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Production of Nondendritic Semisolid ZA3 Alloy through Heat Treatment

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Abstract: ZA3 is a zinc-based alloy with aluminium as its main alloying element. Producing ZA3 product by semisolid metal processing (SSM) can offer significant advantages such as the reduction of macrosegregations, porosity and low forming efforts. The aim of this study was to produce nondendritic semisolid ZA3 alloy through heat treatment. The thermal and microstructure analysis of ZA3 alloy were studied using Differential Scanning Calorimeter (DSC) and Scanning Electron Microscopy (SEM). The solidus and liquidus of the alloy can be determined by DSC analysis. The changes to the microstructures in response to two different isothermal treatments were investigated. They are heating at 100°C for 3-6 h and at 280°C for 0.5-5 h, respectively. Subsequently, all of the treated samples are partially remelt at 383°C for 15 min. The initial as-cast ZA3 alloy consisted of dendritic microstructure typical of a cast ingot. The major effort in the semi-solid technologies is the generation of small and spherical morphologies. The results indicated that when the respective heat-treated ZA3 alloy at 100°C for 4.5 h and 280°C for 3 h was subjected to partial remelting into its semisolid zone, the dendritic arms coalesced and coarsened into fine solid grains of 34±17 μm with corresponds to 0.84 of shape factor and 33±16 μm with the best shape factor of 0.85.

Key words: Solidus, liquidus, dendritic, partially remelt, spherical morphologies

INTRODUCTION

The initial work that led to the interest in semi-solid metal processing (SSM) can be traced back to studies by researchers at The Massachusetts Institute of Technology in the early 1970s. This work was originally directed at the problem of hot tearing in alloy castings but it was later realised that a new technology for near-net shaping of complex shapes had been discovered (Flemings, 1991). This SSM technology can be generally defined as a forming process that shapes metal components in their semi-solid state (Flemings, 1991; Kirkwood, 1994; Omar *et al.*, 2005, 2009).

Semi-solid metal forming (SSM) has become a widely accepted metal processing technique because it combines the elements of both casting and forging, offering significant advantages, such as the reduction of macrosegregations, porosity and low forming efforts (Kirkwood, 1994; Chen *et al.*, 2002). Other major advantages include prolonged die life due to decreased thermal shock (forging below liquidus as against castings), weight savings in components with less porosity than conventionally, plus improved usage of feedstock materials because of improved designs (Omar *et al.*, 2009). Because of the advantages mentioned above, work on SSM processing have been actively carried out involving high and low melting point alloys such as steels and aluminum alloys (Birol, 2009; Alfan *et al.*, 2010).

Work in searching for alternative materials in engineering applications to reduce the cost of production without sacrificing the functional requirements of the components is still actively ongoing. Zinc-based alloys are of recent interest in this regard, offering a number of benefits over their conventional counterparts like aluminum casting alloys, copper-based alloys, bearing bronzes and cast iron in various engineering applications. These alloys feature clean, low-temperature, energy-saving melting, excellent castability, high strength and equivalent or often superior bearing and wear properties as compared to standard bronze bearing. Cast Zn-Al (ZA) alloys have been popular for engineering components including those in the automotive industry (Abou El-khair *et al.*, 2004).

The main requirement for alloys to be shaped in the semi-solid state is that they should exhibit a fine spheroidal or nondendritic grain structure (Chen *et al.*, 2002). From the previous research, nondendritic semisolid

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microstructure could not be obtained if the traditional cast alloy with developed dendrites was directly subjected to partial remelting. The alloy must be pretreated, such as by mechanical stirring during solidification, modifying prior to pouring, or subjected to deformation prior to remelting. These pretreatments not only brought about melt contamination and gas absorption during mechanical stirring or melt contamination from refine, but also needed some special high-cost equipments (e.g., stirring equipment for magnetohydrodynamic stirring and rolling or pressing machine for predeformation) (Zhu *et al.*, 1999; Chen *et al.*, 2006). In this study, the development of nondendritic microstructures of ZA3 was investigated by applying isothermal heat treatments at various temperatures below its solidus temperature followed by partial remelting direct into its semi-solid zones.

MATERIALS AND METHODS

This research project was conducted from February, 2nd 2008 to August, 31st 2010

Material: ZA3 is a zinc based metal alloy with alloying element of aluminum, magnesium and copper. The addition of copper and magnesium are to increased strength and inhibit intergranular corrosion, respectively. Typical uses are automotive parts, household appliances and fixtures, office and computer equipment as well as building hardware (Robert, 1984). The chemical composition of the as-cast material is given in Table 1.

Differential Scanning Analysis (DSC): DSC analysis was carried out primarily to estimate the solidus, liquidus and liquid fraction within the semi-solid zone of the supplied material. The alloy was cut into small pieces (less than 20 mg) for DSC test using Mettler Toledo DSC 822e. The heating rate employed is 10°C per min. The heating was carried out in a nitrogen atmosphere to prevent oxidation. From the heating curve, phase transformation reactions are also observed.

Heat treatment and partial remelting: Two different isothermal heat treatment procedures were carried out using an electric furnace. The first involved heating the ZA3 samples at 100°C for stabilising treatment, in $\alpha+\eta$ zone, ranging for a range of holding times from 3 to 6 h. The second procedure involved a treatment at 280°C, in $\beta+\eta$ zone, for 0.5 to 5 h. Subsequently, samples from both procedures were quenched before a partial remelting treatment was respectively carried out at 383°C (i.e., in the semi-solid temperature of ZA3) for 15 min.

Image analysis: The microstructural characterisation was carried out using Olympus optical microscope and Philips XL30 Scanning Electron Microscope (SEM) before being further analyzed using an imageJ software to measure the shape and size of grains. In addition, energy dispersive X-ray (EDAX) analysis has been carried out to analyse elemental or chemical characterisation of samples. All samples were etched using etchant (200 g Chromic acid, CrO_3 + 7 g Sodium sulphate, Na_2SO_4 + 2 g Sodium fluoride + 1000 mL Water) (Frank, 1991).

RESULTS AND DISCUSSION

Effect of heating on the solid microstructures: The equilibrium diagram of zinc-aluminum alloy is shown in Fig. 1. Zinc and aluminum form a binary eutectic with a melting point of 382°C at 5% aluminum. ZA3 alloy with aluminum content of about 4% has a melting point of 387°C and a short freezing range of 5°C that has a fine-grained structure (Frank, 1991). Figure 2 shows the microstructures of ZA3 alloy in different condition (i.e., as-cast and after heating for different temperatures and periods). Based on microstructural observation, the as-cast microstructure of ZA3 consists of developed dendrites and interdendritic eutectics (Fig. 2a). The fine dendritic structure is formed by gravity casting of ZA3. However, the main requirement in semi solid metal processing is the development of small globular microstructure. Various processes have been demonstrated so far to achieve that structure. In a semisolid condition, dendrites tend to transform into rosettes and/or spherical particles if the alloy is stirred vigorously. On the other hand, another alternative to achieve the globular structure is by thermal transformation, which relies on the ripening of a more or less dendritic structure when it is heated and held for a period of time (Narimannezhad *et al.*, 2009). Actually, production of nondendritic microstructures of different zinc aluminum alloy with higher aluminum content had been conducted by Chen *et al.* (2006). Here, two different heating procedures were carried out to produce nondendritic semisolid microstructures of ZA3 alloy, the

Table 1: Chemical composition of the ZA3 alloy compared to the nominal

	Chemical composition (wt%)							
ZA3	Al	Cu	Mg	Si	Fe	Pb	Ni	Zn
Nominal	3.5-4.3	0.25 max	0.02-0.05	-	0.1 max	0.005 max	-	balance
Analysis	3.05	0.001	0.004	0.005	0.004	0.0021	0.001	balance

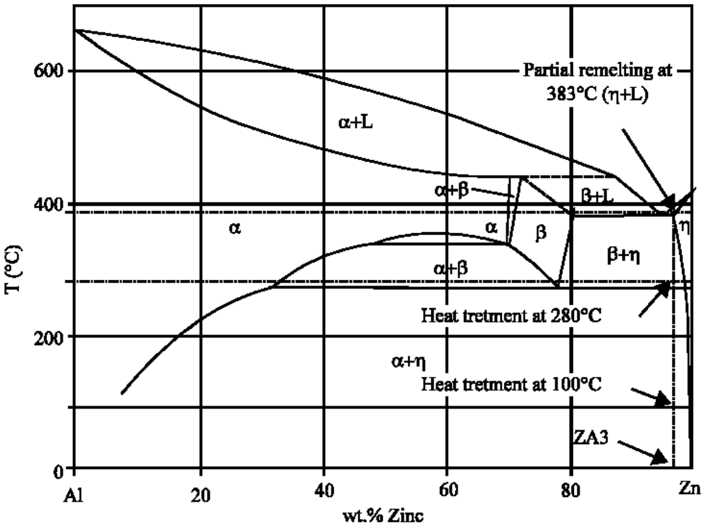

Fig. 1: Binary phase diagram of Zn-Al system

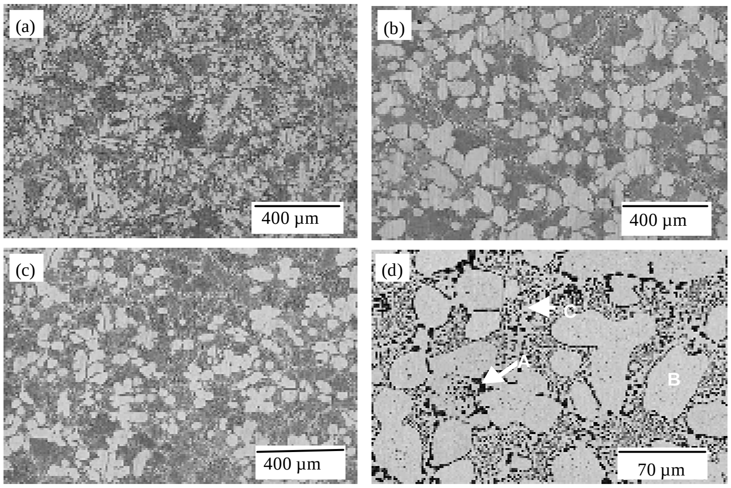

Fig. 2: Microstructures of ZA3 (a) As-cast, (b) Stabilized at 100°C for 4.5 h, (c) Heated at 280°C for 3 h and (d) Detail Observation after Heated at 280°C for 3 h with EDAX microanalysis measurement

first is at a stabilising temperature in α+η zone, 100°C, with various holding times of 3 to 6 h, while the second is in β+η zone, at 280°C, with holding times of 0.5 to 5 h. Both heat treatment procedures have resulted in the coalescence and coarsening of the original dendritic structures (Fig. 2a) into a nondendritic or equiaxed structures as shown in Fig. 2b and c. It could be possible that these equiaxed microstructures of the latter two figures were obtained due to the ripening and coalescence of dendritic arms of the dendrites as shown in the as-cast sample. The ripening and coalescence is further increased with the increased in holding times at the respective 100°C and 280°C stabilising temperatures. The as-cast and treated samples showed that the ZA3 alloy obviously is composed of two different phases (i.e., black and grey structure). When the microanalysis (EDAX) was carried out on the treated sample at 280°C for 3 h, it can be found that the black structure which is marked as A is Al-rich β phase and the grey structure which is marked as B and C are zinc-rich η phase that form separate phases in grains and lamellar structure (Fig. 2d). Table 2 lists the weight percent of Zn and Al according to the result of EDAX for primary phase, grey and black eutectic layers presented in

Table 2: Microanalysis (EDAX) of the sample as shown in Fig. 2d

Group	Zn%	Al%
A (Dark eutectic layers/β phase)	72.88	23.94
B (Primary phase/η phase)	96.57	1.24
C (Bright eutectic layers/η phase)	96.67	1.15

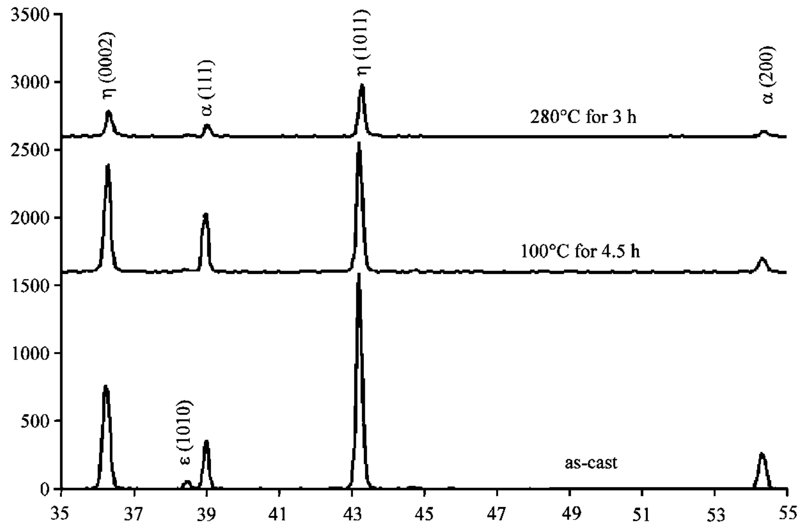

Fig. 3: XRD Pattern of ZA3 alloy at different temperatures

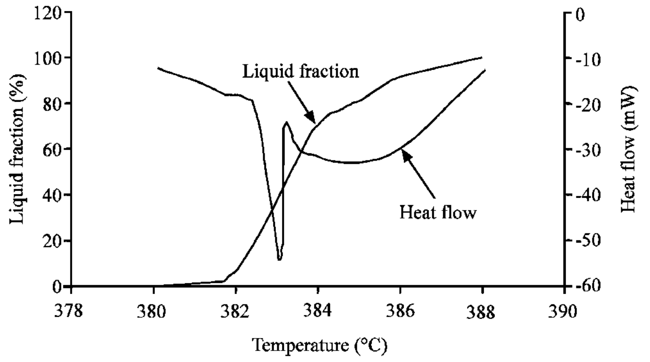

Fig. 4: DSC and Liquid Fraction Curve of ZA3

the microstructure. From the phase diagram in Fig. 1, it can be found that the η phase (solid solution Al in Zn) is the primary grain structure and this structure are embedded in a matrix of the lamellar eutectic which is a mixture of η phase and β phase, where the β phase is solid solution Zn in Al.

XRD pattern of the ZA3 in the as-cast condition, after heating at 100°C for 4.5 h and 280°C for 3h are presented in Fig. 3. It can be observed that the quantity of α and η phase has declined after heat treatment. It is thought that aluminum from α phase dissolved into η phase after heating to 100°C for 4.5 h. This dissolution continues when the sample is heated to 280°C (3 h holding time) into β+η phase (Fig. 1). However, since the XRD analysis was carried out in ambient temperature, the β phase could not be seen in the XRD pattern for the 280°C (3 h holding time) sample. This is so because β phase is not stable in ambient temperature, therefore vanished completely from the XRD analysis (Zhongming *et al*., 2000).

Effect of heating on the semisolid microstructures: The DSC heating curve, together with its corresponding liquid distribution of the as-cast ZA3, is shown in Fig. 4. The solidus is estimated at 380°C and the liquidus at 388°C, while 20 and 50% liquid correspond to 382 and 383°C, respectively. Note that thixoforming is normally carried out at fraction liquid between 20-50% (Kirkwood, 1994). Hence, when the heated ZA3 alloy was partially remelted at 383°C, the corresponding liquid fraction is approximately 50%.

Figure 5 shows some of the typical semisolid microstructures of ZA3 alloy after treating for different periods. Figure 5a shows the microstructure of the as-cast alloy when it was directly subjected to partial remelting at 383°C. Primary phase of as-cast alloy form an intricate structure composed of irregular and interconnected particles. Fig. 5b and c show the nondendritic solid metal structures of ZA3 alloy after partial remelting at 383°C was

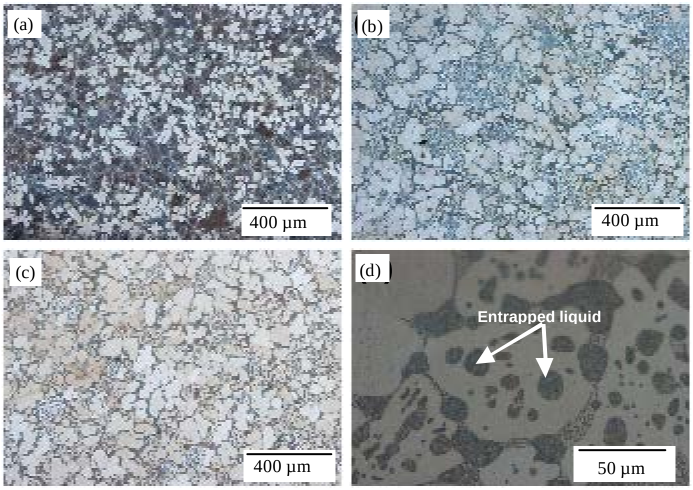

Fig. 5: Microstructure of ZA3 subjected to partial re-melting at 383°C for 15 min on (a) As-cast sample and on samples previously heated at (b) 100°C for 4.5 h, (c) 280°C for 3 h, while (d) is the micrograph of the same sample in (c) at higher magnification showing entrapped liquid

carried out to the 100°C/4.5 h and 280°C/3 h samples respectively. As the previous discussion, when the heat treatment holding time was increased, primary dendritic structure (zinc-rich η phase) could coarsen into nondendritic structure which is embedded in a matrix of the lamellar eutectic. The lamellar structure is composed of the mixture of η+α phase and η+β phase for the samples that were treated at 100 and 280°C respectively where the α and β are Al-rich phase. After partially remelted in semisolid η+L phase (at 383°C), α and β phases have decomposed into η phase and resulting in melting of eutectic phase at the grain boundaries. Similar observation is seen when the holding times were increased more than 4.5 and 3 h for heating at 100 and 280°C respectively. It can be found that the η phase, which formed the lamellar structure in the solid state, has changed into irregular grain structure with some entrapped liquid as shown in Fig. 5d.

To represent quantitatively the shape of grains, shape factor was commonly used to characterize SSM microstructures. Shape factor is defined as $P^2/4\pi A$, where P is the perimeter and A is the area of the particle (shape factor of a circle is equal to 1). For optimum semisolid processing characteristics, the shape factor should be as close to 1 as possible (Legoretta *et al*., 2008). It can be seen that the shape factor has changed to be as close to 1 with an increase of the treatment time. Variations of shape factor and primary grain size of ZA3 subjected to partial re-melting are shown in Fig. 6. After partial remelting at 383°C (i.e., semisolid condition with 50% liquid fraction), the sample that was previously

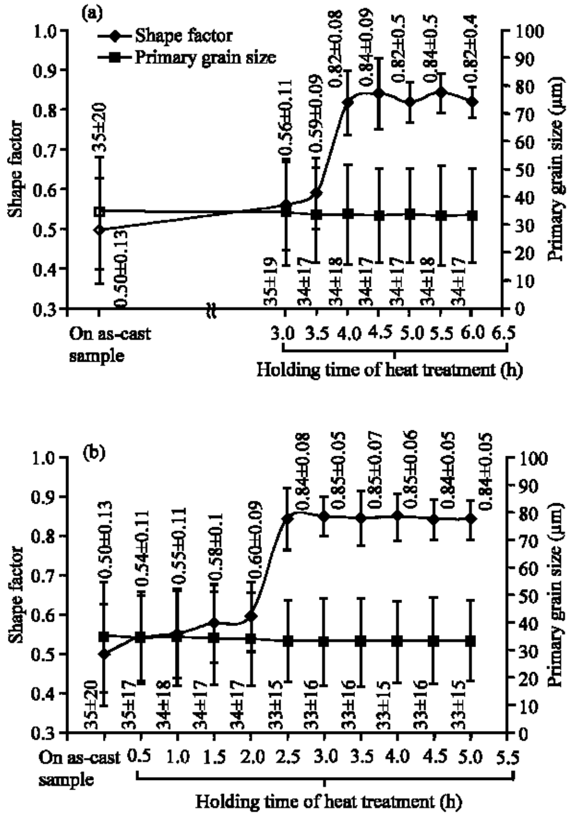

Fig. 6: Variations of Shape factor and primary grain size of ZA3 subjected to partial re-melting at 383°C for 15 min on as-cast sample and on samples previously heated at (a) 100°C and (b) 280°C, (at Various Holding Times)

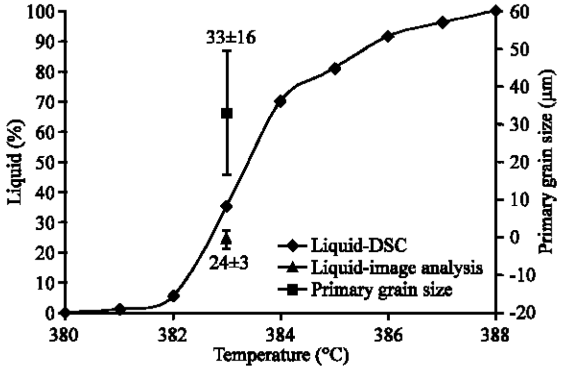

Fig. 7: Liquid fraction and grain size from image analysis plotted with the liquid fraction from DSC

heated at 100°C for 4.5 h has shown an average shape factor of 0.84±0.09 with average sizes of about 34±17 µm (Fig. 6a). Meanwhile, when the sample that was previously heated at 280°C for 3 h subjected to partial remelting at 383°C for 15 min the average shape factor obtained is 0.85±0.05 corresponding to the average sizes of about 33±16 µm (Fig. 6 b). The non-dendritic microstructures are now perhaps suitable for the semi-solid metal processing application. Liquid fraction and grain size from image analysis are plotted against the liquid content from DSC in Fig. 7. The liquid fraction underestimation by the image analysis, as compared to the DSC is due to insufficient cooling rate to instantaneously freeze the microstructure, resulting in further solidification of liquid on the solid phase (Omar *et al*., 2005).

CONCLUSIONS

This study has demonstrated the microstructural evolution of the dendritic as-cast ZA3 alloy to nondendritic semi-solid structures when the alloy was partially remelted into its semi-solid zones. Before partial remelting, the samples were first, respectively heated in solid α+η and β+η phases (i.e., at 100 and 280°C respectively). Both heat treatment processes have resulted in the coalescence and coarsening of the original dendritic structures into a nondendritic or equiaxed structures due to the ripening and coalescence of dendritic arms of the dendrites. When the as-cast and treated samples from both heat treatment processes were partially remelted at 383°C for 15 min, it can be seen that the eutectic η phase start to melt at the grain boundaries. The semisolid microstructures of treated samples at 100°C obtained the best shape factor of 0.84±0.09 when heated for 4.5 h and this corresponds to the grain size of 34±17 µm, while for the samples treated at 280°C, the best shape factor, 0.85±0.05, was obtained at 3 h holding time with the corresponding grain size of 33±16 µm. These nondendritic semisolid microstructures with fine grain sizes are now perhaps suitable for semi-solid metal processing application.

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