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Magnesium 2021

Proceedings of the
12th International Conference on

Magnesium Alloys and their Applications

EDITED BY

Alan Luo · Mihriban Pekguleryuz
Sean Agnew · John Allison
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Warren Poole · Kumar Sadayappan
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The Minerals, Metals & Materials Series

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Preface

The 12th International Conference on Magnesium Alloys and their Applications (Mg 2021) was planned to be held in beautiful Montreal, Quebec, Canada on June 15–18, 2021. However, due to the limits of the COVID-19 pandemic on travel and in-person gatherings, the meeting is virtual for the first time in the 35-year history of this series of international conferences. Held every 3 years since 1986 in Europe, Asia, and North America, this event is considered the premier technical forum for the global magnesium community. We are excited to virtually host Mg 2021 on the same dates planned and with no physical boundaries.

As the lightest structural metal, magnesium has significant growth potential in a variety of applications from transportation and energy storage to electronics and consumer products. Advancements in magnesium have accelerated since the meeting last convened at Mg 2018. We are also seeing a change in the direction of alloy development activities that the conference will present. Notably, magnesium uses have expanded from traditional die casting alloys and aluminum alloying use to groundbreaking new biomedical and energy applications. Biodegradable and biocompatible implant applications are targeting both new alloys and new structures (e.g., scaffolds, foams). In the automotive industry, with the emergence of new automotive engine and alternate fuel technologies, magnesium powertrain casting-alloy research will take a step back while automotive structural and body alloys will step forward, with a focus on wrought and casting alloys with higher ductility/formability, and magnesium-based solid fuels. New understanding in fundamental aspects of magnesium alloys has been made with advanced characterization techniques and modeling methods. These techniques allow researchers to discover new microstructure-property relationships, such as long-period stacking ordered (LPSO) structures. First-principles calculations and machine learning are starting to revolutionize alloy development routes.

Discussions are arranged to explore developments in primary and manufacturing processes, including additive manufacturing, and the progress in advanced joining technologies of linear friction welding and friction stir welding. With the encouraging news that the restrictions on the in-cabin use of magnesium in aircrafts can be lifted, ignition-proof magnesium alloy research has found new impetus. In corrosion science, steps are being taken toward stainless magnesium. These topics and more promise to illuminate and invigorate the minds gathering virtually at Mg 2021.

We are very pleased with the great response to the Call for Abstracts of Mg 2021 from around the world. We received over 180 abstracts, and 26 papers are included in this Proceedings. The conference program features 12 plenary lectures, 155 oral presentations (27 of which are invited), and 17 poster presentations. We are also planning to publish a set of papers presented at the conference in *Metallurgical and Materials Transactions A* in the near future.

We appreciate all the authors and reviewers for their contributions to the Proceedings and their effort to ensure the deadlines were met. We also thank the members of the International Committee for promoting Mg 2021 in the international community and the members of the Organizing Committee for their support to the conference organization. Special thanks go to the TMS staff members who are supporting all of the activities, particularly Kelcy Marini for her tireless efforts in keeping everything in order and Matt Baker for publishing the Proceedings.

Alan Luo
Mihriban Pekguleryuz

Alan Luo is a Professor of Materials Science and Engineering and Integrated Systems Engineering at The Ohio State University (OSU). He leads the OSU Lightweight Materials and Manufacturing Research Laboratory (LMMRL) and is on the steering board of the OSU Center for Simulation Innovation and Modeling (SIMCenter). He is an elected Fellow of ASM International and SAE International. He is presently a Director of the board of the International Magnesium Association and a past Chair of the TMS Light Metals Division and SAE Materials Engineering Division. Prior to joining OSU in July 2013, he was a GM Technical Fellow at General Motors Global Research and Development Center with 20 years of industrial experience. He received his Ph.D. in Engineering Materials from the University of Windsor in 1993.

Professor Luo's research areas include: (1) lightweight materials (aluminum, magnesium, titanium and high-entropy alloys, bio-metals, super-wood, and nanocomposites); (2) advanced manufacturing processes (casting, forming, additive manufacturing, and multi-material manufacturing); and (3) lightweight design and integrated computational materials engineering (ICME).

Mihriban Pekguleryuz is a Professor of Materials Engineering at McGill University and a Fellow of the Canadian Academy of Engineering (CAE). She has 30 years of combined industrial and academic research experience in light metals, specifically in magnesium-based materials some of which have been commercialized by automotive companies and metal producers globally. Her industrial experience ranges from IBM Canada to Noranda Technology (now Glencore) where she worked as Group Leader of Materials Engineering. In academia, she was awarded two industrial Research Chair positions, one with GM of Canada and the other with Alcan (now Rio Tinto). She was a founding member and a past Chair of the TMS Magnesium Committee. She is an Executive Member of the Canadian Institute of Mining, Metallurgy and Petroleum (CIM) and the Metallurgy and Materials Society (MetSoc) and is the Light Metals Section Editor and Editor-in-Chief/Engineering for *Experimental Results*. She received her B.Sc. and M.Sc. degrees in Materials Science and Engineering from the University of Florida, Gainesville (USA) and her Ph.D. in Metallurgical Engineering from McGill University (Canada) in 1987. She is currently leading the Light Metals Research Laboratory at McGill in research activities focused on lightweighting in transport applications (automotive body, ignition-proof Mg for aerospace, Mg materials for fast train and rail); biodegradable and biocompatible Mg implants; aluminum diesel engine alloys; lead-free electronic interconnect materials; corrosion-resistant Mg alloys; and the use of machine learning in light alloy development.

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Part I
Primary Production

A New Hydrometallurgical Process Combined With an Electrolytic Process for Magnesium Primary Production from Serpentine

Joel Fournier

Abstract The FOURNIER PROCESS owned by Alliance Magnesium Inc (AMI) is a hydrometallurgical process combined with an electrolytic process for primary magnesium production. It constitutes an improvement over the former Noranda Magnola Process and uses a combination of best in class technology to produce a high-quality magnesium for use in many applications, including the most demanding, namely, the automotive market. It also introduces a radical breakthrough in technological change by the production of some valuable by-products. AMI made the acquisition of Magnola company and assets in 2017 and is under construction of a commercial demonstration plant to restart the production of primary magnesium in Canada.

Keywords Primary magnesium production · Hydrometallurgy · Electrolysis

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Picture of AMI's site

Picture of the plant under construction

Introduction

The FOURNIER PROCESS, as well as the former Magnola Process, is used to recover magnesium from serpentine rock coming from mine tailing resulting from Asbestos production. Asbestos is a set of six naturally occurring silicate minerals used commercially for their desirable physical properties. They all have in common their eponymous, asbestiform habit: long and thin fibrous crystals. Asbestos became increasingly popular among manufacturers and builders in the late nineteenth century because of its sound absorption; average tensile strength; its resistance to fire, heat, electrical and chemical damage; and affordability. It was used in such applications as electrical insulation for the nineteenth century. For a long time, the world's largest asbestos mine was the Jeffrey Mine in the town of Val-Des-Sources, Quebec. Asbestos production and sale are now banned in most of the countries around the world including Canada for health concern.

The discarded serpentine tailings from asbestos mining constitute the raw material and will be mined themselves by AMI for magnesium production. The tailings contain 24% magnesium, 38% silicate oxide, and minor elements like iron and nickel. It compares advantageously to other sources of mineral magnesium used for metal production.

Magnesium is a commercially important metal with many uses. It is only two-thirds as dense as aluminum. It is easily machined, cast, forged, and welded. It is used extensively in alloys, with aluminum and zinc, and with manganese. The magnesium is an essential ingredient for the lightweighting of transportation industry.

Taking out the magnesium metal from unrefined materials is a force exhaustive procedure requiring nicely tuned technologies. There is thus still a need for improved processes for extracting magnesium from magnesium-bearing ores such as asbestos.

Picture of former asbestos production residues (AMIS's raw material)

The Former Magnola Process

Magnola's magnesium production was based on a hydrometallurgical process followed by an electrolysis process. The production of 58,000 tons of magnesium required about 270,000 tons of serpentine rock (mine tailings) as raw material. Other inputs included magnesium oxide added to the brine neutralization and purification steps; hydrochloric acid to make up for quantities consumed by the process; caustic soda used for cleaning emissions; and sulfuric acid used to dry hydrogen chloride (Fig. 1).

The Magnola magnesium production facility was built and achieved 42% of its nominal capacity in a steady production mode. Certain technological challenges and weaknesses in the process were identified during the development and implementation of the leaching, neutralization, electrolysis, and other ancillary processes, the main ones being:

1. The residual iron, nickel, and silica were extracted from the brine by precipitation. The brine went through agitated neutralization reactors operating at about 110 °C, with a pH close to 4. The addition of anhydrous magnesia or Mg (OH) precipitated iron, calcium, nickel, and chromium. Following this hydrometallurgical step, the non-leached portion was filtered out and sent to the silica-iron

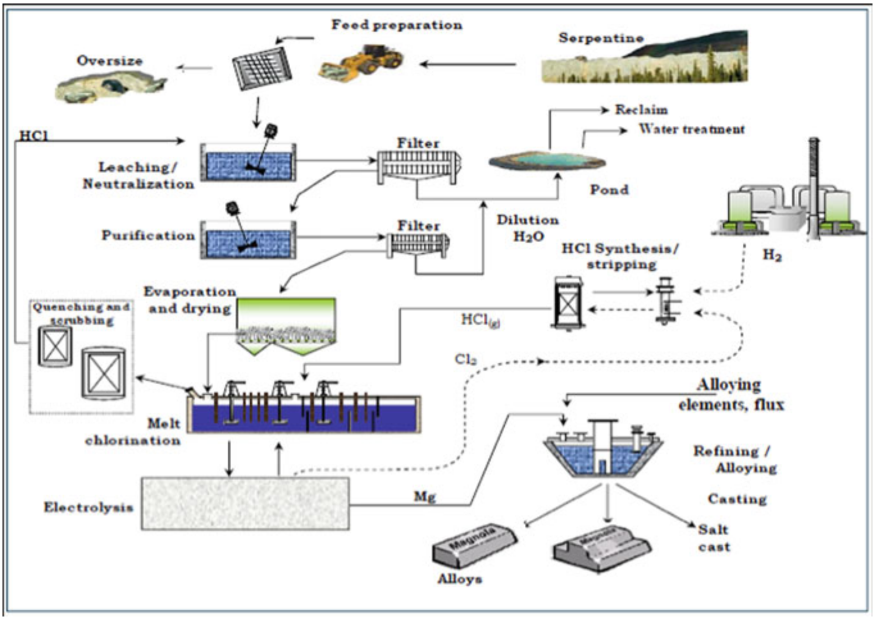

Fig. 1 The diagram depicts the main process stages of material preparation, magnesium extraction, leaching and neutralization, purification and drying, electrolysis and casting, and HCl synthesis and emission treatment. (Color figure online)

storage area. The cake obtained from the filter contained about 50–70% of the original solids. Water was added to bring the solid concentration to about 50%. This residue, called silica-iron residue, has created a large volume of residue in the pound after only 3 years of activities and required a costly operation system to maintain the level of liquid and prevent overflow.

2. The drying of $MgCl_2$ prills was done on a final step using a super chlorinator. This innovative technology at the time was based on the injection of HCl gas into a molten salt electrolysis to dry the $MgCl_2$ before being fed to the electrolysis cells. Generation of magnesium oxide was observed and was detrimental to electrolysis.

The FOURNIER PROCESS

The process described herein allows processing and extracting magnesium from tailings, such as asbestos mine tailings, obtained after processing of magnesium-bearing ores (Fig. 2).

Preparation and Classification

Tailings, and particularly asbestos tailings, can be finely crushed in order to assist the following leaching steps. The tailings have to be crushed sufficiently to shorten the reaction time by few hours (about 2 to 3 h). Screen classifiers can be used to select oversized pieces that can be re-crushed if necessary. After the initial mineral separation, the crushed tailings undergo a magnetic separation to selectively recover magnetite. This step provides an efficient way to reduce hydrochloric acid consumption. The yield of iron removal can reach over 90%. This magnetite is disposed of and will not be submitted to the further leaching step.

Acid Leaching

The crushed classified tailings then undergo acid leaching. Acid leaching comprises reacting the crushed classified tailings with a hydrochloric acid solution during a given period of time which allows dissolving the magnesium and other elements like iron and nickel. The silica remains totally undissolved after leaching. It is interesting to note that the hydrochloric acid leaching destroys 100% of the residual asbestos fibers contained in the serpentine.

The tailings residue is leached at a temperature of about 60° to about 125 °C. These conditions are possible due to the high salt content in the reaction mixture

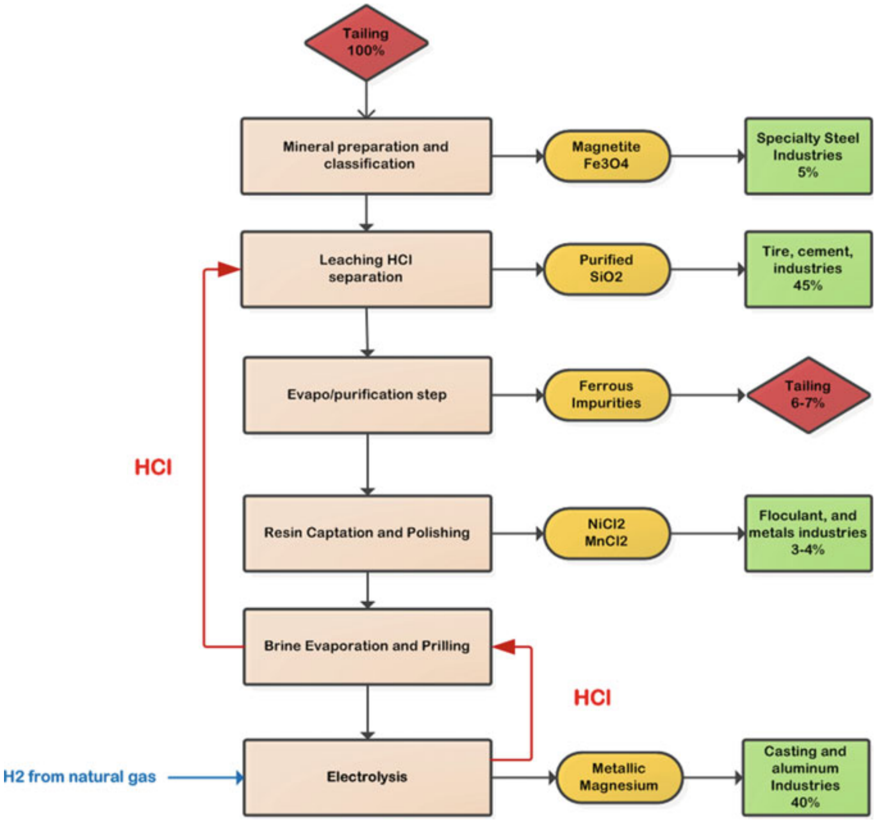

Fig. 2 FOURNIER PROCESS. (Color figure online)

preventing the aqueous solution from boiling. Particularly, the tailings/acid ratio can be about 1:10 (weight/volume), the HCl concentration can be about 25% to about 45 %, and the reaction time can be about 1 to about 7 hours. The leaching reaction converts most magnesium, iron, potassium, calcium, nickel, and manganese into water-soluble chloride compounds. A significant portion of the alumina and all the silica are inert to HCl digestion and remain solid in the reaction mixture.

Liquid/Solid Separation and Washing

Once the extraction is terminated, the solid can be separated from the liquid by filtration, after which it is washed. The corresponding residue can thereafter be washed many times with water so as to decrease acidity and to lower the quantities of sodium hydroxide (NaOH) that are required during this step. The process allows separating the solid from the leachate and washing the solid so as to obtain silica having a purity of at least 85%. The amorphous silica obtained in that step has demonstrated a good potential to be used as a concrete additive.

Resin Captation and Impurity Removal

The spent acid (leachate) containing the metal chloride in solution obtained can then be passed on to a set of ion exchange resin beds comprising a chelating resin system to catch specifically the nickel chloride ($NiCl_2$). For example, the DOWEX^{TM} M4195 chelating resin can be used for recovering nickel from very acidic process streams. Removal of nickel from water and organic solvents is fairly common using strong acid cation resins. Methods of recovering nickel from high magnesium-containing Ni–Fe–Mg lateritic ores are also described in U.S. patent no. 5,571,308. Furthermore, pure nickel (Ni) can be obtained by electrolysis once the nickel chloride has been extracted. Nickel can also be precipitated at this stage as a hydroxide, filtered in a filter press and sold for a value. Iron and other impurity can be precipitated by a change in pH by MgO addition to obtain a very pure $MgCl_2$ brine.

Dehydration

The pure magnesium chloride solution then undergoes multiple dehydration steps, consisting of evaporation, prilling/crystallization, and dehydration.

First, the pure magnesium chloride hexahydrate undergoes a prilling step by using a fluidized bed dryer to essentially obtain a partially hydrated $MgCl_2$ in form of "prills" ($MgCl_2 \cdot 2H_2O$). To remove the water molecules, the prills are sent a second two-step fluidized bed to essentially obtain an anhydrous magnesium chloride with a drying gas containing hydrochloric acid, thereby separating anhydrous magnesium chloride from the remaining water. The drying process is realized by heating gas to about 150°–180 °C and the solution is fed to a concentrator to bring the magnesium chloride concentration up. The magnesium chloride gas-drying is carried out in two stages, targeting two molecules of hydration-water removal in each stage, so that the drying temperatures can be selected to optimize drying and minimize oxidation.

In the fluid bed dryer, dry hydrogen chloride gas heated up to about 450 °C allows fluidization of the particles, producing magnesium chloride granules. The reason for this is to avoid three negative characteristics of the magnesium hydrolysis reaction:

1. It creates magnesium oxide, which will later be concentrated as sludge in the electrolysis cells and will react with the graphite anodes and negatively affect the energy efficiency of the process.
2. Magnesium chloride is lost during the process.

3. The acid gases produced during the reaction must be handled.

The use of gaseous HCl reduces the hydrolysis reactions, thus reducing the concentration of magnesium oxide in the product. In addition, opposite reactions to hydrolysis take place with HCl, which also reduce the magnesium oxide.

$$MgO + HCl\,(g) \rightarrow MgOHCl \tag{1}$$

$$MgOHCl + HCl\,(g) \rightarrow MgCl_2(s) + H_2O\,(g) \tag{2}$$

The HCl from the drying process is transferred to the raw material extraction and preparation process by passing through equipment used for the scrubbing of gaseous emissions. The resulting fluidizing gas contains hydrochloric acid which can be regenerated and brought back to the leaching step.

Electrolysis

Magnesium metal is then obtained by further electrolysis of the magnesium chloride. The magnesium chloride is fed to monopolarelectrolysis cells. The electrolyte composition allows the magnesium metal produced to form a light phase floating on top of the electrolysis bath. The anode can be a high surface area anode, such as, for example, a porous anode in which case hydrogen gas permeates the pores of the anode, such as by diffusion, or molten electrolyte containing the magnesium chloride permeates the pores of the anode, to provide the contact between the hydrogen gas and the chloride ions. This novel design of the electrolytic anode allows the injection of hydrogen in the bath to have an in situ HCl regeneration.

Environmental Benefits

AMI'S technology is a clean technology. It is the most environmental efficient process on the planet measured by the following aspects:

- Mining site remediation.
- Lowest Mg CO_2 emissions.
- Lowest Mg waste/slag generation.
- Lowest Mg energy consumption.

Based on the entire life cycle, each ton of magnesium produced by AMI permits the saving of 20 tons of CO_2 emission, compared with the current average Pidgeon process operated in China.

For each ton of magnesium produced by AMI, only 2.5 tons of CO_2 are emitted compared to traditional Pidgeon plants which produce 21.8 tons of GHS. Also, with AMI over 90% of the residue are converted into valuable product for an equivalent of 0.4 ton/ton of magnesium. (16 tons in Pidgeon plant.)

AMI's plant and the FOURNIER PROCESS are powered by at least 90% renewable hydroelectricity.

Picture of magnesium ingots

Effect of Pre-sintering in Silicothermic Reduction of MgO and Reduction Using Ca_2SiO_4 Instead of CaO

Takeru Saimura, Taiki Morishige, and Toshihide Takenaka

Abstract It was shown in our previous study that the contact condition between MgO, CaO, and Si strongly affected Mg metal production by silicothermic reduction of magnesium oxide derived from salt evaporation ponds. In this study, the influence of the contact condition of MgO, CaO, and Si in the reduction was studied; the dependence of the reduction rate on the preparation procedure of MgO–CaO mixture and pre-sintering before the reduction was examined. A short-term sintering improved the reduction rate, but a longer sintering worsened the rate. Sintering seems effective in the improvement of contact condition, but causes the surface oxidation on Si. In this study, Si reduction with Ca_2SiO_4 instead of CaO was also attempted to reduce CaO consumption, but it was shown that MgO was lost by $CaMgSiO_4$ formation.

Keywords Silicothermic reduction · Calcium silicate · Effect of pre-sintering

Introduction

The reduction in energy consumption and CO_2 generation in the production of Mg primary metal is necessary to wider use of Mg materials. Our laboratory has been researching the Mg material production using bittern-derived materials; the energy and CO_2 generation in Mg production can be reduced compared with the current Mg production using dolomite, and the bittern can be supplied from sea water in Japan, too.

In our previous studies, it is shown that the silicothermic reduction of MgO derived from bittern was possible, and that CaO addition was necessary [1]. The reduction rate was slightly lower than that of dolomite-derived material, even when enough CaO was added to MgO. The difference between the mixtures derived from bittern and

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dolomite can explain their mixed state; MgO and CaO were mixed at the molecular level in dolomite-derived material, while they were not in bittern-derived material. These results suggest that the preparation procedure of the MgO–CaO–Si mixture could affect the reduction rate because CaO is rarely contained in MgO derived from bittern. The minimum amount of CaO–MgO for efficient reduction must be clarified to reduce the added amount of CaO.

In this study, the mixture of MgO and CaO was prepared with two procedures; one is dry and involves calcination of $Mg(OH)_2$ and $Ca(OH)_2$ solution, and the other is dry mixing of MgO and CaO in a mortar. The influence of the procedures was evaluated by the change in the reduction rate. The effect of pre-sintering of the MgO–CaO–Si mixture was also studied. In addition, the reduction of the MgO–Ca_2SiO_4–Si mixture instead of the MgO–CaO–Si mixture was investigated to clarify the minimum amount of added CaO in this study.

Experimental

A MgO–CaO mixture was prepared with two procedures; in the wet procedure, $Mg(OH)_2$ and $Ca(OH)_2$ were dissolved in water, and then dried. The dried mixture was calcinated at 1073 K for 3 h to decompose into MgO and CaO. In the dry procedure, MgO and CaO were carefully mixed in a mortar. The prepared MgO–CaO mixture was compacted with Si and pre-sintered at 1073 K for hours. The molar ratio of MgO:CaO:Si was 2:2:1. In this study, a mixture of MgO–Ca_2SiO_4–Si (2:1:1 in molar) was also prepared by dry procedure without pre-sintering. These samples were set on a boron nitride (BN) boat, and heat reduced under vacuum at 1423 K for 3 h with the apparatus shown in Fig. 1.

After the reduction, the product condensed on the inner surface of vessel outside the furnace and the residual material on the BN boat was recovered. The product and residual material were observed and analyzed with SEM-EDX and XRD.

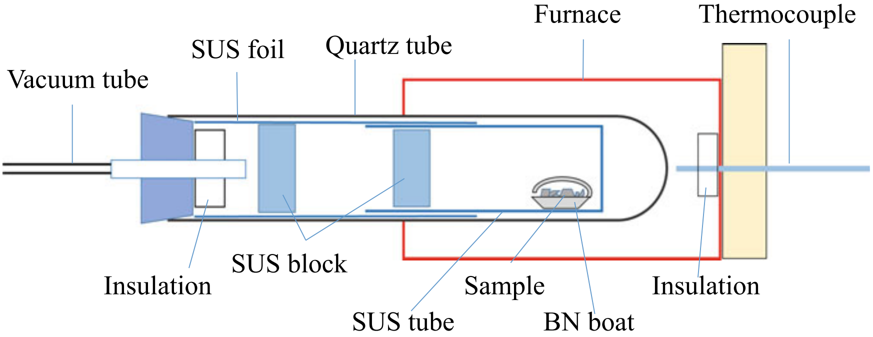

Fig. 1 Experimental apparatus. (Color figure online)

Results and Discussion

Effect of Preparation Procedure of MgO–CaO and Pre-sintering of MgO–CaO–Si

Fine particles mainly consisting of MgO were condensed on the inner surface of vessel outside the furnace regardless of the preparation procedure and pre-sintering. Since the amount of condensed material was very little, XRD analysis and weight measurement could not be performed. It is considered that Mg vapor was formed in the furnace, condensed in the low temperature part, and then oxidized when it was collected after experiment.

The weight of the residual material on the BN boat was always lower than that of the original mixture, and Ca_2SiO_4 was always detected in it. Considering the condensed and the residual materials, it is considered that the silicothermic reduction of Mg shown below occurred, and that Mg vapor and Ca_2SiO_4 were generated.

$$2MgO(s) + 2CaO(s) + Si(s) = 2Mg(g) + Ca_2SiO_4(s) \tag{1}$$

From the reaction (1), the weight change from the original sample to the residual material is thought to be the amount of Mg vapor, and the reduction rate can be calculated as follows:

$$\text{Reduction rate}(\%) = \frac{\Delta m}{m} \times 100 \tag{2}$$

where m is the Mg content in the original specimen and Δm is the weight change.

Figure 2 shows the dependence of the reduction rate on the pre-sintering time for the sample prepared with wet and dry procedures. The reduction rate of the wet-prepared mixture tended to be higher than that of the dry-prepared mixture. This

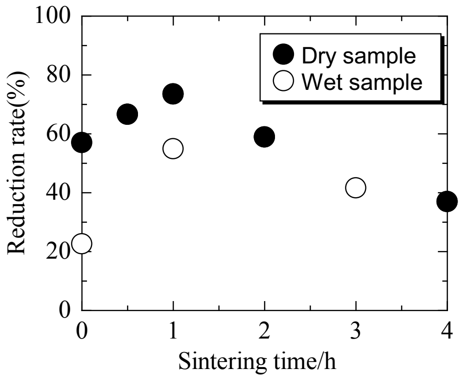

Fig. 2 Effect of sintering time on reduction rate

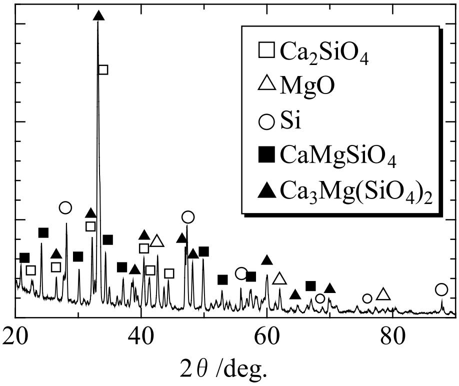

Fig. 3 X-ray diffraction pattern after reduction of MgO-Ca_2SiO_4-Si

result suggests that the mixing procedure strongly influences the reduction efficiency, and that CaO should be added in bittern solution.

The reduction rate tends to increase with the short-term pre-sintering, but decrease with the long-term pre-sintering. It is considered that the contact state of MgO–CaO–Si is improved by the short-term pre-sintering, and that the surface of Si is oxidized by the long-term pre-sintering. The short-term pre-sintering should be effective for efficient silicothermic reduction of MgO derived from bittern.

Reduction Using Ca_2SiO_4 Instead of CaO

Figure 3 shows the XRD results of the residual material on a BN boat after the reduction of MgO–Ca_2SiO_4–Si mixture. Since $CaMgSiO_4$ and $Ca_3Mg(SiO_4)_2$ were detected, it is thought that the reactions occurred as follows:

$$4MgO(s) + Ca_2SiO_4(s) + Si(s) = 2Mg(g) + 2CaMgSiO_4(s) \tag{3}$$

$$4MgO(s) + 3Ca_2SiO_4(s) + Si(s) = 2Mg(g) + 2Ca_3Mg(SiO_4)_2(s) \tag{4}$$

The reduction rate calculated by the formula (2) was about 30%. This value was a half of that using MgO–CaO–Si mixture, and consistent with the reaction (3).

By the reactions (3) and (4), the added amount of CaO can be reduced. However, MgO is unfortunately lost due to the formation of $CaMgSiO_4$ and $Ca_3Mg(SiO_4)_2$. The most desirable reaction for the least CaO addition as follows seems to be rarely achieved.

$$2MgO(s) + Ca_2SiO_4(s) + 2Si(s) = 2Mg(g) + 2CaSiO_3(s) \tag{5}$$

In the reduction of the MgO–CaO–Si mixture, only Ca2SiO4 was formed, and $CaMgSiO_4$ and $Ca_3Mg(SiO_4)_2$ seem not to be synthesized. From the reaction of Gibbs energy of production, γ-Ca_2SiO_4 is stable, and that the reactions (3) and (4) are more likely to occur in β-Ca_2SiO_4. In the reduction of the MgO–CaO–Si mixture under our experimental conditions, γ-Ca_2SiO_4 is thought to be synthesized. The structure of the mineral merwinite $Ca_3Mg(SiO_4)_2$ that seems to be mainly produced is similar to the β-Ca_2SiO_4 [2].

Ca_2SiO_4 used in this experiment was prepared by compaction sintering CaO and SiO_2 at 1673 K, and it is stable in the form of β-Ca_2SiO_4. However, the Ca_2SiO_4 produced by reaction (1) was γ-Ca_2SiO_4 and took the form of olivine. Since the change to β-Ca_2SiO_4 occurs under high pressure [3], it is considered to be γ-type under experimental conditions.

Conclusions

In this study, the dependence of the reduction rate on the preparation procedure of the MgO–CaO mixture and pre-sintering before the reduction was examined. The reduction rate of the wet-prepared mixture tends to be better than that on the dry-prepared mixture, which is thought due to the mixing state of MgO and CaO. The short-term pre-sintering is effective for efficient reduction because of the improvement of the contact condition. Conversely, the long-term pre-sintering worsened the reduction rate because of the surface oxidation of Si.

By the reduction using Ca_2SiO_4 instead of CaO, $CaMgSiO_4$ and $Ca_3Mg(SiO_4)_2$ were generated, which leads to the decrease in the added amount of CaO but the loss of MgO.

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Oxide Films Formed on $MoSi_2$ Anode in Molten $MgCl_2$–NaCl–$CaCl_2$ and Molten LiCl–KCl

Takamasa Miyoshi, Taiki Morishige, and Toshihide Takenaka

Abstract The anodic formation of an oxide film on $MoSi_2$ in molten $MgCl_2$–NaCl–$CaCl_2$ containing oxide ions has been investigated based on our former study, and the compatibility as an inert anode in the melt is discussed in contradistinction in molten LiCl–KCl. A small anodic current flew continuously during potentio-static electrolysis, and gas bubble generation was seen. The weight of $MoSi_2$ was changed by the electrolysis, and an oxide film consisting of SiO_2 and $MgSiO_3$ was formed by the electrolysis above 1.9 V (vs. Mg/Mg^{2+}). The current contributions estimated from the weight change and the film thickness indicate that the reaction other than the Mo dissolution and the oxide film formation enlarged with the increase in the electrolysis duration and the raise in the electrolysis potential. The current contribution other than the Mo dissolution and the oxide film formation became above 90%, which suggests $MoSi_2$ is promising as an inert anode. A SiO_2 film was formed on $MoSi_2$ in molten LiCl–KCl containing oxide ions, but most of the current was consumed for the Mo dissolution and the oxide film formation. It is considered that the formation of $MgSiO_3$ influences the anodic behavior of $MoSi_2$.

Keywords Mg electrolysis · $MoSi_2$ anode · Oxide film

Introduction

Mg is produced by an electrolytic method using a molten chloride salt. The IG method and its improved method are the main methods for electrolyzing Mg. The electrolysis method has the advantages of being easy to scale up, being able to be made into a continuous manufacturing process, and being able to use MgO as a raw material with the generated Cl_2. Li is also produced by electrolysis like Mg. The production process of Mg and Li has been studied in order to be more efficient [1–3]. One of them is related to the anodic reaction.

Carbon-based materials are used for the anode in the molten chloride of Mg and Li. Carbon-based material has advantages in chemical stability in the bath.

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However, since chloride salt has a high hygroscopic property, carbon-based material is consumed by electrochemical reaction with dissolved O^{2-}, for example, reaction (1).

$$C + xO^{2-} \rightarrow CO_x + 2xe \tag{1}$$

An inert anode is desired for the continuous formation of Mg, and it has been reported that glassy carbon [4] and boron-doped diamond [5] behaved as an inert anode in molten LiCl–KCl at 700 K. However, an inert anode which can be used at higher current density and at higher temperature has not been studied well. The authors proposed an inert anode by forming a stable passivation film on the electrode. A SiO_2 film was formed in molten LiCl–KCl containing oxide ions, but the anodic protection was insufficient [6, 7]. An oxide film consisting of SiO_2 and $MgSiO_3$ was formed in molten $MgCl_2$–NaCl–$CaCl_2$ containing oxide ions, and the anodic oxidation seemed to be inhabited.

In this paper, the anodic behaviors of $MoSi_2$ in molten $MgCl_2$–NaCl–$CaCl_2$ were compared with that in molten LiCl–KCl, and the protection property and the effect of $MgSiO_3$ were discussed.

Experimental

The experimental apparatus is illustrated in Fig. 1. In a glove box filled with Ar, about 50 g of $MgCl_2$–NaCl–$CaCl_2$ (about 20: 50: 30 in weight) was put in a transparent quartz glass crucible, and the saturation amount of MgO (99.9%, anhydrous) was added. The mixture was placed in an electric furnace with observation ports.

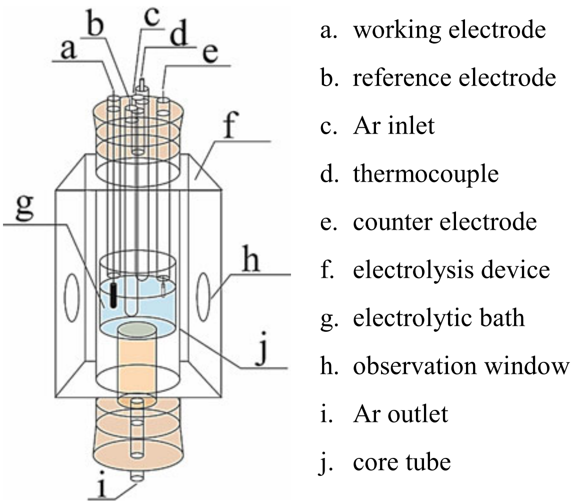

Fig. 1 Apparatus for electrochemical measurement and electrolysis. (Color figure online)