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Corrosion and passivation behavior of Mg–Zn–Y–Al alloys prepared by cooling rate-controlled solidification

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ABSTRACT

Highly corrosion-resistant nanocrystalline Mg–Zn–Y–Al multi-phase alloys have been prepared by consolidation of rapidly solidified (RS) ribbons. The relation between corrosion behavior and microstructure evolution of Mg–Zn–Y–Al alloys with a long period stacking ordered phase has been investigated. In order to clarify the influence of rapid solidification on the occurrence of localized corrosion such as filiform corrosion, several $Mg_{96.75}Zn_{0.75}Y_2Al_{0.5}$ (at.%) alloys with different cooling rates are fabricated by the gravity casting, copper mould injection casting and melt-spinning techniques and their corrosion behavior and microstructures are examined by the salt water immersion test, electrochemical measurements, GDOES, XRD, SEM and TEM. To clarify the effect of aluminium addition on the improvement in corrosion resistance of the alloys, several $Mg_{97.25-x}Zn_{0.75}Y_2Al_x$ alloys with different aluminium contents are fabricated by consolidating RS ribbons and the formation of corroded films on the Mg–Zn–Y–Al alloys have been investigated. Rapid solidification brings about the grain refinement and an increase in the solid solubility of zinc, yttrium and aluminium into the magnesium matrix, enhancing microstructural and electrochemical homogeneity, which in turn enhanced corrosion resistance. The addition of aluminium to magnesium can modify the structure and chemical composition of surface films and improves the resistance to local breakdown of the films.

1. Introduction

Standing first on the list of light structural materials, magnesium alloys have been attracting great attention as one of the key engineering materials for automobile, railway, and aeronautical applications where weight reduction is of importance [1,2]. Moreover, it also deserves special mention that the advantages of magnesium metal are not confined to their light weight. Recently magnesium has proved to be a suitable candidate for metallic implants such as stents that requires mainly bio-compatibility and bio-absorbability [3,4]. Generally speaking, however, commercially available magnesium alloys prepared by traditional ingot metallurgy (I/M) processing are inferior with respect to strength, ductility and corrosion resistance in comparison with commercially available aluminium alloys. For magnesium alloys to find wider application in various fields of industry, it is essential that they acquire higher corrosion resistance as well as higher strength and ductility.

The last decade witnessed the appearance of high-strength and heat-resistant Mg–Zn–rare earth (RE) alloys [5–9]. The Mg–Zn–RE alloy consists of an α-Mg matrix phase and a long period stacking ordered (LPSO) phase [10–13]. The LPSO phase in Mg–Zn–Y is mainly 18R, in which both zinc and yttrium are enriched in four atomic layers at six period intervals in stacking of closely packed planes [14–19]. The role of the LPSO phase in Mg–Zn–Y alloys in the formation of their superior mechanical properties has been a matter of intense interest as is evident from a great abundance of concerning mechanical characteristics of the LPSO phase and LPSO phase-containing magnesium alloys [20–26]. The LPSO phase acts as alloy-strengthening component because of their unique plastic deformation behavior. From the viewpoint of corrosion science, however, the LPSO phase may be considered as a secondary phase causing potential difference from the α-Mg matrix phase. The main reason for the low corrosion resistance of magnesium alloys is galvanic attack due to impurities, alloying elements and secondary phases [27,28]. The two-phase magnesium alloy often shows low corrosion resistance. The development of the technology that improves the corrosion resistance of α-Mg/LPSO two-phase alloy is required.

The application of rapid solidification processing to magnesium alloys results in microstructure refinement, extended solid solubility and improved chemical homogeneity with consequent improvements in mechanical properties and corrosion resistance [29–35]. Rapidly solidified (RS) ribbon-consolidation is a more

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Table 1
Alloy designations, nominal compositions and estimated cooling rates for various solidification techniques.

Designation	Composition (at.%)	Estimated R Cooling Rate ($K\,s^{-1}$)	Techniques
GC-A0.5	$Mg_{96.75}Zn_{0.75}Y_2Al_{0.5}$	1.0×10^1	Gravity casting
IC-A0.5	$Mg_{96.75}Zn_{0.75}Y_2Al_{0.5}$	5.5×10^2	Copper mould injection casting
RS_{10}-A0.5	$Mg_{96.75}Zn_{0.75}Y_2Al_{0.5}$	1.8×10^4	RS Ribbon-consolidation (V_{rc}: $10\,m\,s^{-1}$)
RS_{20}-A0.5	$Mg_{96.75}Zn_{0.75}Y_2Al_{0.5}$	3.5×10^4	RS Ribbon-consolidation (V_{rc}: $20\,m\,s^{-1}$)
RS-A0.5	$Mg_{96.75}Zn_{0.75}Y_2Al_{0.5}$	1.4×10^5	RS Ribbon-consolidation (V_{rc}: $40\,m\,s^{-1}$)
RS-A1.0	$Mg_{96.25}Zn_{0.75}Y_2Al_1$		
RS-A1.5	$Mg_{95.75}Zn_{0.75}Y_2Al_{1.5}$		
RS-MZY	$Mg_{97.25}Zn_{0.75}Y_2$		

recent technique that was developed to obtain a large-sized highly corrosion-resistant α-Mg/LPSO two-phase alloy [33–35]. Rapid solidification followed by the consolidation of RS ribbons produces nanocrystalline α-Mg/LPSO two-phase alloy containing the stacking fault-like LPSO phase that is dispersively precipitated in the dynamically recrystallized matrix grains. A morphologic change of the LPSO phase from a massive block-shaped LPSO phase to a highly dispersed LPSO phase in the grain interior brings about an improvement in corrosion resistance without any compromise in excellent mechanical properties of the alloys owing to increased electrochemical homogeneity. The Mg–Zn–Y RS alloy exhibits passivation behavior in anodic polarization in 0.1 M NaCl neutral aqueous solution [33]. A more recent preliminary investigation for determining an optimum composition in the Mg–Zn–Y ternary system and for exploring the effect of adding a fourth element showed that the aluminium-containing $Mg_{97.25-x}Zn_{0.75}Y_2Al_x$ RS ribbons have the highest corrosion resistance among all materials tested [35]. It is also well-known that the addition of aluminium to the magnesium alloys results in an improvement in repassivation rate in chloride solution in both as-cast and rapidly solidified conditions [29,30,36–39]. In overall consideration of these findings, this study aimed to improve corrosion resistance of the α-Mg/LPSO two-phase alloys by adding aluminium to the Mg–Zn–Y alloys. Large-sized Mg–Zn–Y and Mg–Zn–Y–Al bulk nanocrystalline alloys were fabricated by consolidating RS ribbons. Corrosion and electrochemical behavior of these alloys was investigated. Meticulous attention was paid to make sure if the passivation behavior of α-Mg/LPSO two-phase alloys would vary with increasing cooling rate and aluminium content.

2. Material and methods

2.1. Sample preparation

Master alloy ingots of nominal compositions, $Mg_{97.25}Zn_{0.75}Y_2$ (at.%) and $Mg_{97.25-x}Zn_{0.75}Y_2Al_x$ ($x = 0.25$, 0.5, 1.0, 1.5), were prepared by high frequency induction heating in an argon atmosphere. In the steel mould gravity casting, the master alloy ingot was remelted in a carbon crucible by high frequency induction heating and cast into a steel mould (30 mm diameter, 300 mm high). In the copper mould injection casting, the master alloy ingot was remelted in a quartz nozzle by high frequency induction heating, and then injected into a copper mould (1 mm thick, 10 mm wide, 30 mm high). Three kinds of RS ribbons were prepared by a single-roller melt-spinning method at a roll-circumferential velocity (V_{rc}) of $10\,m\,s^{-1}$, $20\,m\,s^{-1}$ and $40\,m\,s^{-1}$. The cooling rate (R_c) for the RS alloys was calculated from the interlamellar spacing and sample thickness using an eutectic alloy of composition $Al_{83}Cu_{17}$ [40]. The alloy designations and the estimated cooling rates used in various techniques of solidification are listed in Table 1. A large-sized $Mg_{97.25-x}Zn_{0.75}Y_2Al_x$ bulk alloy was prepared by consolidation of RS ribbons. RS ribbons were pressed into a copper billet and degassed for 15 min at 523 K. Extrusion was performed at an extrusion ratio of 10 at 623 K and an extrusion ram speed of $2.5\,mm\,s^{-1}$. The RS ribbon-consolidation process was described in detail in a previous report [35]. The alloy compositions were determined by inductively coupled plasma emission spectrometry (ICP) as shown in Table 2.

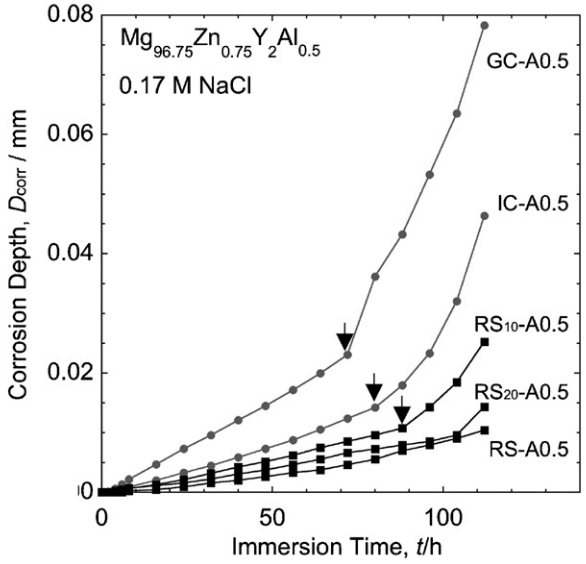

Fig. 1. Change in the corrosion depth of gravity-cast, injection-cast, and RS ribbon-consolidated $Mg_{96.75}Zn_{0.75}Y_2Al_{0.5}$ alloys as a function of immersion time in a 0.17 M NaCl neutral aqueous solution (pH 6.8) open to the air at 298 K.

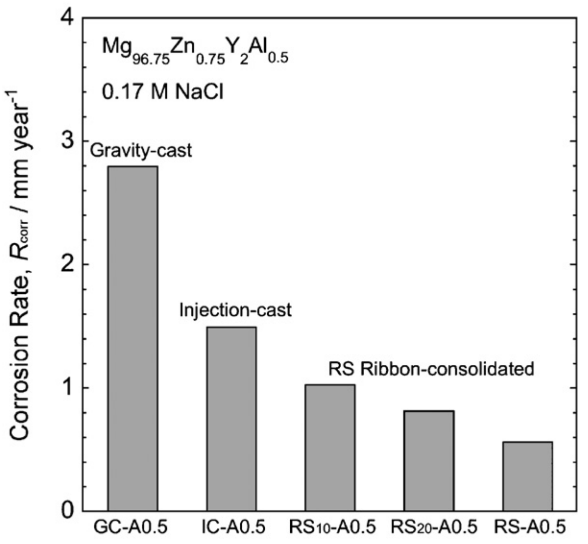

Fig. 2. Corrosion rate of gravity-cast, injection-cast, and RS ribbon-consolidated $Mg_{96.75}Zn_{0.75}Y_2Al_{0.5}$ alloys in a 0.17 M NaCl neutral aqueous solution (pH 6.8) open to the air at 298 K.