Cerium extraction by metallothermic reduction using cerium oxide powder injection


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Abstract: This work presented the feasibility of cerium recovery by Al-Mg alloy through the metallothermic reduction of CeO₂ to obtain a master alloy Al-4%Ce. The master alloy obtained in this investigation was for the grain refinement and modification of Al-Si alloys. The reagent was incorporated into a molten alloy using the submerged powder injection technique, and metallic samples were obtained during injection. Chemical and microstructural analyses (by inductively coupled plasma (ICP) and scanning electron microscopy (SEM), respectively) confirmed the possibility of Ce uptake in the bath (0 to 4 wt.%), as CeO₂ was reduced through metallothermic reactions in the molten alloys. Based on the characterization of reaction products, the sequence of the reaction was proposed.

Keywords: cerium recovery; metallothermic reduction; reaction products; rare earths

Al-Si alloys are mainly used in the automotive and aerospace industries[1]. The demands on their mechanical properties require a strict control on the additions of refinements and modifying agents in the molten bath. The wide variety of alloys that are produced has led to the production of master alloys that are of great importance in the aluminum smelting (Al-Sr, Al-Ce) industry. The use of rare earth metals such as cerium has been the focus on changing the morphology of the silicon eutectic in Al-Si alloys, resulting in better physical and mechanical properties[2]. Cerium is the most abundant element in the family of rare earth metals or lanthanide elements[3,4]. The objective of this study was to make a master Al-Mg-Ce alloy employing the submerged powder injection technique (reactive; CeO₂) due to its very attractive advantages from both a technological and economic point of view. Also, the results concerning the feasibility to incorporate metallic cerium into an Al-Mg liquid alloy from a metallothermic reduction of cerium oxide on a laboratory scale were presented.

1 Experimental

The experimental trials were carried out in a high-frequency induction furnace with a 15 kg molten aluminum capacity. The powder injection equipment allowed for continuous and controlled feeding of solid material through an inert carrier gas. This equipment is frequently used in the process of Mg and Sb removal from molten aluminum alloy[5,6] and in the fabrication of master alloy Al-Mg-Sr[7,8]. The reactant elements used in the experiments were Al and Mg (98% purity) and CeO₂ (–140+200 mesh[7]). The selected experimental variables and their levels were temperature of treatment (800 and 850 °C) and magnesium content (0.5 wt.%, 3.0 wt.% and 4.0 wt.%). The following parameters were kept constant: amount of liquid alloy (8+/–0.1 kg) and powder flow rate to carrier gas flow rate ratio (8 g CeO₂/min:6 L Ar/min). The experimental trials were conducted as follows. The Al-Mg alloy was melted in the induction furnace to the required temperature. The injection equipment loaded with CeO₂ particles was positioned right above the top of the furnace. During experiments, a graphite lance was submerged into the melt to an 85% depth from the surface of the bath[9]. No fluxing or degassing of the melt was performed after melting in the final alloy, so the alloy was only treated for cerium increase. Finally, to obtain kinetic and metallographic information, the samples obtained were taken at 10 min intervals and analyzed by X-ray fluorescence, inductively coupled plasma spectrometry and scanning electron microscopy. In each experiment, dross samples taken at the end were analyzed by means of X-ray diffraction for the qualitative identification of the compounds.

2 Results and discussion

2.1 Chemical analysis

From the chemical analysis results shown in Fig. 1 (a), it is observed that cerium oxide is being reduced by a metallothermic mechanism because the cerium content in the liquid bath increases with the injection time. The cerium content in
the Al-Mg alloy increased to 4.3 wt.% according to the following conditions: temperature, 850 °C; magnesium content, 4 wt.%; CeO₂ powder particle size, −140+200 mesh; treatment time, 60 min. Both the temperature and initial magnesium concentration affected the cerium incorporation rate as shown in Fig. 1 (b). As can be observed, for all initial magnesium contents and both temperatures, 800 and 850 °C, the reaction rate between the CeO₂ particles and the melt alloy increased as the initial magnesium contents or temperatures increased, obtaining higher final cerium levels in the treated alloy.

This behavior is associated with the chemical activity of both Mg and Al present in the bath during the treatment process. According to the literature [10,11], this phenomenon is due to the surfactant nature of magnesium because the surface tension values of this element are lower compared with those of pure aluminum (γ_{Al}=0.914 N/m, γ_{Mg}=0.559 N/m). Therefore, we have concluded that the addition of magnesium reduces the surface tension of the liquid aluminum bath, which leads to an improvement in the wettability between the solid reactant and the liquid metal and, thereby, increases the kinetics of the reactions taking place at the solid-liquid interface. In this way, Mg enhances the reactions that take place at the solid-liquid interface and increases the amount of dissolved cerium in the molten bath. During testing, the initial Mg content decreased from 4 wt.% to 3.2 wt.%; at the same time, the cerium incorporation increased from 0 up to 4.3 wt.%. Similar tests [7] have been carried out in maintaining an Al-Mg liquid at a temperature of 850 ºC for up to 2 h. The reported results indicated that the loss of magnesium by oxidation or evaporation was not significant. Therefore, it can be assumed that the loss of magnesium is due to reduction reactions that occur during the stirring process.

2.2 X-ray diffraction and scanning electron microscopy

Dross generated during the tests of CeO₂ powders injection at 750 and 850 °C was analyzed through X-ray diffraction to identify qualitatively the crystalline compounds that are formed as reaction products. The results suggest that CeO₂ is reduced alternatively by Al and Mg, forming intermediate reaction products. The XRD results of the dross sample include the following (Fig. 2.1 and (2)): MgO (71–1176), MgAl₂O₄ (75–1796) and CeO₂ (89–89–8436). The presence of cerium oxide in the dross sample is due to partially reacted CeO₂ particles due to dragging of the particle trapped into the melt toward the melt surface by injection period. The presence of MgAl₂O₄ and MgO as reaction products establishes that magnesium and aluminum reduce cerium oxide through a metallothermic mechanism. The cerium content in the Al-Mg alloy increased to 4.3 wt.% after 60 min of treatment (See Fig. 1). The high cerium content benefits the precipitation of the primary Al₁₁Ce₃ phase as can be seen in the XRD pattern of Fig. 2 (3).

Fig. 3 shows an SEM micrograph using the EDS technique in which a bright phase that is associated with cerium flakes randomly distributed into the black aluminum matrix can be observed. The results of the energy dispersive X-ray
Fig. 3 SEM micrograph of Al-Mg-Ce master alloy with 4.3 wt.% Ce after 60 min of treatment and EDS analysis of phase Al-Ce.

Semi-quantitative analysis shown in Fig. 3 also present intermetallic compound that is constituted of Al (55 wt.%) and Ce (45 wt.%), indicating the ratio stoichiometrically of the primary phase Al$_{11}$Ce$_3$. This result agrees qualitatively with results reported in the literature[12], in which the microstructure is composed of primary intermetallic phase embedded in a matrix of $\alpha$-Al.

Fig. 4 shows a photomicrograph (SEM) of a partially reacted CeO$_2$ particle. According to the results of the energy dispersive X-ray analysis, the particle contains unreacted CeO$_2$, as only cerium and oxygen were determined. The layer surrounding the center of the particle contains Ce, Mg, Al and O, indicating the presence of MgAl$_2$O$_4$ as a reaction product. The experimental results indicate the formation of a layer of reaction products around the tablet surface and its later growth until the CeO$_2$ nucleus has disappeared. In this case, the process description corresponds to the mechanism of a “decreasing nucleus model”[6].

According to the results obtained and taking into account the stages of the decreasing nucleus model, it is expected that in the very early moments of contact between the CeO$_2$ particles and molten aluminum, the cerium oxide reduction begins through the dissolution of Mg and Al in the bath by equations$^{[13]}$ (1) and (2), and the cerium is incorporated into the molten bath.

\[
\begin{align*}
2\text{Mg} + \text{CeO}_2 &\rightarrow 2\text{MgO} + \text{Ce} \quad (1) \\
\Delta G_{\text{f}}^{\circ} &\text{[KJ]} = -102.449 \text{KJ} \\
4\text{Al} + 3\text{CeO}_2 &\rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Ce} \quad (2) \\
\Delta G_{\text{f}}^{\circ} &\text{[KJ]} = -70.493 \text{KJ}
\end{align*}
\]

The reaction products from Eqs. (1) and (2) (MgO and Al$_2$O$_3$), react into the molten bath to give a result as the following equations:

\[
\begin{align*}
2\text{MgO} + 2\text{Al}_2\text{O}_3 &\rightarrow 2\text{MgAl}_2\text{O}_4 \quad (3) \\
\Delta G_{\text{f}}^{\circ} &\text{[KJ]} = -27.549 \text{KJ}.
\end{align*}
\]

In a general way, these equations can be related between them in the next equation

\[
\begin{align*}
2\text{Mg} + 4\text{Al} + 4\text{CeO}_2 &\rightarrow 2\text{MgAl}_2\text{O}_4 + 4\text{Ce} \quad (4) \\
\Delta G_{\text{f}}^{\circ} &\text{[KJ]} = -200.491 \text{KJ}.
\end{align*}
\]

3 Conclusions

The viability of cerium incorporation from cerium oxide by using submerged powder injection was proved on a laboratory scale. The most important reaction during the injection process was that which occurred between CeO$_2$ and Mg. The rate of reaction was enhanced by increasing the initial amount of magnesium.

The cerium content in the Al-Mg alloy increased to 4 wt.% after 60 min of treatment with the next parameters: temperature of the molten metal, 850 °C, powder size between 140+200 mesh, 4 wt.% Mg and injection time of 60 min using 8 g CeO$_2$/min.

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