STUDY ON THE NONEXISTENCE OF LIQUID MISCIBILITY GAP IN THE Ce-Mn SYSTEM

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Abstract

To ascertain whether the liquid miscibility gap exists in the Ce-Mn system, 3 key alloys are prepared by arc melting the pure elements, annealed at specified temperature for 20 minutes, quenched in ice water and then subjected to X-ray diffraction (XRD) analysis for phase identification and to scanning electron microscopy (SEM) with energy dispersive X-ray analysis for microstructure observation and composition analysis. The XRD examination indicated that terminal solutions based on Ce and Mn exist in the water-quenched alloys. No compound was detected. Microstructure observation and composition analysis indicate the nonexistence of the liquid miscibility gap. The newly assessed Ce-Mn phase diagram was presented.

1. Introduction

The Ce-Mn system is an important sub-binary system in multi-component high-strength and lightweight Al-based alloys containing nanoquasicrystalline particles [1-3]. Rapidly solidified nano-icosahedral reinforced Al-Ce-Mn alloys exhibit attractive properties such as good bending ductility and high tensile strength up to 1320MPa [1]. The specific strength of rapidly solidified $Al_{93}Mn_5Ce_1Ni_1$ (at.%) alloy is evaluated to be as high as 3.9×10^5 Nmkg^{-1}, which is considerably higher than the highest value (3.6×105 Nmkg^{-1}) obtained for the Al-based amorphous single phase and three times higher than that for the conventional Al-based crystalline alloy (7075-T6) [2]. The Ce-Mn system is a system with a high glass forming ability ($Ce_{100-x}Mn_x$, x=20-80 at.%) [4]. Knowledge of the phase equilibria is of fundamental importance to understand the physical properties, chemical behavior and the glass-forming ability of the alloys.

The Ce-Mn phase diagram was first investigated by Rolla and Iandelli [5], who found a narrower miscibility gap for the liquid than that in the La-Mn system. Subsequently, Iandelli [6] determined the complete phase diagram using the alloys prepared from 99.5 wt.% purity Ce and 99.8 wt.% purity Mn, and suggested the existence of the miscibility gap close to 998 ºC in the composition range of 45 to 64 wt.% Mn on the basis of the thermal analysis measurements. However, the existence of the miscibility gap was not confirmed by Mirgalovskaya and Strel'nikova [7], who reinvestigated the phase relations in the Ce-Mn system using a combination approach of thermal analysis and metallography. They [7] argued that the separation of the two liquids might be difficult because the densities of two liquid phases are approximately equal. The flat liquidus at 998 ºC was attributed to an anomalous behavior of the alloys resulting from the decomposition of γMn to βMn and liquid at 998 ºC. The observed thermal effect at 1087 ºC is interpreted as the transformation from δMn to γMn and liquid [7].

The phase relation of the Ce-Mn system was reinvestigated by Thamer [8] as well as Perkins et al. [9]. The Ce-Mn system was evaluated by Massalski [10] as well as Palenzona and Cirafici [11], who considered the previous experimental data [5-9]. The assessed Ce-Mn phase diagram [11] was presented with several uncertainties. The major uncertainty is the issue on the miscibility gap. The aim of the present work is to experimentally ascertain whether the liquid miscibility gap exists.

2. Experimental

Ce rods (purity: 99.9 mass %) and Mn pieces (purity: 99.9 mass %) were used as starting materials. The surfaces of Ce rods were ground, polished, cleaned with ethanol and acetone, and then kept in acetone before use. Mn pieces were treated with dilute nitric acid to remove the surfacial oxides, washed with water, ethanol and acetone, and subsequently kept in acetone. The alloys with the weights about 3-4 grams were prepared by arc melting pure elements under argon (purity: 99.999 %; further purified by Ti-gettering) on a copper hearth using a nonconsumable tungsten electrode. The key alloys with nominal compositions of 73, 75 and 77 at.% Mn were selected based on the assessed phase diagram [11]. The buttons were remelted 4 times to improve their homogeneity. Inductively coupled plasma mass spectrometry (ICP-MS) (IRIS Advantage 1000, Thermo Elemental, USA) was employed to determine the weight loss ratio of Mn during arc melting. Based on ICP-MS measurements of the alloys, slightly excessive Mn was added so that the derivation of the finally prepared alloys from the nominal compositions can be kept within ±1 at.%.

Each sample was cut into several pieces for annealing at different temperatures. Except one piece in as-cast state, the other pieces were for annealing. The samples were wrapped in Ta-foil to avoid the reaction of samples with quartz tube, sealed in evacuated quartz tubes, and then annealed in a high-temperature diffusion furnace (L-45-1-135, QingDao, China) at temperatures of 1012 to 1052ºC for 20 minutes. After completion of annealing, the samples were rapidly quenched into ice water.

After standard metallographic preparation, the microstructure observation and composition analysis of the specimens were performed with scanning electron microscopy (SEM) (JSM-5600LV, JEOL, Japan) with energy dispersive X-ray analysis (EDX). The identification of the phases was carried out using X-ray diffraction (XRD) analysis with monochromatic Cu Kα (Rigaku D/max2550VB, Japan).

3. Results and discussion

Table 1 summarizes the alloy compositions determined by ICP-MS technique, the phases identified by XRD, and the liquid phase compositions

measured by EDX for the alloys annealed at different temperatures for 20 minutes. The XRD examination indicated that the terminal solutions based on Ce and Mn exist in the water-quenched alloys. No compound was detected. This is consistent with the previous works [5-8].

Table 1 Summary of the alloy compositions, the phases identified by XRD, and the compositions obtained by EDX

No	Composition Nominal	(at. % Mn) Analysed[a]	Temperature (^{O}C)[b]	Phases	Composition (at.% Mn)[c]			
					A	B	C	D
1	75	74.5	1012	(Ce)+(Mn)	18.11	28.32	100	98.15
2	75	74.5	1032	(Ce)+(Mn)	20.71	25.05	100	98.72
3	75	74.5	1042	(Ce)+(Mn)	22.35	31.99	100	98.12
4	75	74.5	1052	(Ce)+(Mn)	23.43	25.97	100	98.67
5	73	72.8	1042	(Ce)+(Mn)	22.45	26.12	100	98.35
6	77	76.6	1042	(Ce)+(Mn)	22.67	30.05	100	98.28

[a] Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the compositions.

[b] The alloys were annealed at specified temperatures for 20 minutes.

[c] The locations corresponding to points A, B, C and D are marked in Fig. 2.

The backscatter electron images of the representative quenched alloys are presented in Fig. 1. The observed microstructures of all quenched alloys are similar to those published by Iandelli [6] and Mirgalovskaya and Strel'nikova [7]. Microstructure observation does not indicate the existence of the liquid miscibility gap as claimed by Rolla and Iandelli [5-6]. Figure 2 shows the EDX measurement regions. The measured compositions corresponding to the points A, B, C and D are indicated in Table 1. These EDX measurements show that the liquid composition (point A and B) is from 18.11 to 31.99 at.% Mn. No liquid phase with a composition larger than 75 at.% Mn reported by Iandelli [6] was observed. The composition (point C) for the large dark area in Fig. 2 almost corresponds to pure Mn, i.e., primary crystal Mn, whereas that for the dark area in dentrite (denoted by D) is about 98 at.% Mn.
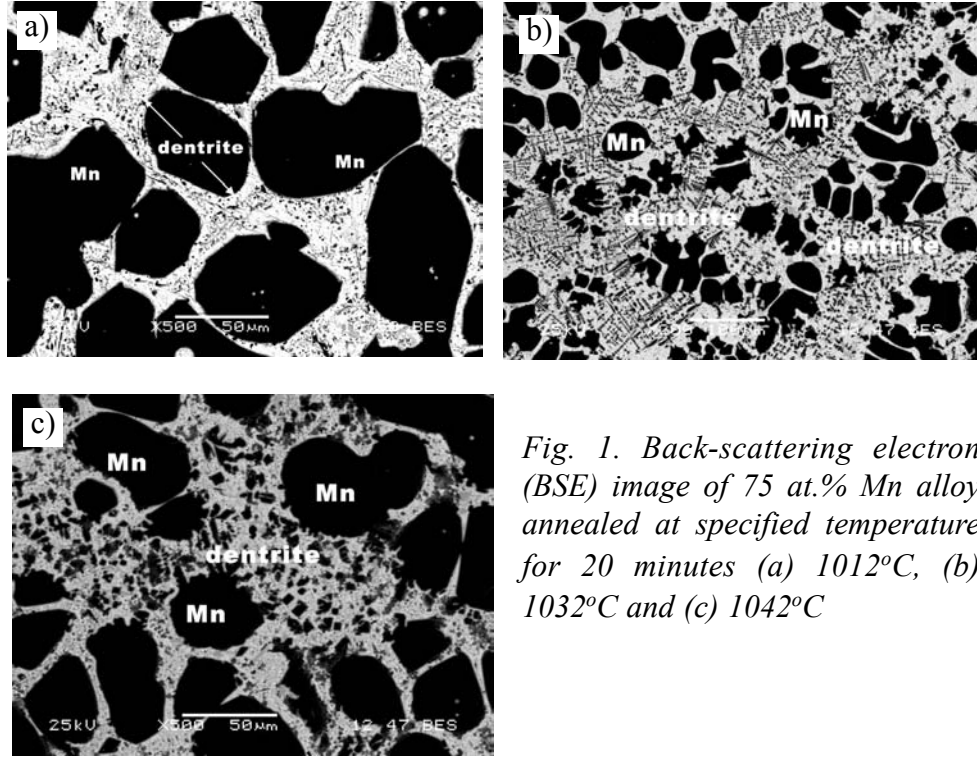
Fig. 1. Back-scattering electron (BSE) image of 75 at.% Mn alloy annealed at specified temperature for 20 minutes (a) 1012ºC, (b) 1032ºC and (c) 1042ºC
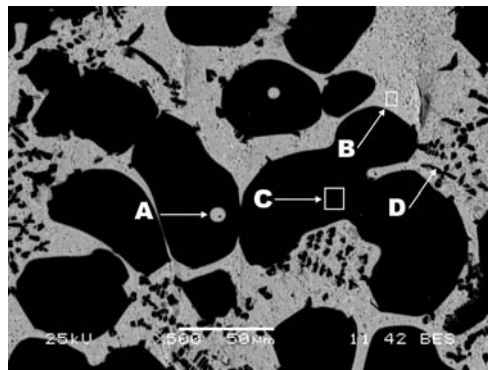

Fig. 2. Schematic illustration of EDX measurement dot for the alloy 75 at.% Mn annealed at 1032 ºC for 20 minutes.

The existence of primary crystal Mn also suggests the nonexistence of miscibility gap in the Ce-Mn system. As a consequence, the measured liquid composition and the existence of primary crystal (Mn) do not indicate that a liquid miscibility gap exists in Ce-Mn system, as suggested by Rolla and Iandelli [5, 6].
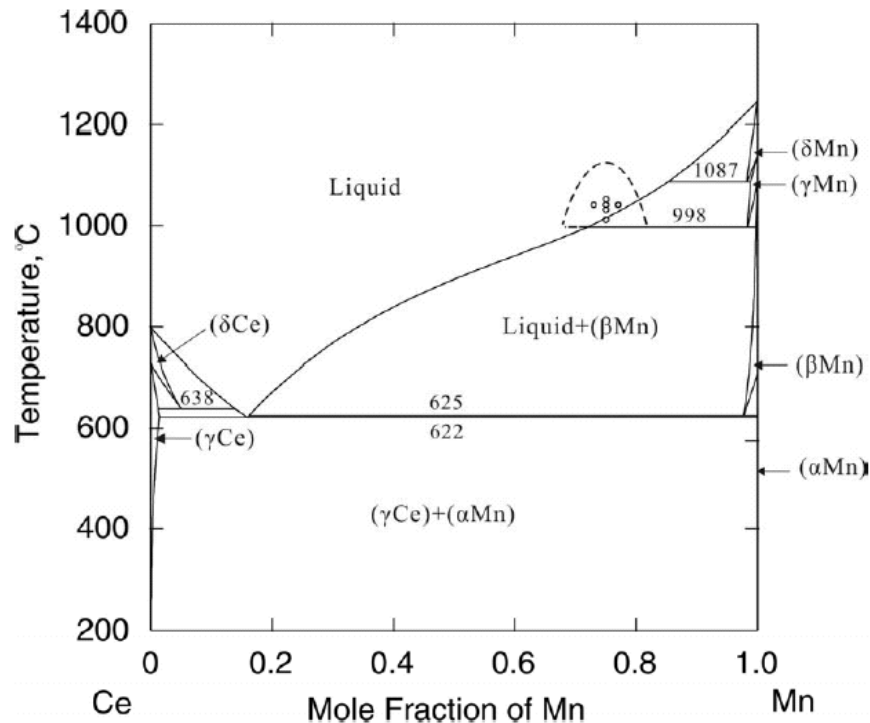

Fig. 3. Assessed Ce-Mn phase diagram according to the present work and the literature data [6-8]. The dash line represents the liquid miscibility gap region claimed by Iandelli [6]. The small circles denote the presently prepared samples, showing of only single liquid phase at the specified temperature. The reaction (βMn = αMn + Liquid) occurs at 625°C, and the reaction (Liquid = γCe + αMn) occurs at 622°C

Based on the experimental results from the present work and the previous work [6, 7], the newly assessed Ce-Mn phase diagram is presented in Fig. 3. The assessed Ce-Mn phase diagram can be used to interpret the presently observed microstructure. For the investigated alloys, primary crystal (Mn) was first precipitated from a liquid alloy accompanying temperature decrease

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during quenching. Since large cooling rate and the supercooling accompany during quenching, the dentrite, consisting of solidified liquid and βMn, was found in the quenched alloys.

4. Conclusion

The nonexistence of the liquid miscibility gap in the Ce-Mn system was confirmed by means of XRD and SEM methods applied to three key alloys. Based on the experimental results and reliable literature data, the newly assessed Ce-Mn phase diagram is presented. The observed microstructure can be interpreted using the assessed phase diagram.

Acknowledgements

References

1. A. Inoue, M. Watanabe, H. M. Kimura, F. Takahashi, A. Nagata and T. Masumoto, *Mater. Trans. JIM*. 33 (1992) 723.
2. H. M. Kimura, K. Sasamori, M. Watanabe, A. Inoue and T. Masumoto, *Mater. Sci. Eng*. A181/182 (1994) 845.
3. F. Schurack, J. Eckert and L. Schultz, *Acta Mater*. 49 (2001) 1351.
4. Y. Obi, S. Murayamab, Y. Amakaib and K. Asano, *Physica* (B) 359-361 (2005) 299.
5. L. Rolla and A. Iandelli, *Ber. Deut. Chem. Ges*. 75 (1942) 2091.
6. A. Iandelli, Lincei-Rend. *Sc. fis. mat. e nat*. 13 (1952) 265.
7. M. S. Mirgalovskaya and I. A. Strel'nikova, *Tr. Inst. Met. Akad. Nauk* SSSR 2 (1957) 135.
8. B. J. Thamer, J. *Less-common Met*. 7 (1964) 341.

9. R. H. Perkins, L. A. Geoffrion, J. C. Biery, *Metall. Trans. AIME* 233 (1965) 1703.
10. T. B. Massalski, in: Binary Alloy Phase Diagrams, Vol. 1, Metals Park, Ohio: Am. Soc. Metals, 1986, p.724.
11. A. Palenzona and S. Cirafici, *J. Phase Equilibria* 17(1) (1996) 53.