論 文

A Novel Slury-Making Process for AZ91-Alloy Rheocasting

Ji-Young Byun†, Soon-Il Kwon*, Jin-Kook Yoon, and Seon-Jin Kim*

Abstract

본 논문은 레오캐스팅용 AZ91 합금 슬러리를 제조하는 새로운 방법에 관한 것이다. 그 원리는 AZ91 합금 액상에서 Mn의 용해도차에 의해 생성되는 $Al_8(Mn,Fe)_5$ 정출물을 α-Mg 초정 생성을 위한 불균일 핵생성 자리로 사용하고자 하는 것이다. 제조된 슬러리의 미세조직 분석결과 $Al_8(Mn,Fe)_5$ 정출물이 α-Mg 내에 위치하고 있어, 이로부터 정출물이 효과적으로 불균일 핵생성 자리로 작용하고 있음을 알 수 있었다. 또한 Mn 함량의 증가는 $Al_8(Mn,Fe)_5$ 정출물 수를 증가시켜, 고상분율이 일정할 때 슬러리 내 α-Mg 고상의 크기를 감소시키고 구형도를 향상시킨다. 이외에도 냉각속도 및 유지시간이 슬러리 미세조직에 미치는 영향에 대해서도 보고하였다. (Received April 12, 2003)

Keywords: Mg alloy, AZ91, Rheocasting, Solidification, Heterogeneous nucleation, Intermetallics.

1. Introduction

Semi-solid forming of Mg alloys has received much attention because the process can overcome problems of pore formation and hot tearing which are usually observed in the high pressure die casting (HPDC) process.[1,2] It is well known that there are two semi-solid processes: rheocasting and thixocasting.[2] The route of thixocating is composed of the manufacture of billets of the desired micro-structure, and the subsequent reheating and forming of the billet in the semi-solid state. On the other hand, the rheocasting is the process to form the semi-solid feed materials called slurry, which are manufactured directly from the liquid state. Such a process simplification leads the rheocasting to become more cost-effective than the thixocating.

One of key technologies in the rheocasting is to manufacture the high quality slurry. To the date, the NRC (New Rheocasting) process has been well known as the slurry forming technique for Mg alloys.[1]. The primary Mg phase with globular shape can be formed by the method avoiding con-stitutional supercooling during precipitation of the primary Mg on a steel cup. As nucleation sites for the method are on the cup wall, great cares are necessary to keep nucleation and to avoid remelting of the primary phase. Thus, the NRC method indispensably accompanies some inconveni-ences in control of cooling pattern.

In the present study, a simple method is suggested for the production of the slurry used for the semi-solid forming of AZ91 Mg alloy. The basic principle of the method is utilization of $Al_8(Mn,Fe)_5$ as a heterogeneous nucleation site for the primary Mg and the principle is explained in the below.

2. Basic principle of the method

Solubility of Mn in Mg alloy melts varies as a function of temperature. Thorvaldsen and Aliravci[3] have obtained the following equation.

$$[Mn]_{sol} = [Al]^{-0.45} e^{11.97-11398/T}$$

where, $[Mn]_{sol}$ and [Al] are the solubility of Mn in the melt and the Al concentration in weight %, respectively, and T is the temperature in Kelvin. The Mn solubility in AZ91 alloy melt at several temperatures is calculated in Table 1. As shown in Table 1, the Mn solubility varies

한국과학기술연구원 재료연구부(Div. of Mat., Korea Institute of Science and Technology)
*한양대학교 재료공학부(Div. of Mat. Sci. and Eng., Hanyang University)
†E-mail : jybyun@kist.re.kr

significantly with temperature. Table1 shows that the saturation solubility temperature for the AZ91 alloy with 0.23% Mn, which is used as a raw material in the present work, is 642°C. When this alloy is solidified after holding at a higher temperature than 642°C, super-saturated Mn is likely to precipitate. It is well known that the Mn in AZ91 alloy precipitates as a form of Al_8Mn_5 rather than pure Mn. In most cases the AZ91 alloy melt contains Fe. Thus, the actual precipitate normally becomes $Al_8(Mn,Fe)_5$.[4] When the melt reaches 598°C which is the liquidus temperature of AZ91 alloy,[5] about 0.108% Mn will be precipitated as a form of $Al_8(Mn,Fe)_5$ as far as solidification does not exceedingly deviate from the equilibrium condition. If these precipitates act as heterogeneous nucleation sites, the primary Mg will be formed as illustrated in Fig. 1. Slurries are formed when the melt is held at a two-phase region (585°C) after partial solidification.

3. Experimental procedure

In the present work, AZ91 alloys with 0.23% and 0.45% Mn are used. Chemical compositions are listed in Table 2. The alloy with 0.23% Mn was prepared by machining the primary AZ91 ingot (Hydro Magnesium). The AZ91 alloy with 0.45% Mn was prepared by the following procedure. Approximately 20 kg of AZ91D primary ingots in a steel crucible was flux-melted at 740°C in an electric resistance furnace. In order to add the Mn in the melt, 200 g of anhydrous $MnCl_2$ were added into the AZ91 alloy melt. The melt was mechanically agitated for half an hour and its temperature was lowered to 700°C. After held for 1 h to allow for settling of precipitated particles, the melt were cast into a steel mold to make samples with 0.45% Mn.

A vertical tube furnace was used for slurry making. A 25 g sample was charged to a graphite crucible and held at 740°C for 10 minutes to form a single liquid phase under an inert atmosphere of Ar gas. The fully homogenized melt was drawn up near the Ar inlet and the Ar flow rate was increased for quick cooling. Change in the melt temperature was monitored by a K-type thermocouple that was inserted into the melt through the lid of the crucible. When the melt temperature approached around the liquidus temperature, the crucible was gently moved down for holding the crucible at a solid liquid two-phase region. The temperature of the solid liquid two-phase region was controlled about 585±3°C. Samples were held for 5 and 20 minutes and they were quenched into an ice water bath. Slurry microstructures were characterized using an optical microscope (Cal Zeiss Co., Axioplan 2) and a scanning electron microscope (SEM, Hitachi, S-4200). Chemical analysis of precipitates was carried out by the electron probe microanalysis (EPMA, Cameca SX-51) technique. The size and roundness of the primary Mg were measured from the optical micrographs using the image analyzer program

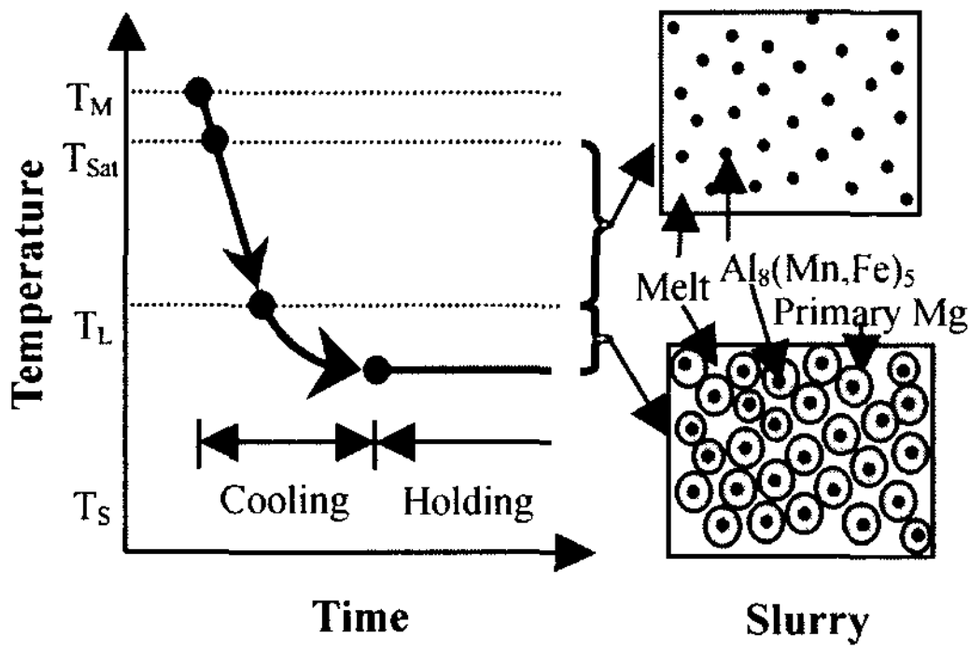

Fig. 1. A Schematic illustration for slurry forming of AZ91 Mg alloy.

Table 1. *Temperature dependence of Mn solubility in liquid AZ91 alloys*

Temperature (°C)	598	610	630	642	650	670	690	710
Mn Solubility (wt.%)	0.122	0.146	0.194	0.230	0.255	0.331	0.425	0.541

Table 2. Composition of AZ91 alloys used in the study (wt.%)

Alloys	Al	Zn	Mn	Fe	Si	Ni	Cu	Mg
Low Mn	9.0	0.80	0.23	0.003	0.02	<0.001	0.002	Remainder
High Mn	9.0	0.80	0.45	0.0029	0.02	<0.001	0.002	Remainder

(Media Cybernetics Co., Image-Pro Plus). The roundness is expressed as $P^2/4pA$, where A is a particle area and P is its perimeter.[6] The solid fraction in the slurry was also measured by the same program based on Delesse's principle[7] which states that the area fraction of non-classically shaped objects measured on the 'two-dimensional' random sections is an unbiased estimate of its volume fraction.

4. Results and discussion

4.1 Microstructure of AZ91 slurries

Microstructures of the slurries made from the AZ91 alloy with 0.23% Mn were shown in Fig. 2. Fig. 2(a) is an optical micrograph of the slurry obtained under conditions that the cooling rate from the single phase melt to two-phase region (585°C) was 2.5°C/s and the holding time at 585°C was 5 minutes. Fig. 2(b) is a magnified SEM image of Fig. 2(a). Dark particles in the optical micrograph or white particles in the SEM image were observed to be within the primary Mg phase. From the electron probe micro analysis (EPMA) of 30 particles, the particles were identified as the $Al_8(Mn,Fe)_5$ phase with composition of Table 3. If the $Al_8(Mn,Fe)_5$ phase did not act as a heterogeneous nucleation site for Mg crystallization, it would be pushed by the solid-liquid interface of the primary Mg into the eutectic region. Existence of the $Al_8(Mn,Fe)_5$ particles within the primary Mg phase rather than the eutectic region indicates that the particles act as the heterogeneous nucleation site[8]. On the other hand, the slurry made with the cooling rate of 0.08°C/s shows quite different morphology. As shown in Fig. 3, branched dendrites are formed and the size of each isolated primary Mg dendrite is larger than that formed with higher cooling rate. The branched morphology typically appears when the nucleation mode is homogeneous. If we look at the microstructure of Fig. 3, precipitates are rarely found. This is due to the sedimentation of $Al_8(Mn,Fe)_5$ particles when the cooling rate to the mixed phase region is excessively slow, considering that the density of $Al_8(Mn,Fe)_5$ phase is calculated to be 4.4 g/cm^3 from its

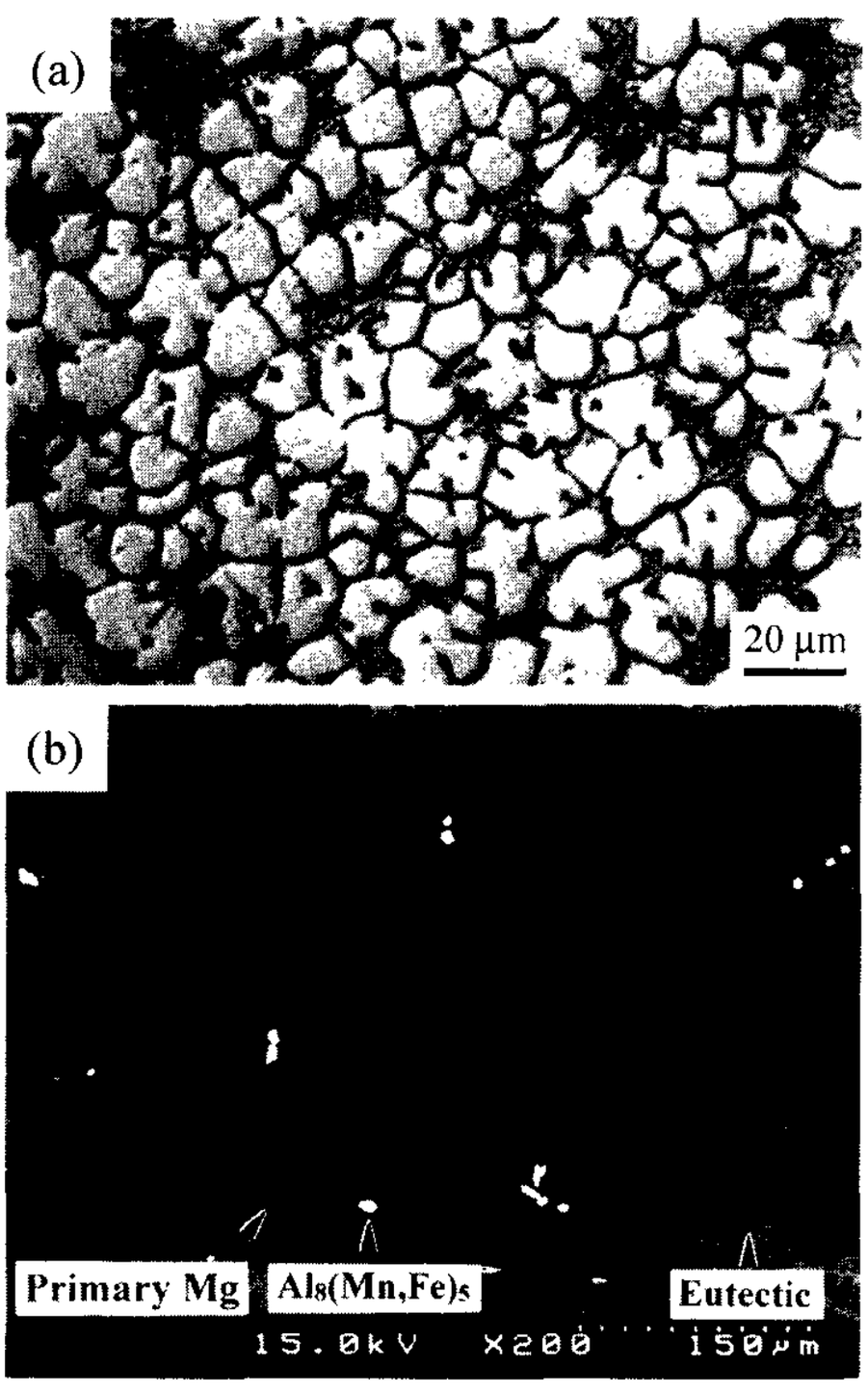

Fig. 2. Microstructures of an AZ91 Mg alloy slurry with 0.23 wt.%Mn (Cooling rate is 2.5°C/s and holding time is 5 min.); (a) an optical image and (b) a back-scattered SEM image.

Table 3. Composition of $Al_8(Mn,Fe)_5$ phase

Chemical composition, at.% (wt.%)		
Al	Mn	Fe
62.5 ± 1.3 (44.9 ± 1.3)	37.1 ± 1.1 (54.5 ± 1.1)	1.3 ± 0.4 (0.5 ± 0.6)

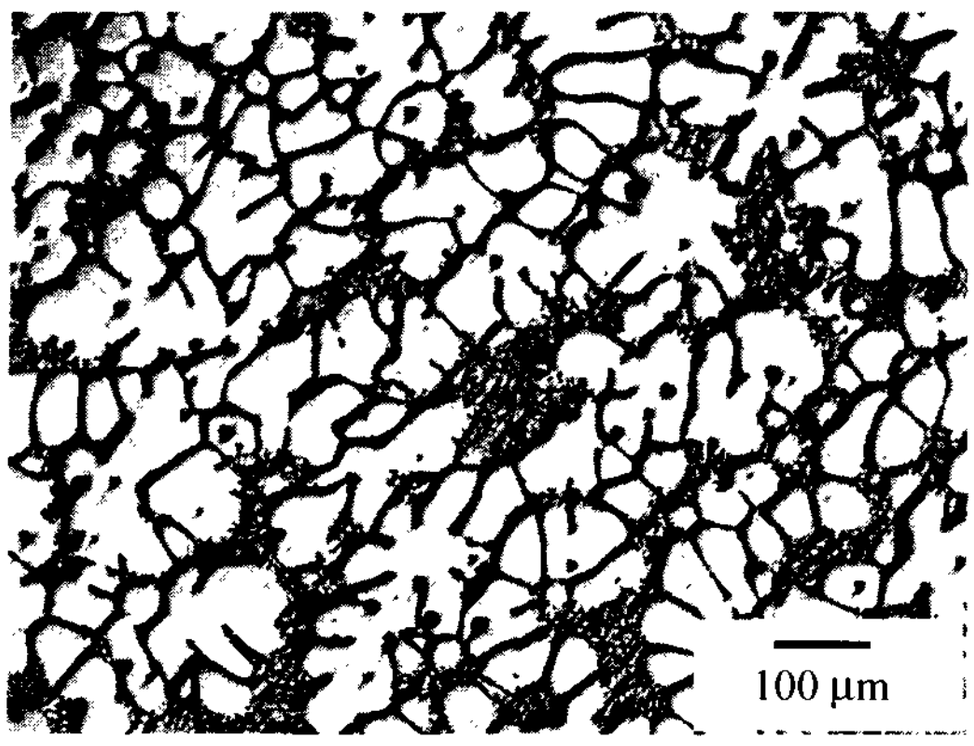

Fig. 3. An optical image of an AZ91 Mg alloy slurry with 0.23 wt.%Mn (Cooling rate is 0.08°C/s and holding time is 5 min.).

crystallographic data and the density of liquid AZ91 alloy is 1.6 g/cm^3.[5] In this case the nucleation mode is expected to be homogeneous because most $Al_8(Mn,Fe)_5$ particles exist at the bottom of the crucible. Therefore, it can be concluded that the moderate cooling rate is required to get $Al_8(Mn,Fe)_5$ particles in the melt for the heterogeneous nucleation.

4.2 Effect of Mn content on the microstructure of AZ91 slurries

The AZ91 alloy melt with 0.45% was cooled from 740°C to 585°C and held for 5 minutes to compare the size of the primary Mg phase with that of the alloy with 0.23 wt% Mn. In this case the cooling rate was 2.4°C/s. The microstructure of the slurry with 0.45% Mn was shown in Fig. 4. If we compare microstructures of Figs. 2(a) and 4, we can clearly distinguish the difference in size and morphology of the primary Mg phase with Mn content.

With higher Mn content, smaller and more globular primary Mg appears. Image analysis for quenched slurries with different amount of Mn shows that average sizes of the primary Mg phase are 102±40 mm and 55±18 mm when the Mn contents were 0.23% and 0.45%, respectively. The liquid fraction was 0.56 in both cases. It was also observed that the roundness of the slurry with 0.45% Mn is 1.23±0.22 and that with 0.23% Mn is 1.62±0.60.

Considering the Mn solubility at the liquidus temperature of AZ91 alloy is 0.122%, in the AZ91 alloy melt with 0.45% Mn, solid $Al_8(Mn,Fe)_5$ corresponding to the amount of 0.328(= 0.45-0.122)% Mn should be precipitated before the formation of the primary Mg phase.

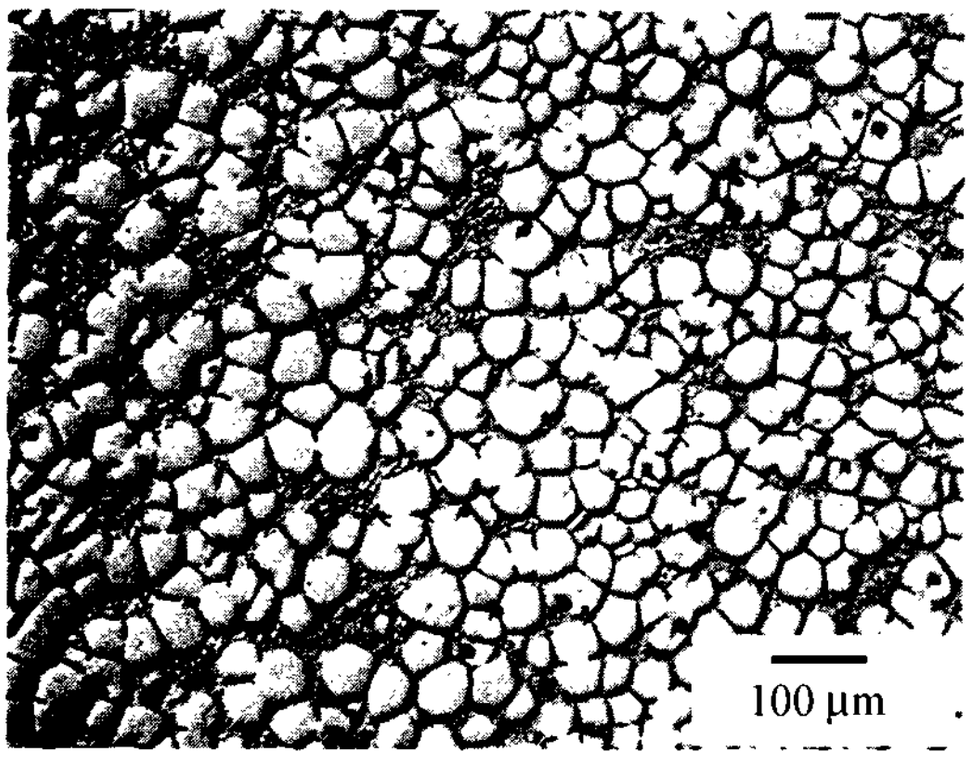

Fig. 4. An optical image of an AZ91 Mg alloy slurry with 0.45 wt.%Mn (Cooling rate is 2.4°C/s and holding time is 5 min.).

From the composition of $Al_8(Mn,Fe)_5$ phase in Table 3, the amount of solid $Al_8(Mn,Fe)_5$ is calculated to be 6.0 g per 1 kg of AZ91 alloy. This amount is more than that in the alloy with 0.23% Mn, 2.0 g of $Al_8(Mn,Fe)_5$ per 1 kg of AZ91 alloy. From Figs. 2(a) and 4, one hundred particles of $Al_8(Mn,Fe)_5$ were also counted and it was determined that the average particle sizes of $Al_8(Mn,Fe)_5$ were 10.58±3.33 mm and 9.16±3.35 mm, respectively. The increase in Mn content in the AZ91 alloy increases the number of the $Al_8(Mn,Fe)_5$ particles in the AZ91 alloy melt at its liquidus temperature. If total volume of the primary phase is same and the heterogeneous nucleation is dominant, the size of the primary Mg phase is expected to decrease due to increased heterogeneous nucleation sites. Assuming that each primary Mg nucleates on each $Al_8(Mn,Fe)_5$ particle, we can calculated the size of the primary Mg in the slurry at a given liquid fraction of 0.56 as a following equation.

$$(4/3)\pi(r_{Mg})^3 \times N = V_{sol}$$

where, r_{Mg} is the radius of each primary Mg. N, the number of $Al_8(Mn,Fe)_5$ precipitates per 1 kg AZ91 melt, is calculated by an equation of $N = W_{pre}/((4/3)\pi(r_{pre})^3 \times d_{pre})$, where W_{pre} is the amount of $Al_8(Mn,Fe)_5$ precipitates per 1 kg AZ91 melt and r_{pre} and d_{pre} are the average size and density of precipitates, respectively. In case of the AZ91 alloy with 0.23%Mn, N is calculated to be 7.33×108, whereas in the alloy with 0.45%Mn, N is 3.39×109. Under the assumption that density of the primary Mg at 585°C is the same as that of the remained melt (density = 1.6 g/cm^3), Vsol, the volume of solid (primary Mg) phase per 1 kg AZ91 melt, is calculated to be 275 cm^3 at the solid fraction of 0.44. Thus, the average sizes of the primary Mg in the slurries with 0.23% and 0.45% Mn was 89 mm and 53 mm, respectively. Considering the existence of more than one $Al_8(Mn,Fe)_5$ particle in a certain primary Mg and the

standard deviation of $Al_8(Mn,Fe)_5$ particle sizes, the calculated values are reasonably agreed with the determined values.

At a given liquid fraction, smaller primary Mg due to more heterogeneous nucleation sites has much less the branched dendrites. This means that smaller primary Mg more rapidly stabilizes its interface with the remaining liquid in order to reduce its interfacial energy. One can see that the primary Mg phase is more globular with increasing the Mn content. Additionally precipitated phase is easily branched when nucleation sites are small. Therefore, large amount of Mn content in AZ91 is advantageous for the production of sound slurry as far as it does not cause other deteriorating effects.

4.3 Effect of holding time on the micro-structure of slurries

The effect of the holding time on the morphology evolution of the primary Mg was investigated. Fig. 5 shows the microstructure of the slurry with 0.45% Mn, which were held at 585°C for 20 minutes. From comparing with Fig. 4, one can see that the primary Mg became more globular with increasing the holding time. The size of the primary Mg phase was also increased.

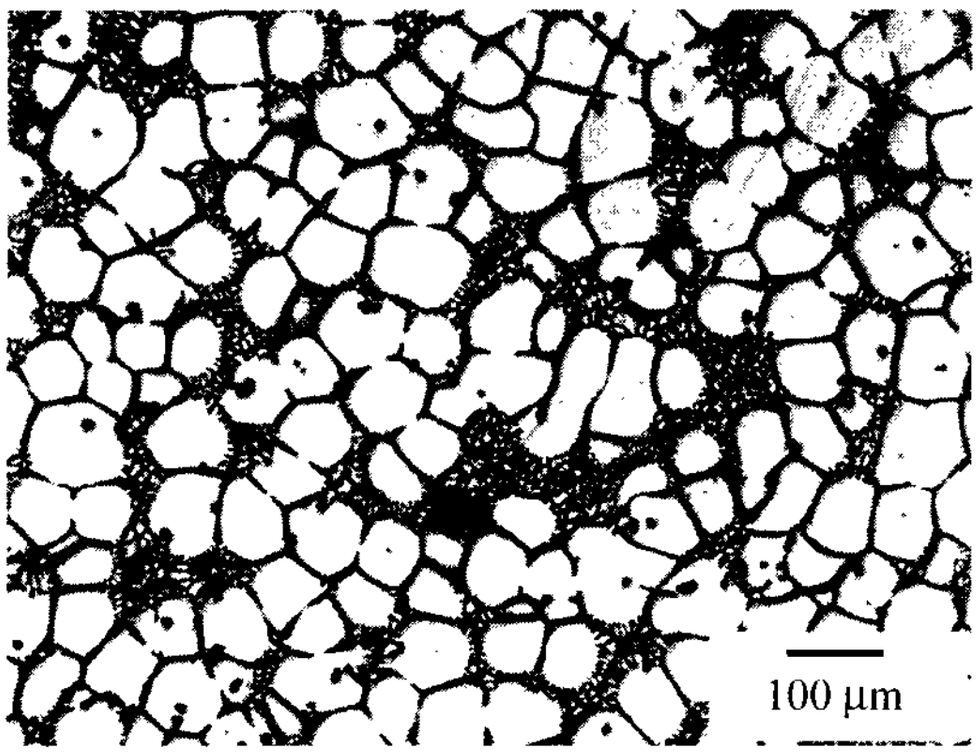

Fig. 5. An optical image of an AZ91 Mg alloy slurry with 0.45 wt.%Mn (Cooling rate is 2.4°C/s and holding time is 20 min.).

Average size of the primary Mg became 115 mm. This kind of change would be attributed to the Ostwald type ripening and coalescence of each primary Mg.

5. Conclusions

From the above experiment the following conclusions have been drawn. When Mn content in AZ91 alloy is higher than equilibrium solubility at the liquidus temperature, Mn precipitates as $Al_8(Mn,Fe)_5$ before precipitation of the primary Mg phase. It acts as a heterogeneous nucleation site for the precipitation of the primary Mg phase. Existence of $Al_8(Mn,Fe)_5$ within the primary Mg phase and decrease of the size of the primary Mg phase with increase of Mn content in AZ91 alloy prove that nucleation mode is heterogeneous. More globular type morphology of the primary Mg phase was found with increase of Mn content within AZ91 alloy. The morphology of the primary Mg changed to globular with increasing holding time and holding temperature at mixed phase region.

References

[1] H. Kaufmann and P. J. Uggowitzer : Adv. Eng. Mat., "Fundamentals of the new rheocasting process for magnesium alloys", 3 (2001) pp. 963-967.

[2] M. C. Flemings : 6th Int Conf on Semi-Solid Processing of Alloys and Composites, "SSM: Some thoughts on past milestones and on the path ahead", Turin (Italy), Sep. 27th-29th, 2000, ed. by G. L. Chiarmetta and M. Rosso, pp. 11-21.

[3] A. Thorvaldsen and C. A. Aliravci : 31st Annual Conference of Metallurgist, "Solubility of manganese in liquid Mg-Al alloys", The Metallurgical Society of CIM (1992) pp. 277-288.

[4] O. Holta, H. Westengen, and J. Roen : Proceedings of the 3rd International Magnesium Conference, "High purity magnesium die casting alloys: Impact of metallurgical principles on industrial practice", April 10th-12th, 1996, pp. 75-87.

[5] Magnesium and Magnesium Alloys, Ed. by M. M. Avedesian and H. Baker, ASM International (1999) 232.

[6] F. Czerwinski, A. Zielinska-Lipiec, P. J. Pinet, and J. Overbeeke : Acta Mater., "Correlating the microstructure and tensile properties of a thixomolded AZ91D magnesium alloy", 49 (2001) pp. 1225-1235.

[7] P. S. Mohanty and J. E. Gruzleski :Acta mater., "Grain refinement mechanisms of hypoeutectic Al-Si alloys", 44 (1996) pp. 3749-3760.