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Diffusion behavior and reactions between Al and Ca in Mg alloys by diffusion couples

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ABSTRACT

The diffusion behavior and reactions between Al and Ca in Mg alloys by diffusion couple method were investigated. Results demonstrate that Al_2Ca is the only phase existing in the diffusion reaction layers. The volume fraction of Al_2Ca in diffusion reaction layers increases linearly with temperature. The standard enthalpy of formation for intermetallic compounds was rationalized on the basis of the Miedema model. Al-Ca intermetallic compounds were preferable to form in the Mg-Al-Ca ternary system under the same conditions. Over the range of 350–400 °C, the structure of Al_2Ca is more stable than that of Al_4Ca, $Al_{14}Ca_{13}$and Al_3Ca_8. The growth constants of the layer I, layer II and entire diffusion reaction layers were determined. The activation energies for the growth of the layer I, layer II and entire diffusion reaction layers were (80.74 ± 3.01) kJ/mol, (93.45 ± 2.12) kJ/mol and (83.52 ± 1.50) kJ/mol, respectively. In layer I and II, Al has higher integrated interdiffusion coefficients $\tilde{D}_i^{Int,\, layer}$ than Ca. The average effective interdiffusion coefficients $\tilde{D}_{Al}^{eff}$ values are higher than $\tilde{D}_{Ca}^{eff}$ in the layer I and II.

1. Introduction

Mg-Al based alloys, possessing the highest strength to weight ratio among the common structural materials, have received increasing attention for their applications in aerospace and automotive industries [1–3]. For Mg-Al based alloys, β-$Mg_{17}Al_{12}$ is an essential phase that plays an important role in strengthening grain boundary and suppressing high-temperature grain-boundary sliding, whereas the softening of the phase at elevated temperature is detrimental to the creep property of the alloys [4,5]. Therefore, the utilization of such Mg alloys is limited. Significant improvements can be achieved by alloying strategy. Additions of rare earth elements show improvement in mechanical properties as a result of formation of strengthening precipitates [6,7], but high costs are indispensable. As a lower cost element, the addition of Ca to Mg-Al alloys can significantly refine the as-cast microstructure [8–10], and significantly improve the mechanical properties at ambient and high temperatures [11–13], which is attributed to the formation of thermally stable Al_2Ca intermetallic compound.

The Mg-Al-Ca system is experimentally investigated at 400 °C using diffusion couples and key experiments, and the isothermal section of Mg-Al-Ca phase diagram at 400 °C is constructed [14]. Solid solubilities for Mg_2Ca, Al_2Ca, Al_4Ca, $Al_{140}Mg_{89}$ phases were determined. A (Mg-30wt%Ca)/Al diffusion couple was assembled and heat-treated at 415 °C. From the cross section of the diffusion couple, backscatter electron microscopy coupled with electron probe microanalysis indicated the existence of $Al_2(Mg,Ca)$ [15]. Ternary Al-Ca-Mg phase equilibria were investigated using X-ray diffraction, metallography, scanning electron microscopy, and differential thermal analysis [16]. However, few studies regarding inter-diffusion and reaction between of Al and Ca in Mg alloys have been carried out.

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Table 1
Chemical compositions (wt%) of Mg-40Al and Mg-20Ca Mg alloy.

Materials	Al	Ca	Si	Cu	Fe	Ni	Mg
Mg-40Al	39.37	–	0.0049	0.0063	0.0037	0.0011	Bal.
Mg-20Ca	–	18.78	0.0053	0.0042	0.0047	0.0028	Bal.

The present paper investigates the diffusion behaviors of Al and Ca, and the forming process of the intermetallic compounds in Mg alloys by (Mg-40Al)/(Mg-20Ca) diffusion couples. Interfacial morphology and formation of Al_2Ca intermetallic compound are examined. Growth kinetics of the diffusion reaction layers is determined.

2. Experimental

Pure Mg (99.98 wt%), pure Al (99.99 wt%) and commercial Mg-20Ca(Mg-20wt%Ca) master alloy were used. Melting point of Mg-20Ca master alloy is 585 °C. Al was added into Mg to form of Mg-40Al(Mg-40wt%Al) master alloy which starts liquefying at 460 °C. These master alloys were melted several times to ensure the composition homogeneity in a vacuum induction furnace. Chemical composition of Mg-40Al and Mg-20Ca master alloys are presented in Table 1. Mg-40Al master alloy is brittle and fragile, and also its melting point is lower than that of Mg-20Ca master alloy. It is not feasible to make solid diffusion couples by the jig method. So a solid-liquid contact method was employed to produce the (Mg-40Al)/(Mg-20Ca) diffusion couples. The Mg-40Al master alloy was melted under the protection of SF_6 and CO_2 mixed gas at 500 °C. Then, a rectangular piece of Mg-20Ca master alloy polished with 200 grit SiC paper that make sure an oxide free surface. Then, Mg-20Ca master alloy was immediately submerged into Mg-40Al master alloy melt, and Mg-20Ca master alloy piece attached by Mg-40Al master alloy melt was taken from the furnace. Due to at higher thermal expansion coefficient of Mg-40Al master alloy than that of Mg-20Ca master alloy, an intimate contact between Mg-40Al and Mg-20Ca master alloys was formed during solidification and the diffusion couple samples were obtained. The diffusion couples were then sealed in an evacuated quartz tube to minimize oxidization during diffusion annealing. The quartz tube was evacuated and purged with Ar three times before finally sealing it with the inside pressure of about 10^{-3} torr. The diffusion couples were then annealed at 350 °C, 375 °C and 400 °C, respectively, and the annealed times of each temperature were 24 h, 48 h and 72 h. After annealing, the quartz capsules were quenched in water.

The diffusion couples were cut perpendicular to the diffusion contact plane using a low speed diamond saw. They were then ground and polished to reveal the cross-sections of the interfaces. Samples were grind with ground papers from 200, 400, 600, 800–1000 grit for cross-sectional SEM examinations. Each diffusion couple was examined using optical microscopy to ensure that the diffusion reaction layers at the interface were well developed. The diffusion reaction layers were studied via scanning electron microscopy (SEM, TESCAN VEGA 2 SEM). The intermetallic compounds in the diffusion reaction layers were identified by energy dispersive spectroscopy (EDS) and X-ray diffractometer (XRD). XRD

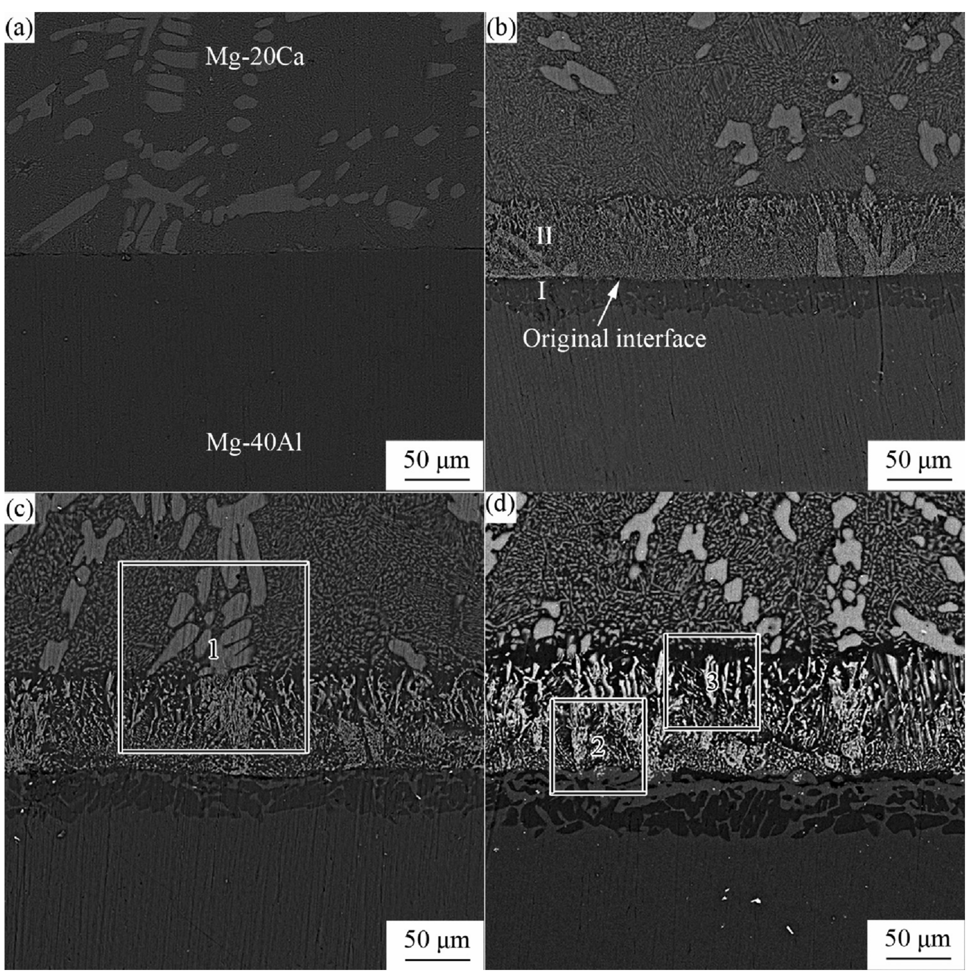

Fig. 1. BSE micrographs from (Mg-40Al)/(Mg-20Ca) diffusion couples (a) prior to annealing before, and annealed at (b) 350 °C, (c) 375 °C and (d) 400 °C for 72 h.