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JOURNAL OF RARE EARTHS
JOURNAL OF RARE EARTHS, Vol. 33, No. 1, Jan. 2015, P. 70
www.re-journal.com/en/

Effect of Ce/La microalloying on microstructural evolution of Mg-Zn-Ca alloy during solution treatment

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Received 4 April 2014; revised 25 August 2014

Abstract: The effect of Ce/La misch metal addition on the microstructural evolution of as-cast and as-soluted Mg-5.3Zn-0.5Ca (wt.%) alloys was systematically investigated. It was found that Ce/La could effectively refine the as-cast alloy and restrain grain growth during solution treatment, which was derived from the constitutional supercooling during solidification process and the formation of stable intermetallic compounds $CeMg_{12}$ and $Mg_{17}La_2$. Furthermore, Ce/La microalloying and solution treatment resulted in an evolution from the original lamellar $Ca_2Mg_6Zn_3$/α-Mg to the divorced eutectic structure. The thermal stability of Mg-Zn-Ca alloy could be effectively improved by Ce/La addition, because the low-melting-point binary Mg-Zn phase was transformed to Mg_xZn_y-Ca-(Ce/La) phase with higher thermal stability and the amount of $Ca_2Mg_6Zn_3$/α-Mg eutectic structure was reduced.

Keywords: Mg-Zn-Ca alloy; Ce/La; solution treatment; Mg_xZn_y-Ca-(Ce/La) phase; rare earths

The requirement of reducing energy consumption and CO_2 emission from engines can be fulfilled by vehicle-weight reduction. Magnesium and its alloys, known by their lightweight, high specific strength and outstanding castability, can be a good candidate for transportation industry[1]. However, the applications of Mg alloys are still limited by their poor strength and ductility at room temperature[2]. In order to overcome these shortcomings, numerous attempts have been made to develop the Mg alloys with superior mechanical properties. Microalloying is an effective method for the improvement of mechanical properties of Mg alloys[3] via grain refinement[4], modifying the morphology, size and distribution of intermetallic compounds[5,6].

Most of commercial alloys are those based on Mg-Al system, however, the strengthening effect and corrosion resistance derived from γ-$Mg_{17}Al_{12}$ precipitates along grain boundaries are dramatically decreased above 125 ºC due to their poor thermal stability[7,8]. Therefore, the improvement of strength and corrosion resistance at elevated temperature has become a pressing problem for the widespread application of Mg alloys. It is found that a solutionized Mg-Zn alloy will exhibit a high hardness followed by the age hardening, due to the precipitation of coherent MgZn, $MgZn_2$ and Mg_2Zn_3 particles[1]. In addition, Zn can effectively refine the grain size and increase strength and corrosion resistance of Mg alloys[8,9]. Furthermore, Ca behaves as a grain refiner for Mg alloys, also contributes to the formation of a stable high-melting-point intermetallic compound Mg_2Ca, and can improve the creep and oxidation resistance at elevated temperature[8,10]. Zn and Ca together with Mg may form the stable intermetallic compound $Ca_2Mg_6Zn_3$ (a=b=0.97 nm, c=1.0 nm)[11–13], which is beneficial for the age hardening behavior of the alloy. Thus, many researches have been made to develop new high-strength and creep-resistant magnesium alloys based on the Mg-Zn-Ca system recently[3,14]. To date, some mechanical properties of Mg-Zn-Ca alloys have been reported. For instance, Somekawa et al.[15] reported that the as-extruded Mg-0.3 Ca-1.8Zn (at.%) showed a good balance of yield strength and plane-strain fracture toughness, which were higher than those of conventional wrought Mg alloys. The mechanical properties could be improved by controlling grain refinement and the dispersion of precipitates in the matrix. Levi et al.[16] reported that the as-cast and as-soluted Mg-1.6Ca-3.2Zn (wt.%) alloy exhibited an obvious age-hardening response during aging treatment at high temperature. And the age hardening response of this alloy correlated with the precipitation of $Ca_2Mg_6Zn_3$, not

Foundation item: Project supported by the National Natural Science Foundation of China (51401200), Natural Science Foundation of Jilin Province (20140520099JH), National Science & Technology Pillar Program (2012BAE01B04), Chinese Academy of Sciences of Western Action Plan Project (KZCX2-XB3-06), the National Natural Science Foundation of China Major Project (91122030), National High Technology Research and Development Program of China (2011AA03A407) and National Natural Science Foundation for Creative Research Group (20921002)

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DOI: 10.1016/S1002-0721(14)60385-9

$CaMg_2$. In addition, some investigations about the microstructure and properties of rapidly solidified (RS) Mg-Zn-Ca alloys have also been reported[10,11].

However, the distribution of coarse intermetallic compounds of as-cast Mg-Zn-Ca alloys is not homogeneous, resulting in a poor dispersion strengthening effect. And the hardness and strength of the Mg-Zn-Ca alloys obviously decreased at the elevated temperatures (≥200 °C)[14]. Thus, RE (rare earth elements) can be added to modify the size, composition and distribution of intermetallic compounds, and further improve the mechanical properties of Mg-Zn-Ca alloys at high temperature[17]. Ce/La misch metal as a byproduct of Nd/Pr separation process has aroused wide interest from more and more investigators due to its low price. In addition, Ce and La have a strong grain boundary strengthening effect, because they can easily concentrate on the grain boundaries and form intermetallic compounds with high melting point. Although a few studies were reported on the microstructure and mechanical properties of Mg-Zn-Ca-(Ce or La)[6,11], there is lack of systematic researches on the effect of Ce/La misch metal on Mg-Zn-Ca alloys. Therefore, in order to develop a low-cost and high-performance Mg alloy, a small amount of Ce/La misch metal was added into Mg-Zn-Ca alloy. The present work investigated the effect of Ce/La microalloying on the microstructural evolution, phase compositions and the distribution of secondary phases of as-cast and as-soluted Mg-5.3Zn-0.5Ca (wt.%) alloy. In addition, the present work made a preliminary research on the Mg-Zn-Ca-Ce/La alloy, and established a foundation for the further research of high-temperature performances.

1 Experimental

This investigation involved three alloys, which were based on Mg-5.3Zn-0.5Ca (wt.%) with 0, 0.5 wt.%, and 1.0 wt.% Ce/La misch metal addition. Commercially pure Mg, Zn and Mg-30 wt.%Ca, Mg-20 wt.%Ce/La master alloys (the mass ratio of Ce and La is approximately 3:1) were used to prepare these alloys. The melting was carried out in a well-type resistance furnace under a protective atmosphere composed of CO_2 and SF_6 with a ratio of 40:1 at 750 ºC. Before pouring the melt into a permanent mold which was preheated to 200 ºC, another 20 min was allowed to ensure a homogenous composition. The cast ingots were soluted at 385 ºC for 8, 16, 24 h and then quenched into water at 70 ºC. The chemical compositions were analyzed using an inductively coupled plasma (ICP) analyzer, and the results are shown in Table 1. The average grain size was calculated by the software of Nano Measure with grain number of more than 1000. The microstructures were observed by an Olympus GX71 optical microscope (OM) and a Hitachi S4800 field-emission scanning electron microscope (FE-SEM). The specimens for optical observation were ground, polished and etched in a picric acid solution. The crystallographic structure and distribution of elements were characterized by X-ray diffraction (XRD, a Bruker D8 Focus diffractometer with Cu Kα radiation) and an X-ray energy-dispersive spectrometer (EDS). The thermal properties were analyzed through the differential scanning calorimetry (DSC) in a purified argon atmosphere using NETZSCH STA 449F3 instrument with the scanning rate of 10 ºC/min.

Table 1 Chemical composition analysis of investigated alloys (wt.%)

Alloy	Zn	Ca	La	Ce	Al	Fe	Mn	Mg
Mg-Zn-Ca	5.689	0.765	–	–	0.004	0.002	0.015	Bal.
Mg-Zn-Ca-0.5La/Ce	5.644	0.713	0.135	0.205	0.011	0.010	0.016	Bal.
Mg-Zn-Ca-1.0La/Ce	5.772	0.534	0.320	0.389	0.003	0.010	0.019	Bal.

2 Results and discussion

2.1 Microstructural observations and phase analysis

Fig. 1 shows the microstructures of as-cast and as-soluted Mg-Zn-Ca-*x*Ce/La (*x*=0, 0.5 wt.%, 1.0 wt.%) alloys. As-cast Mg-Zn-Ca alloy (Fig. 1(a)), with an average grain size of 114 μm, was composed of Mg matrix, network eutectic structure along the grain boundaries and small amounts of spherical second phase randomly dispersed within grains. After 8 h solution treatment (Fig. 1(b)), a uniformly equiaxed grain structure was observed. With further solution, there was a tendency of grain growth (Fig. 1(c)). After 24 h (Fig. 1(d)), the grain boundaries became smooth and grain size was obviously increased. In addition, the amount of spherical secondary phases was remarkably decreased. For Ce/La-containing alloys, some finer grains were observed (Fig. 1(e), (i)), as a result, the average grain size of Mg-Zn-Ca alloy was decreased obviously. After solution, there were no significant changes in the average grain size (Fig. 1(f–h), (j–l)). It should be noted that after solution treated for 24 h (Fig. 1(h), (l)), the volume fraction of secondary phase along grain boundaries was declined, and nearly concentrated on the grain boundary triple junctions only.

The average grain size against solution treatment time curves of the Mg-Zn-Ca-*x*Ce/La alloys are shown in Fig. 2. The grain growth rate of Mg-Zn-Ca alloy was more obvious than that of Ce/La-containing alloys, especially after solution for 8 h, which indicated that the trace Ce/La misch metal addition would effectively hinder the grain growth at 385 °C. Compared with the Mg-Zn-Ca-0.5Ce/La alloy, the average grain size of Mg-Zn-Ca-1.0Ce/La alloy was further decreased. It suggested that the addition of Ce/La misch metal can effectively refine the grains of as-cast Mg-Zn-Ca alloy and restrain the grain growth during the solution treatment. According to