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A kinetic study of the strontium extraction by metallothermic reduction using submerged SrO powders injection

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Abstract

This work reports the results of laboratory experiments conduced to follow the kinetics of strontium recovery into the Al–Mg alloy by metallothermic reduction of SrO. The reagent was incorporated to molten alloy by the use of submerged powders injection technique. The variables analyzed were the injection time, the melt temperature and the initial magnesium content. Magnesium is added to the melt to increase the reactivity and reduce the surface tension of the molten aluminum. It was possible to increase the strontium content from 0 to 5 wt.% after 60 min of treatment. The results were fitted to a general kinetic equation, which allowed it to obtain the kinetic parameters, i.e. order of reaction and activation energy of the process. As the main mechanism of the strontium recovery process is of diffusive type, the global process rate increases as the temperature and initial amount of the magnesium increased.
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1. Introduction

Until recently, strontium was one of the less important elements from the production volume point of view. This situation has been changed due the increased application for strontium in the automobile and aerospace industries resulting in growing demand for the metal. This metal is frequently used in master alloy form, such as Al–Sr and Al–Sr–Mg [1]. Strontium is a reactive metal making it difficult and costly to produce except under carefully controlled processes.

Nowadays, the most effective method for strontium production is the metallothermic reduction of its oxide. This process, named "Melt Leach Evaporation" (MLE), is under development for the extraction of valuable Group IIA metals of the Periodic Table. The MLE process consists of mixing and contacting the value metal source material, which might be an ore or concentrate, with an excess of molten metal which is acting as a reductant and lixiviant. In the process, the value metal extracted from the source material is dissolved in the excess molten metallic solvent and is subsequently extracted as

a vapour by vacuum distillation [2]. For the extraction of strontium from its oxide, different methods have been developed, which work under vacuum conditions and high temperatures. These conditions increase the production cost.

In light of the foregoing, the process of strontium extraction from SrO through the use of submerged powders injection of strontium oxide is very attractive alternative from both the technological and the economic points of view. So in this paper, the results obtained about the feasibility to incorporate metallic strontium to Al–Mg liquid alloy from metallothermic reduction of strontium oxide at scale laboratory are presented.

2. Materials and methods

The experimental trials were carried out in a high frequency induction furnace 15 kg molten aluminum capacity. The powders injection equipment, whose scheme is presented in Fig. 1, allowed the 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 [3,4]. The reactants used in the experiments were as follows: Al (99% purity); Mg (99% purity); SrO (−70+140 mesh [5]).

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1) Molten aluminum; 2) Reaction Zone; 3) Argon supply
4) Lance; 5) Pressurized chamber; 6) Powders container
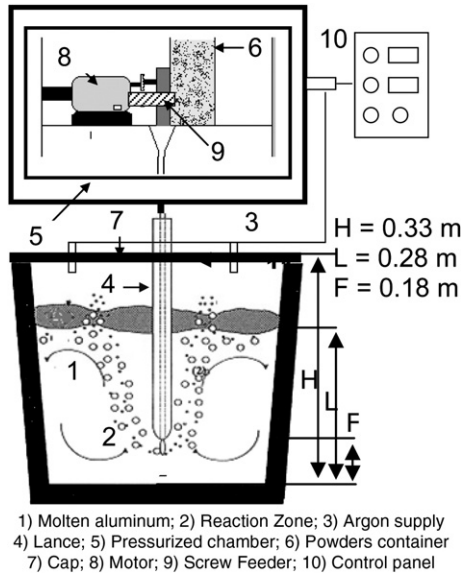7) Cap; 8) Motor; 9) Screw Feeder; 10) Control panel

Fig. 1. Schematic diagram of the powder injection system.

The selected experimental factors and their levels were temperature (973, 1023, 1073 K), magnesium content in the alloy (1, 2, 3 wt.%) and injection time (15, 30, 45, 60 min). To simplify the process of powder injection, the following parameters were kept constant: amount of liquid alloy: 10 ± 0.1 kg; powder flow rate to carrier gas flow rate ratio: 17 g SrO/min / 12 L Ar/min.

The typical experimental trial was conducted as follows: First, the alloy with the initial chemical composition was melted in the induction furnace. Then, the injection system was attached to the furnace and fixed. The graphite lance was submerged into the melt at the specified depth and position (Fig. 1) [6]. Argon gas (UHP 99.99%) was blown into the melt for 3 min before introducing the particles of the reactive powder to avoid powder clogging. No fluxing or degassing of the melt was performed after melting, so the alloy was only treated for strontium increase.

Finally, to obtain kinetic information and metallographic, samples were taken at 15 min intervals and analyzed by using inductively coupled plasma spectrometry (ICP) and Scanning Electron Microscope (SEM) respectively. Dross samples were taken at the end of each experiment and analyzed by X-ray diffraction (XRD) for the qualitative identification of the crystalline compounds.

3. Results and discussion

3.1. Chemical analysis

From the chemistry analysis results (Fig. 2a) is observed that strontium oxide is being reduced by metallothermic mechanism, because the present strontium content in the liquid bath is increased through injection time. Strontium content in the Al–Mg alloy was increased to 5 wt.% by using the following conditions: temperature, 1073 K; magnesium content, 3 wt.%; particle size, $-70+140$ mesh; the powder flow rate to carrier gas flow rate ratio, 17 g SrO/min/12 L Ar/ min; and pressure, 1 atm (out vacuum).

The effect of temperature and initial concentration of magnesium on the strontium recovery rate could be observed in Fig. 2a. As can be seen for all cases, increasing temperature, the reaction rate between SrO

particle and melt alloy is increased, obtaining higher final strontium levels in the treated alloy. This behavior may be explained due to the thermally activated nature of the mechanisms governing the kinetics of the process, diffusion and chemical reaction [7].

The rates of strontium recovery to the melt with magnesium additions increased steadily with time for all experiments, such as shown in Fig. 2a. A previous investigation on strontium recovery from $SrCO_3$, established that magnesium improved the rate and extent of extraction by excess molten aluminum. These experiments were performed in a mechanically stirred molten aluminum bath with different levels of magnesium at 1273 K. It concluded that the beneficial effect was due to magnesium decreased the surface tension favoring the wettability and, therefore, improving the solid–liquid contact. This way enhancing the reactions that take place in the interphase, as well as increasing the amount of strontium dissolved into the excess molten reactive [8].

The analysis of Fig. 2b shows the magnesium loss from the molten bath, as a function of time, for different strontium contents obtained at the end of treatment. The magnesium content decreases respect to the increment of strontium into the molten bath. Preliminary tests were conduced to determine the magnesium loss due to oxidation. The Al–Mg molten alloy was kept at 1073 K during 2 h. The decrease of magnesium content into the Al–Mg alloy was not significant. Therefore, the overall magnesium loss is due to the occurring reaction between strontium oxide and liquid magnesium. Consequently, increasing the initial amount of
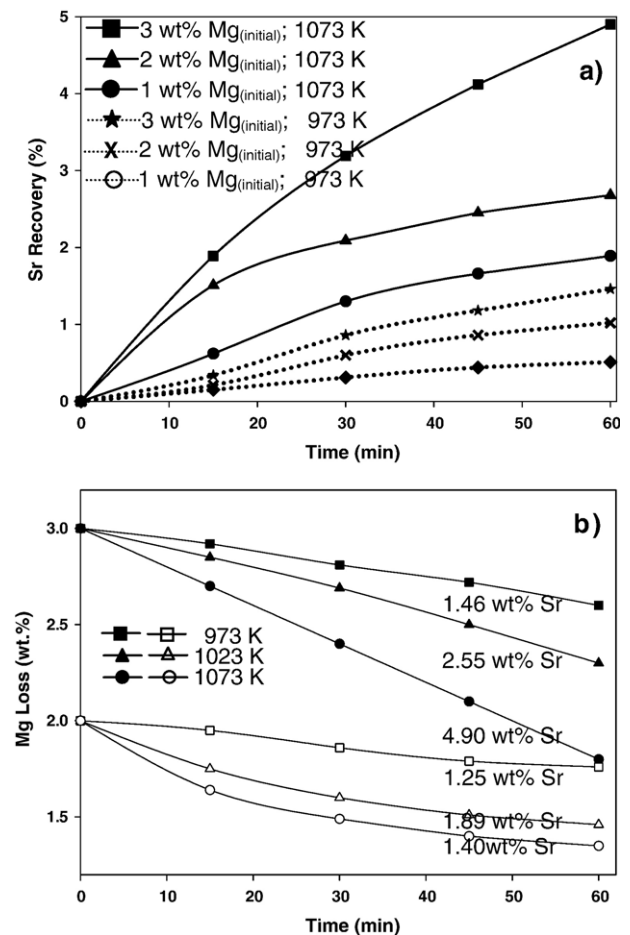

Fig. 2. Results of progresses of elements from the molten bath as a function of time. a) Strontium recovery for the temperature and initial concentration of magnesium indicated. b) Magnesium loss for the temperature, initial concentration of magnesium and final concentration of strontium indicated.

reactive (Mg) in the molten bath, the reactivity between Mg and SrO is enhanced, which contributes to the final strontium recovery.

3.2. X-ray diffraction and scanning electron microscope

The compounds present in the dross sample included: MgO (79-0612), MgAl$_2$O$_4$ (21-1152), SrF$_2$ (88-2294), Al (4-0787), KCl (72-1540), SrO (72-0057). The presence of strontium oxide in the dross sample is due to the partially reacted SrO particle, while SrF and KCl compound are formed due to the addition of flux at the end of experiment. The presence of MgO and MgAl$_2$O$_4$ as reaction products, establishes that aluminum and magnesium are reducing to strontium oxide through a metallothermic mechanism. This may indicate that the principal reaction that takes place during the injection of SrO is the following:

$$SrO + Mg = MgO + Sr \tag{1}$$

The strontium content in the Al–Mg alloy was increased to 5 wt.% after 60 min of treatment. The high strontium content benefits the precipitation of primary Al$_4$Sr phase. It can be seen in Fig. 3.

The primary Al$_4$Sr phase exhibits two-dimensional planar growth slablike form (faceted growth mode). The primary Al$_4$Sr phase in this process is slablike, growing fast in two planar directions and slowly in the normal direction of the slabs. Previous investigation [9] about the formation of microstructure of an Al-10 wt.% Sr alloy prepared by electrolysis and mixing, established that the primary Al$_4$Sr phase is dendritic in the electrolysis-prepared alloy and slablike in the mixing-prepared alloy. These forms of growth are product of the undercooling degree that occurs in the solidification process. When the primary Al$_4$Sr phase grows from the melt prepared by mixing method (undercooling
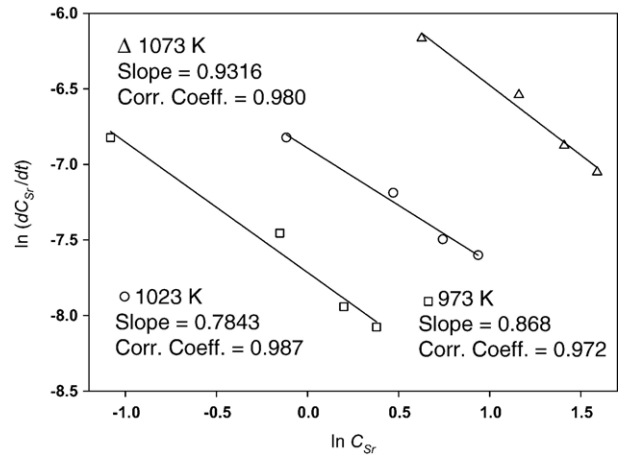

Fig. 3. SEM image showing a partially reacted particle and EDS characteristic patterns of the indicated zone.

Fig. 4. Linear plot of ln(dC_{Sr}/dt) vs. ln C_{Sr}, for the determination of reaction order.

278.7 K [9]), the preferred direction is [110] and it exhibits a planar growth mode, and finally grows into slabs, as seen in Fig. 3. For the melt from electrolysis, however, the relatively higher undercooling (289.4 K [9]) enhances the instability of the solid–liquid interface and the occurrence of a dendritic growth mode, and facilitates the branches of dendrites. The undercooling for this investigation was 285 K.

Also in Fig. 3 is observed a photomicrograph (SEM) of a partially reacted SrO particle. According to the results of the energy dispersive X-Ray analysis, the center of the particle is unreacted SrO, as only strontium and oxygen were determined. The layer surrounding the center of the particle contains Sr, Mg, Al, and O, indicating the presence of MgO as a reaction product. This may indicate that the occurring reaction during the injection of SrO is given by Eq. (1). This assumption is supported by the X-Ray diffraction analysis of the slag. Finally, intermetallic compound surrounding the partially reacted SrO particle is constituted by Sr and Al, indicating the presence of the primary phase Al$_4$Sr.

3.3. Kinetic study

According to the classical kinetic theory (differential method), the rate of strontium recovery during the injection of SrO could be determined by the following equation:

$$V\frac{dC_{Sr}}{dt} = K\left(C_{Sr} - C_{Sr(eq)}\right)^r S_m \tag{2}$$

Where V represents the volume (m^3), t is the time (s), K is the mass transfer coefficient (m (wt.%)$^{1-r}$s^{-1}), r is the reaction order, S_m is the initial concentration of magnesium (wt.%) in the molten bath and $C_{Sr.eq}$ is the volumetric concentration of the Sr at equilibrium (wt.%).

Eq. (2) can be simplified considering that the value of $C_{Sr(eq)}$ is close to zero at the investigated reaction temperature range. The value of the constant K_m considers the effects of the initial concentration of magnesium and the volume of the melt. With the considerations made previously, Eq. (2) can be written as follows:

$$\frac{dC_{Sr}}{dt} = K_m(C_{Sr})^r \tag{3}$$

It is possible to measure the kinetic values of Eq. (1) as a function of temperature. Thus, the logarithm format of Eq. (3) can be written as:

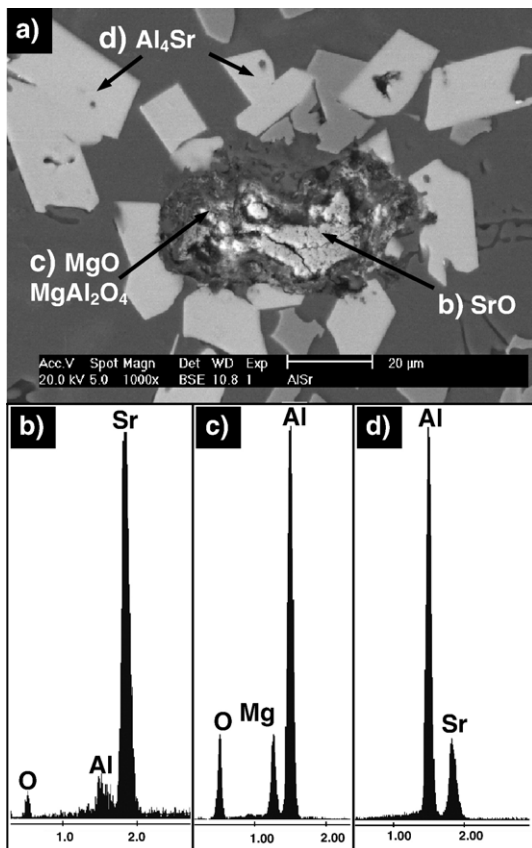$$\ln\left[\frac{dC_{Sr}}{dt}\right] = \ln K_m + r \ln C_{Sr} \tag{4}$$
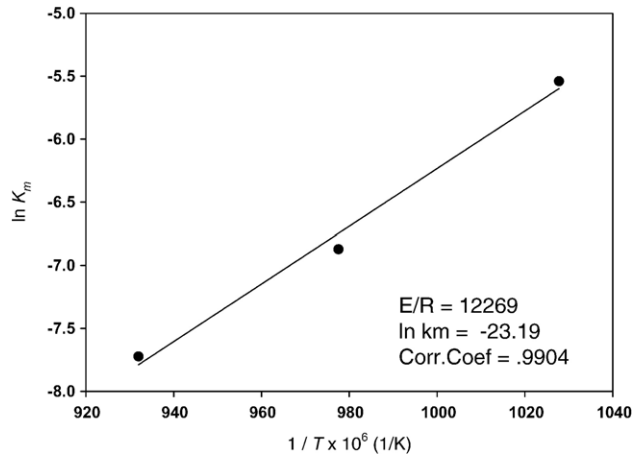
Fig. 5. Linear plot of $\ln K_m$ vs. $1/T$ for determination of the activation energy of strontium recovery.

Fig. 4 shows the linear plot of $\ln(dC_{Sr}/dt)$ against $\ln C_{Sr}$ for the same experimental condition as that shown in Fig. 2a. The slope and interception values of each line, in Fig. 4, indicate the reaction order (r) and the value of the $\ln K_m$, respectively. Using the least squares method, the reaction order was found to be about 1, indicating that the reaction corresponds to a first order kinetics. The value of K_m depends on temperature according to the Arrhenius equation:

$$K_m = f(T) = k_m \, \exp\left(-\frac{E}{RT}\right) \qquad (5)$$

Where E is the activation energy for the reaction (J mol^{-1}) and R is the universal constant of gases (8.314 J mol^{-1} K^{-1}).

Fig. 5 is a linear plot of $\ln K_m$ versus $1/T$, from which the activation energy of the process was obtained to be 102 kJ mol^{-1}. This value is close to the one reported for typical diffusion processes [10].

4. Conclusions

The viability of strontium extraction from strontium oxide by using submerged powders injection has been proved at a laboratory scale. The strontium content in the Al–Mg alloy was increased to 5 wt.% after 60 min of treatment.

The rate of reaction enhanced with increasing the initial amount of magnesium.

The most important reaction during the injection process is that occur between SrO and the Mg.

The experimental data of study kinetic were fitted to a general kinetic formula, having determined that the reaction between Mg in the molten metal and SrO is approximately first order.

The studies were conducted in the range of temperatures between 973 and 1073 K, at a magnesium concentration of 3 wt.% Mg. It was obtained a value of the activation energy for the overall process equal to 102,004 J mol^{-1} K^{-1}. This value indicates that strontium recovery is controlled by diffusion of Mg from the bulk to the powder interface.

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