

CORROSION BEHAVIOR OF VARIOUS STEELS BY AZ31 MAGNESIUM MELT

Cheuk Kin Tang, Marie-Aline Van Ende, In-Ho Jung,
McGill University; 3610 University Street, Montréal, Québec, H3A 2B2, Canada

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Abstract

During the production of magnesium and its alloys, the melt is in contact with steel at various stages of the process. Steel can be eroded and corroded through chemical reactions with molten magnesium and the protective gases such as SF₆ or SO₂. The dissolution rate and corrosion mechanism of steels in molten magnesium were investigated by the rotating cylinder method. The corrosion behavior of four steel grades, i.e. high carbon and low carbon steel, stainless steel 316 and 400 were examined for AZ31 melt under N₂-1% SF₆ gas atmosphere. The corrosion rates were found to be different depending on steel grades. It is found that the corrosion mechanism of steels in magnesium melts involves a two-stage process consisting of oxidation of Fe and its reduction by magnesium melt.

Introduction

Magnesium and its alloys have become a more and more attractive material primarily owing to its light weight. In order to produce the final Mg products of cast alloys or wrought alloys, all Mg alloys should be once melted in a furnace at about 700 °C. A complete melting and casting equipment consists of a pre-heating and charging equipment, melting and holding furnaces, a protective gas mixing device and a metal feed to the casting machine [1]. The Mg melt in the furnace is always under a protective gas atmosphere to prevent Mg burning. Typical protective gas used in Mg industry is N₂-SF₆, dry air-SF₆ and dry air-SO₂ mixture. Since the solubility of Fe in liquid Mg is low (0.04 wt% Fe at 750 °C), steel makes a good candidate for holding and transporting liquid magnesium during its fabrication process. Even most of the tools used for liquid Mg are made of steels. However, Fe is one of the most harmful impurities in Mg alloys as it reduces considerably the corrosion resistance even at low concentration.

Minimizing the corrosion and maintaining the original shape of the steel crucible are important for long service life, easy cleaning and to minimize the contamination of the melt by Fe. Two steel materials have been proven useful for holding the Mg melt. Although expensive, ferritic stainless steel has shown to work best when low wall thicknesses are required for crucible design. However, the most common material used is a bimetal in which a heavy steel plate is joined with an exterior rolled cladding. The Ni-Cr components inherent in stainless steel and the exterior rolled cladding are essential in preventing oxidation at these high temperature conditions [2]. The upper zone of the steel crucible in which the liquid oscillates at horizon is subjected to higher wear than the other zones. However, no comprehensive study on the corrosion of steel near the Mg melt level has been reported. Furthermore, a comparative corrosion study of various steel grades against liquid Mg has not been performed.

In the present study, a laboratory furnace system was designed to investigate the corrosion behavior of steel by molten Mg under a N₂-SF₆ protective gas atmosphere. The goal of the present study is to provide a preliminary understanding of the corrosion mechanisms of various steels by Mg melt, which will be useful for extending the steel crucible life time and selecting future crucible materials.

Experimental

Materials

Four steel grades were investigated using the rotating cylinder experiments: Low carbon steel, high carbon steel, stainless steel 316 and stainless steel 400. These steel types were welded together to form a cylindrical rod exposing each steel types' sides to the liquid. The liquid Mg alloy used for this study is commercial AZ31 magnesium alloy, provided by RIST (Research Institute of Industrial Science and Technology), Korea.

Rotating Cylinder Experiments

The experimental setup is custom-made for the present experiments and is mainly composed of a resistance furnace containing a steel crucible, a rotation motor with steel specimen rod and a protection gas supply unit. A boron nitride coated steel crucible (diameter 23 cm x height 11.5 cm) is placed inside an open-well type resistance furnace. A removable cover is used to facilitate the sample insertion process as well as provide protection from atmospheric exposure to the Mg liquid. The removable cover has three small holes and one large hole used respectively for the gas inlet, thermocouple, hanging wire and observation glass cover. Temperature of the furnace interior and the liquid melt are measured by means of two thermocouples to control the melt temperature within ± 5 °C. Due to the fact that the process takes place at temperature above the melting point of magnesium (649 °C), the whole liquid system was kept under a protective gas atmosphere during the entire course of the present experiment above 300 °C. The protective gas mixture consists of N₂-1% SF₆, where the amount of SF₆ is higher than the normal industrial standard, and the flow rate of the protective gas was maintained at 200 ml/min, which is enough to protect the Mg melt from burning.

Several pieces of AZ31 ingots amounting to approximately 1.2 kg were placed within the holding crucible to give a liquid pool depth of about 8 cm; after attaining a temperature of 150 °C and evaporating the whole moisture for 30 minutes, the temperature was then raised to 700 °C for melting under protective atmosphere. After melting, the molten metal temperature was stabilized for 1 h. The steel rod was preheated above the melt in the crucible to about 400 °C. The steel rod was immersed up to approximately 2 to 3 cm in the liquid metal. The steel bar was then rotated at a speed of 100 rpm for 5 h. After the rotation

experiment, the steel bar was pulled out and suspended in the steel crucible for several minutes to cool down to about 400 °C under the protective gas atmosphere and then pulled out of the crucible to cool it down to room temperature. Fig. 1 illustrates the experimental procedure in the present study.

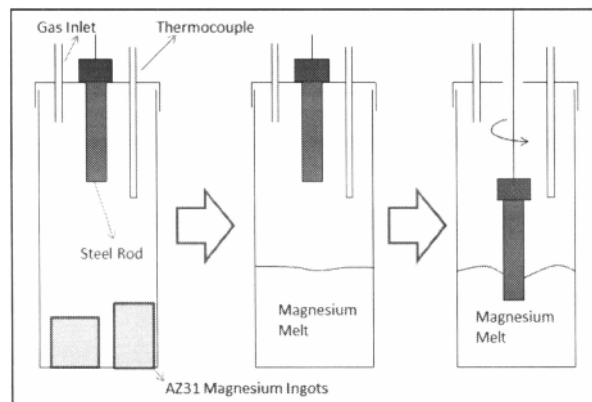


Figure 1. Schematic diagram of the experimental arrangements.

After the experiment, cross section morphologies and chemical compositions of the steel rod were examined using a PHILIPS XL-30 Scanning Electron Microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX from EDAX). Standard metallographic techniques were used for specimen preparation. Table 1 lists the experimental conditions and steel grades used in the present study.

Table 1. Experimental conditions for the rotating cylinder experiments and typical composition of the investigated steel grades.

Experiment	Duration (h)	RPM	% SF ₆	Temperature (°C)
AZ31 alloy	5	100	1	700

Steel grade	Chemical composition (wt%)
Low carbon	<0.1 C, <0.4 Mn
High carbon	0.6~1 C, 0.3~0.9 Mn
Stainless 316	<0.08 C, 16~18 Cr, 10~14 Ni, 2~3 Mo, <2 Mn
Stainless 400	<0.05 C, <1 Mn, 12~13 Cr, <1 Si

Results and Discussion

Figure 2 shows a sample steel rod after the rotating experiment. Brown crusts were observed to form on both of the carbon steels surfaces. Interestingly, XRD patterns indicate that the brown crust is a mixture of Fe₂O₃ (hematite) and MgFe₂O₄ (magnesium ferrite). MgF₂ and FeS were not detected. On the contrary, the Ni-Cr content inherent to the stainless steel's nature limited excess iron oxide formation and no visible crust formation was observed besides a slight discoloring on the surface. In addition, a white and yellowish powder (XRD pattern indicates the powder to be MgO) was collected from the specimen after experiment just above the melt level. This means that, although the protective N₂-1% SF₆ gas was used in the experiment, a small amount of oxygen entered into the crucible chamber through the small holes on the steel crucible cover and oxidized the steel bar to form Fe₂O₃, MgFe₂O₄ and MgO.

The SEM BSE micrographs of the respective steel samples at liquid Mg alloy interface are presented in Figs. 3 to 6. The micrographs were taken at two locations: one above the liquid level (exposed to the protective gas atmosphere) and one below the liquid level (immersed in liquid Mg alloys).

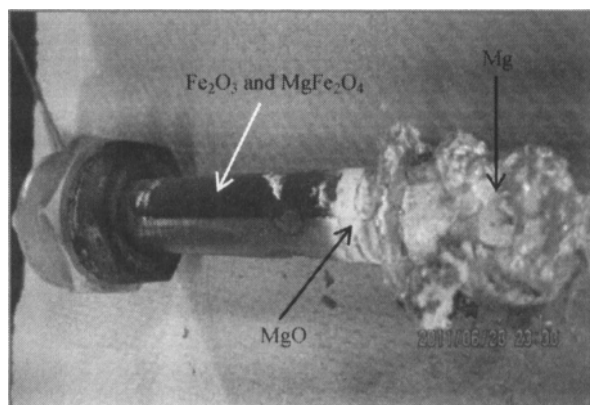


Figure 2. Typical view of steel rod after the rotating cylinder experiment. A thin layer of brown crust developed on top of both high and carbon steel and small amount of liquid Mg is still attached on the bottom of steel.

High Carbon Steel

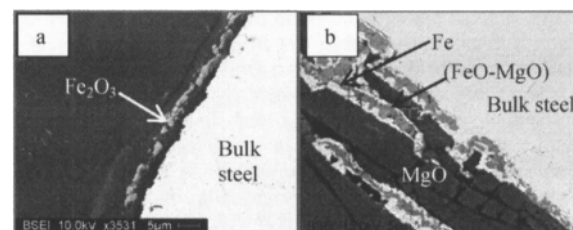


Figure 3. Surface of high carbon steel (a) above liquid level and (b) below liquid level after 5 h rotation cylinder experiment.

Despite being kept under a protective N₂-1% SF₆ atmosphere, it seems that the high carbon steel was still subjected to a high degree of oxidation throughout the entire experiment from the preheating up to the rotation stage. As can be seen in Fig. 3 (a), EDS analysis showed that a continuous Fe₂O₃ layer of 2 to 3 μm thickness was formed on the steel surface above the liquid level. It should also be noted that MgFe₂O₄ was detected on the brownish surface crust as shown in Fig. 2. This means that Fe₂O₃ is formed in the inner side of the oxidation layer and MgFe₂O₄ was formed later. Most probably, the Fe₂O₃ layer was formed during preheating at about 400 °C before Mg was molten. Then, Mg vapor is generated after the melting of Mg, which can be oxidized on the Fe₂O₃ layer to form MgFe₂O₄. It should be noted that oxidation of steel can easily occur even under protective gas atmosphere of N₂-1% SF₆ with very small leakage of atmospheric air, which can happen in real practice of a Mg melting furnace.

Fig. 3 (b) shows the degradation behavior of the pre-oxidized high carbon steel. Interestingly, the Fe₂O₃ layer was changed to MgO and Fe. Then, the MgO layer was torn off from the surface of the matrix steel. Occasionally, a (MgO-FeO) mixed oxide layer was also detected between MgO and Fe.

Low Carbon Steel

Similar to the high carbon steel, Fe_2O_3 was formed on the steel surface above the liquid level, as can be seen in Fig. 4(a). The layer is less continuous in comparison with the high carbon steel. It also has been reported by Lai [3] that low carbon steel is generally more resistant to corrosion than medium and high carbon steels. The degradation behavior of steel below liquid level by the molten Mg, shown in Fig. 4(b), is similar to that of high carbon steel. However, the amount of MgO formed on the surface was much smaller and therefore less degradation can be expected.

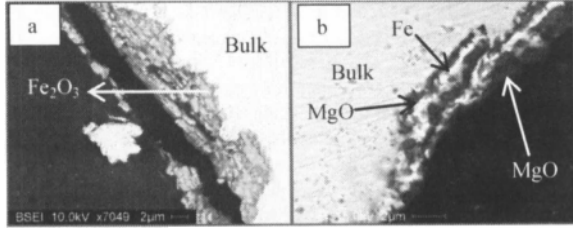


Figure 4. Surface of low carbon steel (a) above liquid level and (b) below liquid level after 5 h rotation cylinder experiment.

Stainless Steel 316

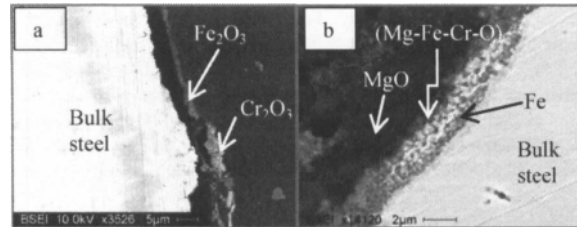


Figure 5. Surface of stainless steel 316 (a) above liquid horizon (b) below liquid horizon after 5 h rotation cylinder experiment.

As shown in Fig. 5(a), well known Cr_2O_3 and minor amount of Fe_2O_3 oxides were observed at the steel surface. Fig. 5(b) shows a micrograph image of steel sample 316 that was immersed in the Mg melt. The morphology of the steel surface is different from those of the above carbon steels. The external layer was MgO, and a network-shaped metallic Fe is covered by a mixed oxide of Mg-Fe-Cr-O, which seems to be a $\text{MgCr}_2\text{O}_4\text{-FeCr}_2\text{O}_4$ layer. Although small piece of Fe islands surrounded by MgO oxide was observed around the surface of stainless steel 316, the Mg-Fe-Cr-O layer seems to be strongly attached to the stainless steel matrix by the network-shaped Fe, which reduced the degradation of the stainless steel 316 by molten Mg.

Stainless Steel 400

Similar to stainless steel 316, EDS analysis indicate that Cr_2O_3 is formed at the surface of stainless steel 400 exposed to the protective gas, as seen in Fig. 6(a). However, Cr_2O_3 is formed inside the steel, while it formed a distinctive layer on the surface of stainless steel 316. That is, internal oxidation occurred for stainless steel 400, while external oxidation occurred for stainless steel 316. Consequently, the morphology of the steel degradation by molten Mg is different from the case of the stainless steel 316. Very complex network-shaped Fe (Fig. 6(b)) is directly connected to the steel matrix, and MgO oxide is formed in between the network. No trace of detached Fe or steel piece was observed near

stainless steel 400, which shows the very limited degradation of stainless steel 400 by liquid Mg.

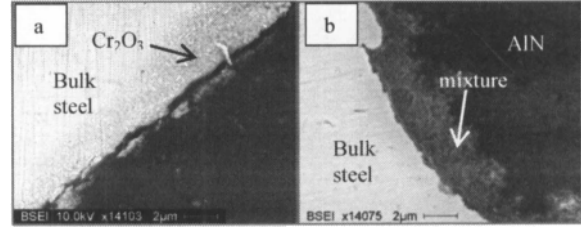
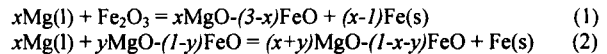


Figure 6. Surface of stainless steel 400 (a) above liquid level and (b) below liquid level after 5 h rotation cylinder experiment.

Corrosion Mechanism: Carbon Steels

Molten metal corrosion of a containment metal is often described by its solubility in the molten metal. This type of corrosion is simply a direct dissolution attack. A containment metal with high solubility to the molten metal would generally exhibit higher corrosion rates. In addition, as the temperature rises, the diffusion rate would also increase. Since the solubility of Fe in Mg at temperature below 700 °C is very limited (400 ppm), a direct dissolution type of corrosion is restricted.

The corrosion mechanism of steel by liquid Mg observed in the present study can be summarized as an "oxidation and reduction" process. Although Fe itself has very limited solubility in liquid Mg, once Fe oxide is formed on the steel surface, it can be reduced by Mg melt. This reaction can be easily understood by the following chemical reactions:



It is well known that MgO is more stable than Fe_2O_3 . The ΔG^0 of reaction (1) for $x = 3$ is equal to $-9.2 \cdot 10^5 \text{ J}$ at 700 °C [4-5]. Moreover, MgO and FeO can form a complete solid solution below 1300 °C. Therefore, the reduction of Fe_2O_3 by Mg can occur as in reaction (1) with the formation of the MgO-FeO magnesio-wustite solid solution. This can explain the formation of a mixed MgO-FeO layer in low and high carbon steels. Near the liquid Mg interface, the FeO in magnesio-wustite solid solution can be further reduced to lower FeO containing solid solution according to reaction (2) and eventually form pure MgO. The reduced solid Fe is already physically detached from the steel matrix and can be suspended in molten Mg. Part of them can be dissolved in molten Mg but most of them are expected to simply sink to the bottom of the crucible.

This two-stage corrosion mechanism involving the oxidation of the steel interface followed by a reduction by Mg is schematically illustrated in Fig. 7. At the oxidation stage (Fig. 7(a)), the steel surface can be oxidized by air leaked into the protective $\text{N}_2\text{-SF}_6$ gas atmosphere. Then, as this oxidized steel is immersed into molten Mg, the latter can react with Fe_2O_3 (Fig. 7(b)). In particular, if there are cracks in the Fe_2O_3 layer, liquid Mg can easily penetrate into the solid Fe_2O_3 layer and begin to reduce Fe_2O_3 to form a MgO-FeO solid solution. With the progress of the reduction, the Fe containing MgO-FeO particles can be detached from the surface of the steel matrix (Fig. 7(c)).

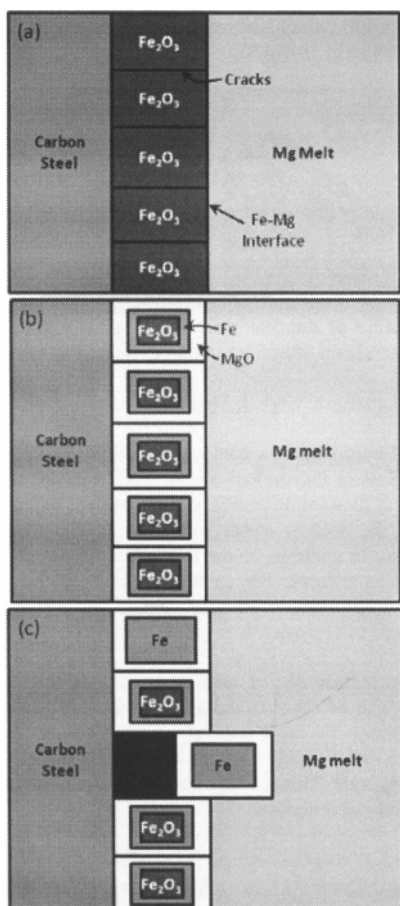
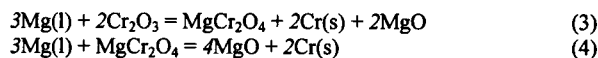


Figure 7. Schematic illustrating the two-step corrosion mechanism of carbon steel by Mg melt: (a) oxidation of the steel surface; (b-c) reduction of Fe_2O_3 and MgO-FeO solid solution by Mg melt.

Corrosion Mechanism: Stainless Steels

In the case of stainless steels, their corrosion mechanism is slightly different from that of carbon steel due to the formation of Cr_2O_3 oxide. Like Fe, the solubility of Cr in molten Mg is also very limited. Therefore, the reduction reactions can be:



The ΔG^0 of reactions (3) and (4) are, respectively, $-6.7 \cdot 10^5$ and $-5.7 \cdot 10^5$ J at 700°C [4-5], indicating that the reactions proceed spontaneously towards the reduction of Cr_2O_3 and MgCr_2O_4 by liquid Mg. The shape of Cr_2O_3 determines the reduction behavior. In the case of stainless steel 400, the internal oxidation behavior results in very interesting morphology after reduction as shown in Fig. 6(b).

Corrosion Resistance and Industrial Perspective

Among the four steel grades tested in the present study, the corrosion resistance against liquid Mg can be concluded as (from the more resistant to the less resistant): Stainless steel 400 > stainless steel 316 > low carbon steel > high carbon steel.

In the real operation of a Mg furnace, a steel crucible is typically used. In particular, low carbon steel is typically used in practice. As well-known, the presence of Fe in Mg alloys can cause severe corrosion problems through the formation of galvanic corrosion assemblage with the Mg matrix. In order to reduce the Fe concentration in molten Mg as much as possible, small amount of Al and Mn are added to make stable precipitates, $\text{Al}_3\text{Mn}_2\text{Fe}_2$. In this way, the soluble Fe concentration in liquid Mg can be reduced from several hundreds wt ppm level to 10-20 wt ppm level. Unfortunately, no alloying elements have been revealed to reduce the Cr or Ni levels in Mg like Fe. As Cr and Ni are enriched in Mg melt and their concentrations are hard to reduce, stainless steels are less common for Mg furnace materials.

However, from a purely corrosion view point, stainless steels 400 or 316 are superior to the carbon steels. In order to reduce the Fe pickup as much as possible, the oxidation of steel should be controlled well. One possibility to reduce Fe and Cr pickup from steel crucible is to replace the crucible of low carbon steel clad by stainless steel 400 only for the liquid Mg line.

Summary

Laboratory experiments on the corrosion of steels by liquid AZ31 were performed in this study. Four different steel grades were investigated in the present study: stainless steel 400, stainless steel 316, low carbon steel, and high carbon steel. It is found that the corrosion of the steels occurs by a two-stage process: oxidation of steel and reduction of the oxides by Mg melt. The corrosion resistance against Mg melt was found to be in the order of stainless steel 400 > stainless steel 316 > low carbon steel > high carbon steel.

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