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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Zn25Al3Cu BASED COMPOSITES WITH LARGE Al_2O_3 PARTICLES AT ROOM AND ELEVATED TEMPERATURES

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Abstract

Microstructure and compressive properties of Zn25Al3Cu alloy and Zn25Al3Cu/Al_2O_3 particulate composites with large reinforcing particles (250 μm) were examined. The composites were obtained by compocasting technique through infiltration of 3, 8 and 16 wt. % Al_2O_3 particles into the semi-solid metal matrix. The influence of temperature in the range from room temperature to 170 °C on compressive yield strength of the matrix alloy (as-cast Zn25Al3Cu) and composites was investigated. From 70 °C compressive yield strength of all materials starts to decrease, but the rate of decrease is different for the matrix alloy (as-cast) and composites It was found that the abrupt decrease of compressive yield strength of the matrix alloy occurred at temperatures higher than 70 °C, whereas composites retained relatively high values of compressive yield strength till the end of testing temperature range regardless on the amount of reinforcing particles.

Key words: Metal-matrix composites, zinc–aluminum alloys, Al_2O_3 particles, compocasting, compressive yield strength

Introduction

Among the zinc-based foundry alloys the alloys with relatively high content of aluminum (zinc–aluminum or ZA alloys) are distinguished by excellent bearing properties. The alloys are designated 8, 12 and 27 corresponding to their approximate aluminum content. These alloys are also characterized by favorable combination of physical, mechanical and technological properties (low melting point, excellent castability, high strength, good machining and tribological properties), as well as by low

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manufacturing costs. The alloys are suitable for a wide application range (industrial fittings and hardware, pressure tight housings, sleeve bearings, thrust washers and wear plates). However, ZA alloys are applicable at operating conditions up to 80 °C, due to a deterioration of mechanical properties at elevated temperatures [1].

ZA27 alloy is the lightest of the ZA alloys and offers excellent bearing and wear resistance properties. The alloy is characterized by the dendrite microstructure [2,3] and a non-uniform distribution of chemical elements in the alloy phases [4]. ZA27 alloy solidifies in a wide temperature range and is suitable for processing in the semi-solid state. Compocasting technique [5] was used to produce ZA-based composites. This technique is characterized by infiltration of reinforcing particles into the semi-solid metal matrix. It was shown that physical and a number of mechanical characteristics (elasticity modulus, hardness, wear resistance, linear thermal expansion coefficient) of ZA27 alloy-based composites with addition of Al_2O_3, SiC [6-9] and ZrO_2 [10] particles were better with respect to the matrix alloy at room temperature. Cornie et al. [6] carried out investigation of mechanical properties of ZA27 alloy strengthened by SiC particles and Al_2O_3 whiskers at room temperature. However, the results at elevated temperatures have not been reported.

Compressive properties of commercial bearing alloys at room and elevated temperatures (about 100 °C) are of exceptional importance for their application in manufacturing of sliding bearings [11]. ZA27 alloy is suitable bearing material for heavy and light load pressures with low and high surface speeds. Particulate composites with base ZA27 alloy were developed in order to overcome the deterioration of alloy mechanical properties at elevated temperatures.

It is well-known that the size of reinforcing particles significantly affects mechanical properties of composites. At uniform particles distribution better mechanical properties were achieved by using small particles [12, 13]. Hard particles as SiC, Al_2O_3 and ZrO_2 [6, 7, 14] and soft particles as graphite, coke dust [15, 16] were used for producing composites with base ZA27 alloy. The size of particles was mostly from 50 to 150 μm. There are only a few papers [8, 17-19] concerning composites with reinforcing particles larger than 200 μm. Addition of these particles to the matrix alloy offers several advantages which are as follows:

- due to the particle size infiltration of particles into the semi-solid melt of matrix alloy can be easily performed with dosator,
- mixing of composite semi-solid melt during compocasting process can be carried out in the laminar flow regime with the minimum vortex and small energy consumption,
- large (250 μm) particles are not prone to agglomeration contrary to small (12 μm) particles [8]. Small particles exhibit significant tendency towards formation of B type agglomerates as was defined by Tszeng [20],
- it is possible to develop a compocasting procedure with the reduced time of mixing and favorable distribution of reinforcing particles in the matrix.

Thus, in relation to composites with small reinforcing particles, except that a more balanced distribution of particles may be obtained, this process from the economic point of view may be more favorable due to its shorter duration and lower energy consumption.

Besides, it was recently shown that the wear resistance of the ZA27/Al_2O_3 particulate composites with large particles (250 µm) was higher with respect to as-cast ZA27 alloy at room temperature [17, 18].

In this work large Al_2O_3 particles were used for processing of composites with Zn25Al3Cu matrix alloy. Compressive properties of the matrix alloy and the composites were studied. The effect of the amount of reinforcing particles (3, 8 and 16 wt. % Al_2O_3) on the compressive yield strength of composites was examined at room and elevated temperatures (from 70 to 170 °C).

Chemical composition of studied Zn25Al3Cu alloy is very similar to that of ZA27 alloy except that amount of copper is slightly higher than recommended by EN 12844 [21]. Murphy′s investigations related to ZA27 alloy [3] and the results reported in [22] for Zn25Al3Cu alloy indicate microstructural similarity and close mechanical properties of both alloys. Therefore**,** experimental results obtained within this work can be compared with the results for ZA27 alloy based composites with ceramic particles.

Experimental procedure

Test samples

Zn25Al3Cu alloy was processed in the Department of Materials Science "Vinca" Institute. The nominal composition (in wt. %) of the alloy was as follows: 27 Al, 3 Cu and Zn remainder. The alloy casting was performed at 580 °C into the steel mold preheated up to 100 °C. The as-cast samples were cylindrical with 36 mm in diameter and 120 mm in height.

Compocasting

In the first stage of the process previously as-cast Zn25Al3Cu alloy was charged into the crucible of electro-resistance furnace [23].The alloy was melted and preheated up to 550 °C to clean the slag from the melt surface. The melt was left to cool down to 485 °C at 5 $°C\ min^{-1}$ cooling rate (approximately isothermal regime) and the active part of paddle stirrer was then immersed into the melt. Mixing of the matrix semi-solid melt was performed within the temperature range between liquidus and solidus temperature with the gradual increase of stirrer rotation speed. Stationary mixing regime (i.e. mixing was performed under the constant temperature and the mixing rate) was achieved at rotation speed of 450 rpm and at 461 °C. Large Al_2O_3 particles (3, 8 and 16 wt. %) were infiltrated continuously with mixing into the semi-solid melt. No previous chemical preparation of Al_2O_3 particles has been performed. Al_2O_3 particles were preheated at 200 °C for 1 h in order to eliminate moisture and reduce thermal shock during infiltration. Reinforcing particles were added into the zone next to the shaft of the active part of stirrer. Compared to speed of 450 rpm (melt without added Al_2O_3 particles), mixing of melt with infiltrated particles was done at relatively lower speeds, i.e. at 200 rpm for 3 and 8 wt. % Al_2O_3, and at 100 rpm with addition of 16 wt. % Al_2O_3 particles. Lower speeds were applied in order to prevent segregation of reinforcing particles in the peripheral zones of castings as well as to avoid air penetration into the melt. Mixing temperature of melt and infiltration time were dependant on the amount of reinforcing particles as presented in Table 1.

Table 1 Parameters of compocasting process

δ (μm)	250		
G (%)	3	8	16
t (°C)	461	464	468
τ_{inf} (min)	3	4	5
τ_{tot} (min)	30		

The composite semi-solid melt was poured into the steel mold preheated to 300 °C. The composite samples were cylindrical, 36 mm in diameter and 120 mm in height. Hot-pressing of all composites which was done at 230 °C and 250 MPa was applied in order to eliminate porosity as much as possible.

Characterization of the matrix alloy and the composites

Microstructural investigations

Optical microscopy (OM) and scanning electronic microscopy (SEM) were used as well as energy dispersive spectroscopy (EDS) for microstructural characterization of the matrix alloy and composites.

Samples were machine-cut from ingots and then ground and polished. Grinding was performed with 80, 360 and 600 grits emery paper, while polishing was done using polishing cloth and polishing paste with Al_2O_3 particles. Polished samples were used for SEM and EDS analysis, whereas samples for OM examination were etched in 9 % v/v HNO_3.

Compression tests and hardness

Compression tests were performed at room (20 °C) and elevated temperatures: 70, 120 and 170 °C. This temperature interval is similar to that applied for tensile tests of zinc-based alloys [1], since there are no data in the literature on the temperature range for compression tests. The operating temperature was maintained within ± 1 °C. The tests were done on cylindrical specimens (4 mm in diameter and 8 mm in height) using a tensile test machine with a hot chamber. The specimens were heated for 20 minutes prior to compression test. Loading rate of 1 mm min^{-1} was applied. Three specimens of the matrix alloy (as-cast) and three specimens of each composite type were tested and the average value of compressive yield strength was calculated.

The room temperature hardness tests were conducted in accordance with ASTM E10 using Brinell hardness tester with a ball indenter of 2.5 mm diameter and a load of 62.5 kg. The load was applied for 30 s. Tests were performed on specimens with 36 mm in diameter and 10 mm in height. Five hardness readings were taken for each specimen at different locations.

Results and discussion

Microstructure

Zn25Al3Cu as-cast

General appearance of as-cast microstructure can be seen in Fig. 1a,b. Alloys which solidify through peritectic reaction during cooling are characterized by this kind of structure. A typical dendrite structure indicates a non-equilibrium solidification process. The dendrite core consists of α phase, while $\alpha + \eta$ phase mixture prevails at the dendrite periphery. Interdendrite space is filled with η phase. The presence of ε phase ($CuZn_4$) was also noticed. This phase is distributed in the form of mainly elliptical particles within η phase (Fig. 1b). It was reported that ε phase had a beneficial effect on the mechanical and wear properties of Zn25Al3Cu alloy, particularly after certain heat treatment regimes [3]. Prolonged etching caused considerable dissolution of η phase resulting in a vague appearance of other constituents of Zn25Al3Cu alloy.

Variations of chemical composition along the L line (in Fig. 1a) are shown in Fig. 1c. Concentrations of zinc and copper increase reaching the maximum and then decrease while the variation of aluminum concentration is quite opposite. It is noticeable that copper concentration is significantly lower in regard to zinc concentration. These results show that that dendrite cores are rich in aluminum while the amount of zinc is rather high in the interdendrite space.

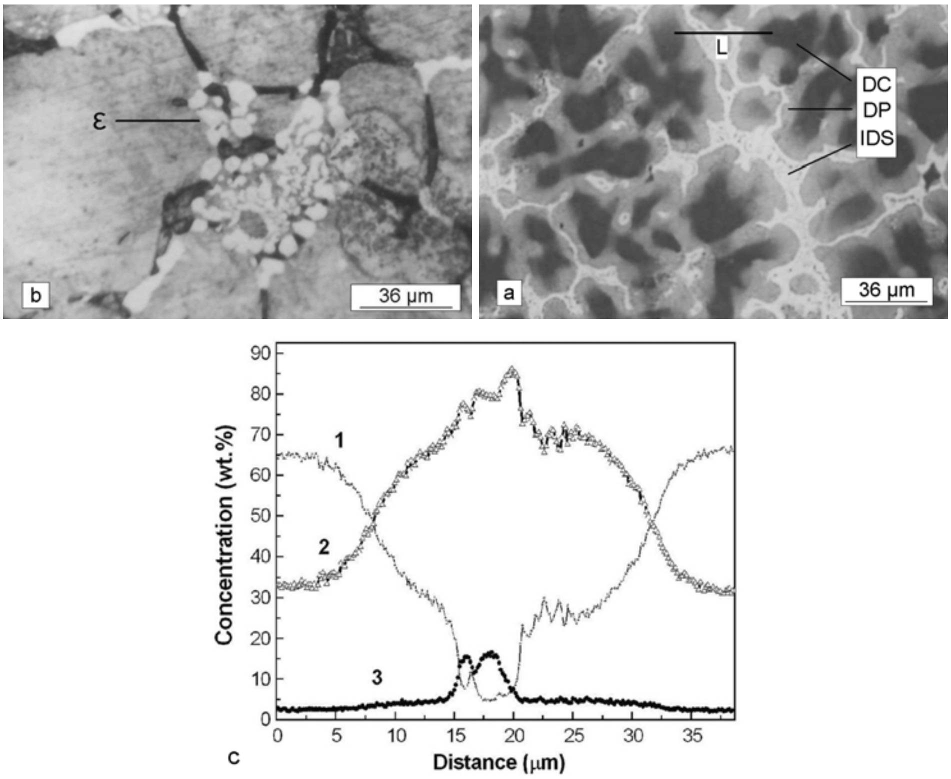

Figure 1. Microstructure of as-cast Zn25Al35Cu. (a) SEM, polished DC – dendrite core; DP-endrite periphery; IDS-interdendrite space; (b) OM detail of ε phase, etched; (c) variation of chemical composition along the L line (Fig. 1a), 1 - Al; 2 - Zn; 3 - Cu.

$Zn25Al3Cu/Al_2O_3$ composites

The microstructure of composites is shown in Fig. 2a-c. Large Al_2O_3 particles are uniformly distributed in the matrix alloy regardless of their amount. Segregation of the reinforcing particles was not noticed neither their tendency to form agglomerates.

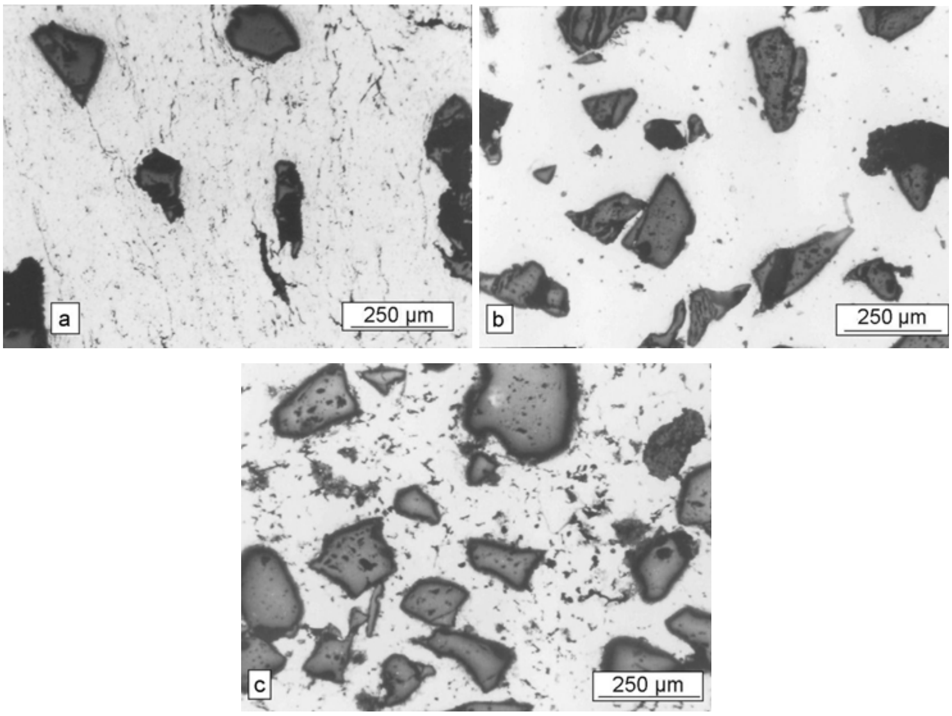

Figure 2. Microstructure of $Zn25Al3Cu/Al_2O_3$ composites, OM, polished (a) Zn25Al3Cu + 3 wt. % Al_2O_3; (b) Zn25Al3Cu + 8 wt. % Al_2O_3; (c) Zn25Al3Cu + 16 wt. % Al_2O_3

Details of microstructure of the composite with 3 wt.% Al_2O_3 particles are shown in Fig. 3 a, b. The microcracks along the matrix/particle interface (A) and the microcracks starting from the reinforcing particle towards the matrix (B) can be seen more clearly at higher magnification (Fig. 3 a). The microcracks are also observed at the boundary between η and $\alpha + \eta$ phases (Fig. 3b).

Microstructure of an etched sample of the composite with 3 wt. % Al_2O_3 particles is shown in Fig. 4a. Large primary particles of α phase are visible in the composite matrix. Porosity at the interface between a large reinforcing particle (RP) and the matrix was not observed at this level of applied magnification.

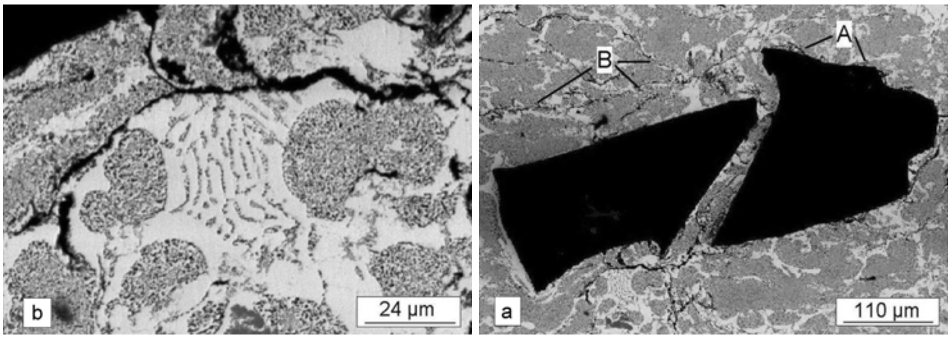

Figure 3: Microstructure of Zn25Al3Cu/Al_2O_3 composite (3 wt.% Al_2O_3), SEM, polished (a) interface and microcracks; (b) microcracks development

A detail of microstructure corresponding to the composite with 16 wt. % Al_2O_3 is presented in Fig. 4b. Large Al_2O_3 particle is cracked into smaller fragments kept together by the metal matrix. No scattered fragments detached into the matrix have been observed. Fragments of particles can form agglomerates behaving as a source of initial microcracks imposing negative effect on mechanical properties of composites. The cracks in particles are probably induced by the thermal stress. As there is a large mismatch between thermal coefficients of the matrix (linear thermal expansion coefficient for ZA27 alloy is 26μmm^{-1}K^{-1}) [5] and Al_2O_3 particles (7.6μmm^{-1}K^{-1}) [24], there will be a large thermal stress during cooling of the composites. The large Al_2O_3 particles will be under the influence of a tensile stress and may crack during cooling.

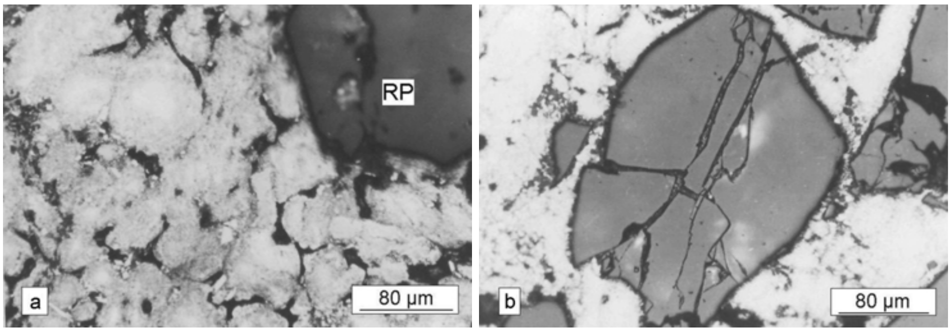

Figure 4. Microstructure of Zn25Al3Cu/Al_2O_3 composites, OM, etched. (a) 3 wt. % Al_2O_3, RP - reinforcing particle; (b) 16 wt. % Al_2O_3, a detail - fractured Al_2O_3 particle

Mechanical properties

Compressive yield strength and hardness at room temperature

Experimental results of compressive yield strength as dependence on temperature are presented in Fig. 5. Compressive yield strength of 420 MPa for as-cast Zn25Al3Cu alloy (Fig. 5,) is somewhat higher (8 %) than the value prescribed by the standard for ZA27 alloy [20]. This increase is probably due to a slight increase of the copper content in the investigated alloy than in the standard ZA27 alloy since the addition of copper favors the formation of ε phase.

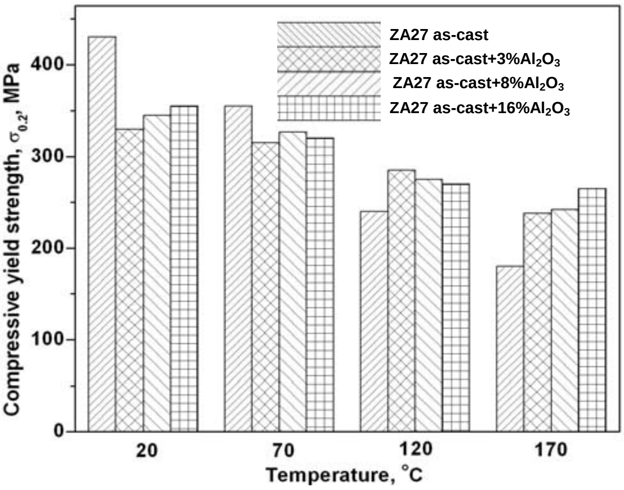

Figure 5. Compressive yield strength dependence on temperature. 1 - Zn25Al3Cu as-cast; 2 - Zn25Al3Cu + 3 wt. % Al_2O_3; 3 - Zn25Al3Cu + 8 wt. % Al_2O_3; 4 - Zn25Al3Cu + 16 wt. % Al_2O_3.

On the other side, compressive yield strength of Zn25Al3Cu/Al_2O_3 composites is lower with respect to the as-cast alloy. Values of compressive yield strength of composites are lower regardless of the amount of reinforcing particles although one might expect higher values for composites bearing in mind mechanism of composites hardening proposed by Arsenault [19]. According to this mechanism the density of dislocations increases with amount of volume fraction and decreases with size of strengthening particles, but is always higher compared to the non-strengthened matrix alloy. The lower compressive strength of composites may be ascribed to the negative effect of microcracks formed either along the matrix/particle interface or microcraks situated at the boundaries between α + η and η phases (see Fig. 3a,b, respectively). This effect was also previously reported [25].

The results of Brinell hardness test are presented in Table 2.

Table 2 Hardness of Zn25Al3Cu alloy and Zn25Al3Cu/Al_2O_3 particulate composites at room temperature

Material	Hardness (BHN)
Zn25Al3Cu, as-cast	111
Zn25Al3Cu + 3 wt. % Al_2O_3	85
Zn25Al3Cu + 8 wt. % Al_2O_3	113
Zn25Al3Cu + 16 wt. % Al_2O_3	118

These results confirmed that hardness of composites increases with increase of the amount of reinforcing particles. Hardness of composites with 3 and 8 wt. % Al_2O_3

particles is similar to hardness of the matrix alloy (as-cast) while hardness of the composite with 16 wt. % Al_2O_3 particles is higher. This is in accordance with results reported by Cornie et al. [6].

Compressive yield strength at elevated temperatures

In the temperature range from 70 to 170 °C compressive yield strength of all materials decreases, but the rate of decrease is different for the matrix alloy and composites (Fig. 5). The abrupt decrease of compressive yield strength of the matrix alloys occurred at temperatures higher than 70 °C, whereas composites retained relatively high values of compressive yield strength which is similar for all composites in the whole range of testing temperatures (from 70 °C to 170 °C). Compressive yield strength of composite with 16 wt. % Al_2O_3 at 170 °C is somewhat higher comparing to composites with lower amount of Al_2O_3 particles.

The deterioration of compressive yield strength of the matrix alloy above 70 °C originates from the effect of thermally activated processes which are coupled with an external load. Climbing is the basic mechanism of dislocations motion under the influence of an external load and elevated temperatures [26]. This statement is valid for pure metals when $T > 0.5\ T_m$ (where T is the testing temperature and T_m is the melting temperature), but as a first approximation may be applied in the case of ZA27 alloy. The melting temperature of ZA27 alloy is 373 °C (T_m = 646 K) [1] and if the testing temperature is 100 °C (T = 373 K), which roughly equals to the middle part of the test temperature range of this study, then $T = 0.57\ T_m$. At temperatures above 70 °C easier movement of dislocations in matrix alloys is enabled by diffusion processes resulting with the rapid decrease of compressive yield strength.

Although in this study the size of Al_2O_3 particles was rather high (250 μm) the effect of these particles on the matrix strengthening cannot be neglected. Nevertheless, the density of dislocations which might arise as a result of the difference in thermal expansion between the metal matrix and Al_2O_3 particles is higher in composites than in the matrix alloy. The addition of Al_2O_3 particles induces higher dislocation density and being hard these particles act as barriers to the movement of dislocations within the matrix aggravating their mobility. The net effect is the slow decrease of compressive strength of composites at elevated temperatures. For the composite with 16 wt. % Al_2O_3 these effects are more pronounced at 170 °C. The similar conclusion was reached by Seah et al. [14] studying ZA27 alloy strengthened by the addition of SiC particles with size between 100 and 150 μm.

Conclusions

1. Large Al_2O_3 particles are uniformly distributed in the matrix Zn25Al3Cu alloy regardless of the amount of reinforcing particles. Porosity of the particle/matrix interface and segregation of the reinforcing particles have not been noticed at the level of applied magnification.

2. Cracks in large Al_2O_3 particles could be induced by thermal stress. As there is a large mismatch between the thermal coefficients of the matrix and the particles, a large stress gradient will be formed during cooling. The large Al_2O_3 particles which

have low thermal expansion coefficients will sustain a tensile stress and may crack during cooling.

3. Hardness of Zn25Al3Cu/Al_2O_3 particulate composites increases with increase of amount of reinforcing particles.

4. Zn25Al3Cu alloy (as-cast) exhibit higher compressive yield strength with respect to Zn25Al3Cu/Al_2O_3 composites at room temperature. In the temperature range from 70 to 170 °C compressive yield strength of all materials decreases, but the rate of decrease is different for the matrix alloy (as-cast) and composites. The abrupt decrease of compressive yield strength of the matrix alloy occurred at temperatures higher than 70 °C, whereas composites retained relatively high values of compressive yield strength similar for all composites, except that of composite with 16 wt. % Al_2O_3 at 170 °C which is somewhat higher.

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