A Kinetic Study on the Preparation of Al-Mn Alloys by Aluminothermic Reduction of Mn₃O₄ and MnO Powders

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Abstract: The study of aluminothermic reduction in manganese compounds is a complex challenge in preparing Al-Mn alloys. The primary objective of this study was to ascertain the activation energy values for the aluminothermic reduction of MnO and Mn₃O₄ oxides derived from alkaline batteries. The study melted aluminum found in beverage cans and utilized the technique of powder addition with mechanical agitation. The kinetics of the reaction were studied under the effects of temperature (750, 800, and 850 °C), degree of agitation (200, 250, and 300 rpm), and the initial concentration of magnesium in molten aluminum (1, 2, 3, and 4% by weight). Kinetic measurements for Mn₃O₄ particles suggest a reaction mechanism that occurs in stages, where manganese undergoes oxidation states [Mn³⁺] to [Mn²⁺] until it reaches the oxidation state Mn⁰, which allows it to dissolve in the molten aluminum, forming alloys with up to 1.5 wt.% of Mn. Therefore, the kinetic of the aluminothermic reduction of MnO is described by the geometric contraction model, while the mechanism of Mn₃O₄ reduction occurs in two stages: geometric contraction, followed by an additional stage involving the diffusion of chemical species to the boundary layer. In addition, this stage can be considered a competition between the formation of MnO and the chemical reaction itself.

Keywords: alkaline batteries recycling; aluminothermic reduction; aluminum recycling; Mn₃O₄; MnO; Al-Mn alloys

1. Introduction

Alkaline battery disposal represents a challenge, and various processes have been promoted to ensure the correct and most effective recovery of battery components, as documented in [1–9]. However, the results of these processes are limited to the recovery of components with high purity, such as sulfates or salts rich in manganese (Mn) or zinc (Zn) [10–15]. For manganese oxides (MnO), each alkaline battery discharged makes it possible to obtain 40% of high-purity Mn₂O₃. Statistics indicate that battery recycling has been increasing in recent decades, targeting the most developed countries, where batteries recycling is performed for approximately 14% [16]. The metal thermal reduction of cathodes found in recycled alkaline batteries for aluminum casting processes has been successfully tested in manufacturing aluminum-manganese (Al-Mn) alloys applied in components for the automotive industry [17,18]. Consequently, recycling cathodes from alkaline batteries represents similar techniques to the aluminum beverage can recycling process [19].

From the thermodynamic point of view, the reduction of Mn₂O₃ to Mn may involve the formation of other oxides, given the various valences that Mn can have. This implies that at a certain point, there is a formation of Mn₂O₃, Mn₃O₄, or MnO [18] until metallic Mn is obtained, and then such a component is incorporated into the molten Al alloy. This is why it is important to study the kinetics of such reactions to achieve the conditions in which
a weight of up to 3% is obtained of metallic Mn. If the kinetics are accelerated up to 5% by weight, additional magnesium must be added to the molten alloy, which is consumed by the aluminothermic reduction reactions. This magnesium (Mg) loss is associated with increasing the effectiveness of the chemical reduction reaction, as well as improving the wettability of particles of Mn oxides by the molten alloys [19,20]. In particular, kinetic information about the aluminothermic reduction rate by which MnO can be reduced is essential for the development of new sustainable products and processes that apply the recycling of both aluminum and alkaline batteries [16,17]. Therefore, this paper proposes to study the aluminothermic reduction rate of the following reactions:

\[
3\text{Mn}_3\text{O}_4(s) + 8\text{Al}(l) \rightarrow 4\text{Al}_2\text{O}_3(S) + 9\text{Mn}(l)
\]

\[\Delta G^\circ_{800 \, ^\circ\text{C}} = -2300.67 \text{ kJ/mol} \] (1)

\[2\text{Al}(l) + \text{Mg}(l) + \text{Mn}_3\text{O}_4(s) \rightarrow 3\text{Mn}(l) + \text{MgAl}_2\text{O}_4(s)\]

\[\Delta G^\circ_{800 \, ^\circ\text{C}} = -453.45 \text{ kJ/mol} \] (2)

\[3\text{MnO}(s) + 2\text{Al}(l) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{Mn}(l)\]

\[\Delta G^\circ_{800 \, ^\circ\text{C}} = -245.037 \text{ kJ/mol} \] (3)

\[2\text{Al}(l) + \text{Mg}(l) + 4\text{MnO}(s) \rightarrow 4\text{Mn}(l) + \text{MgAl}_2\text{O}_4(s)\]

\[\Delta G^\circ_{800 \, ^\circ\text{C}} = -418.851 \text{ kJ/mol} \] (4)

**Aluminothermic Reduction Reactions**

A metallothermic process refers to the obtaining of metals and alloys by reducing their oxides or halides with metals, according to the following reaction:

\[\text{AX} + \text{B} \rightarrow \text{A} + \text{BX} \] (5)

where X represents oxygen, chlorine, or fluorine; and A and B represent the two metals, such as manganese and aluminum (or magnesium). The metals mainly used as reducers include Al, Ca, Mg, and Na. The affinity of these elements for oxygen is higher than other elements since the reactions of these elements with oxygen are predominant due to the negative values found in each elements’ Gibbs free energy. The process of the aluminothermic reduction of oxides is described by the following reaction when the liquid aluminum that is used as a reducing agent has a high initial content of Mg [21–25]:

\[2\text{Al}(l) + \text{Mg}(l) + 4\text{MnO}(s) \xrightarrow{\Delta} 4\text{Mn}(l) + \text{MgAl}_2\text{O}_4(s) \] (6)

This type of solid–liquid reaction has a disadvantage as the phenomena at the interface govern the reduction rate. This rate depends on the physical properties of the solid and liquid, such as the density, liquid surface tension, solid surface area, and porosity. Generally, when reduction reactions occur, a new solid precipitate around the particle, or transformations occur at the periphery of the particle. When the solid particle is immersed in the liquid, it will try to occupy as much contact area as possible with that liquid. Then, the first stage of the reaction occurs, having, as first obstacle, the saturation of the production at the surface of the solid; this saturation stops the reaction. Such first layer of products must be removed for the reaction to progress. Once the first layer of products is formed,
the idea that the reactions will take place in the solid state up to a specific limit—where the coating of products is enriched and reaches a reaction limit is discarded. When this layer of products is removed, more active sites can be released on the surface of the particle, resulting in a continuation of the reduction reaction. A porous particle may perform better due to the penetration of liquid into the pores of the solid and may or may not break the same particle with the formation of products. Previous research on the reduction of Mn$_2$O$_3$ particles analyzed the effect of mechanical agitation for refining aluminum [26]. This system is ideal for breaking down this layer of products and maintaining the course of the reaction.

A critical factor is the effect of the initial concentration of Mg in the liquid alloy on the dissolution of solid particles of Mn oxides due to the tense-active nature of this element in molten aluminum. This leads to an improved wettability between the solid reagent and the molten metal, thus increasing the kinetics of the reactions at the solid–liquid interface [27–30].

Therefore, the primary objective of this study is to determine the reaction rate of the aluminothermic reduction of MnO and Mn$_3$O$_4$ oxides using the powder addition technique with mechanical agitation. On the other hand, the effects of initial magnesium concentration are also investigated, as this element is known to improve the reaction rate, not only by its effect on the chemical reactivity of the molten bath but also by increasing wettability between the particles added and the molten bath itself. It is also important to determine the kinetic model that best adjusts the experimental results since Mn presents various oxidation states, where the formation of reaction product layers of various oxides could limit the sequence of reaction, thus limiting the reaction kinetics. In processes where the elements to be reduced undergo different oxidation states, the control of the reaction rate can be of the mixed type, where the solid–liquid interface controls the chemical and mass transport steps and therefore the reaction rate. This is analyzed experimentally in the sections below.

2. Materials and Methods

Because of the necessity for a preliminary basis for the subsequent presentation of results and discussion, we characterized Mn$_3$O$_4$ and MnO powders using scanning electron microscopy and chemical analysis by atomic absorption spectrophotometry, utilizing the Philips Scanning Electron Microscope model XL30 (Philips, Eindhoven, The Netherlands). The first technique allowed us to determine the morphological characteristics of the powder particles, while the second technique helped us ascertain the purity of both oxides. We acquired these oxides from the company Merck Aldrich’s Mexican subsidiary (Toluca, Mexico). Subsequently, we prepared the Al-Mg alloys from the aluminum found in beverage cans (the chemical composition is provided in Table 1) and commercial-grade Mg (99% by weight) using a medium-frequency induction furnace. The unit presented in Figure 1 has a tailored-made stirring system that employed a Crafmo brand graphite impeller coupled to a variable speed motor manufactured by KB controls (Santa Fe Springs, CA, USA); the rest of the unit was custom-made and assembled within the lab.

Table 1. Chemical composition of the aluminum cans for beverages used in this study in wt. %.

<table>
<thead>
<tr>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Ni</th>
<th>Zn</th>
<th>Ti</th>
<th>Co</th>
<th>Sr</th>
<th>V</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.26</td>
<td>0.73</td>
<td>0.18</td>
<td>0.6</td>
<td>0.9</td>
<td>0.012</td>
<td>0.12</td>
<td>0.01</td>
<td>0.004</td>
<td>0.001</td>
<td>0.01</td>
<td>97.2</td>
</tr>
</tbody>
</table>

With the melting system described above, the liquid bath was maintained perfectly mixed; in addition, a close to constant temperature control was permitted, with variations not exceeding 5 °C. Batches of alloys with different initial concentrations of magnesium, namely 1, 2, 3, and 4% by weight, were prepared.
In the second stage, melting tests were carried out considering a constant temperature, degree of agitation, and initial concentration of Mg. For such tests, a factorial design of random blocks 2k was considered, and the design of experiments yielded 16 trials. The Mn$_3$O$_4$ and MnO powders used in the tests were covered with aluminum foil (6.25 g of each powder), added at intervals of 15 min until reaching the amount stoichiometrically required according to the reactions (2) and/or (4), to obtain a concentration of Mn of up to 1.5% by weight, in maximum treatment times of 4 h.

During each treatment, a sample of the metal bath was taken every 15 min to subsequently construct graphs of the Mn or Mg concentration against time for each value of the operating parameters selected, according to the experimental design shown in Table 2. At the end of each experiment, the slag generated was collected to characterize the reaction products using X-ray diffraction.

### Table 2. Experimental design performed.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Oxide</th>
<th>Temperature (°C)</th>
<th>Stirring Speed (RPM)</th>
<th>Mg (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type and range</td>
<td>MnO, Mn$_3$O$_4$</td>
<td>750, 800, 850</td>
<td>200, 250, 300</td>
<td>1, 2, 3, 4</td>
</tr>
</tbody>
</table>

The reaction speed involving a solid phase is expressed in the following equation:

$$\frac{d(\alpha)}{dt} = Ae^{-\frac{E_a}{RT}}$$  \hspace{1cm} (7)

The conversion fraction for gravimetric measurements is usually calculated as follows:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}$$  \hspace{1cm} (8)

where $m_0$ is the initial mass of Mn in the alloy, $m_t$ is the actual mass, and $m_f$ is the final mass of Mn that passed to the molten alloy. The kinetic parameters of all the reactions considered in this study were calculated from the experiments performed. The mass of each element in every reaction was calculated from the conversion fraction of the respective reaction, allowing the formulation of mass balance equations concerning the reactions described by Equations (1) through (4), defining the change in the chemical concentration of the species.
concerned during the development of the aluminum–thermal reaction, depending on the treatment time.

3. Results and Discussion
3.1. Characterization of the MnO and Mn$_3$O$_4$ Powders

First, we present the results of the characteristics of MnO. Morphological characteristics of the oxide particles used were observed in the scanning electron microscope. It should be noted that the purity determined by atomic absorption spectrophotometry was 97% by weight for Mn$_3$O$_4$ and 99% by weight for MnO. The micrographs in Figures 2 and 3 display the irregular shapes of the MnO and Mn$_3$O$_4$ particles. The micrograph in Figure 2a shows particles with small cracks. The pore shape was irregular with an average size of around 1 µm. This was seen and analyzed in a previous study, where it was mentioned that Mn$_3$O$_4$ had an octahedral morphology with oxygen vacancies at the electrolyte interface [31]. The micrograph in Figure 3a shows this octahedral morphology of the particles of Mn$_3$O$_4$, which were rather spherical, with average diameters in the order of 100 nm. The micrograph in Figure 3b shows some agglomerates of particles.

![Figure 2](image-url)

**Figure 2.** SEM micrographs using back-scattered electrons for MnO particles; (a) group of particles, and (b) close-up to an individual particle.

![Figure 3](image-url)

**Figure 3.** SEM micrographs using back-scattered electrons for Mn$_3$O$_4$ particles; (a) close-up to a group of particles, and (b) agglomerated particles.

The morphological differences between the two oxides are essential in explaining the possible efficiency of the thermal reduction reaction. As concluded by J. Yang et al. [32], the morphology of manganese oxides controls capacitance properties due to the higher surface area associated with its porous structure. For this case, the absence of pores in the particles of Mn$_3$O$_4$ can reduce the reaction rate. However, since their average particle size is smaller, this could counteract such an effect. As for impurities, Mn$_3$O$_4$ powders contain 3% by weight of other MnO, mainly Mn$_2$O$_3$. However, it could be considered that this impurity content would not significantly affect the reaction kinetics from probabilistic reasons.
3.2. Aluminothermic Reduction

The results of the experiments carried out with different values of the operating parameters, such as temperature, degree of agitation, and initial concentration of Mg, are presented in Figures 4 and 5. Figure 4 shows the graphic aluminothermic reduction reaction results of MnO addition, where Figure 4a shows the increment in Mn content, and Figure 4b the decrement of Mg content, respectively. Figure 5 depicts the graphic aluminothermic reduction reaction results of Mn$_3$O$_4$ addition, where Figure 5a depicts an increment in Mn content, and Figure 5b the decrement of Mg content.

**Figure 4.** (a) Effect of treatment time on the increase in the Mn concentration and (b) the decrease in the concentration of Mg in molten aluminum, during the aluminothermic reaction of MnO particles, at the indicated temperatures. The initial concentration of Mg was 1% by weight, and a stirring speed of 300 rpm was used.

**Figure 5.** (a) Effect of time treatment on the increase in the Mn concentration and (b) the decrease in the concentration of Mg in molten aluminum, during the aluminothermic reduction reaction of particles of Mn$_3$O$_4$, at the indicated temperatures. The initial concentration of Mg was 1% by weight, and a stirring speed of 300 rpm was used.

Figure 6 shows the results of the effect of treatment time on the increase in Mn concentration, at the indicated stirring rates, during the aluminothermic reduction of MnO powders at a constant temperature and degree of agitation. In this graph, the Mn concentrations can be observed close to 1.5% by weight, which was reached at the highest rate of agitation. In turn, Figure 7 presents the effect results of the treatment time for the increment considering the Mn concentration, at the indicated stirring speeds, during the aluminothermic reduction of Mn$_3$O$_4$ powders.
Figure 6. Effect of treatment time on the increase in the Mn concentration and the decrease in the Mg concentration in molten aluminum, during the aluminothermic reaction of MnO particles, to the levels of agitation indicated. The initial concentration of Mg was 1% by weight, and a temperature of 850 °C was used.

Figure 7. Effect of time treatment on the increase in the Mn concentration and the decrease in the Mg concentration in molten aluminum, during the aluminothermic reduction reaction of particles of Mn$_3$O$_4$, to the levels of agitation indicated. The initial concentration of Mg was 1% by weight, and a temperature of 850 °C was used.

Figure 8 depicts the effect of treatment time on the Mn increase concentration in the alloy and on the decrease in magnesium concentration for different initial concentrations of magnesium in the alloy as indicated, using a constant temperature of 850 °C and at 300 rpm for the addition of MnO powders.

Figure 9 shows the effect of treatment time on Mn and Mg concentrations for the initial magnesium concentrations indicated and on the operating conditions indicated in each figure during the aluminothermic reduction reaction of Mn$_3$O$_4$ powders.
Figure 8. (a) Effect of treatment time on the increase in the Mn concentration and (b) the decrease in the Mg concentration in molten aluminum, during the aluminothermic reduction reaction of particles of Mn$_3$O$_4$, to the initial concentrations of magnesium indicated. The temperature was 850 °C, and the stirring speed was 300 rpm.

Figure 9. (a) Effect of treatment time on the increase in the Mn concentration and (b) the decrease in the Mg concentration in molten aluminum, during the aluminothermic reduction reaction of particles of Mn$_3$O$_4$, to the initial concentrations of magnesium indicated. The temperature was 850 °C, and the stirring speed was 300 rpm.

In general, a substantial effect of temperature, degree of agitation, and initial magnesium concentration in the molten alloy can be observed on the aluminothermic reduction reactions of Mn oxides. Depending on the type of oxide used, the highest final concentrations of Mn occur at the highest temperature, at the highest level of agitation, and at the highest initial Mg concentration. It should be noted that in experiments with Mn$_3$O$_4$ particles, lower final concentrations of Mn are reached compared to those achieved when using MnO particles. This can be explained by various effects such as the physical characteristics of the particles (average size, porosity, etc.), in addition to the possible lower oxide chemical reactivity or the case where it presents more stages during the aluminothermic reduction reaction. However, it can be shown based on slag analysis that the low efficiency is due mainly to an intermediate reduction reaction like Mn$_2$O$_3$ occurring when Mn$_3$O$_4$ is reduced to MnO [9].
3.3. Analysis of the Slags

The decrease in the concentration of Mg in all cases indicates that this element is consumed during the aluminothermic reduction, promoting its oxidation in the form of spinel and/or periclase. The X-ray diffraction patterns can be observed in Figures 10 and 11. These patterns correspond to the analysis of the typical slags obtained when adding MnO particles (Figure 10) and when adding Mn$_3$O$_4$ particles (Figure 11), respectively.

![X-ray diffraction pattern for a slag obtained during aluminothermic reduction experiments using MnO particles, at the temperature of 850 °C, at a stirring speed of 300 rpm and an initial concentration of Mg of 4% by weight.](image)

Figure 10. X-ray diffraction pattern for a slag obtained during aluminothermic reduction experiments using MnO particles, at the temperature of 850 °C, at a stirring speed of 300 rpm and an initial concentration of Mg of 4% by weight.

The mineralogical species determined for the slags obtained in the aluminothermic reduction experiments of the two types of oxides used varied significantly, since when MnO was used, the main products were MgO, MgAl$_2$O$_4$, and AlN, in addition to MnO, which passed into the slag without reacting. Meanwhile, when using Mn$_3$O$_4$ powders, the main reaction products, in addition to MgO, MgAl$_2$O$_4$, and AlN, contained MnO, indicating that Mn$_3$O$_4$ had been partly reduced to MnO, explaining the low reaction efficiency when using these powders. In both types of experiments, the presence of AlN is explained based on the high affinity of aluminum for nitrogen at temperatures above 700 °C, as discussed by Nabi [33].

3.4. Kinetic Study

In the next part of this work, the results of the kinetic measurements are presented and discussed. To do this, the conversion fraction ($\alpha$) was considered to determine the progress of the reaction calculated according to the formula given in Equation (8) to immediately determine which of the mathematical models reported in the literature review best fit the experimental data [34]. The variation of $\alpha$ to the treatment time to match the best value set of the operating parameters, for the cases of both MnO and Mn$_3$O$_4$ particles, was a temperature of 850 °C, a stirring speed of 300 rpm, and an initial concentration of Mg of 1 and 4% by weight. Figure 12 shows in graphical form the representation of the conversion fraction values ($\alpha$) against time and the predictions of the models for geometric contraction for the best operating conditions indicated.
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Figure 12. Variation of the conversion fraction against time for the aluminothermic reduction of (a) MnO and (b) Mn₃O₄ to 850 °C, with a stirring speed of 300 rpm and initial concentrations Mg of 1 and 4% by weight. Predictions of the indicated kinetic models of geometric contraction are included.

Figure 13 depicts the experimental data and predictions of the kinetic diffusion models for (a) MnO and (b) Mn₃O₄, at the experimental conditions indicated in each part of such figure.

Figure 13. Variation of the conversion fraction against time for the experimental data and its comparison with the predictions of the diffusion models for (a) MnO and (b) Mn₃O₄, to the experimental conditions indicated in each figure.
After that period of time, the reaction became slower, and the efficiency of Mn incorporation (329 kJ/mol), as compared to the energy required for the aluminothermic reduction reaction, was found to be 25%. Therefore, it can be stated that it is more efficient to prepare alloys with a concentration of up to 1.5 wt.% Mn starting from MnO powders. In the case of Mn3O4 particles, the aluminothermic reduction reaction released only a small amount of Mn that passed directly to the molten metal. To this point, it can be stated that it is more efficient to prepare alloys with a concentration of up to 1.5 wt.% Mn starting from MnO powders. In the case of Mn3O4 particles, operating parameters such as temperature, agitation speed, or initial Mg concentration in the melt must be enhanced in order to reach for higher efficiencies of reduction, as it can be seen in Figure 13b.

Figure 13. Variation of the conversion fraction against time for the experimental data and its comparison with the predictions of the diffusion models for (a) MnO and (b) Mn3O4, to the experimental conditions indicated in each figure.

Table 3. Activation energy values for the aluminothermic reduction reactions of MnO and Mn3O4 powders at a constant agitation speed of 300 rpm.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Ea (kJ/mol)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO (Al-1%Mg)</td>
<td>329.56</td>
<td>0.93</td>
</tr>
<tr>
<td>Mn3O4 (Al-4%Mg)</td>
<td>35.88</td>
<td>0.99</td>
</tr>
</tbody>
</table>
At the melting temperature of aluminum, no such changes have been reported [36–39]. The progress of the reaction, it will stop and only achieve a partial reduction (Mn volumetric contractions are expected as the particle is consumed; these changes can be optimizations of Mn powders at a constant agitation speed of 300 rpm.

Plot of Ln(k) versus 1/T for the Ea calculation during the aluminothermic reduction reactions of Mn$_3$O$_4$ and MnO at a constant initial concentration of Mg and a constant agitation speed, and simple lines are the lineal regression of the experimental points.

3.5. Thermodynamic Consideration

The aluminothermic reduction of Mn oxides contained in the by-products of discharged alkaline batteries could be reduced by molten Al-Mg as follows. The reduction reactions occur in stages, from Mn$_3$O$_4$ to MnO, until releasing Mn metal that is dissolved by the molten Al-Mg alloy. It could be inferred that the reaction will only take place at the solid–liquid interface, leaving a sequence in two main steps:

\[
2\text{Al}(l) + \text{Mg}(l) + 4\text{Mn}_3\text{O}_4(s) \xrightarrow{\Delta} 12\text{MnO}(s) + \text{MgAl}_2\text{O}_4(s)
\]

\[
\Delta G^\circ_{800 \text{ C}} = -1078.72 \text{ KJ/mol}
\]  

(9)

\[
2\text{Al}(l) + 4\text{MnO}(s) \xrightarrow{\Delta} 4\text{Mn}(l) + \text{MgAl}_2\text{O}_4(s)
\]

\[
\Delta G^\circ_{800 \text{ C}} = -418.851 \text{ KJ/mol}
\]  

(10)

The thermodynamic considerations assume that the particle will break at each step and fractionate as the reaction progresses. Smaller particles resulting from the sequence of the reduction reaction have a lower oxidation state. However, this reduction effect only manages to release metallic Mn in the last step, so if there is an obstacle that prevents the progress of the reaction, it will stop and only achieve a partial reduction (Mn$_3$O$_4$→MnO). At the melting temperature of aluminum, no such changes have been reported [36–39]. The volumetric contractions are expected as the particle is consumed; these changes can be caused by a fracture or the appearance of pores in the solid body that improves the rate of reduction. The following equations are highly probable at the solid–liquid interface of the MnO and Mn$_3$O$_4$ particles.

\[
2\text{Al}(l) + \text{Mg}(l) + 3\text{Mn}_3\text{O}_4(s) \xrightarrow{\Delta} 3\text{Mn}(s) + 2\text{Mn}_2\text{O}_3(s) + 2\text{MnO}_2(s) + \text{MgAl}_2\text{O}_4(s)
\]

\[
\Delta G^\circ_{800 \text{ C}} = -398.53 \text{ KJ/mol}
\]  

(11)
\[
\text{Mn}^{(s)} + 4\text{Mn}_2\text{O}_3^{(s)} \xrightarrow{\Delta} 3\text{Mn}_3\text{O}_4
\]

\[
\Delta G^\circ_{800 \, ^\circ C} = -318.26 \frac{\text{kJ}}{\text{mol}} \quad (12)
\]

\[
3\text{Mn}_3\text{O}_4^{(s)} \xrightarrow{\Delta} 3\text{Mn}_2\text{O}_3^{(s)} + 3\text{Mn}^{(s)}
\]

\[
\Delta G^\circ_{800 \, ^\circ C} = -82.38 \frac{\text{kJ}}{\text{mol}} \quad (13)
\]

\[
3\text{MnO}^{(s)} \xrightarrow{\Delta} \left[3\text{Mn}^{(s)} + 3\text{O}^{(s)}\right] \xrightarrow{\Delta} \text{Mn}^{(s)} + 4\text{Mn}_2\text{O}_3^{(s)}
\]

\[
\Delta G^\circ_{800 \, ^\circ C} = -1230.74 \frac{\text{kJ}}{\text{mol}} \quad (14)
\]

It can be inferred that the reduction of Mn$_2$O$_3$ particles begins and continues at the interface once the reaction is reached. This will happen until stopped by the saturation of reaction sites. Then, the particle isolated and immersed in molten aluminum will undergo structural changes due to temperature as if it were a heat treatment. Such consideration is the reason why it is estimated that Mn$_2$O$_3$ will reappear (when the reaction product detaches, a new surface of Mn$_2$O$_3$ is exposed and is likely to continue reacting) in the reduction of Mn$_3$O$_4$ when this is not direct. When incorporating metallic Mn into liquid Al, the solid–liquid interface governs the reaction. However, reactions can play an essential role in the core of the particle, where solid-state reactions take place. Next, the equation for the reduction of the Mn$_3$O$_4$ particle partially, given by:

\[
2\text{Al}^{(l)} + \text{Mg}^{(l)} + 16\text{Mn}_3\text{O}_4^{(s)} \xrightarrow{\Delta} 12\text{Mn}_2\text{O}_3^{(s)} + 24\text{MnO}^{(s)} + \text{MgAl}_2\text{O}_4^{(s)}
\]

\[
\Delta G^\circ_{800 \, ^\circ C} = -749.18 \frac{\text{kJ}}{\text{mol}} \quad (15)
\]

4. Conclusions

All the operational variables analyzed in this paper directly influenced the rate of aluminothermic reduction rates of the MnO and Mn$_3$O$_4$ particles. In the case of MnO, the highest reaction efficiency was achieved when the Mg content in the aluminum-based alloy was increased. The transformed fraction achieved was equal to 1 in just 120 min when it was used at an initial concentration of 4% by weight Mg. Hence, the concentration of the mentioned 4% Mg was reported as highly important, because the value of the activation energy (329.56 kJ/mol) was 10-times lower than the value required when the initial Mg concentration was equal to 1%. Such results show that the increment in temperature and degree of agitation are less important than the initial concentration of Mg.

In turn, it was identified that the aluminothermic reduction of Mn$_3$O$_4$ occurred in stages, where reaction first started at the reaction interface, followed by the chemical species diffusion through the layers of reaction products. Then, simultaneously, the Mn valence changed, but we also recognized an aluminothermic reduction competition of the oxides that were being formed, mainly Mn$_2$O$_3$, as it was deducted by the composition of the slags produced at the end of these experiments. Despite the smaller value of activation energy of the aluminothermic reduction reaction of Mn$_3$O$_4$ particles (35.88 kJ/mol), the efficiency of the reaction was very low as compared to that of MnO, and it was due to the parallel formation of MnO during the aluminothermic reduction reaction, which passed directly into the slag without reacting.

Therefore, the mechanism of aluminothermic reduction of MnO is described by the geometric contraction model, while the mechanism of Mn$_3$O$_4$ reduction occurs in two
stages: geometric contraction, followed by an additional stage involving the diffusion of chemical species to the boundary layer. In addition, this stage can be considered a competition between the formation of MnO and the chemical reaction itself.

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