Materials Transactions, Vol. 44, No. 4 (2003) pp. 552 to 557
Special Issue on Platform Science and Technology for Advanced Magnesium Alloys, II

Observation of Manganese-Bearing Particles in Molten AZ91 Magnesium Alloy by Rapid Solidification

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Magnesium alloy AZ91 contains 0.1 to 0.3 mass% manganese as an alloying element. Such manganese always reacts with aluminum and produces various compounds. Actually, numerous Mn-bearing particles are visible in polished surfaces under an optical microscope. Some Mn-bearing particles are also expected to be present in molten alloy. We believe that some Mn–Al compounds are closely related to the superheating effect. However, it is not clear specifically what compounds exist in molten alloy and how contribute to grain refinement by superheating. In order to study this subject, we utilized a diffusionless process based on rapid solidification. Two grams of AZ91 alloy was melted in a stainless steel tube and then injected onto a copper wheel rotating at high-speed under various conditions to obtain cast ribbons. Cast ribbon was analyzed by an X-ray diffractometer, an electron probe micro-analyzer and a transmission electron microscope. These analyses indicated that the cast ribbons consist of single phase and that the structure is quite homogeneous, *i.e.*, diffusionless solidification occurs due to rapid cooling. Manganese-bearing particles completely disappear in the melt around 963 K and superheat temperatures, which is inconsistent with presently accepted superheat mechanisms, the temperature-solubility nucleation theory and the temperature-phase relationship theory. In the meantime, cross-shaped Mn-bearing particles are often observed in the ribbons when the melt is cooled from superheat temperatures to the injecting temperature (973 K) before injecting. This treatment may facilitate the formation of these particles.

(Received October 22, 2002; Accepted December 9, 2002)

Keywords: *AZ91, Mn-bearing particles, rapid solidification, grain refinement, superheat treatment*

1. Introduction

Magnesium alloys are attractive as a light-weight structural material due to recent environmental problems. New magnesium alloys and processes are thus being intensively studied and developed in industrial countries.

Magnesium-alloy components are generally produced by casting processes. Mg–Al based alloys, such as AZ and AM series magnesium alloys, are the most commonly used commercial materials in automotive fields. In these alloys, manganese is a beneficial element that reduces the influence of harmful iron.[1)] Usually, manganese is normalized 0.1 to 0.35 mass% to improve corrosion resistance.[2)] Manganese forms various compounds with aluminum and removes harmful iron by absorbing it into compounds. These compounds form metallic brown particles that are easily found by metallographic observation. Existence of variously shaped compounds suggests that some of them are effective nucleation matter about fine-grained microstructure by superheat treatment.[3,4)] However, it is not clear how and when these compounds are produced.

Superheat treatment is a useful method for obtaining fine-grained cast microstructure of Mg–Al based alloys. In general, this treatment reduces the average grain sizes to quarter approximately. This treatment consists of just a simple heat cycle in which molten metal is held at an elevated temperature, quickly cooled to the casting temperature and then poured. Many researchers[2–8)] discussed theories of why the treatment effectively produced fine grains, but they could not establish a mechanism. To date, there have been many hypotheses of this grain-refining mechanism. In particular, the temperature-solubility nucleation theory and the temperature-phase relationship theory are widely accepted as explaining the general mechanisms of superheat refinement. However, experimental methods to verify these hypotheses are quite difficult. Nonetheless, it is important to precisely control cast microstructure of magnesium alloys.

In this study, we investigate the presence of manganese-bearing particles in molten AZ91 magnesium alloy at various temperatures using rapid solidification of single-roll method, and discuss the previous hypotheses to determine the relationship between the effect of superheat treatment and the presence of manganese-bearing particles.

2. Experimental Procedures

2.1 Rapid solidification

Table 1 shows the chemical composition of AZ91 magnesium alloy. A 2-gram sample of the alloy was cut off from the ingot and charged into a 10 mm-diameter stainless steel tube. The tube end is worked into a slit (0.3 mm) and the tube inner wall is coated with BN. We melted the charged alloy by induction heating and then injected in onto a copper wheel rotating at high speed. In this process, we successfully obtained magnesium alloy ribbon. SF_6 and CO_2 were utilized to prevent burning throughout this experiment, and Ar was used to push the melt from the stainless steel tube onto the copper wheel.

Table 1 Chemical composition of AZ91 magnesium alloy.

(mass%)

Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
8.5	0.71	0.23	<0.01	0.001	<0.001	0.002	bal.

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2.2 Microscopic examination

We determined the metallographic features of alloy ribbons by an optical microscope (OM), an X-ray diffractometer (XRD), a scanning electron microscope (SEM), an electron prove microanalyzer (EPMA) and a transmission electron microscope (TEM) equipped with an EDS-unit. XRD was conducted using X-rays of CuKα, an applied voltage of 40 kV and a current of 20 mA. SEM and EPMA were performed with an acceleration voltage of 15 kV, and TEM, with an acceleration voltage of 200 kV.

In order to determine the microstructures, the appropriate size of the ribbon cemented on the aluminum block was polished with Al_2O_3 suspension, and the freshly surface were revealed. Particularly, samples for a TEM were prepared by twin-jet electropolishing and ion thinning. The electroyte consist of ethanol (100 mL), 2-n-butoxyethanol (15 mL), acetic acid (3 mL) and sodium thiocyanate (17.5 g), and the ion thinning was subsequently carried out at 15° and 4 kV.

2.3 Experimental conditions

The alloy ribbons were prepared under the following conditions.

① Molten alloys were held for 300 s at temperatures of 893, 903, 913, 923, 933, 943, 953, 963, 973, 1023 and 1073 K and then injected at these temperatures.

② In superheat treatment, the molten alloy must be held for a given time at elevated temperatures (the superheat temperatures). We therefore held the melts for 60, 180 and 300 s at 1123 K, 1173 K and 1223 K, and then injected the melt at each temperature. In addition, superheat treatment does not produce enough grain refinement if the superheated melt is subsequently held below the temperatures of superheat region. Thus, we immediately cooled the melts after the elapsed time from the superheat temperatures to injecting temperature (973 K) and then injected them.

3. Results and Discussion

3.1 Microscopic examination

Figure 1 shows the 10 mm-wide, 50 μm-thick alloy ribbons. The ribbons have bright metallic surfaces that facilitate metallographic observation. These were freshly polished and then placed in an etchant consisting of acetic acid (20 mL), nitric acid (1 mL), ethylene glycol (60 mL) and distilled water (90 mL) for 5 seconds before the optical metallographic studies.

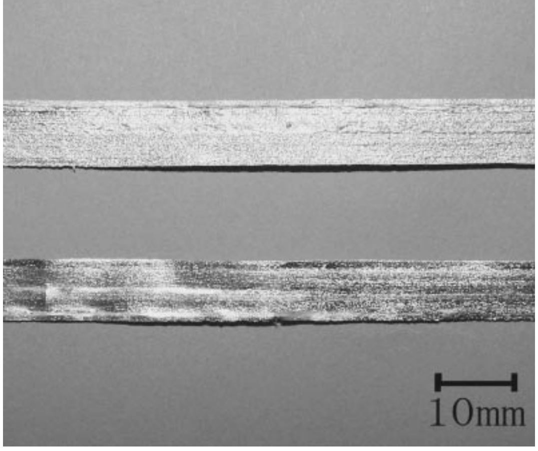

Fig. 1 Rapid-solidified alloy ribbons.

Figure 2(a) shows the cast microstructure of permanent mold castings. Figures 2(b) and (c) are optical micrographs of alloy ribbons injected at 973 and 1223 K. We observed micro-segregation of aluminum and non-equilibrium eutectic compounds of $Mg_{17}Al_{12}$ in permanent mold castings. In the meantime, the ribbons consist of single-phase material with quite fine-grained structure. Considering a binary Mg–Al alloy, we can predict that the solidification process of the ribbons is depicted as in Fig. 3. From this figure, the entire process probably progressed below the solidus temperature (Ts) in a supercooled condition since the single-roll method generally attains a cooling rate of 10^6 Ks^{-1} with continuous chilling of the copper wheel.[9] On the other hand, the cooling rate of permanent mold casting is about 50 Ks^{-1}. The single-roll method hinders movement of the solute elements, so

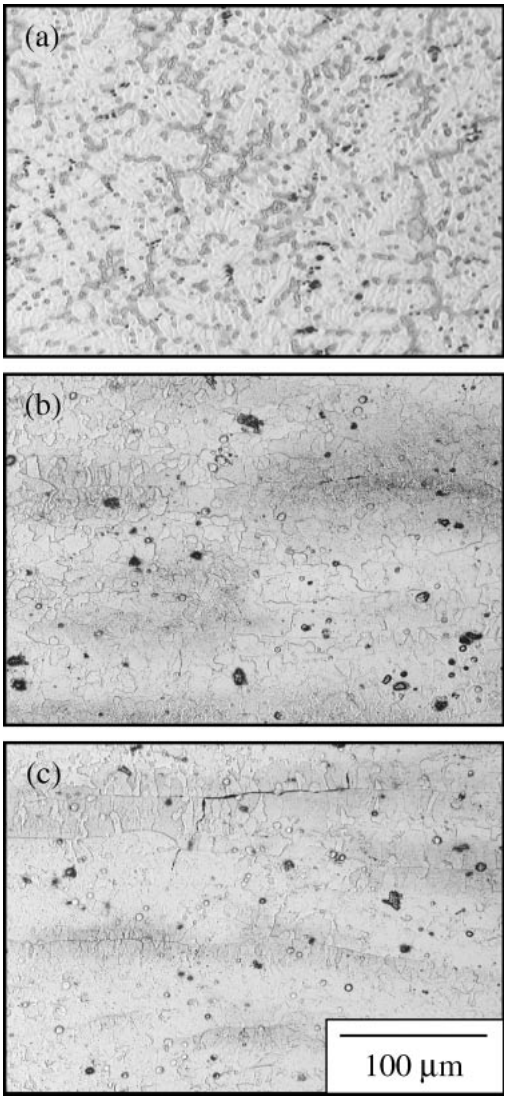

Fig. 2 Optical micrographs of AZ91 magnesium alloy, permanent mold casting (a), rapid-solidified alloy ribbon injected at 973 K (b) and at 1223 K (c).

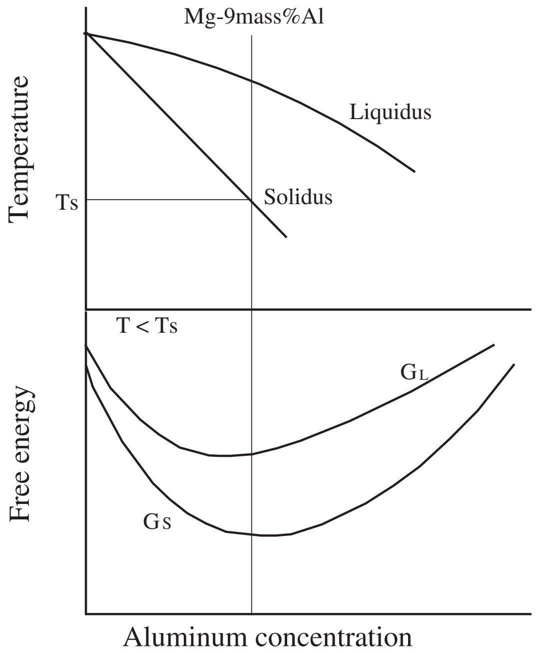

Fig. 3 Schematic diagram of rapid solidification.

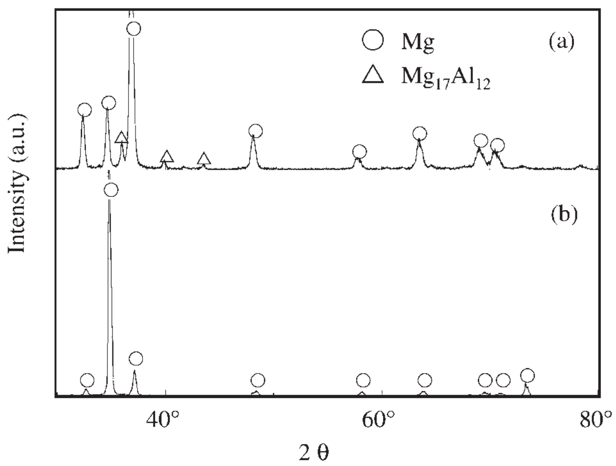

Fig. 4 X-ray diffraction patterns of AZ91 magnesium alloy, permanent casting (a) and rapid-solidified ribbon (b).

Table 2 With or without of manganese-bearing particles.

Melt temp. (K)	Particles
893	○
903	○
913	○
923	○
933	○
943	○
953	○
963	×
973	×
1023	×
1073	×

with ○, without ×

diffusionless solidification ($G_L > G_S$) schematically exhibited in free-energy composition diagram occurs[9–11] and therefore, provably prevents manganese compounds from precipitating. The result of XRD proved the ribbon to be single-phase magnesium solid solution. For example, Fig. 4 presents a XRD pattern without an $Mg_{17}Al_{12}$ peak.

Figure 5 depicts back-scattered electron images of alloy ribbons, where the melts were injected at 893, 923 and 973 K. Undissolved manganese-bearing particles are always found in microstructure injected at 893 and 923 K, but not at 973 K. We could not find any particles in the ribbon injected at 973 K. This is also inconsistent with earlier work[3] in which compounds, such as $MnAl_6$, are stable in the alloy below the superheating temperature.

Table 2 summarizes the manganese-bearing particles found at various melt temperatures. In this table, if manganese particles are observed, the cell is filled with a circle (○); if they are not observed, the cell is filled with a cross (×).'' Normally, we observed a 1 cm^2 piece of each of three portions of an alloy foil to judge the existence of the particles. As a result, we confirmed some Mg–Al compounds existed in a temperature range from 893 to 953 K, but completely disappeared at temperatures above 963 K.

The temperature-solubility nucleation theory in superheat treatment states that some materials with particles too large at normal temperatures to be effective as nuclei are dissolved into solution at higher temperatures and then reprecipitate to form fine nuclei during the cooling process.[3,8] In this experiment, however, we could not detect such particles.

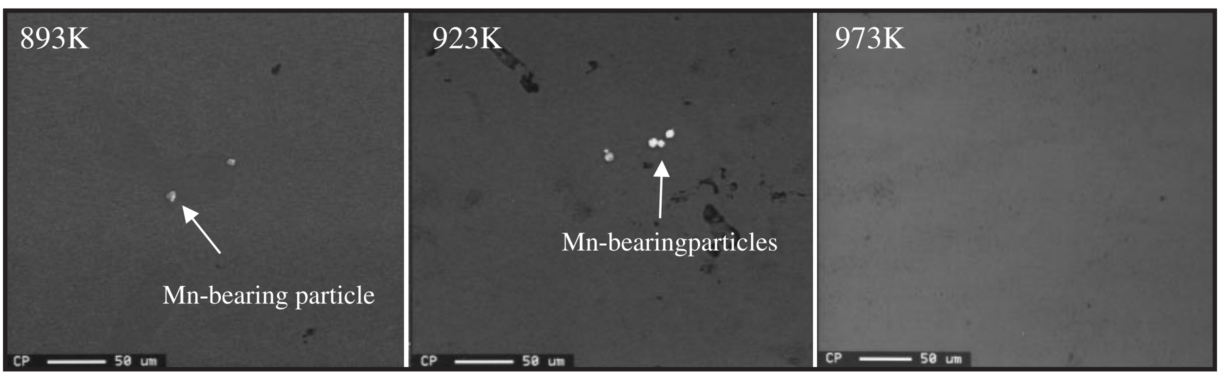

Fig. 5 Back-scattered electron images of alloy ribbons injected at 893 K, 923 K and 973 K.

Furthermore, manganese compounds completely disappeared at 973 K, which is about 100 K below the superheat temperature.

3.2 Superheat treatment and manganese compounds

The relationships between superheat treatment and the presence of manganese-bearing particles are listed in Table 3. Micrographic examination did not reveal any particles in alloy ribbons injected at holding temperatures corresponding to the superheat region (1123 K to 1223 K), independent of melt-holding time. This does not seem to support the previous temperature-phase relationship theory in superheat treatment since this theory states that the manganese compounds with hexagonal crystal habit, such as $MnAl_4$, is stable at the range of superheating temperatures provide effective nucleation material of primary magnesium.

In this experiment, however, cross-shaped particles could be often observed as shown in Fig. 6 when the melt was rapidly cooled to 973 K before injecting. This tendency is likely to be more remarkable if the melt is cooled from higher temperatures. Generally, it is difficult to characterize these particles in conventional castings because variously kinds of and shaped compounds are mixed with them. Figure 7 shows the EPMA analysis of the particles. From this figure, the particles obviously consist of aluminum, manganese and iron. Furthermore, there seems to be much more iron at the center than in outer regions. Figure 8(a) shows the TEM bright field image of the particle, where the electron diffraction patterns of the portions numbered 1 and 2 were taken. As can be seen from Fig. 8(b), electron diffraction produced the same patterns of single crystal both at the center and in the outer regions. Furthermore, the EDX analysis (Fig. 9) identifies that the particle is composed of aluminum, manganese and iron, consistent with the result of the EPMA

Table 3 With or without of manganese-bearing particles in superheated melt.

Melt temp. (K)	Holding time (s)	Injecting temp. (K)	Particles
1123	0	973	○
		1123	×
	60	973	×
		1123	×
	180	973	×
		1123	×
	300	973	○
		1123	×
1173	0	973	×
		1173	×
	60	973	○
		1173	×
	180	973	○
		1173	×
	300	973	○
		1173	×
1223	0	973	○
		1223	×
	60	973	○
		1223	×
	180	973	○
		1223	×
	300	973	○
		1223	×

with ○, without ×

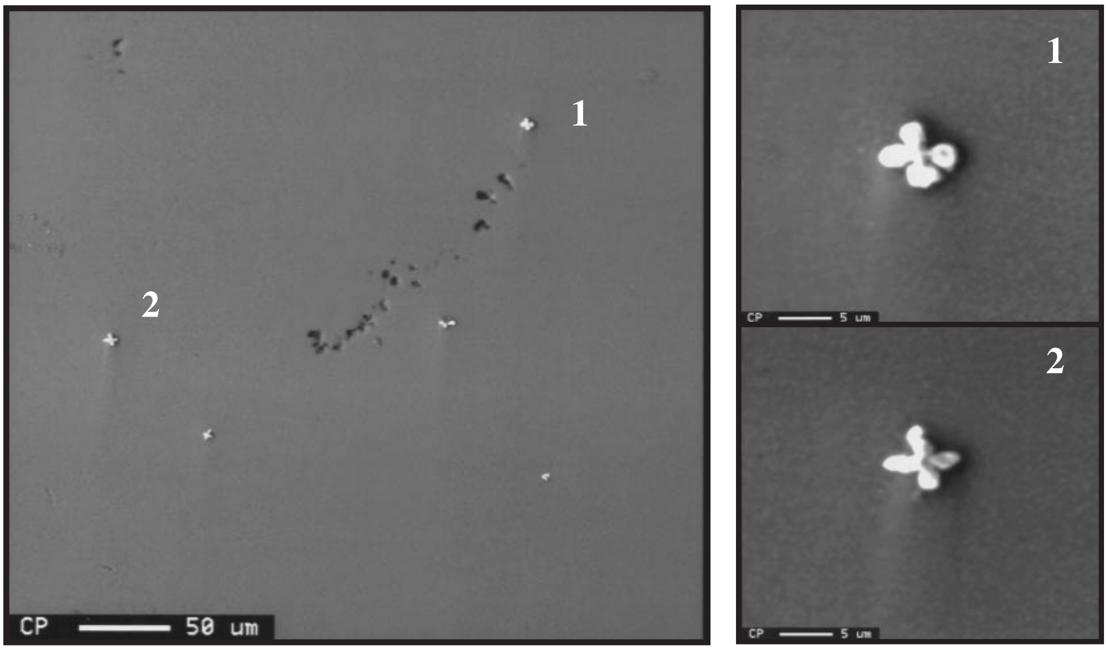

Fig. 6 Cross-shaped particles dispersed in alloy ribbon.

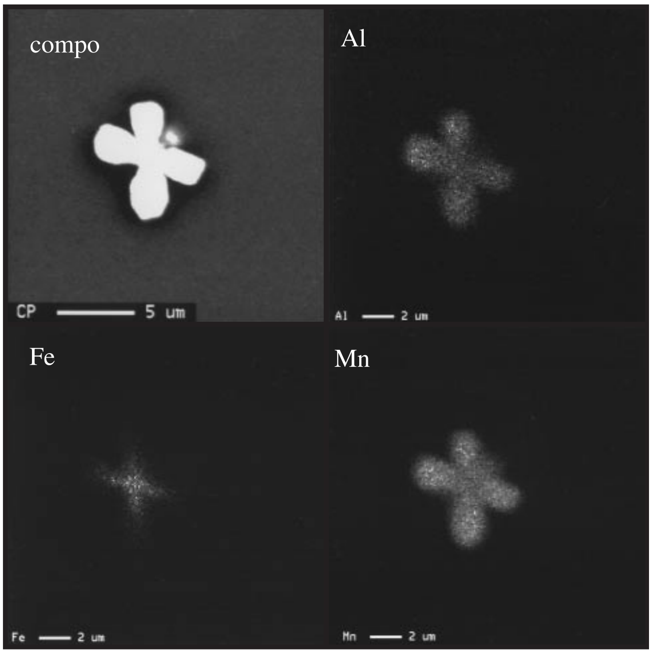

Fig. 7 EPMA analysis of cross-shaped particle.

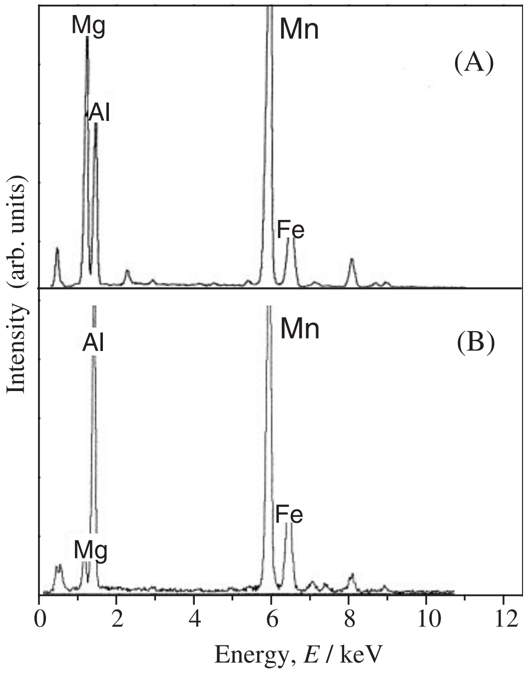

Fig. 9 EDX analysis about the cross-shaped particle in Fig. 7, portions numbered 1 (A) and 2 (B).

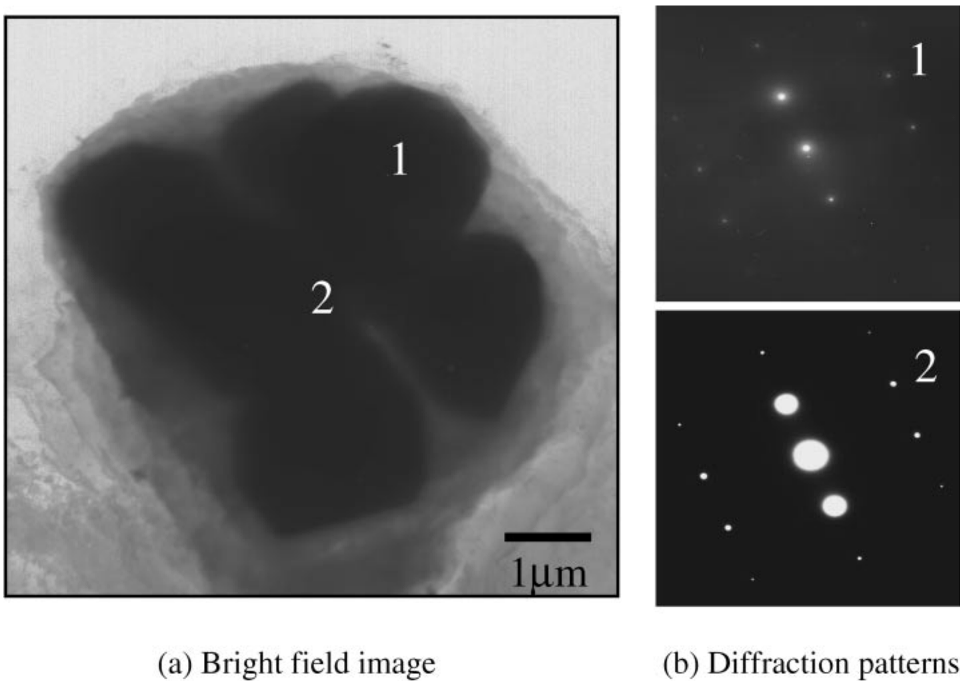

Fig. 8 TEM observation of cross-shaped particle.

analysis. Consequently, during the cooling process, manganese-bearing particles containing much iron may first crystallize from the melt and develop cross-shaped features with decreasing iron content; superheat treatment may facilitate the formation of these particles.

Although cross-shaped particles will produce effective nucleation sites for magnesium, the temperature-solubility nucleation theory has already been rejected above. For this reason, it is possible that iron from the stainless steel tube contaminated the superheated melt and promoted the crystallization of manganese. Actually, chemical analysis reveals an increase of iron content before and after the experiment. For example, iron content of the raw material is 0.0022 per cent, while that of the alloy foil is 0.0030 per cent. However, we have not clarified to what extent compositional differences bring about manganese precipitation.

4. Conclusion

In this experiment, we investigated manganese compounds in molten AZ91 magnesium alloy by rapid solidification and discussed the previous general hypotheses about the mechanisms of superheat grain refinement. The results obtained are as follows:

(1) The Temperature-Solubility Nucleation Theory in grain refining by superheat treatment is not valid because large particles in AZ91 magnesium alloy, such as manganese compounds, completely disappear in the melt around 963 K.

(2) The Temperature-Phase Relationship Theory is not valid because no manganese compounds that are expected to become nucleation sites are formed when the melt was held at superheat temperature.

(3) In some cases, cross-shaped manganese-bearing particles are crystallize from melt during the cooling process before injecting if the melt is cooled from superheat temperature.

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