Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 22(2012) 2906−2912
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Microstructure evolution of hot pressed AZ91D alloy chips reheated to semi-solid state

XU Hong-yu, JI Ze-sheng, HU Mao-liang, WANG Zhen-yu
School of Material Science and Engineering, Harbin University of Science and Technology, Harbin 150040, China

Received 9 August 2012; accepted 15 October 2012

Abstract: AZ91D magnesium alloy chips, which were directly collected on the spot of machining process, were recycled to prepare billet via hot pressing for semi-solid processing. The semi-solid microstructure evolution of the billet during reheating was investigated. The results indicate that there are three stages during reheating to semi-solid state: the dissolution of $Mg_{17}Al_{12}$ and diffusion of Al into α-Mg matrix, the melting of the region with high content of solute and formation of isolated solid particles, and spheroidization and growth of solid particles. Meanwhile, a number of entrapped liquid droplets form within solid particles. In addition, the number and size of entrapped liquid droplets rely on the holding time in the semi-solid temperature range. With increasing isothermal holding time, the solid fraction remains unchanged when the solid-liquid system reaches the dynamic equilibrium at last, while the solid particles become more globular and the average size of solid particles increases owing to the decreasing of interfacial energy and the effect of interfacial tension.

Key words: AZ91D alloy; chips; semi-solid microstructure; microstructure evolution; recycling; entrapped liquid droplet; interfacial energy; interfacial tension

1 Introduction

Since the discovery of semi-solid metal 40 years ago, semi-solid metal processing has drawn great attention because of its outstanding features. Compared with traditional cast materials, materials formed by semi-solid processing have less segregation and porosity because of the nonturbulent filling of the die, and therefore have better mechanical properties [1,2]. Recently, thixoforming, one of the main semi-solid forming processes, has been widely applied in industries [3−6]. In semi-solid processing, the required feedstock is the thixotropic slurry with a fine spheroidal or non-dendritic morphology of solid particles [7,8]. Thus, the preparation of semi-solid billets is of great importance. So far, a number of processes are used to produce semi-solid alloys, such as taper barrel rheomoulding process (TBR) [9], introducing grain process (IGP) [10], serpentine channel pouring rheo-diecasting (SCRC) process [11−13], equal channel angular extrusion (ECAE) process [14] and strain-induced melt activation (SIMA) process [15].

The SIMA process is the most typical method among solid-state routes. However, in traditional SIMA process involving severe hot working by compressing or extrusion, there may be variation in the amount of stored work across the section. Due to nonuniform deformation, the semi-solid microstructure evolution speed varies from area to area during reheating. That is to say, nonuniform deformation results in inhomogeneity of semi-solid microstructure and a longer isothermal holding time is needed to eliminate the difference of microstructure [16−18]. In recent years, alloy chips machined by cutting are used to prepare semi-solid billets via hot pressing [19−21]. This is a modified process based on SIMA method, and can well solve the problem of inhomogeneity. Moreover, it is also a promising recycling process of alloy chips.

In this work, AZ91D magnesium alloy chips, which were directly collected on the spot of machining process, were recycled to prepare billet via hot pressing for semi-solid metal processing and their semi-solid microstructure evolution was investigated during reheating.

2 Experimental

In the present work, clean AZ91D magnesium alloy chips were directly collected on the spot of machining

Foundation item: Project (50974048) supported by the National Natural Science Foundation of China
Corresponding author: JI Ze-sheng; Tel: +86-13804517924; E-mail: qinghejin@sina.cn
DOI: 10.1016/S1003-6326(11)61549-5

process and used as the experimental material. AZ91D chips with 0.2−0.6 mm in thickness and 2−5 mm in width were machined by dry cutting in a lathe. Certain amount of machined chips with various dimensions were mixed, filled into a cylindrical mold, preheated to 300 °C and held for 20 min, and pressed into some billets with a diameter of 40 mm and a height of 15 mm using a pressure of 500 MPa on a hydraulic machine. The chemical composition of AZ91D magnesium alloy was checked by an ICP spectral analyzer and listed in Table 1.

Table 1 Composition of AZ91D magnesium alloy (mass fraction, %)

Al	Zn	Mn	Si	Be
8.96	0.68	0.20	0.02	<0.01

Fe	Cu	Ni	Mg
<0.01	<0.01	<0.01	Bal.

Billets were isothermally held in the furnace with a heating rate of 10 °C/min under a protective gas flow of argon, and then were immediately quenched in water to freeze the semi-solid microstructure. Isothermal holding temperatures were 400, 500, 550, 570, 580 and 590 °C, respectively. Isothermal holding times were 5 min, 30 min and 60 min, respectively. A thermocouple was located in the centre of the sample and a PID temperature controller with an accuracy of ±1 °C was used to accurately monitor and control the temperature of billets. Preparation of metallographic specimen consisted of wet grinding, polishing and etching with 4% nitric acid and 96% ethanol for several seconds. Microstructure observation on the cross-section of specimen was performed by optical microscope and scanning electron microscope equipped with energy-dispersive spectrum (EDS). Quantitative metallography analyses including the volume fraction, size and morphology of solid phase were conducted by the image-pro-plus analysis software.

3 Results and discussion

3.1 Microstructure of recycled AZ91D alloy chips

Figure 1 shows the microstructures of recycled AZ91D alloy chip. From length−width direction, chip was observed to have a sawtooth-like feature. The machined chip is severely deformed during cutting frequently accompanied by cracks, especially at the root position, as pointed out by the arrows in Fig. 1(a). In as-cast condition, the dendritical microstructure of AZ91D alloy chip is characterized by the presence of primary α-Mg, divorced eutectic α-Mg, divorced eutectic β-$Mg_{17}Al_{12}$ and precipitate β-$Mg_{17}Al_{12}$, which are shown clearly in Fig. 1(b). It can be seen that α-Mg grains are surrounded by coarse and reticular β-$Mg_{17}Al_{12}$ phase which is black in Fig. 1(a) but white in Fig. 1(b). The presence of divorced eutectic is due to non-equilibrium solidification caused by the fast cooling rate of casting processes. During solidification, the remaining liquid is quite rich in aluminum at the end of solidification, resulting in the inhomogeneity of Al content. When the Al content in liquid is close to the eutectic composition, remaining liquid transforms to the divorced eutectic α+β. In the further cooling procedure, β-$Mg_{17}Al_{12}$ precipitates into α-Mg matrix, especially in the divorced eutectic α-Mg matrix for its high aluminum content.

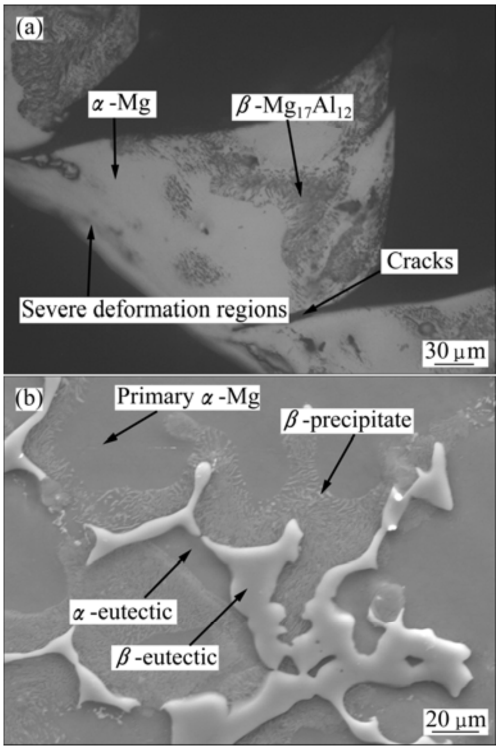

Fig. 1 Microstructures of recycled AZ91D alloy chip: (a) OM micrograph; (b) SEM micrograph

3.2 Microstructure of hot pressed AZ91D chip after isothermal holding

Figure 2 shows the deformed microstructures and semi-solid microstructures of the billet. The billet was heated to 580 °C and isothermal held for 30 min. The microstructure observations were carried out on both the transverse section and the longitudinal section of the pressed billet. Chips are compacted and coalesced into billet during hot pressing. The α-Mg dendrites are distorted severely and slightly orient in the direction that is vertical to the compressive direction. Comparing Figs. 2(a) with (c), no distinct difference of deformation occurs between the transverse section and the longitudinal section. When heated to semi-solid state, the solid particles uniformly distribute in the liquid matrix (Fig. 2(b) and (d)). Therefore, hot pressing of chip is more effective to induce uniform strain in comparison with other asymmetrical predeformation process, such as compressing [16,17] and extrusion [18]. Due to the severe plastic deformation occurring in chipping and pressing, energy is stored in forms of dislocation multiplication, elastic stress and vacancies, which make a good strain induced effect to promote the morphological transition from dendritic to globular structure [22].

Differences in alloying elements distribution in semi-solid microstructure are presented in Fig. 3 as the results of SEM+EPMA analysis. In the elemental maps, there are mainly Mg, Al and Zn. It is clearly seen that Zn element mostly distributes homogeneously in Mg matrix whereas Al concentration is higher at the region between the solid particles. In the freezing semi-solid microstructure, the formation of β-$Mg_{17}Al_{12}$ because of the fast cooling causes that Al enriches around the solid particles and these areas constitute liquid phase. During the study of semi-solid microstructure, it is also obviously found that apart from liquid between solid particles (like area marked as 2 in Fig. 3(a)), there are a number of phases akin to liquid within solid particles (like area marked as 1 in Fig. 3(a)). A further analysis was conducted by EDS, as shown in Table 2. As a consequence, it is confirmed to be liquid containing the close content of Al and Zn, which is called entrapped liquid droplet. Although most liquid is concentrated around the solid particles, entrapped liquid droplets within solid particles still account for about 10% revealed by quantitative metallography. This must adversely affect the uniformity of semi-solid slurry because it is unavailable to wet the surfaces of globules to provide flowability. The formation and transformation of the entrapped liquid droplet is illustrated in detail in

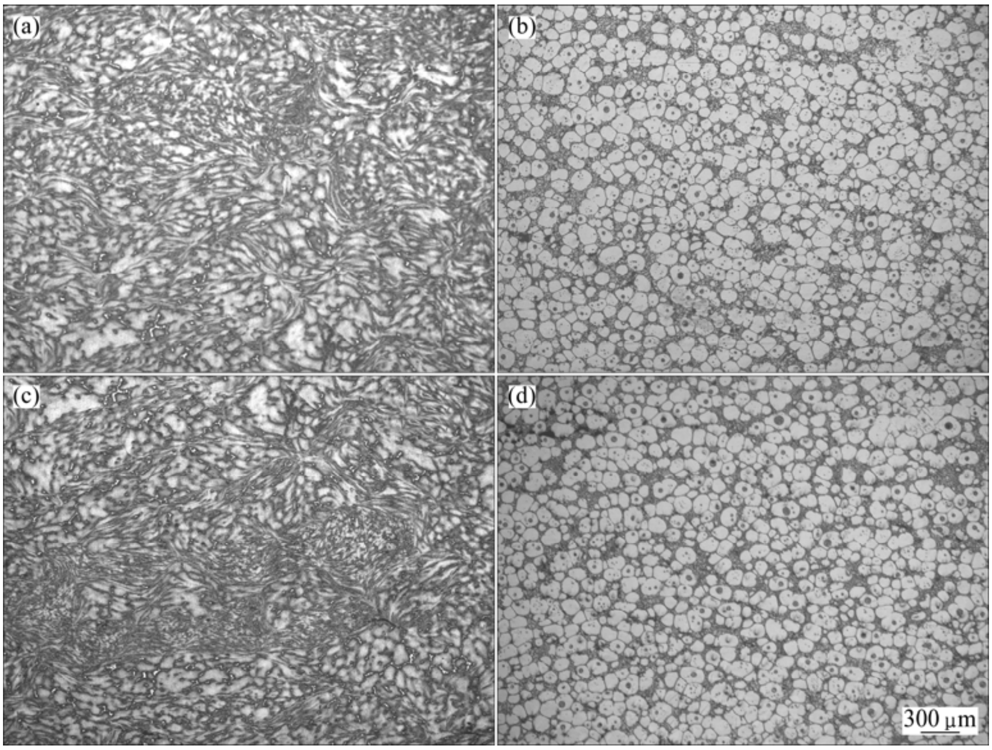

Fig. 2 Deformed microstructures (a, c) and semi-solid microstructures (b, d) of billet: (a), (b) Transverse section; (c), (d) Longitudinal section

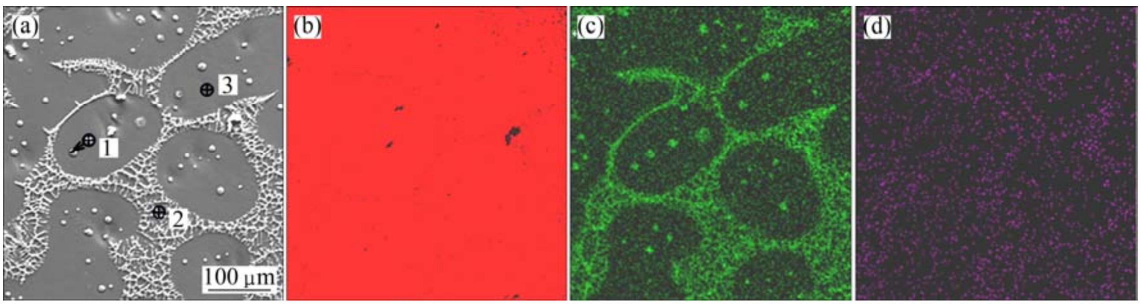

Fig. 3 SEM image and elemental maps by EPMA of AZ91D alloy billet reheated to 580 °C and isothermally held for 30 min: (a) SEM image; (b) Mg element; (c) Al element; (d) Zn element

Table 2 Analysis results of some points in semi-solid microstructure of AZ91D alloy by EDS in Fig. 3(a)

Scanning point	w(Al)/%	w(Zn)/%	w(Mg)/%
1	36.76	0.277	59.95
2	37.39	0.280	59.40
3	4.43	0	95.57

the following part of the paper.

3.3 Influence of temperature on microstructure evolution

The microstructures of AZ91D alloy after reheating to different temperatures are shown in Fig. 4. Isothermal holding time is 5 min for all temperatures. At 400 °C, compared Fig. 4(a) with Fig. 1(b), the precipitates β-$Mg_{17}Al_{12}$ have disappeared because of the diffusion of solute atom at the grain boundaries. When heated to 500 °C (Fig. 4(b)), the residual β-$Mg_{17}Al_{12}$ and the near region where Al concentration is higher firstly melted at the grain boundaries. Liquid has appeared along grain boundaries and is also as tiny entraped liquid droplets within the grains close to grain boundaries. With heating continuously to 550 °C (Fig. 4(c)), liquid phase increased, the grain boundaries almost melted and the primary α-Mg grains have incompletely segregated so as to form small irregular polygon solid particles. A typical semi-solid structure is obtained after heating to 570−590 °C (Fig. 4(d)−(f)), namely, round solid particles distribute uniformly in the liquid matrix. Moreover, the relative solid fractions are 67.6%, 52.3% and 36.5%, respectively. Therefore, based on the experiment condition, 580 °C is better for semi-solid forming.

Microstructure of billet transforms significantly

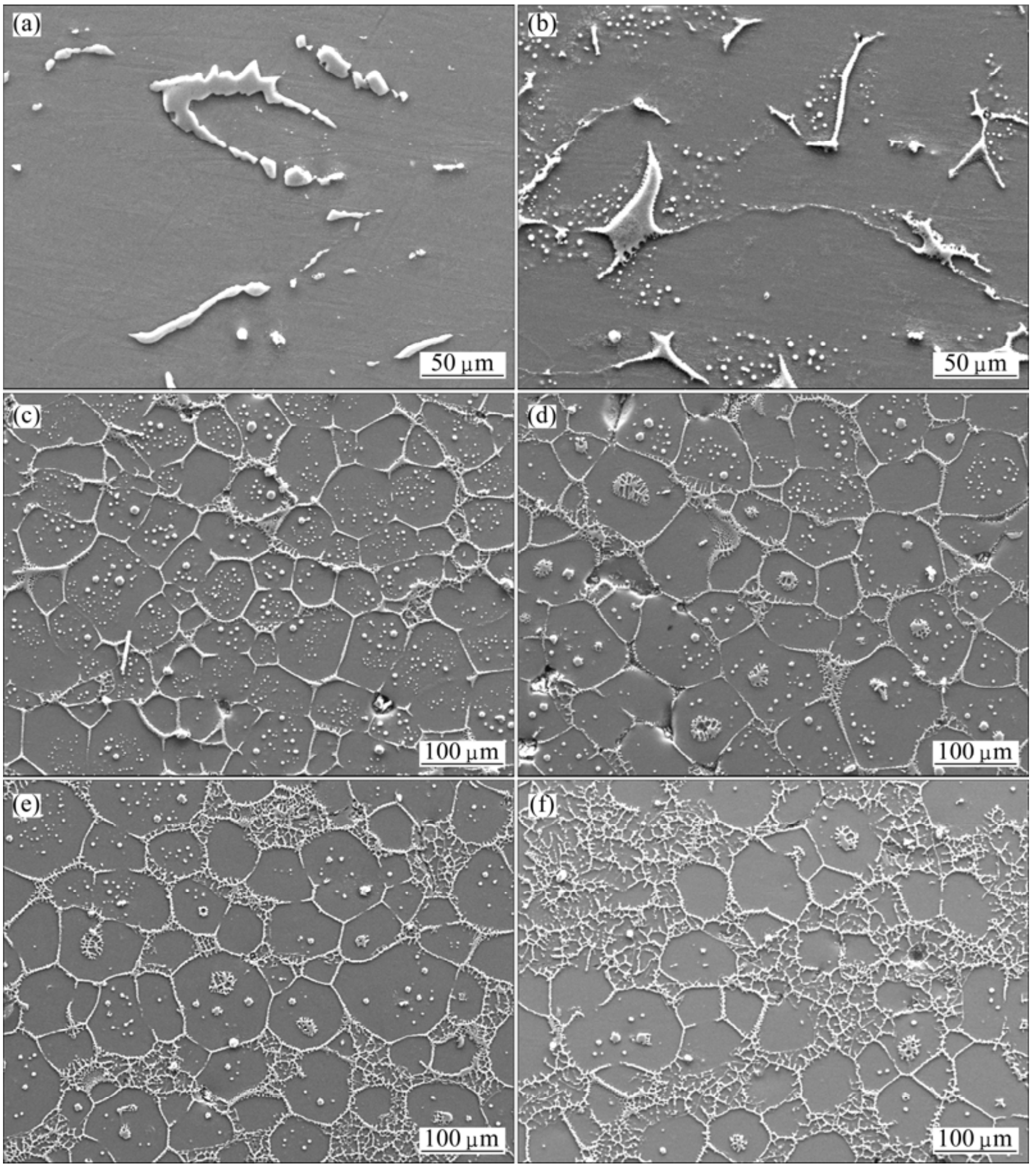

Fig. 4 SEM images of AZ91D alloy heated to 400 °C (a), 500 °C (b), 550 °C (c), 570 °C (d), 580 °C (e), 590 °C (f) and isothermally held for 5 min

during reheating. With increasing reheating temperature, the solid solubility of Al in α-Mg increases. Thus, the metastable $Mg_{17}Al_{12}$ primarily dissolves and the diffusion of Al atoms into α-Mg occurs until completely disappears. However, since diffusion of Al in α-Mg is rather slow at 400 °C, time is too short to allow complete homogenization. Hence, the concentrations of the solute at the primary α-Mg grain boundaries and in the circumjacent region within α-Mg grain are relatively high, i.e. chemical microsegregation. Theoretically, a feedstock material containing microsegregation is prerequisite for semi-solid processing, which enhances SSM processability by reducing the necessary processing temperature and lowering the temperature sensitivity of the volume fraction of liquid [23]. The solidus temperature decreases with increasing solute content. Above the solidus temperature of alloy, melting starts in the region with high content of Al. When the liquid dissolves more Al than the solid, the adjacent solid becomes depleted in Al and hence the local solidus temperature is increased, which prevents further melting into the solid grain unless the reheating temperature is raised. This is called self-blocking remelting process and the detailed description is given in Ref. [24]. These entrapped liquid droplets mainly originate from the internal inhomogeneity of the primary solid, which is caused by chemical segregation. Within the grains, the original Al content has been preserved as the nominal Al level, leading to no change of solidus temperature. Therefore, melting may starts simultaneously everywhere inside the grains, namely many tiny entrapped liquid droplets develop. When the reheating temperature is high enough, more liquid forms, grain boundary penetration takes place and the remaining solid is broken up into isolated particles, finally nearly spherical particles suspend in the liquid matrix.

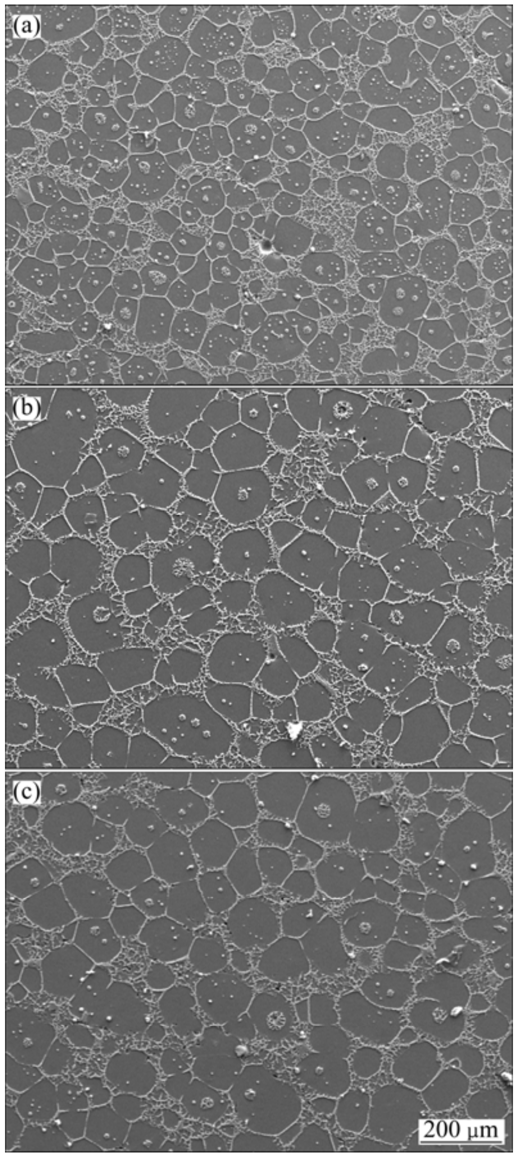

Fig. 5 SEM images of AZ91D alloy heated to 580 °C and isothermally held for 5 min (a), 30 min (b) and 60 min (c)

3.4 Influence of holding time on microstructure evolution

A certain soaking time in the semi-solid temperature range is needed to obtain semi-solid slurry with sufficient fluidity for proper die filling. The microstructure of AZ91D alloy during isothermal holding at 580 °C is illustrated in Fig. 5. After 5 min holding time, the semi-solid microstructure of sample is inhomogeneous, namely, some coarse particle and fine particle coexist in microstructure, which is surely not suitable for semi-solid processing. When held for 30 min, the transformation into proper semi-solid slurry is mainly completed, while the size of the solid grains gradually increases. A further holding only leads to undesirable grain growth. Simultaneously plenty of very small entrapped liquid droplets develop in the early stage of isothermal holding. The number and size of these entrapped liquid droplets rely on the holding time in semi-solid temperature range. With increasing holding time, some contiguous entrapped liquid droplets gradually merge into some big entrapped liquid droplets by coalescence. On the other hand, the number of small entrapped droplets also decreases by migration to some huge liquid entrapped droplets by diffusion through the solid phase. Subsequently, these entrapped liquid droplets become rounded in order to decrease the interfacial energy between solid and liquid phase.

The specific relevance of the solid fraction, the average size and the shape factor of the solid particles with holding time can be revealed from Fig. 6. During the semi-solid isothermal treatment with the extension of holding time, more liquid phase generated in surrounding or inside the primary solid particles. On the contrary, the solid fraction has a downward trend. With further increasing isothermal holding time, it almost remains unchanged according to the lever law when it reaches dynamic equilibrium. This is attributed to diffusion of solute atom, leading eventually to complete equilibrium between solid and liquid. Meanwhile, the average size and shape factor of the solid particles increase in succession with the time going on. It is concluded that in the initial stage of isothermal holding, melting is in the lead and contributes to the reduction of the solid fraction and spheroidization of solid particles. Due to high interface curvatures and high solute gradients in the liquid around the particles, the protuberant parts of the solid particles primarily melt off, which makes the solid particles more globular. With further increasing the isothermal holding time, the solid particles begin to grow and coarsen based on coalescence ripening mechanism and the Ostwald ripening mechanism [25].

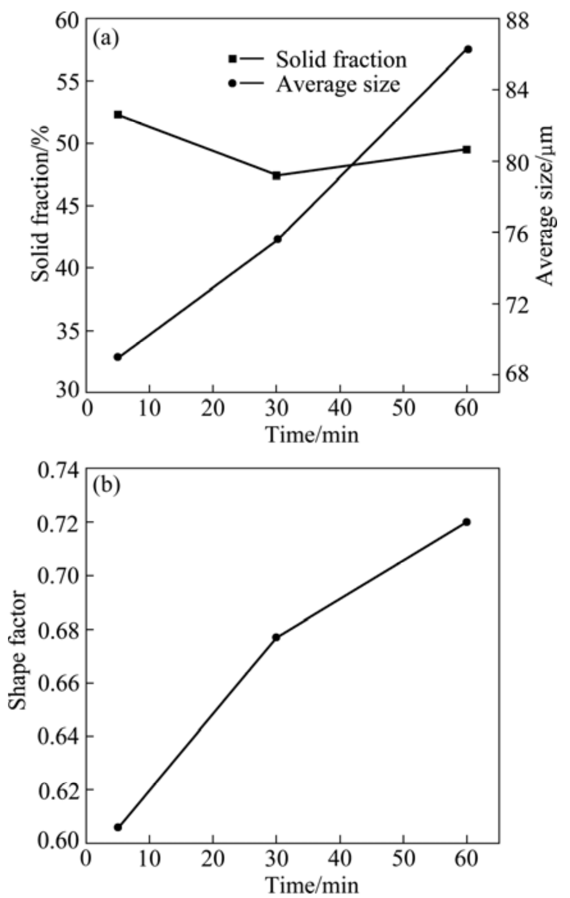

Fig. 6 Effects of time on solid fraction and average size (a) and shape factor (b) of particles

4 Conclusions

1) AZ91D magnesium alloy chips which were directly collected on the spot of machining process are successfully recycled to prepare billet for semi-solid processing via hot pressing. And the optimal semi-solid isothermal treatment condition is at 580 °C for 30 min. This provides a potential recycling method of chips or other machining scraps.

2) A number of entrapped liquid droplets form within remaining solid particles, which is attributed to the difference of local solute content as a result of microsegregation and inhomogeneous diffusion. In addition, the number and size of these liquid droplets rely on the holding time in the semi-solid temperature range. A short holding time results in many small liquid droplets, which became fewer and bigger and rounder by growth and coalescence with increasing holding time.

3) The microstructure evolution of hot pressed AZ91D alloy chips during reheating to the semi-solid state consists of three stages. First, the $Mg_{17}Al_{12}$ dissolved and the Al atoms diffused into α-Mg. Second, the remaining eutectics melted along the primary α-Mg grain boundaries. Finally, the grains became separated from each other and spheroidized in the semi-solid temperature range due to the penetration of liquid.

4) During semi-solid isothermal holding, the solid fraction decreased until the solid-liquid system reached its equilibrium state. However, the average size and shape factor of the solid particles increase in succession with the time going on owing to the decreasing of interfacial energy and interface curvature.

References

[1] FLEMINGS M C. Behavior of metal alloys in the semisolid state [J]. Metallurgical and Materials Transactions A, 1991, 22(5): 957−981.

[2] KAUFMANN H, UGGOWITZER P J. Fundamentals of the new rheocasting process for magnesium alloys [J]. Advanced Engineering Materials, 2001, 3(12): 963−967.

[3] ZHANG Y F, LIU Y B, CAO Z Y. Microstructure characteristics and solidification behavior of thixomolded Mg−9%Al−1%Zn alloy [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(2): 250−256.

[4] HUANG H J, CHEN T J, MA Y, HAO Y. Microstructural evolution during solution treatment of thixoformed AM60B Mg alloy [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(4): 745−753.

[5] DU Z M, CHEN G, CHENG Y S, XIE S S. Inhomogeneity of density and mechanical properties of A357 aluminum alloy backward extruded in semi-solid state [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(10): 2285−2293.

[6] CHEN Y N, WEI J F, ZHAO Y Q, ZHANG X M. Tensile properties and microstructure of Ti14 alloy after semi-solid forging [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(12): 2610−2616.

[7] CZERWINSKI F. Semisolid extrusion molding of Mg−9%Al−1%Zn alloys [J]. Journal of Materials Science, 2004, 39(2): 463−468.

[8] TZIMAS E, ZAVALIANGOS A. Evolution of near-equiaxed microstructure in the semisolid state [J]. Materials Science and Engineering A, 2000, 289(1−2): 228−240.

[9] YANG L Q, KANG Y L, ZHANG F, XU J. Microstructure and

mechanical properties of rheo-diecasting AZ91D Mg alloy [J]. Transactions of Nonferrous Metals Society of China, 2010, 20(S3): s862−s867.

[10] CHEN Z Z. Preparation of semi-solid A356 Al-alloy slurry by introducing grain process [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(6): 1307−1312.

[11] CHEN Z Z, MAO W M, WU Z C. Mechanical properties and microstructures of Al alloy tensile samples produced by serpentine channel pouring rheo-diecasting process [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(7): 1473−1479.

[12] CHEN Z Z, MAO W M, WU Z C. Influence of serpentine channel pouring process parameters on semi-solid A356 aluminum alloy slurry [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(5): 985−990.

[13] YANG X R, MAO W M, SUN B Y. Preparation of semisolid A356 alloy slurry with larger capacity cast by serpentine channel [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(3): 455−460.

[14] JIANG J F, LIN X, WANG Y, QU J J, LUO S J. Microstructural evolution of AZ61 magnesium alloy predeformed by ECAE during semisolid isothermal treatment [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(3): 555−563.

[15] BOLOURI A, SHAHMIRI M, CHESHMEH E N H. Microstructural evolution during semisolid state strain induced melt activation process of aluminum 7075 alloy [J]. Transactions of Nonferrous Metals Society of China, 2010, 20(9): 1663−1671.

[16] ZHANG Q Q, CAO Z Y, LIU Y B, ZHANG Y F, ZHANG L, ZHANG M L,WU R Z. Effect of asymmetrical deformation on the microstructure evolution of semisolid AZ91D alloy [J]. Materials Science and Engineering A, 2008, 488(1−2): 260−265.

[17] ZHANG Q Q, CAO Z Y, ZHANG Y F, SU G H, LIU Y B. Effect of compression ratio on the microstructure evolution of semisolid AZ91D alloy [J]. Journal of Materials Processing Technology, 2007, 184(1−3): 195−200.

[18] LUO S J, CHEN Q, ZHAO Z D. An investigation of microstructure evolution of RAP processed ZK60 magnesium alloy [J]. Materials Science and Engineering A, 2009, 501(1−2): 146−152.

[19] XU H Y, JI Z S, HU M L, WANG Z Y. Microstructure of AZ91D magnesium alloy semi-solid billets prepared by SIMA method from chips [J]. Transactions of Nonferrous Metals Society of China, 2010, 20(S3): s749−s753.

[20] WANG Z Y, JI Z S, HU M L, XU H Y. Evolution of the semi-solid microstructure of ADC12 alloy in a modified SIMA process [J]. Materials Characterization, 2011, 62(40): 925−930.

[21] WANG Z Y, JI Z S, SUN L X, XU H Y. Microstructure of semi-solid ADC12 aluminum alloy adopting new SIMA method [J]. Transactions of Nonferrous Metals Society of China, 2010, 20(S3): s744−s748.

[22] WANG J G, LU P, WANG H Y, LIU J F, JIANG Q C. Semisolid microstructure evolution of the predeformed AZ91D alloy during heat treatment [J]. Journal of Alloys and Compounds, 2005, 395(1−2): 108−112.

[23] TZIMAS E, ZAVALIANGOS A. Synthesis of lightweight metals III [M]. Warrendale: Minerals, Metals and Materials Society, 1999: 195−203.

[24] KLEINER S, BEFFORT O, UGGOWITZER P J. Microstructure evolution during reheating of an extruded Mg−Al−Zn alloy into the semisolid state [J]. Scripta Materialia, 2004, 51(5): 405−410.

[25] FAN Z. Semisolid metal processing [J]. International Materials Reviews, 2002, 47(2): 49−85.

热压制工艺回收 AZ91D 镁合金屑的半固态组织演变

许红雨，吉泽升，胡茂良，王振宇

哈尔滨理工大学 材料科学与工程学院，哈尔滨 150040

摘 要：以从机械加工现场直接收集的 AZ91D 镁合金屑料为原料，采用热压制工艺再生制备半固态加工所需的坯料，研究二次加热过程中的半固态组织演变。结果表明，半固态组织演变可分为三个阶段：$Mg_{17}Al_{12}$ 相的溶解和 Al 原子的扩散，高溶质含量区域的熔化和固相颗粒的生成，固相颗粒的球化和长大。同时，在固相颗粒内部形成大量的嵌入式液滴。这种嵌入式液滴的数量和尺寸随着保温时间的变化而变化。随着保温时间的延长，固、液两相最终达到动态平衡，固相率不再发生变化。由于界面能降低和界面张力的作用使固相颗粒尺寸逐渐增大，并且越来越圆整。

关键词：AZ91D；屑；半固态组织；组织演变；再生；嵌入式液滴；界面能；界面张力

(Edited by YANG Hua)