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Solid-state phase equilibria in the Mg corner of the Mg–Gd–Sm phase diagram

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Abstract

The solid-state phase equilibria in the Mg corner of the Mg–Gd–Sm phase diagram were investigated by optical and scanning electron microscopy, X-ray diffraction and electrical resistivity measurements. The experiments showed that in the Mg corner of the system there are only three solid phases in equilibrium: the Mg solid solution and the two Mg-richest compounds of the adjoining binary systems. Each of the binary compounds take into solution significant quantities of the second rare-earth metal. Gd and Sm mutually reduce their solubility in the Mg solid solution. Isothermal sections of the phase diagram at 500 and 300°C are presented.

Keywords: Mg–Gd–Sm system; Phase diagram; Magnesium alloys; Rare earth metal

1. Introduction

Mg-base alloys with rare-earth metals are interesting as light construction materials having high mechanical strength [1–3]. They are also interesting owing to the clearly manifested differences between the individual rare-earth metals when their influences on the properties of Mg are compared. This is supposed to be connected with the quite different solubility of individual rare-earth metals in Mg solid solution. So, Eu is practically insoluble in solid Mg, but the solubility of Lu in Mg is as high as 8.80 at.% [4,5]. There are certain similarities as well as differences in compound formation in the systems of Mg with rare-earth metals [6,7]. Also, this may be responsible for the quite different influence of the individual rare-earth metals on the properties of magnesium alloys. There is enough information about the binary phase diagrams of Mg with the different rare-earth metals, but the phase diagrams of ternary systems of Mg with two rare-earth metals have hardly been studied. Only two ternary phase diagrams of this type have been investigated. One of these is the Mg–La–Ce system [8], and the second is Mg–Pr–Nd [9]. Both systems were studied in the Mg-rich region and included two rare-earth metals belonging to the same subgroup and being the closest neighbours in the lanthanide row. In addition, the Mg-rich parts of several ternary phase diagrams were investigated, where one of the rare-earth metals was Y, not belonging to the lanthanide row [10–12]. Despite the investigations of these ternary phase diagrams, many features of the physico-chemical interaction between Mg and two different rare-earth metals are still not clear and difficult to predict. One of the systems, where the interaction of two rare-earth metals with Mg may be different from that in the already investigated systems, is Mg–Gd–Sm. In this system the two rare-earth metals are close in the lanthanide row and, therefore, have similar atomic radii, but they belong to different subgroups. This system is also interesting because both Gd and Sm are quite good prospects for improving the strength properties of Mg alloys [13,14].

In this work, the phase equilibria in the Mg corner of the Mg–Gd–Sm phase diagram were investigated as part of a study of this system.

2. Binary systems

The Mg–Gd phase diagram is of the eutectic type on the Mg-rich side with a eutectic point at 8.8 at.% Gd and 548°C [15,16]. The compound Mg_5Gd is in equilibrium with the Mg solid solution [15,17]. Its

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crystal structure is cubic and it has a large number of atoms in its unit cell. Mg_5Gd is formed peritectically from the liquid and Mg_3Gd at 658°C. The solubility of Gd in solid Mg is 4.53 at.% at the eutectic temperature and decreases as the temperature becomes lower [18]. The Mg–Sm phase diagram is of the eutectic type on the Mg side, too [19]. The eutectic point is at 8 at.% Sm and 530°C. The Mg-richest compound in this system is $Mg_{41}Sm_5$ and has a tetragonal crystal structure with 92 atoms in the unit cell. $Mg_{41}Sm_5$ is formed peritectically from the liquid and the next compound Mg_5Sm at a temperature somewhat higher than 530°C. Mg_5Sm has the same crystal structure as Mg_5Gd [19]. The solubility of Sm in solid Mg is significantly lower than that of Gd. It amounts 0.99 at.% at the eutectic temperature [20]. So, in the Mg corner of the ternary system one may anticipate a limited field of Mg solid solution being in equilibrium with at least two compounds belonging to the adjoining binary systems.

3. Experimental details

The alloys used in the experiments were prepared by melting in an electrical resistance furnace in alumina crucibles under a flux of 50% KCl + 50% LiCl. The starting materials were magnesium of 99.96% purity, gadolinium of 99.85% purity, and samarium of 99.83% purity. During melting, gadolinium and samarium were added by the previously prepared master-alloys: Mg–28% Gd and Mg–36% Sm. The flux preserved the melts from burning. After melting the alloys were poured into a steel mould. The ingots were about 18 mm in diameter and 60 mm long. All ingots were analysed chemically and their compositions were assumed in accordance with the results of chemical analysis. The chemical analysis also showed that there was no contamination the alloys by aluminium from the crucible material.

The ingots were cut into pieces which were homogenized at 500°C for 50 h and at 300°C for 100 h followed by quenching in cold water. The homogenization at 300°C followed that at 500°C.

The samples for the optical microscopy investigation were prepared by a common metallographic technique. This included mechanical polishing and etching. The best results were obtained by an etchant of 0.5% nitric acid in alcohol. The X-ray investigation was carried out using an X-ray diffractometer of the DRON-3M type. The X-ray patterns were taken from flat samples, and Fe radiation was used. Measurements of the electrical resistivity were performed by the compensation method. The error in the determination of the specific electrical resistivity of the alloys was estimated to be $\pm 0.7\%$.

Two sorts of equipment were used for scanning electron microscopy. One of them was a Jeol JSM-U3 microscope equipped with a device for energy dispersive X-ray microanalysis. This equipment was used for distinguishing the phases in the structure qualitatively. The other was an Amray KYKY-1000B scanning electron microscope. This was used for quantitative analysis of the phases.

4. Results and discussion

The main problem in the investigation was to distinguish the phases in equilibrium with the Mg solid solution. The X-ray investigation showed only two phases in equilibrium with the Mg solid solution. These phases belonged to the Mg–Gd and Mg–Sm binary systems: Mg_5Gd and $Mg_{41}Sm_5$. However, under the optical microscope both compounds have a similar appearance. They differed distinctly from the white Mg solid solution by virtue of their grey colour, but, depending on the etching conditions each of them could appear darker or lighter. Nevertheless, both phases could reliably be distinguished under the optical microscope, if the process of etching was performed carefully. Figs. 1(a)–1(c) show microstructures of the alloys after homogenization at 500°C. They contain, besides the Mg solid solution, only Mg_5Gd (Fig. 1(a)), only $Mg_{41}Sm_5$ (Fig. 1(b)), and both compounds simultaneously (Fig. 1(c)). In the latter photomicrograph Mg_5Gd containing more rare-earth metal is darker than $Mg_{41}Sm_5$.

The fact of two different phases being in equilibrium with the Mg solid solution was confirmed by scanning electron microscopy. Fig. 2(a) shows the microstructure of an alloy, obtained in the elastically-reflected electron regime in which one distinguishes two phases besides the Mg solid solution. The two compounds in this microstructure are distinguished by a different brightness due to their different heavy metal content. The images in the characteristic X-rays of Gd and Sm (Figs. 2(b) and 2(c)), however, show only weak difference between the two compounds. This corresponds to the fact that these phases have quite close compositions. This fact is confirmed also by the profile lines of the characteristic X-rays of Gd and Sm (Fig. 2(d)). Both lines have similar shapes, although there are also visible differences. The quantitative microanalysis of Gd and Sm in the scanning electron microscope revealed three phases in equilibrium with the following Gd:Sm (at.%) ratios (in limits): 1.74–2.08 for the Mg_5Gd-base phase, 0.80–0.84 for the $Mg_{41}Sm_5$-base phase, and 3.10–3.88 for the Mg solid solution. This means, that about 35 at.% Gd in Mg_5Gd is replaced by Sm, and about 45 at.% Sm in $Mg_{41}Sm_5$ is replaced by Gd.

Homogenization at 300°C resulted in a decomposi-

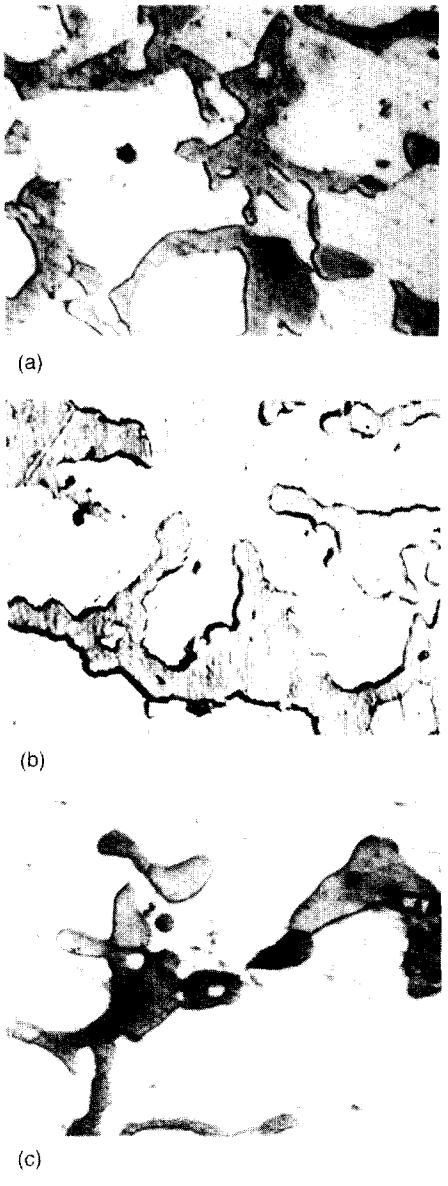

Fig. 1. Optical micrographs (1000×) of Mg–Gd–Sm alloys annealed at 500°C: (a) Mg–4.8at.%Gd–0.7at.%Sm; (b) Mg–0.9at.%Gd–4.75at.%Sm; (c) Mg–3.4at.%Gd–2.1at.%Sm.

tion of the Mg solid solution formed previously during the anneal at 500°C. The precipitated phases differed in appearance from those formed during crystallization. They were small particles extended along certain directions in the Mg solid solution grains. The decomposition patterns of Gd- and Sm-rich precipitates had distinct differences. The Gd precipitates were longer, and the order of their arrangement was stricter (Fig. 3(a)). The latter is manifest from the fixed distance between closest particles extending in the same direction. The Sm precipitates were significantly shorter, and the order of their arrangement was not that strict (Fig. 3(b)). These differences in appearance were used for distinguishing the two phases precipitated from the supersaturated Mg solid solution at 300°C. No decomposition of the Mg_5Gd-base and $Mg_{41}Sm_5$-base phases was observed by microscopic investigation after annealing at 300°C.

The boundaries of the Mg solid solution area were determined more precisely by using the electrical resistivity method. This method is based on the presence of kinks in plots showing the dependence of the resistivity on the concentration of a given alloying element along a certain direction in the phase diagram. The kinks should correspond to a transition from a one-phase region to two-phase or three-phase regions. Fig. 4 displays the results of the resistivity measurements for the alloys of both binary systems and for the alloys along three directions corresponding to constant Gd:Sm (at.%) ratios of 3:1, 1:1, and 1:3. The kinks in the displayed plots show the precise concentrations of the Mg solid solution boundaries at 500 and 300°C between the corresponding one-phase region (open circles) and two- or three-phase regions (filled circles). The solubilities of Gd and Sm in solid Mg determined in these experiments for the binary systems are in accordance with the results of earlier investigations [18,20].

Using the results of the above-mentioned experiments, the isothermal sections of the Mg–Gd–Sm phase diagram at 500 and 300°C were constructed. The sections are presented in Figs. 5 and 6. They show that there are only four different regions in the Mg corner of the phase diagram: (Mg), (Mg) + Mg_5Gd, (Mg) + $Mg_{41}Sm_5$, and (Mg) + Mg_5Gd + $Mg_{41}Sm_5$. The boundaries of the Mg solid solution region in these sections are based on the results of the electrical resistivity method.

The investigated Mg–Gd–Sm phase diagram has the following peculiarities. Unlike the systems Mg–La–Ce [8] and Mg–Pr–Nd [9], the two rare-earth compounds are simultaneously in equilibrium with the Mg solid solution. This result could be anticipated because the Mg-richest compounds in the Mg–Gd and Mg–Sm systems have different crystal structures. Nevertheless, there were some doubts about the crystal structures and compositions of these compounds. So, one could suppose their crystal structures are similar, or quite close, and, consequently, the possibility of forming a continuous solid solution between them could not be ruled out. This investigation enables us to conclude with certainty that the Mg-richest compounds in the Mg–Gd and Mg–Sm systems do not form a continuous solid solution. However, there is a significant mutual solubility of the two rare-earth metals in the two corresponding Mg-rich compounds. There is no other phase in equilibrium with the Mg solid solution besides the two mentioned Mg-rich compounds of the binary Mg systems. This seems to be result of the

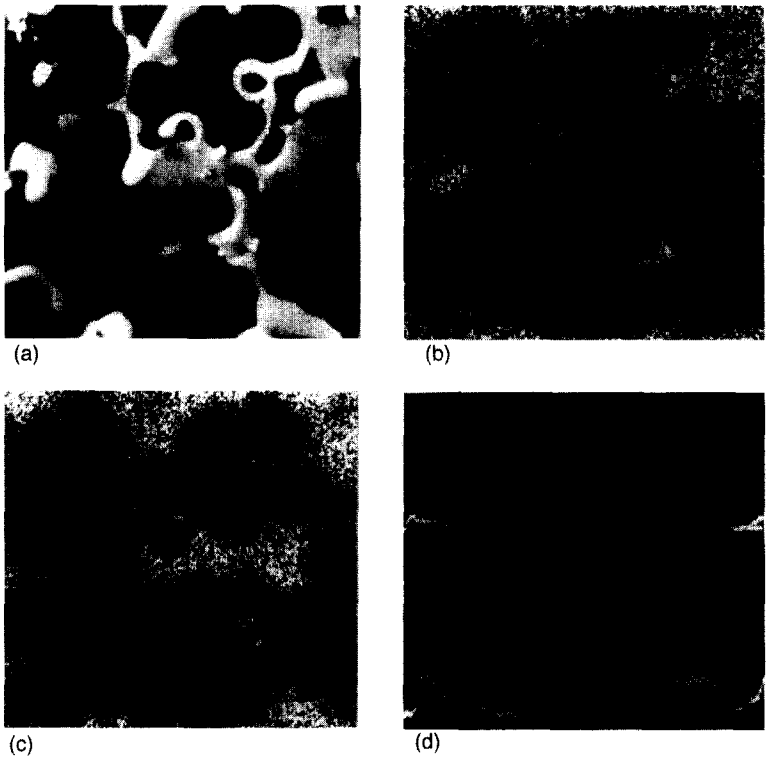

Fig. 2. Scanning electron microscope micrographs (1500×) of Mg–3.4at.%Gd–2.1at.%Sm annealed at 500°C: (a) image in elastically-reflected electrons; (b) the same image in Gd characteristic X-rays; (c) the same image in Sm characteristic X-rays; (d) intensity profiles of Gd (lower) and Sm (upper) characteristic X-rays along the middle of the same image.

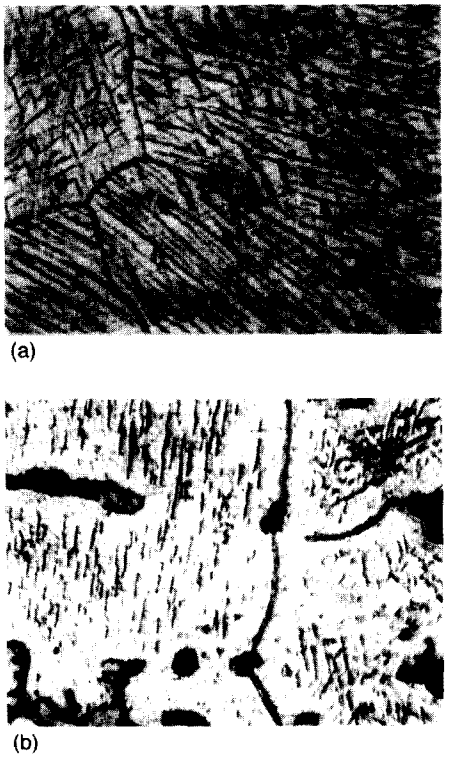

Fig. 3. Optical micrographs (1000×) of Mg–Gd–Sm alloys annealed at 300°C: (a) Mg–2.8at.%Gd, (b) Mg–0.4at.%Gd–1.2at.%Sm.

reluctance of rare-earth metals to form compounds with each other. The shape of the boundary of the Mg solid solution region shows that each of the rare-earth metals reduces the solubility of the other in solid Mg. This suggests that there is some interaction between Gd and Sm atoms in the Mg solid solution.

5. Conclusions

The Mg–Gd–Sm system is characterized by the existence in the solid-state of only two phases in equilibrium with the Mg solid solution. They are solid solutions on the bases of Mg_5Gd and $Mg_{41}Sm_5$ being the Mg-richest compounds of the adjoining binary Mg systems. The isothermal sections for 500 and 300°C of the Mg corner of the Mg–Gd–Sm phase diagram were constructed. They display a one-phase Mg solid solution region, two two-phase regions of (Mg) + Mg_5Gd and (Mg) + $Mg_{41}Sm_5$, and a three-phase region of (Mg) + Mg_5Gd + $Mg_{41}Sm_5$. The mutual solubility of Gd and Sm in solid Mg becomes lower as the temperature decreases. Gd and Sm mutually reduce their solubility in solid Mg.

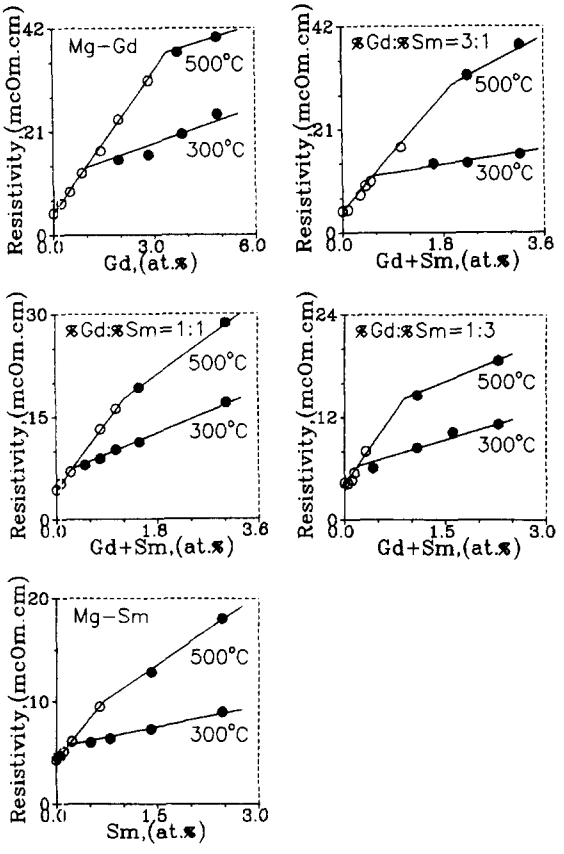

Fig. 4. Electrical resistivity of Mg–Gd–Sm alloys after annealing at 500 and 300°C. Open and filled circles correspond respectively to one-phase regions and two- or three-phase regions, as revealed by the microscopic investigation.

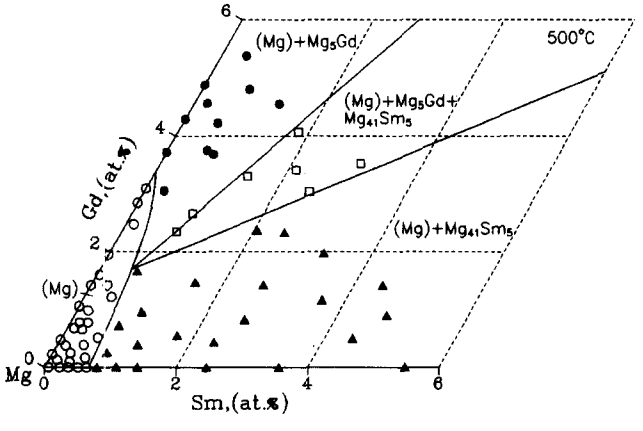

Fig. 5. Isothermal section of Mg–Gd–Sm phase diagram at 500°C.

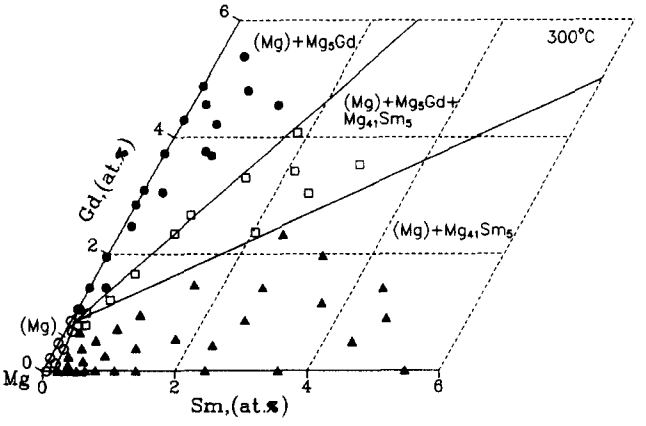

Fig. 6. Isothermal section of Mg–Gd–Sm phase diagram at 300°C.

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