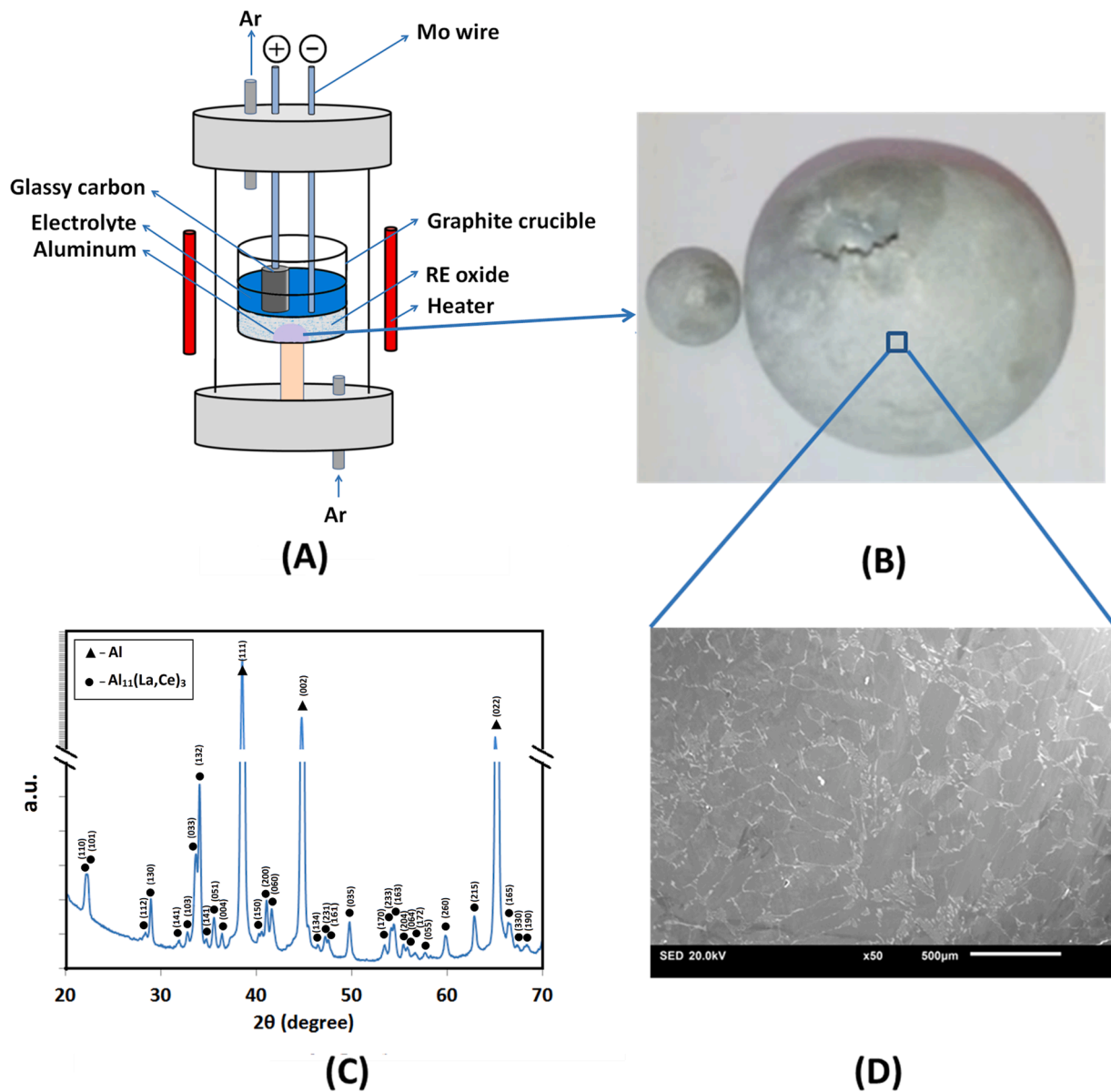


Fig. 5. Fused salt electrolysis of RE oxides in the presence of Al. (A) Electrolysis experimental setup; (B) image of the Al-RE alloy globules formed during cooling from high temperature; (C) XRD pattern of the sample shows $Al_{11}(La, Ce)_3$ intermetallic together with Al; (D) SEM image of the sample cross-section shows a uniform distribution of $Al_{11}(La, Ce)_3$ intermetallic.

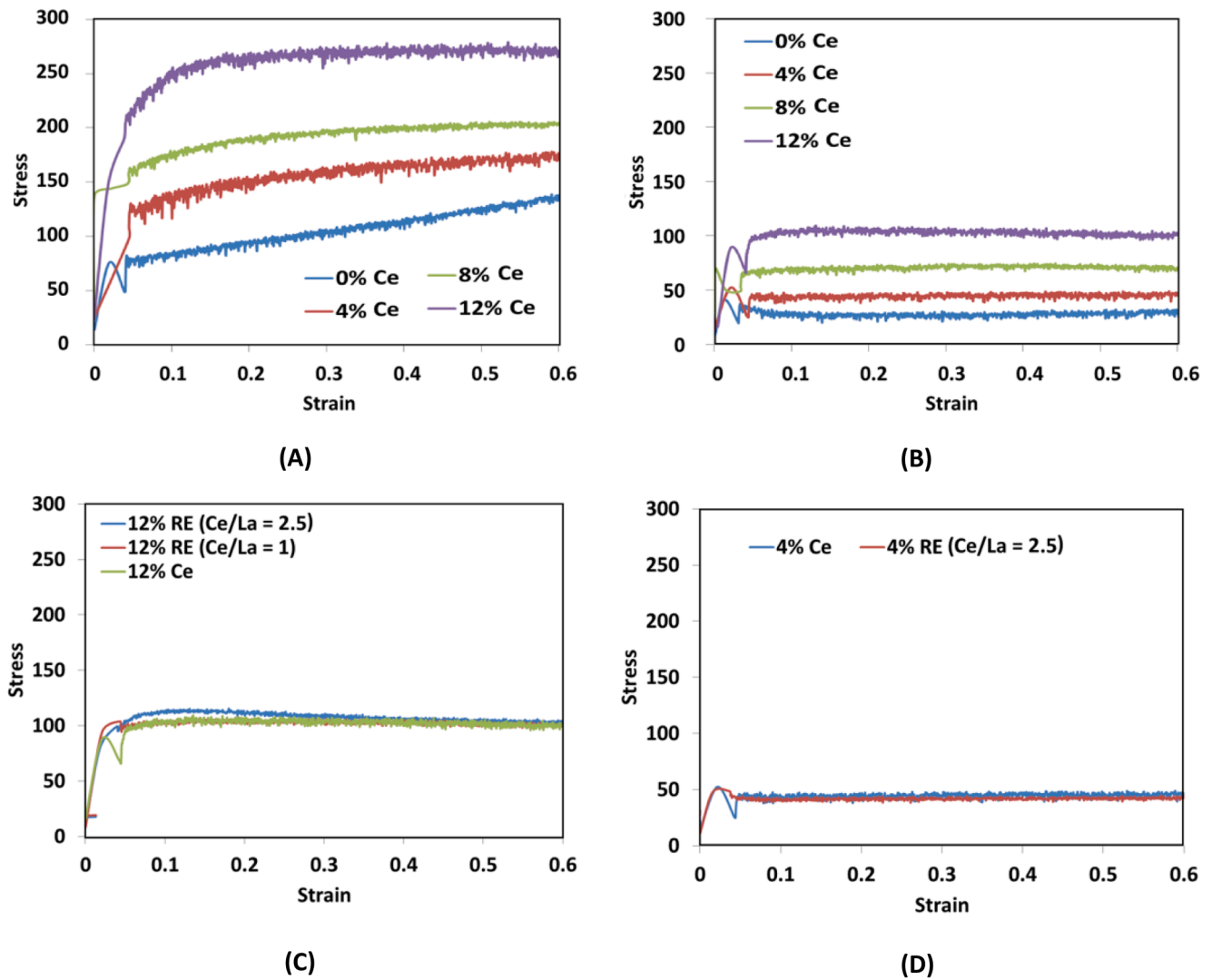


Fig. 6. True stress-true strain curves of different Al-RE alloys at a strain rate of 0.001 s^{-1} . (A) Al-Ce alloys at room temperature show an increase in Ce content increases the strength; (B) Al-Ce alloys at $300 \text{ }^\circ\text{C}$ show about 40% of the room temperature strength can be attained at $300 \text{ }^\circ\text{C}$; (C) Al-12% RE alloys at $300 \text{ }^\circ\text{C}$ with different La/Ce ratios show that Ce replacement with La does not affect strength; (D) Al-4% RE alloys at $300 \text{ }^\circ\text{C}$ show that Ce replacement with La does not affect strength.

the strength is retained even at $300 \text{ }^\circ\text{C}$. La replacement of Ce at a given RE concentration does not have any significant effect on the strength. This is due to the similar chemical properties of La and Ce and their similarity in atomic radii (La 187 pm and Ce 182 pm). Atomic radii were considered as both La and Ce are present in the alloy with zero valence state. Based on the compression test results, it can be concluded that La can be replaced in Al-Ce alloys without significant change in the strength of the alloy at a given RE content. This helps in utilisation of REOs mixture recovered from the polishing waste without further separation of La. This can lead to utilisation of both overproduced primary La and Ce and recovered La and Ce from polishing waste in high value Al alloys.

4. Conclusions

Two different polishing wastes were studied for recovering REEs. Reductive acid leaching of the waste with HNO_3 at $75 \text{ }^\circ\text{C}$ for 4 h with a L/S ratio of 5:1 can dissolve about 70% of REEs. The undissolved RE fluorides and phosphates were converted to oxides/hydroxides by NaOH treatment at $500 \text{ }^\circ\text{C}$ for 4 h followed by water leaching. These hydroxide/oxides can be further purified by reductive acid leaching, followed by selective precipitation with oxalic acid. The recovered rare earth

oxalates can be converted to oxides by calcination at $850 \text{ }^\circ\text{C}$. High purity REOs recovered from the polishing waste were converted to Al-RE alloys with chloride-based fused salt electrolysis at $850 \text{ }^\circ\text{C}$ for 4 h. About 5% RE containing Al alloy was successfully produced from the recovered REOs. However, Misch (La+Ce) metal can also be produced by conventional processes from the recovered REOs and can be used in Al-La-Ce alloy production. Al-La-Ce alloys have similar properties in compression tests compared to Al-Ce alloys at a given RE concentration.

The present study leads to novel process routes for producing high value, and new Al-La-Ce alloys from La and Ce recovered from polishing waste. This can help in the complete utilization of polishing waste. Reductive leaching with a carbohydrate instead of hydrogen peroxide decreases the process cost. Furthermore, an extra alkali treatment step recovers most of the La and Ce present in the polishing waste. The new molten chloride electrolysis process may enable the in-situ production of Al-RE alloy at a low temperature compared to conventional Misch metal production. New alloys developed in this study will allow for the utilisation of both La and Ce.

CRedit authorship contribution statement

Chenna Rao Borra: Conceptualization, Formal analysis, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Thijs JH Vlugt:** Conceptualization, Funding acquisition, Methodology, Resources, Supervision, Writing - review & editing. **Yongxiang Yang:** Conceptualization, Funding acquisition, Methodology, Resources, Supervision, Writing - review & editing. **Jeroen Spooren:** Resources, Writing - review & editing. **Peter Nielsen:** Resources, Writing - review & editing. **Murugaiyan Amirthalingam:** Methodology, Resources, Supervision, Writing - review & editing. **S Erik Offerman:** Funding acquisition, Methodology, Resources, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Chenna Rao Borra

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