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Synthesis and characterization of zircon sand/Al-4.5 wt% Cu composite produced by stir casting route

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Abstract Zircon sand particles of different size and amount have been incorporated in Al-4.5 wt% Cu alloy by stir casting route. Coarser particles of size between 90 and 135 μm can be dispersed in substantial amounts (up to 30 wt%), where as finer particles of size 15 and 65 μm have limited dispersion, 10 and 20 wt%, respectively. The matrix of the composites has cellular structure, where the size of the cell depends on zircon particle size and its amount in the composite. Segregation of copper rich phase ($CuAl_2$) has been found in the vicinity of the particle–matrix interface. The abrasive wear resistance of the composite improves with the increase in amount or decrease in size of zircon particles.

Introduction

Aluminum metal matrix composites (Al MMCs) are being considered as advanced materials for its light weight, high strength, high specific modulus, excellent wear resistance and low co-efficient of thermal expansion compared to conventional metals and alloys [1–3]. The excellent mechanical properties of these materials and the relatively low production cost make them very attractive for a variety of applications in automotive and aerospace industries. There are several fabrication techniques available in manufacturing the MMC materials. According to the type of reinforcement, the fabrication techniques can vary considerably. These techniques include stir casting [4–9], liquid metal infiltration [10], squeeze casting [11], and spray co-deposition [12]. Stir casting route is generally practiced commercially [13–15]. Its advantages lie in its simplicity, flexibility and applicability to large quantity production. Some of the Al matrix composites such as those reinforced with SiO_2, B_4C, Al_2O_3 or SiC are now commercially available in a variety of structural forms. Amongst the various aluminum–ceramic combinations limited studies are done on aluminum–zircon composite as zircon is not readily wetted by liquid aluminum and there is a significant difference between their density values. However, wetting characteristics of the liquid metal with the solid surface may quickly be altered by an appropriate alloying element addition. Despite having disadvantages in synthesizing aluminum–zircon composites, zircon was found to be a promising candidate due to its high hardness, high modulus of elasticity, and excellent thermal stability. Excellent thermal stability is important since fabrication processes undergo enormous changes in temperature, and large volumetric changes due to phase transformation can cause debonding at the interfaces [16].

In the present investigation, stir-casting route has been used for incorporating zircon sand particle of different size and amount in Al-4.5 wt% Cu alloy melt. It has been reported earlier that introduction of zircon in liquid aluminum does not require the formation of a vortex [16]. However, in the present investigation stirring has been done for better distribution and to prevent sedimentation of zircon particles in melt. Effect of particle size and amount on particle distribution, particle settling and matrix structure has been studied and correlated. Abrasive wear behavior of the monolithic alloy and as-cast composites has been evaluated and compared.

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Experimental

Materials

Compositions of zircon sand and Al alloy, used in the present study, are given in Table 1. The as received zircon sand was pulverized in a planetary ball mill and particles of average size of 15, 65, 90 and 135 μm were selected to reinforce the Al-4.5 wt% Cu matrix.

Synthesis

A stir casting setup, which consisted of a resistance furnace and a stirrer assembly was used to synthesize the composite. Clay graphite crucible of 1 kg Al melt capacity was placed inside the furnace. Top pouring arrangement was made to cast the composite in metal mould. The stirrer assembly consisted of a graphite turbine stirrer fixed to a steel rod.

Al-4.5 wt% Cu alloy was prepared in an induction furnace. Approximately 700 g of alloy was then remelted at 820 °C in the resistance furnace of stir casting setup. Preheating of zircon sand at 450 °C was done in a resistance furnace, placed near stir casting setup, to remove moisture and gases from the surface of the particulates [17]. The stirrer was then lowered vertically up to 20 mm from the bottom of the crucible (total height of the melt was 60 mm). The speed of the stirrer was gradually raised to 600 rpm and the preheated zircon sand was added with a spoon at the rate of 20–30 g/min into the melt. The speed controller maintained constant speed, as the stirrer speed reduced due to the increase in viscosity of the melt when particulates were added into the melt. After addition of zircon sand, stirring was continued for 10 min for better distribution. The melt was kept in the crucible for 1 min in static condition and it was then top poured in three identical small metal moulds successively to study the sedimentation of zircon particle in a static melt.

Quantitative assessment of zircon particles

Quantitative assessment of the zircon particulates in the composite sample was carried out using chemical dissolution method. The method involved, measuring the mass of the composite samples and then boiling it in hydrochloric acid to dissolve aluminum. Concentrated nitric acid was then added to dissolve copper, followed by washing and filtering to separate the zircon particulates. Particulates were then dried in furnace at 900 °C and weight fraction was determined.

Table 1 Composition of materials

Material	Composition (wt%)					
Zircon sand	ZrO_2	SiO_2	TiO_2	Fe_2O_3	Volatiles	
	65.90	32.20	0.30	0.87	1.53	
Al–Cu alloy	Cu	Mg	Si	Fe	Mn	Al
	4.5	0.06	0.05	0.08	0.06	95.25

X-ray diffraction and microscopy

X-ray diffraction patterns of zircon particles and composite were recorded by PW 1840 X-ray Diffractometer using the CoK_α radiation.

Microstructural characterization studies were primarily accomplished using an optical microscope and scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). The monolithic alloy and composite samples were metallographically polished and etched with Keller's reagent. All quantitative assessments (particle size, cell size, interparticle distance, etc.) were accomplished with the help of LEICA Image Analyzer using LEICA QWIN software.

Wear test

As cast alloy and composites were subjected to abrasive wear test under dry conditions at a load of 15 N. The tests were conducted on 8 mm diameter, 35 mm long cylindrical specimens, against 220 grit SiC paper affixed to a rotating flat disc of 250 mm diameter. The sliding velocity was fixed at 1.8 m s^{-1} and track diameter was 120 mm. Each test was performed with a fresh abrasive paper. Wear loss was determined by weight loss technique. The weight loss has been converted to volume loss and then wear data have been plotted as cumulative volume loss as a function of sliding distance. The wear rate has been calculated by using the following formula:

$$W\left(\mathrm{mm^3 m^{-1}}\right) = \frac{M(\mathrm{g})/D\left(\mathrm{g/mm^{-3}}\right)}{\text{Sliding distance (m)}}$$

where M = mass loss during abrasive wear, D = density of the respective composite.

Results and discussion

Characterization of zircon particles

Scanning electron micrographs of zircon particles of various average particle size 15, 65, 90 and 135 μm are shown in Fig. 1. It shows that coarser particles are more spherical

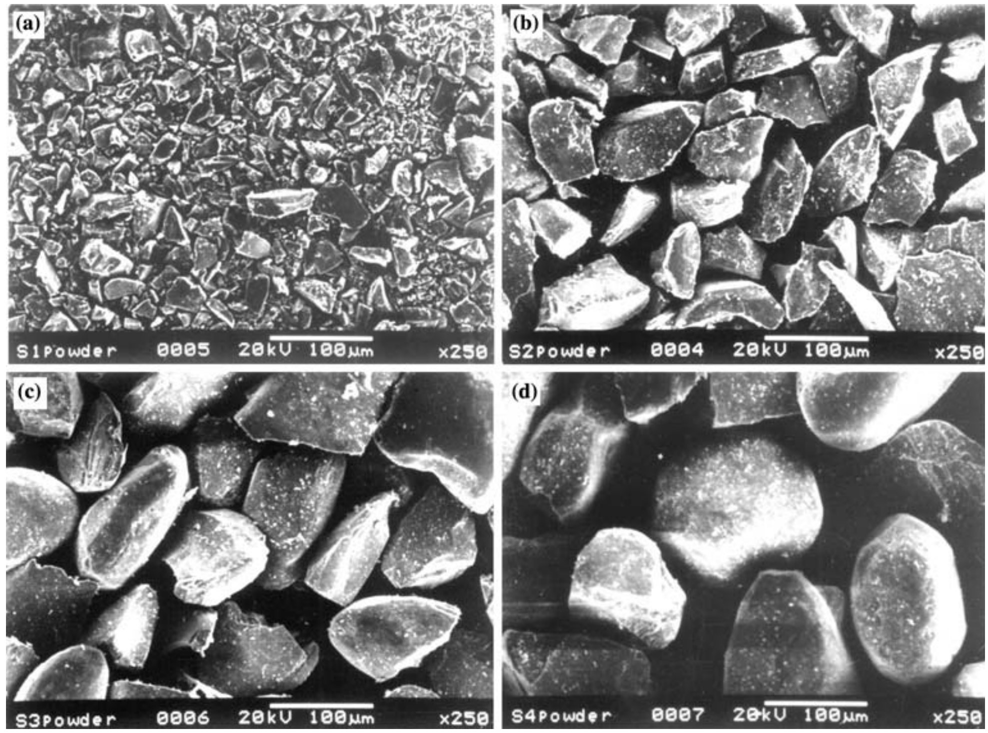


Fig. 1 Scanning electron micrographs of zircon particles of average size (**a**) 15, (**b**) 65, (**c**) 90 and (**d**) 135 µm

in shape compared to the finer ones. Irregular shape of fine particles (15 and 65 µm) is due to the breakage of particles during ball milling.

X-ray diffraction patterns of as received, ball milled and recovered (from composite by chemical dissolution of matrix) zircon particles are identical. This suggests that there is no crystallographic change in the tetragonal zircon due to ball milling and melting operation, confirming the stability of zircon particles.

Effect of zircon particle size and amount on sedimentation

Analyzing the amount of zircon particles in as-cast composites, it is found that there is an increase in particle amount from the first casting to the third one for all compositions. As top pouring was carried out the first casting had the top part of the melt, the second casting had the middle part of the melt and obviously the third casting had the bottom part of the melt. Figure 2a–d shows the effect of particle size and amount on the recovery of zircon in three castings. Figure 2c–d shows severe settling for the composite reinforced with 20 and 25 wt% of 90 or 135 µm zircon particle. It is observed from Fig. 2d that the increase in amount of zircon particles from the second to third casting is less when compared to the increase in zircon particles from first to second casting for the composites reinforced with 90 or 135 µm size particles. This is due to saturation of zircon particles at the bottom of the crucible due to high settling rate of the coarse particle during one minute holding time. The severe settling of zircon particulates in the case of composites reinforced with coarser zircon particles, when added in higher amount can be attributed to the velocity gradient during settling of the coarse particles, which causes acceleration in the melt and drags the near by particle and enhances the sedimentation rate. Where as, in the case of composite reinforced with 65 µm particle size, insignificant amount of settling is observed when compared to settling of coarser (90 and 135 µm) zircon particles. This is due to the ability of the finer particle to be in suspension for longer time compared to coarser particles. Zircon particulates of average size 15 and 65 µm were rejected from the melt when the added amount was more than 10 and 20 wt%, respectively. Fine particles have a tendency to agglomerate during synthesis, when added above a certain amount, depending upon its size. These agglomerates entrap air and there is a decrease in their density. A combined effect of decrease in density, buoyant force of the melt and stirring action results in floatation of these agglomerates on liquid melt during synthesis.

Microstructure of composite

Scanning electron micrographs at low magnification show uniformly distributed zircon particles throughout the matrix (Fig. 3). Scanning electron micrograph of as-cast composite at high magnification shows the presence of

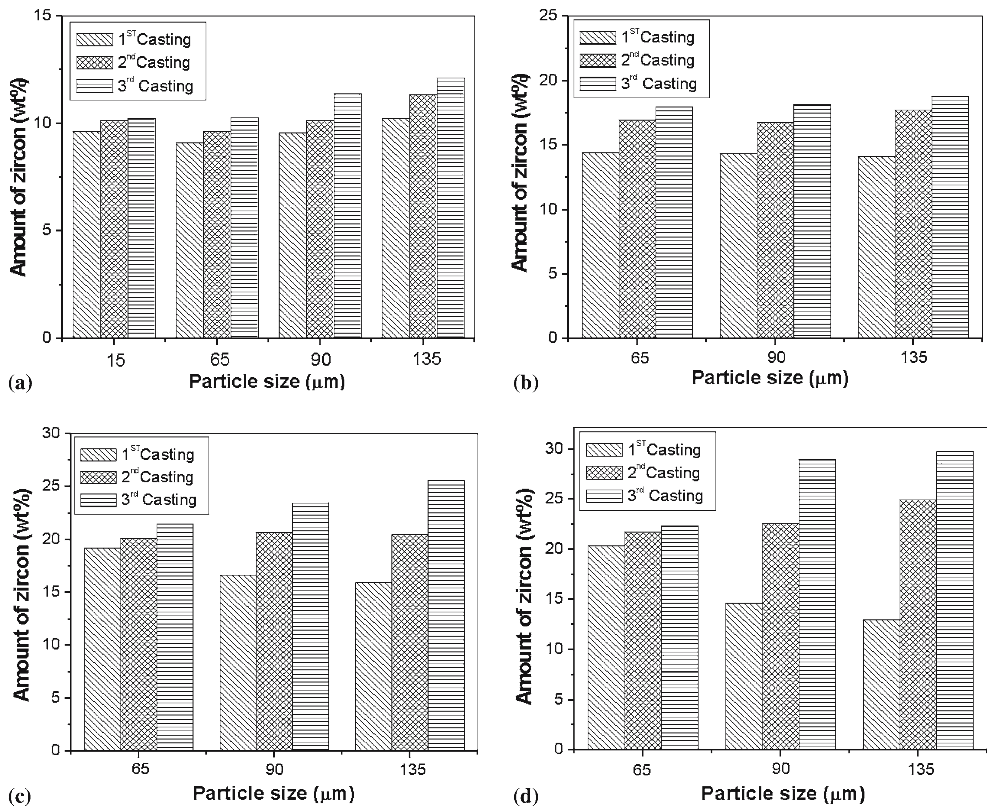


Fig. 2 Effect of particle size on settling for composites reinforced with (**a**) 10, (**b**) 15, (**c**) 20 and (**d**) 25 wt% of zircon particles in composite

uniformly distributed secondary phase in the alloy matrix (Fig. 4). There is no evidence of voids at the particle matrix interface, indicating a strong continuous bond between zircon particle and the alloy matrix.

X-ray dot maps from selected area containing particle and second phase are shown in Fig. 5. Dot maps on particle show the existence of zirconium and silicon confirming the presence of zircon sand and the secondary phase confirms to be copper rich region.

X-ray diffraction pattern of synthesized composite shows the presence of Al, $CuAl_2$ and zircon (Fig. 6). This confirms the presence of zircon particles and $CuAl_2$ phase in the cast composite.

Line profile analysis (LPA) across the particle–matrix interfacial region reveals a high concentration of Cu at the interface (Fig. 7). It can be attributed to the presence of enhanced dislocation density at the interfacial region due to the difference in the thermal coefficient of expansion between the zircon particle and the alloy matrix, promoting the dislocation-assisted diffusion of alloying elements from the adjacent dislocation-lean areas of the matrix. Gupta et al. [18] reported a similar enrichment of Cu in SiC particulate-matrix (Al-2 wt%Cu) interfacial region.

Distribution of zircon particles in cast composite is analyzed quantitatively by measuring the interparticle spacing of the zircon particle from a number of SEM micrographs taken from different portions of the castings. For each composite more than 200 measurements were taken. The average of interparticle spacing, i.e., mean interparticle spacing as a function of size and amount is reported in Fig. 8. Mean interparticle spacings are found to be greater than 75 μm in all the composites.

Effect of zircon particle size and amount on matrix structure

Optical micrographs of the as-cast alloy and some of the composites are shown in Fig. 9. The particles are found in interdendritic regions as they are pushed by the solid–liquid interface during solidification process. A wide variation in matrix structure is observed due to the presence of zircon particulates of different size and amount in the alloy matrix (Fig. 9). Reinforcement may restrict the solute transport processes by diffusion and flow. This may change dendritic morphology towards a cellular one when interparticle distance becomes sufficiently small [19]. Thus, a polished metallography sample may reveal circular grain type morphology of dendrites. In the present investigation, monolithic alloy shows dendritic structure as expected. However, this dendritic morphology changes to cellular one in the composite owing to the above mentioned reason. Average diameter of such cells as a function of size and amount of zircon sand is shown in Fig. 10.

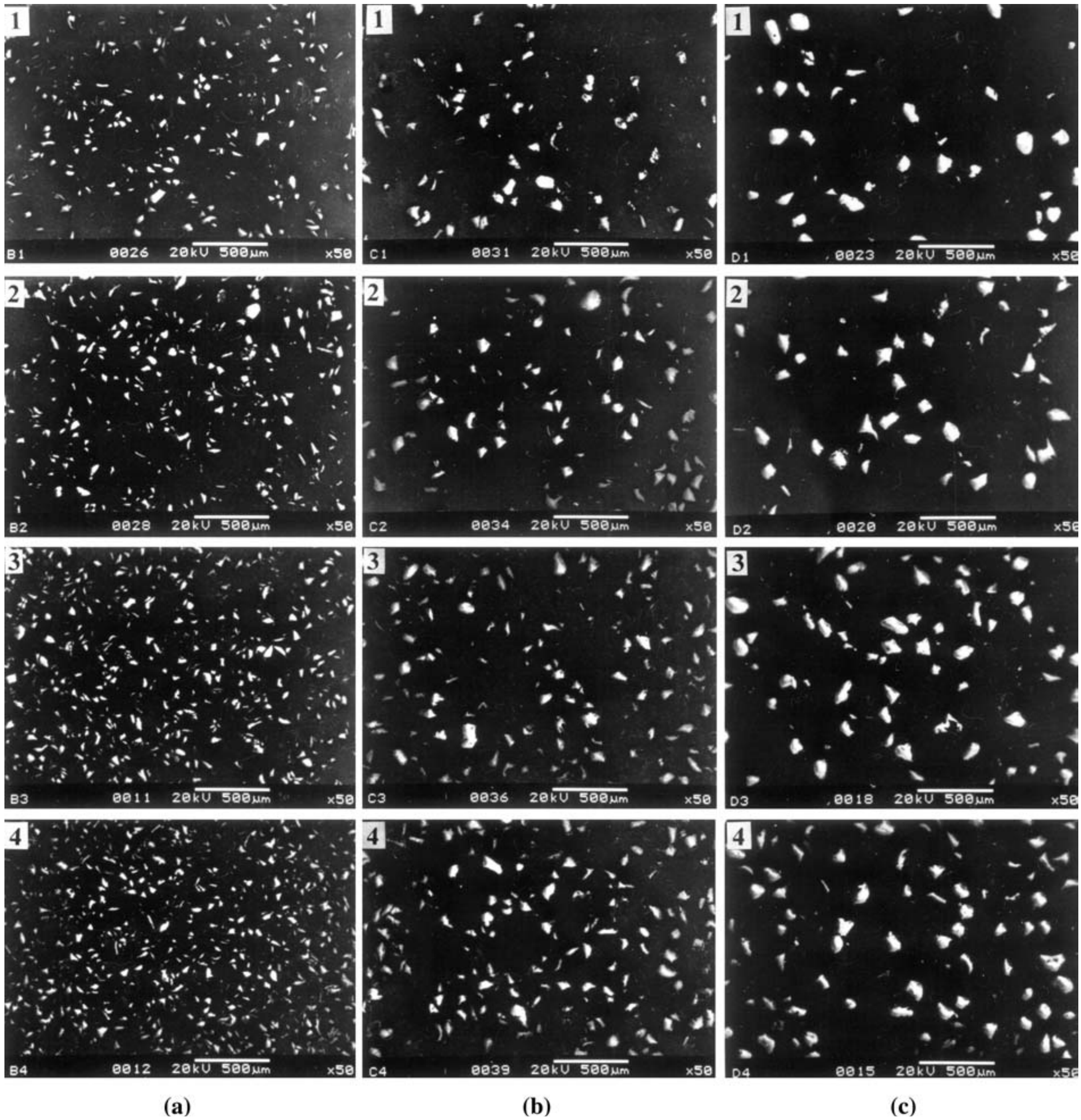


Fig. 3 Scanning electron micrographs of composites reinforced with (**a**) 65, (**b**) 90, and (**c**) 135 μm average size zircon particles (with increasing weight percent from top to bottom figure)

The cell diameter increases with an increase in amount of zircon in the cast composite. It can be attributed to the increase in viscosity of the melt with the increase in particle amount, which reduces the degree of convection in molten composites, and in turn tend to promote large cellular structures. It has been reported that convection is a major factor in determining the matrix structure in a permanent metal mould casting [20]. It is also observed that composite containing coarser particles exhibits a large cell diameter compared to the same in composite containing finer particles (Fig. 10). As finer particle implies lesser interparticle spacing, it discourages cell growth leading to a relative refinement of the matrix structure.

Wear properties

Figure 11a–c shows the cumulative wear volume loss as a function of sliding distance for the Al-4.5 wt% Cu alloy and composites reinforced with zircon particles of various size (65, 90 and 135 μm) at a load of 15 N. It is observed that the abrasive wear resistance improves significantly after addition of zircon sand in Al-4.5 wt% Cu alloy. It is

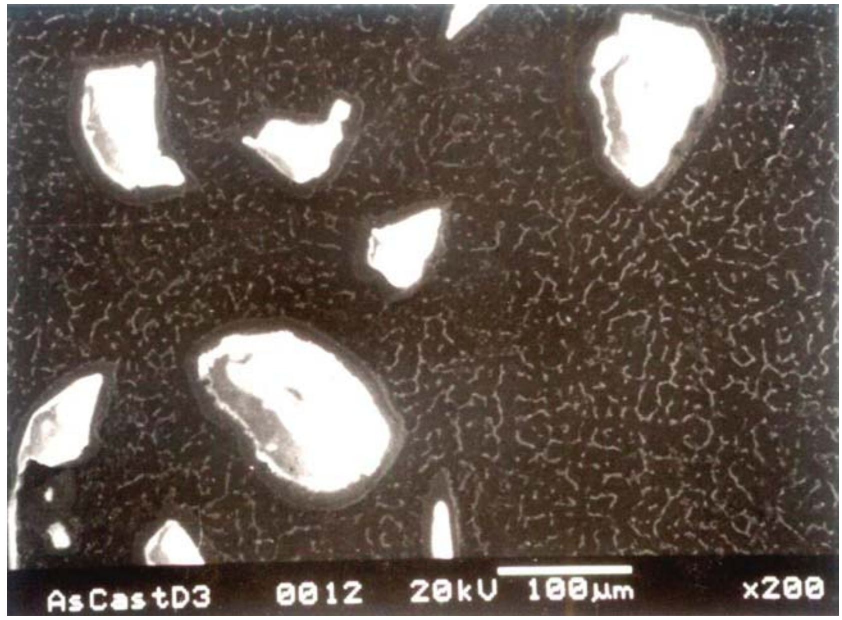


Fig. 4 Scanning electron micrograph of Al-4.5 wt% Cu/Zircon sand composite showing good particle–matrix bonding

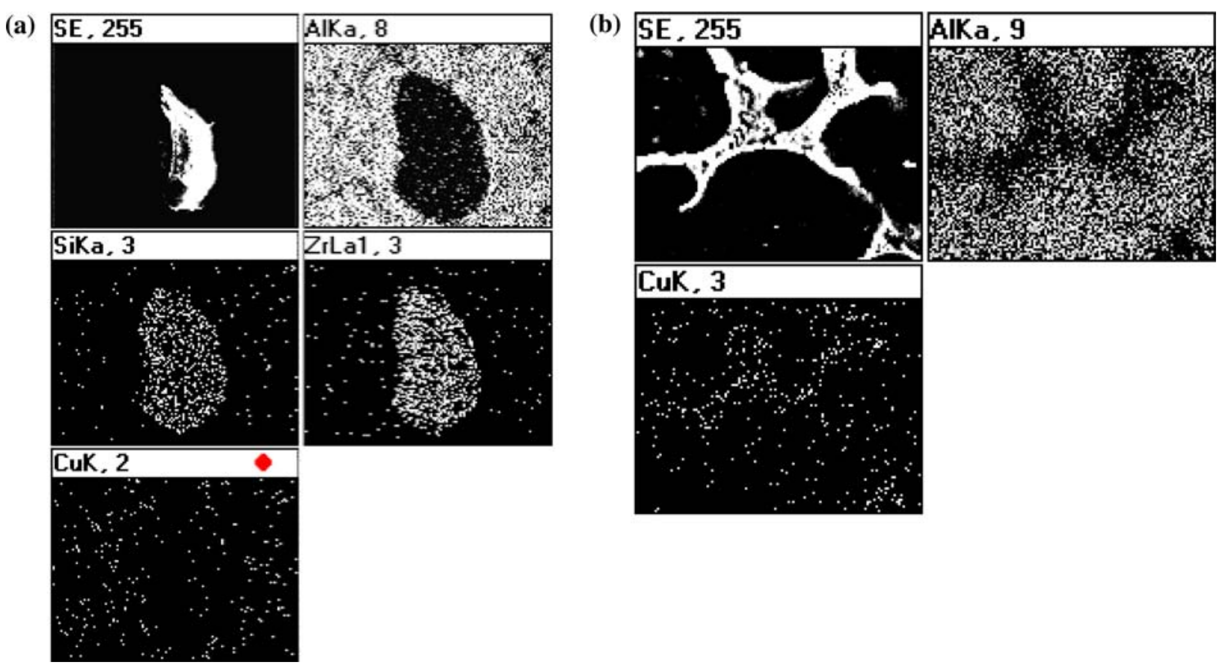


Fig. 5 X-ray dot maps of (**a**) reinforcement particle (**b**) secondary phase

also evident that the increase in particle amount decreases the wear volume of the composite for all particle size. On comparing the wear volume loss as a function of sliding distance, among the composites, it is observed that wear volume loss decreases marginally when the zircon particle amount is increased from 10 to 15 wt% for the composite reinforced with 65 or 90 µm size particle and 10–20 wt% for the composite reinforced with 135 µm size particle. However, the wear volume decreases significantly after further increase in the amount of zircon particle for all the composites. This might be due to the change in wear mechanism as the particle amount is increased.

Figure 12 shows the effect of zircon particle size and amount on the wear rate of composite after 10 min of abrasion. It is observed that wear rate decreases with the increase in particle amount and decrease in particle size. Material removal in a ductile material such as aluminum alloy matrix is due to the indentation and ploughing action of the sliding indenters (SiC abrasive particles) [21]. Incorporation of hard zircon particles in the Al-4.5 wt% Cu alloy

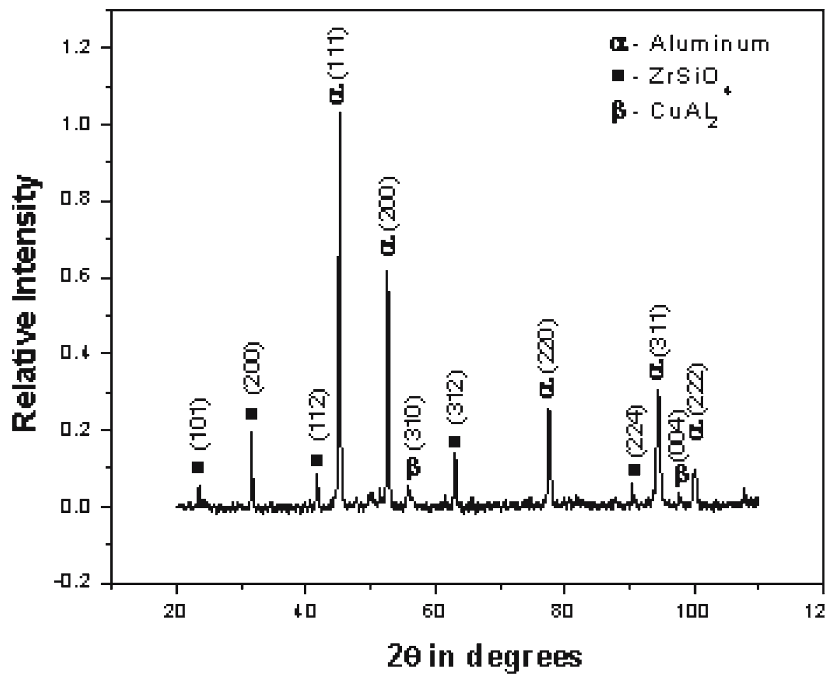


Fig. 6 Typical X-ray diffraction pattern of as-cast composite

restricts such ploughing action of sliding indenters and improves the wear resistance. An increase in zircon particle amount increases the hardness of the composite. The hardness of the material determines the depth of the indentation of the abrasive particle, as previously discussed by Wang and Rack [22]. Hence, the increase in hardness due to increase in particle amount decreases the wear rate of the composite.

The increase in wear rate, as the particle size increases might be due to the shape of zircon particle in the composite. It is evident from Fig. 1 that the finer zircon particles are more angular in shape compared to the coarser one. The sharp edges of the angular particles assist to cut and blunt the abrading silicon carbide particles more effectively compared to coarser particles, which are nearly spherical in shape. Moreover, increase in hardness with decrease in zircon particle size for the same amount, decreases the wear rate.

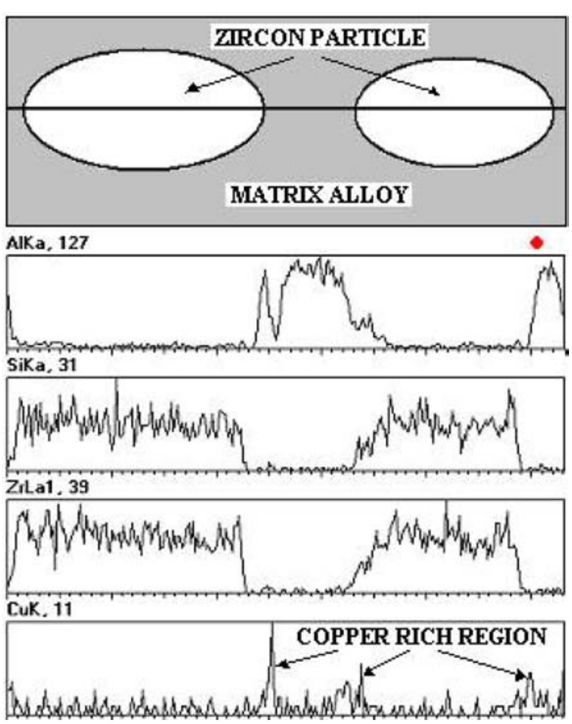


Fig. 7 Line profile analysis (LPA) across particle matrix interfacial region

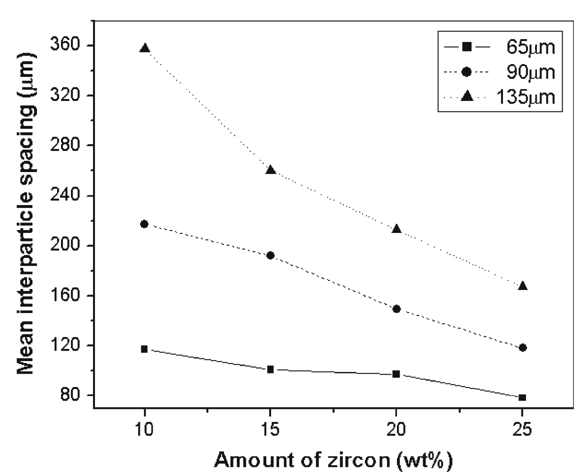


Fig. 8 Mean interparticle spacing of zircon particles in as-cast composite for various size and amount of zircon sand

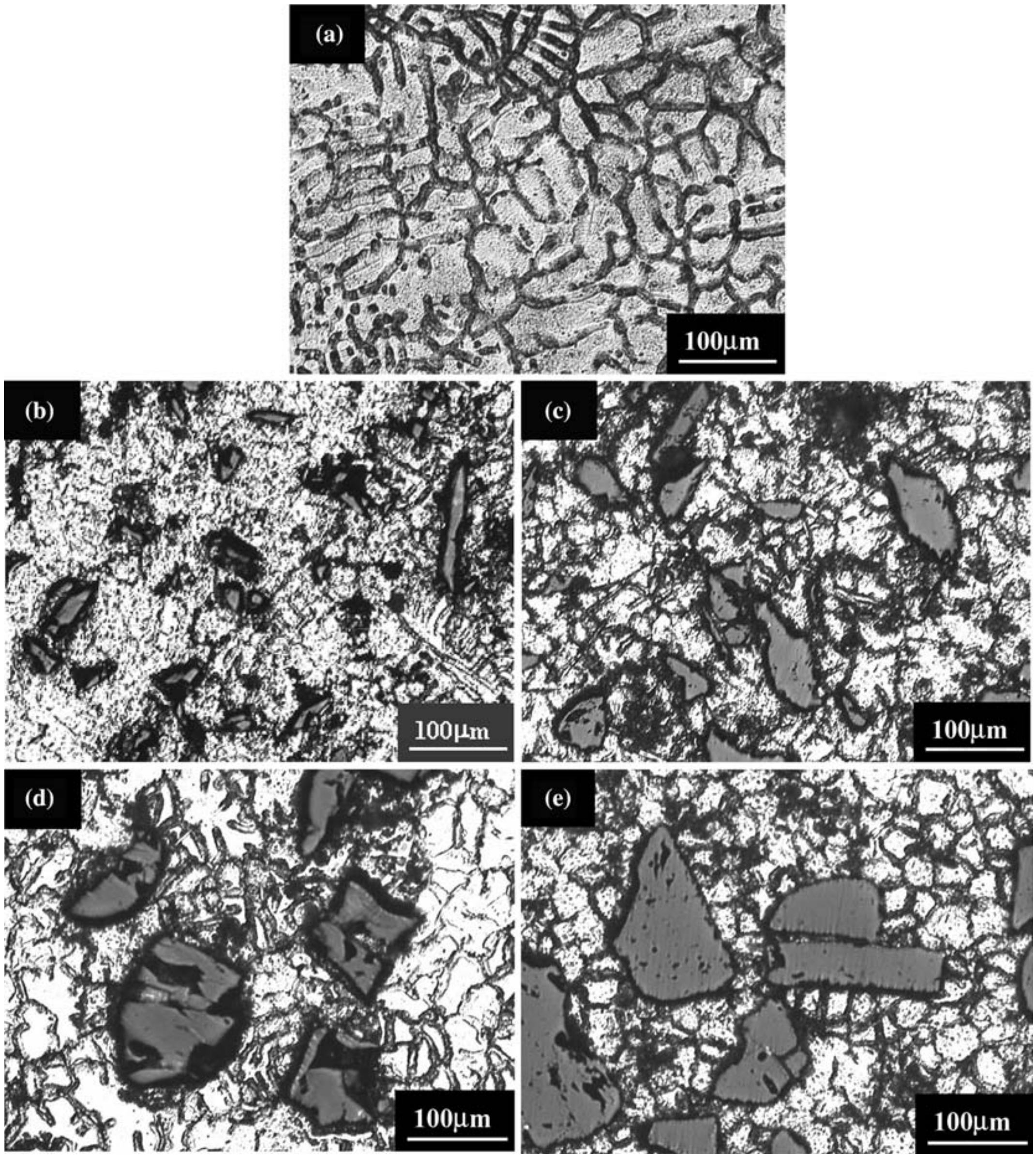


Fig. 9 Optical microstructures of (**a**) Al-4.5 wt% Cu alloy and composite with zircon particle size (**b**) 15 μm (10 wt% zircon), (**c**) 65 μm (20 wt% zircon), (**d**) 90 μm (25 wt% zircon), and (**e**) 135 μm (25 wt% zircon)

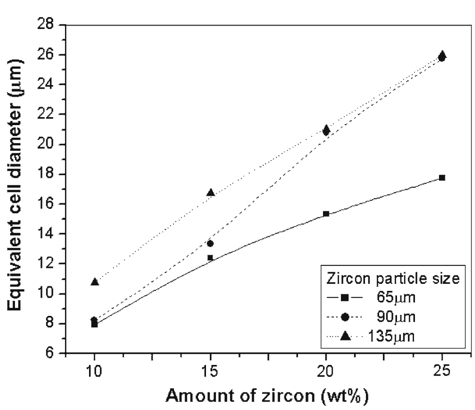


Fig. 10 Effect of zircon particle size and amount on cell diameter of the Al-4.5Cu matrix alloy

Conclusions

The following conclusions can be drawn from the present investigation:

1. Zircon particles can be uniformly dispersed in Al-4.5 wt% Cu alloy by the casting route. Recovery of zircon particles in composite depends on its size and amount. Coarse particles tend to settle earlier compared to fine particles, as expected. However, fine particles form agglomerates and tend to float when added above a certain amount depending on their size.

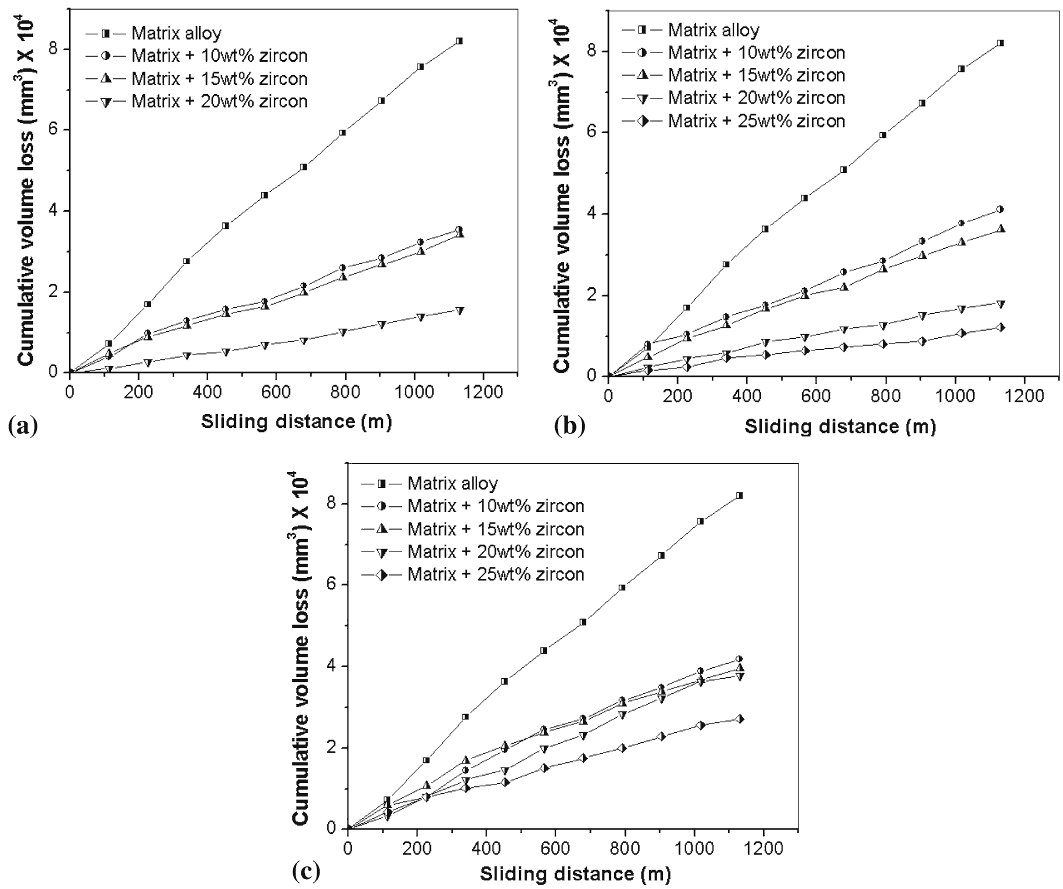
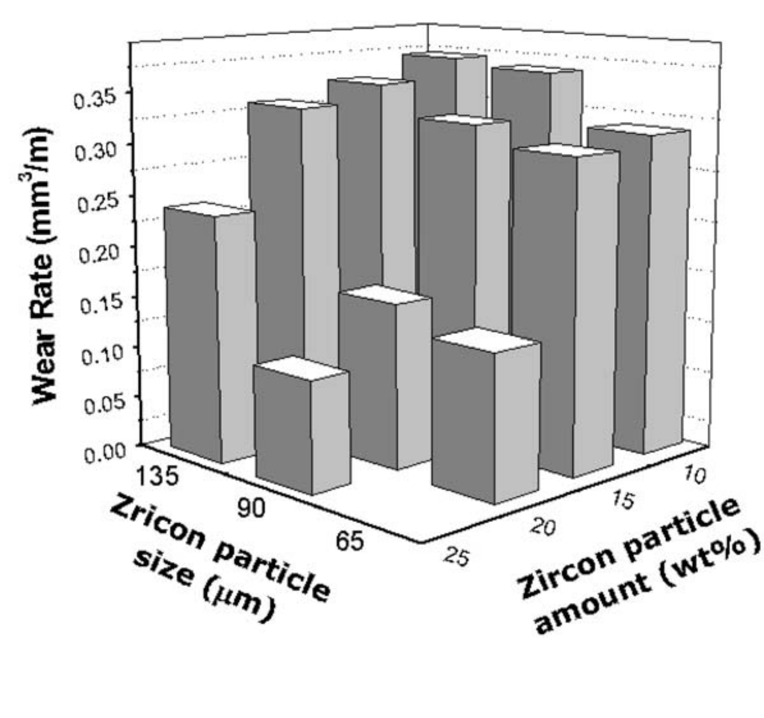


Fig. 11 Variation of cumulative volume loss with sliding distance for (**a**) 65, (**b**) 90, and (**c**) 135 μm size zircon particle reinforced composite with varying particle amount

Fig. 12 Variation in wear rate of the composites as a function of zircon particle size and amount



2. Line profile analysis (LPA) on particle matrix interface shows a high concentration of copper near the periphery of zircon particles due to dislocation-assisted diffusion.
3. The matrix of the composites has cellular structure, where the size of the cell depends on zircon particle size and its amount in the composite.
4. Abrasive wear resistance gets improved with zircon particle reinforcement in Al-4.5 wt% Cu alloy. The abrasion resistance of the composites increases with increasing amount of particle and decreasing particle size.

References

1. McDanels DL (1985) Metall Trans A 16:1105
2. Ralph B, Yuen HC, Lee WB (1997) J Mater Proc Technol 63:339
3. Surappa MK, Rohatgi RK (1981) J Mater Sci 16:983
4. Seo YH, Kang CG (1999) Compos Sci Technol 59:643
5. Skolianos S (1996) Mater Sci Eng A 210:76
6. Kang CG, Yoon JH, Seo YH (1997) J Mater Proc Technol 66:30
7. Yilmas M, Altintas S, Proceedings of the Second International Biennial European Joint Conference on Engineering System, UK, p 119
8. Hanumanth GS, Irons GA (1993) J Mater Sci 28:2459
9. Lee JC, Byun JY, Oh CS, Seok HK, Lee HI (1997) Acta Mater 45:5303
10. Yunsheng X, Chung DDL (1998) J Mater Sci 33:4707
11. Seo YH, Kang CG (1995) J Mater Proc Technol 55:370
12. Zhang S, Cao F, Chen Y, Li Q, Jiang Z (1998) Acta Mater Compos Sin 15:88
13. Bar J, Klubmann HG, Gudlat HJ (1993) Scripta Metall Mater 29:787
14. Sonsino CM, Backer E (1991) Materialistische Wissenschaft und Werkstofftechnik 22:48
15. Gui MC, Wang DB, Wu JJ, Yuan GJ, Li CG (2000) Mater Sci Tech 16:556
16. Banerji A, Surappa MK, Rohatgi PK (1993) Metall Trans B 14B:273
17. Hashim J, Looney L, Hashmi MSJ (1999) J Mater Proc Technol 92–93:1
18. Gupta M, Qin S, Chin LW (1997) J Mater Proc Technol 65:245
19. Asthana R (1998) J Mater Sci 33:1679
20. Dutta B, Surappa MK (1998) Composite Part A 29A:567
21. Robinowicz E (1965) Friction and wear of materials. Wiley, New York
22. Wang A, Rack HJ (1991) Wear 146:337