Diagnosis and Analysis of Oxide Films in Cast Magnesium Alloys by Ultrasonic-Vibration Treatment

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Magnesium alloys with low density are important light metals, widely used in the aerospace and automotive industries and in the manufacture of communication devices, consumer-electronics appliances and computers products in recent years. However magnesium and magnesium alloys are the most reactive metals so that oxide films easily form on them during the melting or pouring process. These films are difficult to observe by optical micrograph. In this study we propose a simple method to observe oxide films entrapped in cast magnesium alloys. The oxide films are fractured as a result of cavitation erosion on the sample surface that occurs during ultrasonic-vibration treatment. The eroded areas become visible as differently shaped foggy marks. This method of observing and identifying foggy marks is shown to be useful in the diagnosis of oxide films in cast magnesium alloys. In addition, the presented method in the diagnosis of oxide films that formed on magnesium and aluminum alloys are also compared. [doi:10.2320/matertrans.MER2007213]

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1. Introduction

Magnesium and magnesium alloys are widely used in the making of automobile parts and in the communications and aerospace industry due to their excellent properties, such as high specific strength, good damping capability and low density. However magnesium alloys are very active and can cause a fire hazard. When magnesium alloys are melted or poured, the molten magnesium oxidizes readily to form an oxide film that easily entraps the metal and often forms at the interface of the matrix and magnesia or intermetallic compound. These oxide films can also serve as nucleation sites for the formation of pores or inclusions in cast magnesium alloys, which of cause accelerates fatigue crack propagation eventually leading to fatigue failure. In other words an oxide film is extremely harmful to the quality of cast magnesium. Consequently gating system design are important for reducing the amount of oxide film entrapped in cast magnesium alloys. Oxide films are relatively difficult to identify based on optical-microscope observations. Huang8 and Chen9,10 et al. proposed an ultrasonic-vibration method for the diagnosis of oxide films entrapped in cast aluminum alloys. The principles of the method are based on the phenomena of acoustic cavitation. A piezoelectric transducer uses mechanical vibration to propagate ultrasound through the liquid. This ultrasound generates alternating acoustic pressures of tension and compression. If the acoustic pressure is high enough that the liquid is subjected to tensile force during the negative cycle of the acoustic waves, the molecules of the liquid can be pulled away from one another and micro-bubbles or cavitation bubbles will form. During the positive ultrasound cycles, these cavitation bubbles will collapse, forming micro-jets and shock waves that instantaneously generate intense local heating and high pressure.11,12 These micro-jet impacts can develop pressures of about $2 \times 10^8$ Pa, and a local heating and cooling rate of above $10^9$ K/s.12 In fact, cavitation damage can be generated by the non-spherical symmetric collapse of a cavitation bubble, either at or near a solid surface. The micro-jets associated with shock waves that develop in the liquid function as a local erosive force or a cleaning action on the surface of the specimen. Oxide films in cast aluminum alloy become visible after an ultrasonic-vibration treatment. They show up on the polished surface of aluminum alloy specimens as white marks, scripts, spots or clouding.

The area of these white marks (foggy marks) increases in extent with an increase in the treatment time. Magnesium and aluminum not only have a different crystalline structure but also the type of oxide film is not the same, and the coherent extent with the matrix is different. Therefore, the diagnosis of oxide films in cast magnesium alloys by the above-mentioned ultrasonic-vibration method is a new approach and application. The purpose of this study is to focus on the diagnosis and analysis of oxide films in cast magnesium alloys. We adopt an ultrasonic-vibration treatment to investigate the cavitation erosion of oxide films entrapped in cast magnesium alloys. This technique combined with scanning...
electron microscopy (SEM) observations provides information for better understanding the shape and distribution of the oxide films in cast magnesium alloys. The elemental constituents present in the region of the oxide film are also evaluated by electron probe microanalyzer (EPMA). A series of schematic illustrations that describe the cavitation erosion of oxide film on the polished surface of magnesium alloys are also included.

2. Experimental Procedure

The experimental setup includes devices for acoustic pressure measurement and bubble capture, as shown in Fig. 1. The materials used in this study include pure magnesium, AM50A, AM60B and AZ91D magnesium alloys, and the chemical compositions of materials as shown in Table 1. Pure magnesium and magnesium alloy ingots were melted in an electric resistance furnace using protective gases of dried air mixed with SF$_6$ and CO$_2$. The molten liquids were poured into chilled copper molds to obtain samples 10 mm in thickness and 40 mm in diameter. After polishing and running spectrometer chemical analysis, the chilled samples were again polished with anhydrous alcohol prior to ultrasonic-vibration treatment.

An ultrasonic cleaner equipped with a stainless steel vessel was used. The vessel was filled with distilled water to a volume of 500–600 ml. During the treatment, the ultrasonic cleaner was operated at a frequency of 46 kHz with an initial ultrasound intensity of about 40 kw/m$^2$. To observe the sequential development of cavitation bubbles, the one side of the ultrasonic cleaner was cut out and sealed with a piece of glass. This served as a window for observing and recording the sequence of cavitation bubble formation. A high-speed digital camera with a top shutter speed of 1/16000 s and flash synchronization of up to 1/500 s, and a flash as a light source was used to capture images of cavitation bubbles that formed on the eroded surface of the sample. A PZT hydrophone, with a Fast Fourier Transfer (FFT) analyzer was used to measure the ultrasonic intensity or acoustic pressure in real time during the ultrasonic-vibration treatment. The hydrophone used to measure the acoustic pressure at the interface of liquid and solid was located 1 mm from the sample surface.

After a polished specimen was set on the bottom of the vessel, a short 10 s ultrasonic-vibration treatment was carried out at 46 kHz. White colored foggy marks with different shapes lumps, flakes, scripts or spots, were gradually revealed on the shiny surface of the specimen as the treatment time increased. The shape and area fraction of the foggy marks were observed and recorded. Each sample underwent the same process twice. After the ultrasonic-vibration treatment, the foggy marks on the polished sample surface could be clearly identified. A scanning electron microscopy (SEM) and an electron x-ray probe microanalyzer (EPMA) was used to observe the eroded oxide film on the surface of the treated samples and to analyze the constituents of the oxide films.

3. Results and Discussion

3.1 Acoustic cavitation bubbles and cavitation damage on the sample surface

The negative ultrasound pressure produced cavitation bubbles. This was related to the tensile strength of liquid, which increases with the purity of the liquid.$^{13-15}$ For pure water, the tensile strength is about 3 x 10$^7$ Pa.$^{16}$ The formation of cavitation bubbles in the liquid is thus mainly based on heterogeneous nucleation. When an ultrasound propagates in water, the existence of solid impurities submerged in the water or crevices in the container wall or on the sample surface can serve as nucleation sites for the formation of heterogeneous cavitation bubbles. These cavitation bubbles are subjected to the traction forces of an ultrasonic field; the bubbles can cluster to form bubble clouds or streaming patterns. These bubble clouds intensified the cavitation erosion on the surface of pure magnesium sample, as shown in Fig. 2. According to the description of
Krautkrämer,\textsuperscript{17}) acoustic impedance is the product of the density of an object and the velocity of the ultrasound, and is proportional to the square of the acoustic pressure. The acoustic impedances of water, Mg, MgO and MgAl\textsubscript{2}O\textsubscript{4} are \(1.48 \times 10^6\), \(10.98 \times 10^6\), \(34 \times 10^6\) and \(23.7 \times 10^6\) (kg/m\textsuperscript{2}/s), respectively. When an ultrasound travels from water into a specimen, the acoustic pressure at the boundary of the specimen intensifies due to the high acoustic impedance. A cavitation bubble can form at a site where a high acoustic pressure is exerted, especially in areas where an oxide film is present. In distilled water, the acoustic pressure measured near the oxide film showed a more distinct intensity than that measured near the magnesium matrix, as shown in Fig. 3. Cavitation bubbles in water occur due to heterogeneous nucleation during ultrasonic-vibration treatment. If such cavitation bubbles occur near an oxide film site, they will...
oscillate under the effects of the high-pressure amplitude. The cavitation bubbles will grow at the emerging site to form bubble clouds. These bubble clouds then collapse, especially near or on an oxide film, which generates large micro-jet impact intensities and shock waves that eroded the oxide film. Finally, the oxide films become detached from the matrix and show up on the sample as surface erosion.

3.2 Observations of foggy marks on the treated sample

In the experiments, polished chilled specimens were set in distilled water and subjected to ultrasonic-vibration treatment for 10 s. Several obvious marks or strips (foggy marks) appeared on the polished surface of the Mg, AM50A, AM60B and AZ91D magnesium alloys, as shown in Figs. 4(a)–(d) respectively. On the pure magnesium sample, the foggy marks mostly appeared as long strips. On the AM50A and AM60B alloy samples, the foggy marks showed up as shiny spots or lumps, and on the AZ91D alloy, they appeared as reveals fine-long strips. There was great variation in area fraction of the foggy marks on the different samples since the oxide film was not evenly distribute.

3.3 Identifying the constituents of the foggy marks on the treated sample

The foggy marks were observed by scanning electronic microscopy (SEM), and the elemental constituents of the foggy marks were studied with an electron x-ray probe microanalyzer (EPMA). The EPMA analysis of foggy marks in cast pure Mg, AM60B and AZ91D alloys are shown in Figs. 5–7 respectively. The results indicate that the foggy marked area was rich in oxygen, meaning that the existences of oxide films were confirmed. Figure 5(a) shows the fractured oxide film and several micro-cracks on the chilled magnesium sample. The EPMA mapping of the fractured oxide film shows that it mainly contains two elements, magnesium and oxygen, identified as MgO; see Figs. 5(b) and (c). These films were originally entrapped in the magnesium alloy ingot; the films displayed a flake-like morphology. Mg-Al alloys contain elemental Al that is soluble in magnesium so it diffuses out to form spinel \((\text{MgAl}_2\text{O}_4)\) during the melting process \((\text{Mg} + \text{Al} + \text{O} \rightarrow \text{MgAl}_2\text{O}_4\) or \(\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4\)). The Gibbs free energy of spinel is lower than that of magnesia therefore spinel could form at the interfacial layer between the magnesia film/or \(\text{Mg}_17\text{Al}_{12}\) and the matrix. The mechanism for the above result is based on the diffusion of a solute Al to the interface, to react with oxygen and magnesia film. The elastic modus of spinel and magnesia are 380 GPa and 250 GPa, respectively. Spinel is more brittle than magnesia, therefore for an oxide film that contains spinel and magnesia, when a polished sample is subjected to ultrasonic-vibration treatment, and micro-jets impact the oxide film, cracks will be initiated in the spinel. EPMA mapping of oxide films entrapped in cast AM60B alloy show that it is rich in elemental Al, O and Mg, as shown in Figs. 6(b)–6(d). The fractured area is rich in aluminum, which shows up locally at the interface between the matrix and the oxide film, indicating the existence of spinel. Oxide films can also serve
as nucleation sites for the formation of pores or inclusions in cast magnesium alloys. Micro-pores and a few particle or needle-like compounds could be found close to the fractured area. These compounds are composed of Al and Mn that usually occurs along with spinel, see Figs. 6(a), 6(b) and 6(e). Mg$_{17}$Al$_{12}$ is the main compound in AZ91D magnesium alloy. It is always located at grain boundaries or at shrinkage holes, which are rich in elemental aluminum and oxygen. Consequently, oxide compounds form was easily, especially spinel compounds owing to the lower free energy. Figure 7(a) shows an oxide film on the polished surface of an AZ91D sample after an ultrasonic-vibration treatment 10 s. The fractured areas along with micro-cracks are rich in elemental Al, O and Mg, as seen in Figs. 7(b)–(d). These cracks propagate along the boundaries of the lengthy Mg$_{17}$Al$_{12}$ compound that existed spinel oxide.

3.4 Fracturing mode of the eroded oxide film
Magnesia and spinel oxides are more brittle than the magnesium matrix and intermetallic compounds, Mg$_{17}$Al$_{12}$ and Al$_8$Mn$_5$. When a polished sample is subjected to an ultrasonic-vibration treatment, micro-jets will impact the oxide film. Since a greater deformation strain can be induced in the magnesium matrix and intermetallic compounds than in the oxide film, cracks initiated at the oxide film sites. These cracks grow and became linked together, leading to fracturing of the oxide film. Small oxide particles can become detached from the oxide film, eventually eroding the surface of the treated sample. The erosion of the oxide film shows up as a foggy mark that can be seen optically. Figures 8(a)–(e) display the eroded surface of pure Mg, AM50A, AM60B and AZ91D alloy samples, after a 10 s ultrasonic-vibration treatment. On pure magnesium, the oxide film is rich in...
Magnesia. There are two fracture modes, a flake-like mode, where oxide films were originally entrapped in cast magnesium ingot, (Fig. 8(a)), and a nodule-like mode, where the fractured surface mostly consisted detached equiaxed magnesia grains, for oxide films that mainly develop in melting or pouring process, (Fig. 8(b)). Observation of the inside of the cavity shows micro-channels which can act as an easy path allowing the diffusion of Mg, which reacts with the oxygen to develop the nodular structure (MgO). Oxidation persists and the nodular structure coarsening causes the micro-channels to gradually fill up the interface between the magnesium matrix and the oxide film. In the AM50A alloy, the fractured surface shows a granular fracture mode. The surface fracturing occurs as long cracks which are produced by the failure of the spinel oxide, (Fig. 8(c)). In the AM60B alloy, the surface fractures mostly consisted of detached plate-like spinel, (Fig. 8(d)). The fractured surface of AZ91D also displayed detached plate-like spinel, (Fig. 8(e)). Some areas were eroded. Cavities were produced from the micro-jet impacts during the collapse of cavitation bubbles. Eventually, the cavities could become linked together, and the oxide films became detached from the matrix, generating surface erosion on the treated sample. In short, the fracture morphology of oxide film depending on the aluminum content in the alloys. Increasing the aluminum content increases the plate-like and decreases the equiaxed-type of surface fractures.

3.5 Mechanisms for cavitation erosion of the oxide film

In the experiments, white marks, script, spots or clouding gradually appeared on the sample surface during ultrasonic-vibration treatment in distilled water. The white marks (or foggy marks) indicated oxide films erosion. Increasing the treatment time increased the extent of the fracturing of the oxide film. The fracturing of the oxide film led to particles being detached from the matrix which produced a rough or eroded surface. The crack sites on the eroded surface can provided potent sites for the nucleation of cavitation bubbles, which eventually formed cavitation clouds. These bubble clouds could develop streaming patterns in distilled water, as shown in Fig. 9.

Figure 10 illustrates the cavitation erosion mechanisms in the oxide films of cast magnesium during ultrasonic-vibration treatment. An oxide film on the sample surface would exert the high acoustic pressure when the magnesium alloy sample was subjected to ultrasonic-vibration treatment in distilled water. The high acoustic pressure produced cavitation bubble nucleation and formation near oxide film sites on the magnesium alloy sample, see Figs. 9 and 10(a). The collapse of a cavitation bubble near the oxide film would forms a micro-jet. The micro-jet has an impact on and fractures the oxide films. The enlargement of ‘a’ shows the fracturing morphologies of oxide film; flake-like and nodule-like mode, as seen in Figs. 8(a) and 8(b). The cracks in the oxide film provided potent sites for the nucleation of bubble clouds, which result in the development of intense micro-jet impacts, see Fig. 9. The micro-cracks were then linked together, leading to oxide particles become detached from the oxide film, generating surface erosion on the treated sample; see Figs. 5(a) and 10(b). The enlarged portion in part ‘b’
confirms that surface erosion tends to encourage the nucleation of bubble clouds. These bubble clouds intensify the impact of the micro-jets and shock waves to form streaming patterns; see Figs. 9 and 10(c). In the end, the surface of the treated sample shows differently shaped foggy marks.

3.6 Comparison of diagnosing oxide films in cast aluminum and magnesium alloys

The description of diagnosing oxide films in cast aluminum alloys proposed by Huang\textsuperscript{8} and Chen et al.\textsuperscript{9,10} that associated with previous results are summarized in Table 2. Cavitation bubbles are readily at the sites neighboring with oxide film, such as the interface of different oxides where the bubbles readily collapse. Therefore micro-jets have great impact to areas near the interfacial boundaries of oxides resulting in micro-cracks initiation. For Mg-based alloys,
Formation of bubble clouds and development of streaming patterns

More bubbles nucleate and initiate at the eroded oxide film site.

Table 2 Comparison of diagnosing oxide films in cast Al-based and Mg-based alloys by ultrasonic-vibration treatment.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Mg-based alloys</th>
<th>Al-based alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pure Mg</td>
<td>AZ91D</td>
</tr>
<tr>
<td>Main oxides</td>
<td>magnesia</td>
<td>magnesia + spinel</td>
</tr>
<tr>
<td>Acoustic impedance (kg/m&lt;sup&gt;2&lt;/sup&gt;/s)</td>
<td>Mg: 10.98 × 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>magnesia: 34 × 10&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td>The site of initiated crack</td>
<td>magnesia/ Mg&lt;sub&gt;17&lt;/sub&gt;Al&lt;sub&gt;12&lt;/sub&gt;</td>
<td>spinel/ Mg&lt;sub&gt;17&lt;/sub&gt;Al&lt;sub&gt;12&lt;/sub&gt;</td>
</tr>
<tr>
<td>Sharp corner effect</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Order of the rate for showing foggy marks</td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>Morphology of foggy marks</td>
<td>long strips</td>
<td>fine-long strips</td>
</tr>
<tr>
<td>Contrast between foggy mark and matrix</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>Fractured mode of the eroded oxide films</td>
<td>flake-like or nodule-like</td>
<td>plate-like</td>
</tr>
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Fig. 10 Schematic illustration showing the sequence: (a) micro-jet formation in collapsing bubble, and the fractured mode of the eroded oxide film; (b) erosion of oxide film (c) bubble cloud intensification and streaming pattern development.
micro-cracks propagate along the boundaries of the lengthy Mg$_{17}$Al$_{12}$ compound that existed spinel oxide. For Al-based alloys, the boundaries between different oxides develop a protruding interface in the polished surface of sample. This protruding boundary acts as potential site for collapsing bubbles to form micro-jets, and leads to sharp corner effect can intensify the subjecting stress to fracture the oxides.

Acoustic impedance is the resistance of sound traveling in the materials. The rate for showing foggy marks is related to acoustic impedance of materials. High acoustic impedance materials such as Al-based alloys have lower rate than Mg-based alloys for showing foggy marks during ultrasonic-vibration treatment. For Al-XSi alloys, the existence of eutectic silicon increases the damping capacity, and reduces the intensity of micro-jet impacts. Therefore the oxide film fractures at the slowest rate to show foggy marks among all the alloys listed in Table 2. The foggy marks which could be visible optically need at specific contrast. Al-based alloys showing the better contrast between foggy marks and matrix. For Al-based and Mg-based alloys, the fracture morphology of oxide films depends on aluminum contents. Increasing the aluminum content increases the plate-like and decreases the equiaxed-type of surface fractures.

4. Conclusions

Cavitation bubbles formed in distilled water due to heterogeneous nucleation. The cavitation bubbles collapsed generating micro-jet impacts and shock waves at or near the oxide film surface. These micro-jet impacts could fracture the oxide film so the oxide particles became detached from the oxide film and eroded the polished surface. This eroded surface showing up visual foggy marks. The foggy marks can indicate the area of oxide film erosion on the treated sample. The morphology of oxide film entrapped in the castings normally depends on its constituents. In this study we not only describe the mechanism for cavitation erosion of oxide films, but also indicate that for magnesium alloys, the fracture morphology of oxide film includes equiaxed, granular, nodular and plate-like shapes, depending on the aluminum content in cast magnesium alloys. Increasing the aluminum content increases the plate-like and decreases the equiaxed-type of surface fractures. The micro-cracks extend into the matrix of the oxide film, can serve as nucleation sites for the generation of intense bubble clouds associated with micro-jet and shock waves. Great impulse pressure is produced, which forces oxide particles to become detached from the oxide film to show up as foggy marks. Comparison of diagnosing oxide films in cast magnesium and aluminum alloys by ultrasonic-vibration treatment. The main differences are the showing rate and the contrast of foggy marks.

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