EFFECT OF SOLIDIFICATION RATE ON CORROSION RESISTANCE OF CAST Al-10Mg₂Si IN-SITU COMPOSITES

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ABSTRACT

The hypoeutectic Al-10Mg₂Si (wt%) composites, also denoted as Al-6.3Mg-3.7Si (wt%) alloy, were cast in a steel step mould, in which different solidification rates were obtained. The microstructural characterizations were made by optical microscope and XRD. Corrosion performances were measured by immersion and electrochemical corrosion tests in 3.5% NaCl solution. Microstructure analysis showed that all the alloys consisted of α-Al, Chinese script type Mg₂Si and needle-like Al₅FeSi phases. Increasing solidification rate resulted in a remarkable refinement of Chinese script-like eutectic Mg₂Si phases. Corrosion tests revealed that increasing solidification rate improved the corrosion resistance of Al-10Mg₂Si composites due to the more uniform distribution of Mg₂Si phases and the stabilization of protective oxide films on the sample surface.

Keywords: Aluminum alloys, solidification, casting, microstructure, corrosion

DÖKÜM Al-10Mg₂Si İN-SİTÜ KOMPOZİTLERİN KOROZYON DİRENCİNE KATILAŞMA HIZININ ETKİSİ

ÖZ

Al-6.3Mg-3.7Si (ağ.%) a尕şımı olarak da adlandırılan hipoötektik Al-10Mg₂Si (ağ.%) kompozitleri, farklı katlaeama oranlarının elde edildiги bir kademeli çelik kalba dökülmüştür. Mikroyapısal karakterizasyonlar optik mikroskop ve XRD ile yapılmıştır. Korozyon performansları %3.5 NaCl çözeltisinde daldırma ve elektrokimyasal korozyon testleri ile ölçülmüştür. Mikroyapı analizleri, tüm a尕şmlarda α-Al, Çin yazısi şekilli Mg₂Si ve iğnemsi Al₅FeSi fazlarının oluştuşunu göstermiştir. Katlaeama hzndaki artı. Çin yazısi şekilli ötektik Mg₂Si fazlarının önemli derece küçülmesine neden olmuştur. Korozyon testleri sonucunda artan katlaeama hızının Al-10Mg₂Si kompozitlerinin korozyon direncini arttırdığı görülmüştür ve bu da Mg₂Si fazlarının daha düzgün dağılımı ve numune yüzeyindeki koruyucu oksit filmlerinin daha kararlı hale gelmesi ile meydana gelmiştir.

Anahtar kelimeler: Alüminyum a尕şmları, katlaeama, döküm, mikroyapı, korozyon

1. INTRODUCTION

Over the past few decades, cast aluminum alloys have attracted special attention mainly in automotive industry because of their high strength, low density and good castability compared to steel counterparts [1,2]. However, there is still need for improving their mechanical and corrosion properties to make them applicable for high performance materials. Regarding this, Al-Mg₂Si in-situ composites can be considered as a potential material since

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they possess high melting temperature, high strength at elevated temperature and low thermal expansion [3]. Mg$_2$Si intermetallic compounds as the reinforcing material in Al matrix are the main reason for the improvement of properties and their size, distribution and morphology specify the final properties of the Al alloys. However, in hypereutectic Al-Mg$_2$Si composites, coarse and skeleton shaped Mg$_2$Si particles contain high stress concentration at their sharp edges and this leads to premature crack propagation and accordingly deteriorates mechanical properties [2,4]. Furthermore, the flake-like eutectic Mg$_2$Si particles cannot impede the crack propagation effectively either [5]. Among the Mg$_2$Si particles with different shapes, truncated octahedron crystals are more beneficial to mechanical properties [6]. Therefore, it is necessary to alter the size and distribution of Mg$_2$Si particles in order to make them beneficial. Recently, much efforts have been made on refinement of Mg$_2$Si compounds by mainly employment of different alloying elements such as Bi [7,8], Sb [9], Ce [2], Sr [10] and Gd [11]. Wu et al. showed that the morphology of the eutectic Mg$_2$Si phase transformed from plate-like structure to a thin coral-like and fibrous one by increasing Bi addition to Al-10Mg$_2$Si alloy [7]. Wang et al. reported that 0.5 wt% Sb addition changed the morphology of eutectic Mg$_2$Si phase from coarse dentrite to small polyhedral shape and significantly improved the mechanical properties of Al-20Mg$_2$Si-4Cu alloy [9]. Nordin et al. showed that after Ce addition, the skeleton Mg$_2$Si transformed to polygonal shape with decreased size and more uniform distribution and flake-like Mg$_2$Si phase changed to rod-like morphology [2]. It was also reported in the same study that the needle-like Al$_3$FeSi phase was refined by Ce addition. Furthermore, it was showed in another study that Sr addition resulted in a transformation of primary Mg$_2$Si phase from imperfect octahedron to polygonal morphology and also a transformation of eutectic Chinese script type Mg$_2$Si phase to fibrous and fish-bone morphology [10]. Ghandvpar et al. showed that 1 wt% Gd addition altered the primary and eutectic Mg$_2$Si morphology from coarse dentritic and flake-like to truncated octahedral and rod-like shape, respectively [3,11]. Apart from this, it has been reported that different cooling conditions may result in a significant microstructural changes and thus mechanical properties [1,3,12]. Wang et al. [12] showed that increasing cooling rate led to a transformation of the morphology of primary Mg$_2$Si phase from perfect octahedron to truncated octahedron. However, there is no study in the literature about the effects of solidification rate on the microstructure of hypoeutectic Al-Mg$_2$Si in-situ composites. Furthermore, there is very limited study on the corrosion properties of Al-Mg$_2$Si in-situ composites and this study aims to clarify the relationship between the microstructural changes caused by different solidification rates and the corrosion properties of Al-Mg$_2$Si in-situ composites.

2. MATERIALS AND METHOD

Al-6.3Mg-3.7Si (wt%) alloy, corresponding to hypoeutectic Al-10Mg$_2$Si alloy, was prepared in an electrical resistance furnace by use of pure Al ingots (≥ 99 wt%), pure Mg ingots (≥ 99.5 wt%) and Al-30Si (wt%) master alloys. Firstly, Al ingots and Al-30Si master alloys were melted at 750 °C and Mg ingots (with an extra addition of 15% to compensate the oxidation loss) were added into the melt at this temperature. Subsequently, 0.5 wt% dry C$_2$Cl$_6$ degassing tablets were applied. After stirring for 10 min and cleaning off the slag, the melt was poured into a steel step mould preheated to 200 °C. As shown in Fig. 1, the stepped design contains different section thicknesses, which provides different cooling rates. The temperature of each section was simultaneously measured at their centre by K-type thermocouples connected to a data acquisition equipment. The thermocouples were already placed in the mould before pouring the melt. After the solidification, the thermocouples were cut off and the cast alloy was sectioned as illustrated in Fig. 1. The chemical composition of the alloy taken from section 2 was measured by wave-length dispersion X-ray fluorescence (XRF-Rigaku-ZSX Primus II) and the results are given in Table 1. Because the chemical composition results were in line with the alloy design, the casting process was not repeated.

Table 1. Chemical compositions of the studied alloy (wt%)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Ca</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-10Mg2Si</td>
<td>6.26</td>
<td>3.85</td>
<td>0.19</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

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Figure 1. Schematic diagram of stepped design permanent mould

Metallographic samples were taken from near centre of each section and standard routine was used for mechanical grinding and polishing. After that, an etchant of 1 vol% HF in water solution was used for 20 s. Microstructures were taken by optical microscope (OM). The constituent phases were analysed by Rigaku Ultima IV X-ray diffractometer (XRD).

The constant immersion corrosion test specimens were cut from the near centre of each section as rectangular shape with the dimension of 20 mm x 10 mm x 2 mm. The samples were ground up to 2500 grid emery paper before the immersion tests. After that, the specimens were immersed in 3.5 wt% NaCl solution for 12 days at room temperature. The removal of corrosion products formed on the surface after the immersion tests was done by dipping in 50 vol% HNO3 solution for 3 min. Then the weight loss measurements were made and corrosion rates were calculated. The cross sections of the corroded surfaces were analysed by OM. At least three specimens were used for the immersion tests for each section. The electrochemical corrosion tests were also carried out in 3.5 wt% NaCl solution. A classical three-electrode cell was used with a graphite rod as counter electrode, a saturated calomel electrode (SCE) as reference electrode and the sample as working electrode. Gamry model PC4/300 mA potentiostat was used for both potentiodynamic polarization and potentiostatic electrochemical impedance spectroscopy (EIS) tests. The polarization curves were obtained at a scan rate of 1 mVs-1, starting from -0.25 V (vs. Eoc) to +0.25 V (vs. Eoc). The corrosion current densities were calculated by Tafel extrapolation method. In the EIS tests, the frequency range was from 60 kHz to 0.4 Hz and the voltage amplitude was set to 20 mV. Both electrochemical tests were repeated at least three times to supply reproducibility.

3. RESULTS AND DISCUSSION

The cooling curves of the Al-10Mg2Si composites simultaneously measured during solidification are presented in Fig. 2. It is evident that the cooling rate during solidification gradually decreased as stepping up in the steel mould, meaning that sections with larger thickness cooled more slowly. The average cooling rate can be estimated by [13]

\[ V_{\text{average}} = \frac{(T_1 - T_2)}{\Delta t} \]  

Eq. 1

where \( V_{\text{average}} \) is the average cooling rate, \( T_1 \) is the initial temperature, \( T_2 \) is the final temperature and \( \Delta t \) is the time passed between these temperatures. Here, the final temperature can be chosen as 500 °C. According to Eq. 1, the average cooling rates of the Al-10Mg2Si composites calculated as 0.78, 0.33 and 0.17 °C/s at the sections of 1, 2 and 3, respectively.
Cooling curves of the Al-10Mg$_2$Si alloys during casting and solidification

Fig. 3 shows the XRD patterns of the Al-10Mg$_2$Si alloy. Since different cooling rates did not lead to any formation of a new compound, only the XRD pattern taken from the Section 2 was presented in Fig. 3. It can be seen that the constituent phases consisted of $\alpha$-Al, Mg$_2$Si and Al$_5$FeSi phases in the Al-10Mg$_2$Si alloy. From Fig. 4, the morphology and distribution of the intermetallic phases can be seen clearly. According to Al-Mg$_2$Si phase diagram [14], $\alpha$-Al + Mg$_2$Si$_{\text{eutectic}}$ phases form after the solidification of Al-10wt% Mg$_2$Si alloy. The eutectic Mg$_2$Si phases formed as the shape of Chinese script consisting of thin strips in a white $\alpha$-Al matrix. Similar Chinese script-like morphology of Mg$_2$Si phases were observed in previous studies [3,7,8,15]. In Fig. 4, the microstructures of the sections having different cooling rates contained nearly the same amount of second phases. However, the size of Chinese script-like eutectic Mg$_2$Si phases exhibited a remarkable refinement with increasing cooling rate. The specimen from Section 1 revealed more refined microstructure whereas the second phases were the largest in the microstructure taken from Section 3. The Al$_5$FeSi phases were identified in the microstructures based on its distinctive needle-like morphology as it has been reported in previous studies [2,16,17]. The Al$_5$FeSi usually form in the remaining solidified liquid when there is Fe in the Al-Si system even with small fraction [16]. This phase is very hard and brittle and does not have a strong bond with the Al matrix [18].

According to sludge factor (SF), which calculated as $\text{SF} = 1 \text{ wt}\% \text{Fe} + 2 \text{ wt}\% \text{Mn} + 3 \text{ wt}\% \text{Cr}$, a SF value below 2 will not give rise to sludge formation at a casting temperature of 650°C and above [19]. In the present study, the SF factor was calculated as 0.3 according to Table 1, which is much lower than 2. Accordingly, no star-like or exploded sludge formation containing high amounts of Al, Si, Fe, Mn and Cr were observed as reported in previous studies for the alloys having SF factor mostly above 2 [18,19]. However, as outlined above, although no Fe addition was made in this study, the formation of Al$_5$FeSi phase was due to the Fe contamination caused by the impurity elements in the ingots used during casting. It is also worth noting that the length of needle-like Al$_5$FeSi phases increased with decreasing cooling rate as it can be seen in Fig. 4. It is because the growth of Al$_5$FeSi phase becomes difficult at faster cooling rates since the precipitation approaches the solidification onset of eutectic Al-Si [20]. Seifeddine et al. [21] showed that needle-like Al$_5$FeSi phase can form even at high cooling rates and high ratio of Mn to Fe. Therefore, the complete removal of these harmful precipitates is challenging.
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Figure 3. XRD pattern of the Al-10Mg2Si alloys taken from Section 2

Figure 4. Microstructures of the Al-10Mg2Si alloys with different magnifications taken from (a,b) Section 1, (c,d) Section 2 and (e,f) Section 3
The weight loss measurements obtained from the immersion tests at different days are presented in Fig. 5. The weight loss values increased gradually with increasing immersion time for all the sections. It seems that the corrosion resistance of Al-10Mg2Si composite was drastically improved as the solidification rate increased. The alloy taken from Section 1 showed the best corrosion performance. The results of the potentiodynamic polarization tests are illustrated in Fig. 6. The results showed that the corrosion potential values (E\text{corr}) did not show a considerable change. However, at the fastest cooling rate, the E\text{corr} values were shifted toward to more noble value. Furthermore, it is agreed that higher corrosion current density values (i\text{corr}) characterize higher corrosion rate [22]. In the present study, the i\text{corr} values, obtained from the polarization curves in Fig. 6, were estimated as 4.78, 5.96 and 11.4 μA/cm² for Section 1, Section 2 and Section 3, respectively. Therefore, the corrosion rate decreased as the solidification rate increased, revealing that the results were in line with the immersion test results shown in Fig. 5.

![Figure 5. Immersion test results of the Al-10Mg2Si alloys](image)

![Figure 6. Potentiodynamic polarization curves of Al-10Mg2Si alloys](image)

The Nyquist plots of the studied alloys with corresponding equivalent circuit are demonstrated in Fig. 7. As it can be seen, all the EIS spectras exhibited one capacitive loop at medium frequencies. The only distinct difference among the EIS spectras seemed to be the diameters of the arcs, indicating that their corrosion rates were different.
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based on the microstructural changes. Generally speaking, the larger medium frequency capacitive loop indicates an improvement of the corrosion resistance. In Fig. 7, the diameter of the capacitive loop for the Section 1 was the larger compared to other sections and it became smaller with decreasing solidification rate. This indicated that the higher solidification rate led to better corrosion resistance due to the stabilization of the protective oxide film on the surface [23]. Furthermore, the EIS test results were fitted in accordance with the equivalent circuit which illustrated as the inset in Fig. 7. In that equivalent circuit model, $R_s$, $R_1$ and $R_2$ represent solution resistance, corrosion product resistance at the sample surface and charge transfer resistance, respectively. CPE$_1$ and CPE$_2$ are the constant phase elements, which characterize the capacity of the oxide film and the electric double layer capacity at the interface of solution and sample. It is generally accepted that the $R_1$ and $R_2$ values have a direct proportional to corrosion resistance. The higher $R_1$ and $R_2$ values indicate more difficult charge transfer between the sample and solution [24,25]. The $R_1$ values of 473, 305 and 118 $\Omega$/cm$^2$ and the $R_2$ values of 1623, 1014, 773 $\Omega$/cm$^2$ were calculated for the alloys taken from Section 1, Section 2 and Section 3, respectively. It is evident that both resistance values showed a decrease as the solidification rate decreased, indicating that higher solidification rate induced more stable protective layer of oxide film and improved corrosion resistance. Ozturk et al. [26] also reported similar capacitive loops for A356 alloy with and without Sr additions and resistance of oxide layer value found the highest in Sr-modified samples, indicating a barrier effect caused by Sr addition.

Both the immersion and electrochemical corrosion tests showed that higher cooling rates of Al-10Mg$_2$Si composites during solidification can improve the corrosion resistance. Since the alloys studied in this study have the same chemical composition but different solidification rates and thus different microstructural characteristics, the difference in the corrosion rates can be explained by only the microstructure differences among the alloys. As outlined earlier, higher solidification rate resulted in finer Chinese script type Mg$_2$Si intermetallics (see Fig. 4). Abdel Rehim et al. showed that the resistance of the protective film increased and the pitting corrosion resistance was improved by Si addition to Al [27]. Additionally, the role of Mg$_2$Si intermetallics on corrosion resistance of Al alloys was investigated by Escalera-Lozano et al. and they reported that Mg$_2$Si tended to form MgO and SiO$_2$ oxides and these oxides protected Mg$_2$Si particles from microgalvanic corrosion with $\alpha$-Al matrix [23]. They also reported that Al-Fe-Si containing intermetallics did not affect the corrosion resistance. However, Arrabal et al. [28] measured the surface potential maps of A356 alloy by Kelvin probe force microscopy and showed that Al-Fe-Si intermetallic had higher potentials than the $\alpha$-Al, meaning that it was cathodic to $\alpha$-Al matrix and Mg$_2$Si intermetallic exhibited more negative potential, indicating an anodic behavior with respect to $\alpha$-Al. It was also reported in several studies that in Al-Mg$_2$Si composites, potential of Mg$_2$Si is negative to that of $\alpha$-Al at the initial stage of corrosion and thus, corrosion initiates at Mg$_2$Si particles by dissolution of Mg and results in an enrichment of Si in these particles [29,30]. Eventually, Mg$_2$Si particles became cathode and led to formation of pits.

The SEM micrographs of the corroded surfaces after 12 h immersion tests are illustrated in Fig. 8. It can be seen that none of the studied alloys exhibited severe corrosion throughout the surface. Furthermore, it is also clear that $\alpha$-Al matrix phase in the studied alloys showed very few dissolution whereas most of the dissolution occurred
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around second phase particles. As stated earlier, Al₅FeSi, having higher potentials than α-Al, always acted as cathode during the corrosion process and caused degradation around (dissimilar to Ref. [23]) it while the adverse effects of Mg₂Si phase on the corrosion propagation were seen as the corrosion proceeded as dissolution of matrix around the particles due to the polarity conversion between Mg₂Si and α-Al. Since the size of Al₅FeSi phase in the alloy Section 1 was much smaller than that in the other sections, the alloy Section 1 exhibited lower weight loss and better corrosion resistance.

Therefore, the corrosion improvement by increased solidification rate in this study can be attributed to the following aspects. Firstly, the formation of more stable oxide films and accordingly protection of microgalvanic coupling of Al₅FeSi and Mg₂Si particles with α-Al matrix. The finer Chinese script type Mg₂Si consisting of tiny Mg₂Si particles with larger surface area and their uniform distribution likely resulted in formation of more MgO and SiO₂ oxides and stabilized the protective surface film. Secondly, the finer Al₅FeSi phases at higher cooling rates resulted in less localized corrosion attack since they can act as local cathodic sites during the corrosion process because of their higher potential compared to α-Al [28,30]. Accordingly, the refinement of Chinese script type Mg₂Si and needle-like Al₅FeSi phases can play a beneficial role on the corrosion protection of Al-Mg₂Si in-situ composites from further attack in NaCl solution.

Figure 8. SEM micrographs of the corroded surfaces after 12 h immersion in 3.5 % NaCl solution after removal of corrosion product: (a) Section 1, (b) Section 2 and (c) Section 3.

4. CONCLUSION

Al-10Mg₂Si alloys were successfully cast in a steel step mould to provide different solidification rates. The corrosion resistances were measured by immersion and electrochemical tests and following conclusions were drawn:

- The constituent phases consisted of α-Al, Mg₂Si and Al₅FeSi phases in the Al-10Mg₂Si alloys.
- The eutectic Mg₂Si phases formed as the shape of Chinese script consisting of thin strips in a white α-Al matrix.
- The Chinese script-like eutectic Mg₂Si phases exhibited a remarkable refinement with increasing cooling rate.
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- Both the immersion and electrochemical corrosion tests showed that increasing solidification rate improved the corrosion resistance of Al-10Mg2Si composites.
- The corrosion improvement by increased solidification rate was attributed to the formation of more stable oxide films and accordingly protection of microgalvanic coupling of Mg2Si particles with α-Al matrix caused by more uniform distribution of tiny Mg2Si particles with larger surface area and decreased local cathodic effects of needle-like Al3FeSi phases with increasing solidification rate.

REFERENCES


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