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Effect of solute atoms and second phases on the thermal conductivity of Mg-RE alloys: A quantitative study

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ABSTRACT

In this study, the room temperature thermal conductivity and microstructure of Mg–Ce, Mg–Sm and Mg–Y binary alloys in as-cast and solution treated conditions were investigated. Quantitative study was conducted on the effect of rare earth elements (in solid solution and intermetallic compounds) on the thermal conductivity of Mg–RE alloys. The reduction in thermal conductivity was determined to be about 123.0 W/(m·K) and 6.5–16.4 W/(m·K), respectively, per 1 at.% RE addition in the form of solid solution or intermetallic compounds with Mg. The thermal conductivities of Mg–RE alloys were fitted using modified Maxwell and EMT models based on the distribution, volume fractions and shape of intermetallic compounds. The modified structural models provide a good fit to the experimental thermal conductivity data.

1. Introduction

With increasing power density requirements of integrated circuits, heat sinks in modern electronic devices must possess high heat dissipation capability to remove excess heat from the devices. The high thermal conductivity of heat sink materials ensures a uniform temperature distribution which reduces thermally induced stresses, thereby improves fatigue properties [1]. The other important requirement for a high-quality heat spreader is light weight, which is important for electronic devices, such as laptops, mobile phones and other communication devices [2]. The low density and relatively high thermal conductivity of magnesium alloys make them an attractive heat dissipation material option [3].

There are a few studies published on the thermal conductivity of Mg alloys, generally for commercial alloys. Rudajevová et al. [4] demonstrated that the thermal conductivity of AM20, AM50 and AM60 alloys were sensitive to their microstructure. The solid solution of Al in Mg had lower thermal conductivity than alloys where $Mg_{17}Al_{12}$ phase was present. This suggests that using alloying elements with a low solid solubility in the Mg matrix will produce Mg alloys with high thermal conductivities. Furthermore, some thermal–mechanical processes can be used to improve the thermal conductivity of Mg alloys by modifying the microstructure. Yuan et al. [5] found that both solution treated and aged Mg–Zn–Mn alloys showed higher thermal conductivities than their as-cast counterparts, which were mainly due to the precipitation of α-Mn from the Mg matrix. Peng et al. [6] reported that weak texture can result in improved thermal conductivity in wrought Mg products. Generally, the thermal conductivity of Mg alloys is influenced by the following factors: solute atoms, intermetallic compounds, grain boundary, dislocation and temperature, etc. [7,8]. Among them, solute atoms and intermetallic compounds have the greatest influence on the thermal conductivity of alloys at room temperature. It is known that solute atoms can reduce the thermal conductivity to a greater extent than intermetallic compounds [9]. In a recent study, Pan et al. [10] experimentally demonstrated that the specific thermal resistivity (the thermal resistivity increment of the alloy per at.% addition) of solute atoms in Mg alloys was in the following sequence: $Zn < Al < Ca < Sn < Mn < Zr$. Similarly, the influence of RE solute

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atoms (Ce, Nd, Y and Gd) on the thermal conductivity of Mg alloys was measured and compared by Zhong et al. [11]. However, these studies only qualitatively compared the effects of solute elements and intermetallic compounds on the thermal conductivity of Mg alloys. In this paper, the representative Ce, Sm and Y were selected because their solid solubilities in Mg are low, medium and high among all the RE elements [12], as they are used in commercial alloys, such as WE43 and WE54. Additionally, the relevant results for Mg–Nd alloys from a previous report were included for comparison [13].

Modelling the effective thermal conductivity of heterogeneous or composite materials is of interest for many heat transfer applications. Some structural models have been proposed to estimate the effective thermal conductivity of multiphase systems according to the distribution and volume fractions of constituent phases [14–17]. The Cheng–Vachon model modified by Carson et al. [18] provided accurate predictions of the thermal conductivity for dispersed aluminum composites. Stadler et al. [19] used the Maxwell model to estimate the thermal conductivity of cast Al–Si alloys. Chen et al. [20] calculated the thermal conductivity values in Al–Si/Cu/Fe/Mg binary alloys using effective medium approximations and the results fit closely to measured results. However, modelling the thermal conductivity of Mg alloys using structural models has not been reported, to the best of our knowledge.

In this study, the effect of solute elements and intermetallic compounds on the thermal conductivity of binary Mg–RE alloys was studied quantitatively. Based on the experiment results, structural models were modified to fit the thermal conductivity of Mg–RE alloys. Furthermore, the thermal conductivity values obtained using the modified models were compared with the measured results. Finally, the effects of these two key parameters (solid solution vs. intermetallic compounds) in the models were discussed, providing important basis for the development of high thermal conductivity Mg alloys.

2. Experimental procedure

Binary Mg–Ce, Mg–Sm and Mg–Y alloys with different concentrations were prepared using pure magnesium (99.95 wt%), Mg–90 wt% Ce, Mg–35 wt% Sm and Mg–20 wt% Y master alloys in an induction furnace protected by high purity Ar gas. The melt was cast at 730 °C into a cylindrical permanent mold (40 mm in diameter and 85 mm in height) preheated to 300 °C. An inductively coupled plasma analyzer (ICAP 6000 Radial) was used to analyze the actual chemical composition of the samples, shown in Tables 1–3.

The most important experimental procedure in this study was to obtain solid solutions containing different concentrations of solute atoms and saturated solid solutions with various amounts of intermetallic compounds. In the case of the Mg–Ce alloys, for example, the solid solubility of Ce in the Mg matrix is 0.13 at.% [12]. Two groups of Mg–x at.% Ce alloys ($0 \leq x < 0.13$ and $x > 0.13$) were solution treated at 580 °C for 12 h followed by water quenching immediately. The solution temperature and time were selected to dissolve as much Ce into the Mg matrix as possible while avoiding overheating (incipient melting) the samples. Thus, the solution treated Mg–x at.% Ce alloys ($0 \leq x < 0.13$) can be regarded as solid solutions. For the solution treated Mg–x at.% Ce alloys ($x > 0.13$), the amount of Ce atoms in the Mg matrix is about 0.13 at.% with the remaining Ce in intermetallic compounds. Similarly, the as-cast Mg–Sm and Mg–Y samples were subjected to the solution treatments at 520 °C for 24 h and 530 °C for 12 h, respectively, followed by immediate water quenching.

Samples for microstructural observation were mechanically ground and polished, but not etched, as some of the intermetallic compounds may be removed during etching. Backscattered electron images were taken using a scanning electron microscope (SEM, JEOL, JSM-7800 F Prime) to distinguish different intermetallic compounds. X-ray diffraction (XRD) analysis was also conducted using a diffractometer (Rigaku Ultima IV) with Cu Kα radiation to identify the intermetallic compounds. The volume fractions of intermetallic compounds in the as-cast alloys were measured using the Image Pro Plus software and SEM images.

Disc samples (12.7 mm diameter and 3 mm thickness) were machined from the alloys for thermal diffusivity measurements, using the laser flash method (Netzsch LFA 447) at 25 °C. The surface of the specimens was painted by carbon-coating before measurement to improve the absorption of the light pulse. At least three samples machined from different areas were measured for each composition. The room temperature density of the alloys was obtained from an electronic balance (Sartorius Quintix124-1CN) with a densimeter (YDK03P), using the Archimedes method. The specific heat capacity of the alloys was calculated according to the Neumann–Kopp rule [21,22].

Thermal conductivity λ [W/(m·K)] was calculated as follow:

$$\lambda = \alpha \cdot C_p \cdot \rho \qquad (1)$$

where α is the thermal diffusivity (m^2/s), C_p is the specific heat capacity [J/(g·K)] and ρ is the density (g/cm^3). The standard deviation for the thermal conductivity data is about 7%.

3. Results

Figs. 1–3 present the SEM backscattered electron images of the as-cast Mg–Ce, Mg–Sm and Mg–Y alloys, respectively. Divorced eutectic intermetallic compounds are evident and the amount of such intermetallic compounds increased with the alloying contents. The XRD results (Fig. 4) indicated that the intermetallic compounds are $Mg_{12}Ce$ (and $Mg_{17}Ce_2$), $Mg_{41}Sm_5$ and $Mg_{24}Y_5$ in the Mg–Ce, Mg–Sm and Mg–Y alloys [23–25], respectively.

3.1. Mg–Ce alloys

As shown in Fig. 1, $Mg_{12}Ce$ and $Mg_{17}Ce_2$ intermetallic compounds mainly exhibited a spherical or rod-like shape and irregular distribution when the Ce concentration was less than 1 wt%. Semi-continuous networks of eutectic structures developed in the

Table 1
Chemical composition and thermal conductivity of Mg–Ce binary alloys.

Nominal (wt.%)	0.15	0.3	0.45	0.6	1.0	2.0	3.0	5.0	7.0	9.0
Actual (wt.%)	0.13	0.31	0.44	0.56	1.04	1.9	3.04	4.90	6.76	8.80
Actual (at.%)	0.02	0.05	0.08	0.10	0.18	0.33	0.54	0.89	1.24	1.65
As-cast TC[a] W/(m·K)	161.6	156.0	152.4	149.6	143.8	134.8	133.2	120.1	115.1	105.2
Solution treated TC W/(m·K)	160.1	154.5	144.7	144.2	133.4	118.4	117.9	112.2	105.7	97.9

[a] Note: “TC” represent “Thermal conductivity”.