EXPERIMENTAL INVESTIGATION OF THE Sm-RICH SIDE IN Sm-Zr SYSTEM

Tian Yin[1], Shuqiang Zhang[1], Zhihong Zhang[2], Jieyu Zhang[1*]

1 State Key Laboratory of Advanced Special Steel, School of Materials Science and Engineering, Shanghai University, Shanghai, 200072, China; 2 Baotou Research Institute of Rare Earths, Baotou, 014030, China

Keywords: Sm-Zr system, diffusion couple, phase equilibrium

Abstract

The information of phase diagram for the Sm-Zr system is deficient. A diffusion couple and two alloys in Sm-rich side of Sm-Zr system were prepared. The phase equilibrium in the alloys at 800 and 900 ℃ were determined by scanning electron microscopy，equipped with energy dispersive X-ray spectroscopy (SEM-EDS) and X-ray diffraction(XRD). The results show that a peritectic reaction exists in the Sm-rich end. The solubility of Sm in (Zr) was detected to be about 2.4 at.% at 800℃ and 2.7 at.% at 900 ℃. The solubility of Zr in (Sm) is negligible. No binary compound is detected in the XRD patterns in all samples.

Introduction

Alloys and compounds contained rare earth elements possesses unique properties. The scope of their applications includes permanent magnet materials，superconductors， sensors，phosphors. Therefore, knowledge of phase equilibria in the systems contained rare earth elements is desirable.

Sm and Zr are the important alloying elements of magnesium alloys to improve their mechanical properties[1-4]. For the advanced development of the Mg-based alloys, knowledge of the phase equilibria of the Sm-Zr system is of fundamental importance. However, the knowledge of the phase equilibria and thermodynamic analysis of this system is deficient. So far, no phase diagram for the Sm-Zr system is available in the literature. Consequently, we present here a preliminary study for Sm-Zr system.

Experimental Procedure

As starting materials, 99.9 wt.% Sm and 99.95 wt.% Zr were used for the preparation of the diffusion couple and Sm-Zr alloys. The Sm/Zr diffusion couple of approximate dimensions of 10 mm×10 mm×10 mm was made of pure block Sm and Zr. In order to decrease the influence of the potential oxidation film to the diffusion of atoms, the diffusion interface between Sm and Zr block was polished and pressed together under the pressure of 6 MPa, 800 ℃ and vacuum(10^{-3}Pa) for 4 hours. After hot pressing, the diffusion couple was encapsulated in quartz tube under a protective argon atmosphere. The diffusion couple was then annealed at 800 ℃ for 30 days, followed by water quenching.

Two alloy samples were synthesized from purity Sm and Zr using cold crucible induction levitation melting method. Due to the high volatility of Sm and the significant difference between the melting points of Sm and Zr, the pure Zr were added to the furnace by two or three

* Corresponding author. Tel.: +86 021 56337920;
E-mail address: zjy6162@staff.shu.edu.cn (Jieyu Zhang)

times respectively. Each alloy was melted several times to ensure good homogeneity. The alloys were wire cut as the size 4 mm×4 mm×4 mm, wrapped with tantalum sheet and then annealed in an evacuated quartz tube. Each sample was annealed at 500℃ for 30 days firstly and then at 800 and 900 ℃ for 7 and 3 days respectively, followed by water quenching.

The compositions of casting alloys were analyzed by optima 7300DV ICP. The HITACHI SU-1500 SEM/BSE equipped with EDS system were used to analyze the microstructure of diffusion couple and alloys. XRD, carried our on a Rigaku D/MAX-rC diffractometer (CuKα radiation，2θ = 25-70°，4°/min) operated at 40 KV and 100 mA, was used to determinate the structure of the alloys. Due to the oxidation of pure Sm in the form of powder, all the XRD samples are rectangle block, which were polished to be mirror surface in alcohol.

Results and Discussion

Analysis of diffusion couple

The BSE images of the microstructure of Sm/Zr diffusion couple annealed at 800 ℃ for 30 days are shown in Figure 1 (a). After the interdiffusion of the Sm and Zr, no intermetallics layer formed. Based on the principle of backscattering, the dark field is Zr and the bright field is Sm. the sample was studied via SEM/EDS and the results of line scanning and point analysis are presented in Figure 1 (b) and (c). The curve in Figure 1 (b) indicates that the diffusion layer is composed of (Sm) and (Zr) solid solution. The Figure 1 (c) shows the similar tendency to Figure 1 (b). The solubility of Zr in (Sm) at 800 ℃ was approximately 0.6 at.%, which is negligible.

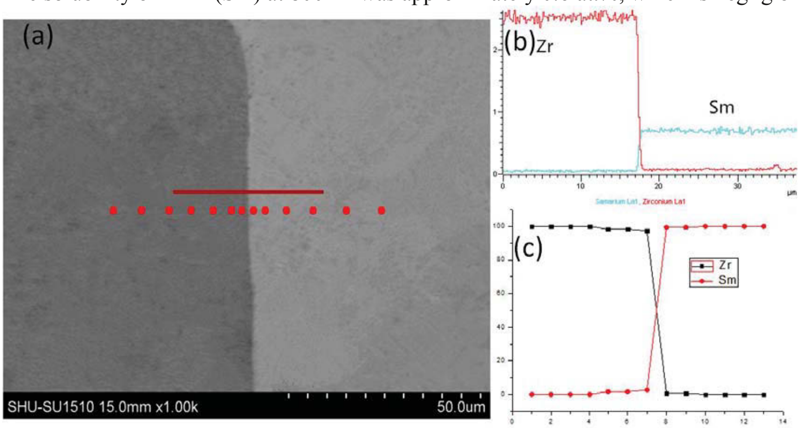

Fig 1. (a) The BSE image of the microstructure of the diffusion couple annealed at 800 ℃ for 30 days; (b) line scanning analysis of the diffusion couple; (c) point analysis of the diffusion couple.

Microstructure and phase identification of Sm-Zr alloys

According to the result detected from Sm/Zr diffusion couple, two alloys had been prepared for phase identification. All the prepared Sm-Zr alloys have been subjected to XRD and SEM/EDS. The analyzed chemical compositions for the alloys, annealing condition and phase identification are shown in Table I.

Table I. Summary of the composition and the annealing temperature of alloys in the present work

Alloy No.	Alloy composition (at.%)	Annealing temperature (℃)	Phase
#1	$Sm_{91.1}Zr_{8.9}$	800	(Sm) (Zr)
		900	(Sm) (Zr)
#2	$Sm_{77.2}Zr_{22.8}$	800	(Sm) (Zr)
		900	(Sm) (Zr)

Figure 2 shows the comparison of the microstructure between the as-cast Sm-Zr alloys and that annealed at 800 ℃ for 7 days and 900 ℃ for 3 days. Based on the principle of backscattering, the dark field is (Zr) and the bright field is (Sm). That is to say, the phase equilibrium relation in each annealed alloys is (Sm) + (Zr).

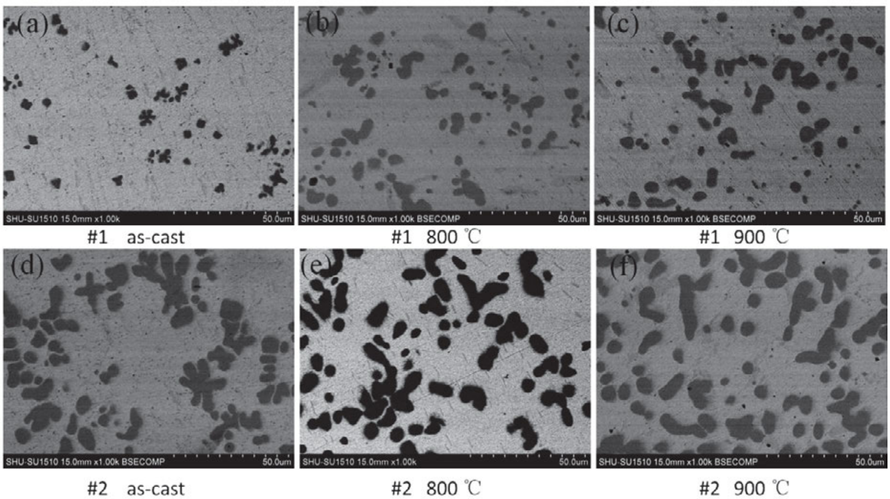

Fig 2. The BSE image of the microstructure of the as-cast Sm-Zr alloys and that annealed at 800 ℃ for 7 days and 900 ℃ for 3 days

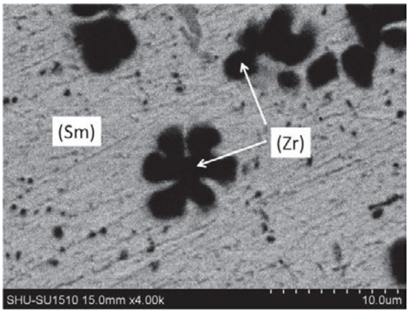

Fig 3. The BSE image of the dendritic crystal in the as-cast Sm-Zr alloys #1

Dendritic crystals shown in Figure 3 can be observed in the as-cast Sm-Zr alloys and that disappear after annealing at 800 and 900 ℃. This phenomenon is similar to the Nd-Zr binary system reported by Cheng[5]. The EDS results indicates that the solubility of Zr in (Sm) is negligible, the same as the results in the samples annealed at 800 and 900 ℃. It can be deduced that primary Zr dendritic crystal forms and grows up firstly at the beginning of the solidification, then surrounds by the peritectic formed (Sm). Therefore, this is a evidence that there is a peritectic reaction on the Sm-rich side in Sm-Zr system. The solubility of Sm in (Zr) was detected to be about 2.4 at.% at 800℃ and 2.7 at.% at 900 ℃. Figure 4 is the XRD patterns of as-cast and annealed Sm-Zr alloys. The XRD results indicates that all the alloys are composed of (Sm) and (Zr), which is in agreement with the results of SEM/EDS.

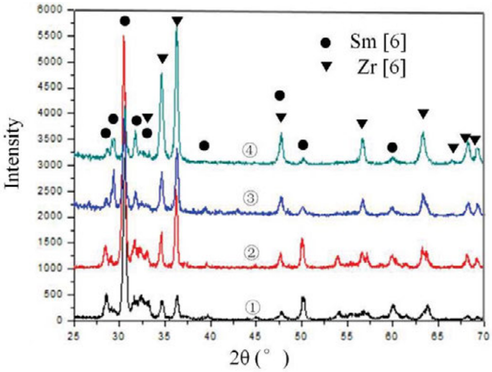

Fig 4. The XRD patterns of (1) as-cast alloy #1, (2) as-cast alloy #2, (3) alloy #2 annealed at 800 ℃ for 7 days, (4) alloy #2 annealed at 900 ℃ for 3 days

Conclusions

We have presented a preliminary study for the Sm-rich side of Sm-Zr system. It is that a peritectic reaction exists in the Sm-rich end. The solubility of Sm in (Zr) was detected to be about 2.4 at.% at 800℃ and 2.7 at.% at 900 ℃. The solubility of Zr in (Sm) is negligible. No binary compound is detected in the XRD patterns in all samples.

Acknowledgements

The authors thank Instrumental Analysis and Research Center of Shanghai University for their support of materials testing and research and Baotou rare earth institute for providing high purity materials.

References

1. Yuan M, Zheng Z. Effects of Zn on the microstructures and mechanical properties of Mg–3Sm–0.5Gd–xZn–0.5Zr (x=0, 0.3 and 0.6) alloy[J]. Journal of Alloys and Compounds, 2014, 590(2):355–361.
2. Wang Q, Li D, Blandin J J, et al. Microstructure and creep behavior of the extruded Mg–4Y–4Sm–0.5Zr alloy[J]. Materials Science & Engineering A, 2009, 516:189–192.
3. Z Zhang, L Peng, X Zeng, P Fu, W Ding. Characterization of phases in a Mg–6Gd–4Sm-0.4Zr (wt.%) alloy during solution treatment[J]. Materials Characterization, 2009, 60(6):555-559.
4. J Zheng, Q Wang, Z Jin, T Peng. The microstructure, mechanical properties and creep behavior of Mg–3Sm–0.5Zn–0.4Zr (wt.%) alloy produced by different casting technologies[J]. Journal of Alloys and Compounds 496 (2010):351–356
5. Cheng K, Zhou H, Hu B, et al. Experimental Investigation and Thermodynamic Modeling of the Nd-Zr and the Mg-Nd-Zr Systems[J]. Metallurgical & Materials Transactions A, 2014, 45(6):2708-2718.
6. S. Delfino, A. Saconne, and R. Ferro: Metall. Mater. Trans. A, 1990, vol. 21A, pp. 2109–14