Cast aluminium alloy containing dispersions of TiO₂ and ZrO₂ particles

A. BANERJI, P. K. ROHATGI
Regional Research Laboratory, Council of Scientific and Industrial Research, Trivandrum-695 019, India

Up to 4 wt% of ultrasonically-pretreated titania and zirconia particles (5 μm average size) were dispersed in Al–11.8 wt% Si–1 wt% Mg alloy castings. The technique employed to prepare the cast composites involved mechanically mixing pretreated oxide particles in aluminium alloy melts in the presence of magnesium, followed by casting the resulting mix in permanent moulds. Pretreatment of the oxide particles consisted of agitating the particles in acetone by ultrasonic vibrations to cause the disintegration of agglomerates and the removal of adsorbed water molecules from the particle surfaces. Infra-red (i.r.) spectroscopy of powders showed desorption of water molecules from oxide surfaces by ultrasonic pretreatment in acetone. Ultrasonic pretreatment of oxide particles before their incorporation into the melt and presence of magnesium in the melt were found to be necessary to disperse TiO₂ and ZrO₂ particles in molten Al. Microscopic studies of the composites indicated dispersed TiO₂ and ZrO₂ particles which exhibited a reaction zone at the periphery of the particles, and microprobe X-ray elemental analysis confirmed preferential segregation of magnesium at the particle–matrix interface. The composites exhibited an increase in hardness as a result of dispersions of titania and zirconia particles, while the tensile-strength values of composites were comparable with that of the base alloy.

1. Introduction

In recent years a number of oxide and other particles including graphite have been dispersed in cast metal matrices by liquid metallurgy techniques [1–6]. Incorporation of ceramic particles in metal matrices has been shown to improve hardness, tensile strength, compressive strength, wear and abrasion resistance [2, 3, 7–9]. However, these dispersoids were generally coarse and ranged in size from 40 to 200 μm. It was found to be difficult to disperse particles less than 40 μm size in liquid metals due to the formation of agglomerates. However, there have been some attempts to disperse sub-micrometre-sized ceramic particles in molten metals by ultrasonic stirring [10, 11]. Hasegawa and Takeshia [12] have reported the dispersion of sub-micrometre-sized zirconia particles in steel by plasma-arc spraying of particles in a stream of molten steel. The present paper describes a new and relatively simpler technique to disperse pretreated titania and zirconia particles of 5 μm average size in aluminium alloy castings. These hard dispersoids are expected to increase the hardness and wear resistance of the composities.

2. Experimental procedure
2.1. Materials

Zirconium dioxide (monoclinic) and titanium dioxide (anatase) particles were obtained from M/s Indian Rare-Earths Ltd, and M/s Travancore Titanium Products, India, respectively. The average size of the particles was 5 μm but a few coarse particles of up to 80 μm size were also present in the powders. Al–11.8 wt% Si alloy was obtained from M/s Bharat Aluminium Co., India. The compositions of the materials are given in Table IA to C.

TABLE IA Composition of titania (wt%)

SiO₂	ZrO₂	Fe₂O₃	Volatiles	TiO₂
0.10	0.05	0.12	0.15	99.58

TABLE IB Composition of zirconia (wt%)

SiO₂	TiO₂	Fe₂O₃	Volatiles	ZrO₂
0.20	0.16	0.14	0.10	99.40

TABLE IC Composition of Al-alloy (wt%)

Cu	Mg	Si	Fe	Mn	Al
0.30	0.05	11.80	0.50	0.05	87.30

2.2. Pretreatment

Batches of as-received titania and zirconia powders of weight 25 g were mixed with 500 cm^3 of acetone in a stainless-steel beaker and ultrasonically agitated (at 25 kHz) for 15 min. The particles were allowed to settle. The excess acetone was decanted. Infra-red (i.r.) spectra of the powders before and after the ultrasonic treatment in acetone were recorded using a Perkin–Elmer 299B infra-red spectrophotometer.

2.3. Process

Batches of aluminium alloy, of weight 3 kg, were melted in a composite caster consisting of a crucible-type electrical resistance furnace provided with a bottom-pouring arrangement, which has been described elsewhere [13]. The melt was de-gassed either with chlorine-containing tablets or with purified nitrogen gas; the slag was then skimmed. The melt was stirred at 300 to 400 r.p.m. by a ceramic-coated steel impeller connected to a variable speed direct current (d.c.) drive, whilst the melt temperature was maintained between 1013 and 1033 K. Freshly pretreated titania or zirconia powder was added at a rate of 50 g min^{-1} using a spatula. 1 wt% magnesium was added (in pieces of 10 cm^3) to the surface of the melt at the same time as the powder was added. When all the powder had been added, stirring was continued for 1 min and the melt was teemed, through the nozzle provided at the bottom of the crucible, into permanent moulds. A few experiments were also performed with as-received titania and zirconia powders without any pretreatment. Composites were also prepared with heat-treated particles. Heat-treatment consisted of heating 100 g batches of powder to 773 K in air and soaking them at

this temperature for 1 h keeping a maximum bed-height of 5 mm. The heat-treated powders were added into the melt in the hot condition.

The castings were machined and visually examined. Polished specimens were studied under optical and scanning electron microscopes. Electron probe microanalysis (EPMA) was carried out on polished specimens across the oxide particles and its surroundings in the composites.

Measurements of hardness, ultimate tensile strength (UTS) and percentage elongation were made on the cast composite specimens.

3. Results

As-received (cold-untreated) TiO_2 and ZrO_2 particles were found to be rejected by Al–Si melts. When 5 wt% as-received TiO_2 or ZrO_2 particles were added into the melt and cast, the castings contained only 0.5 wt% TiO_2 or ZrO_2, which corresponds to only 10% recovery. These castings also exhibited excessive blow holes. When preheated powders were added onto the melt, slightly better recoveries (about 20%) were obtained, but the particles were found to be present as agglomerates in the castings. Fig. 1 shows a scanning electron micrograph (SEM) of a region of such a casting showing agglomerated TiO_2 particles. Since as-received powders were found to contain many agglomerates of particles (see Fig. 2) they were subjected to ultrasonic vibrations in an acetone
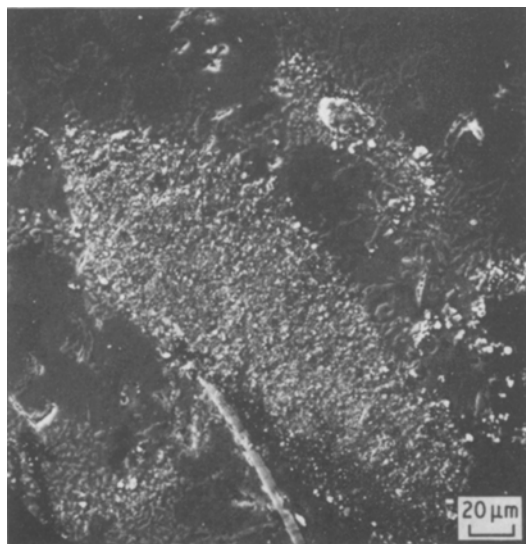

Figure 1 Scanning electron micrograph of cast Al–11.8 wt% Si–1 wt% TiO_2 composite showing agglomerated TiO_2 particles.
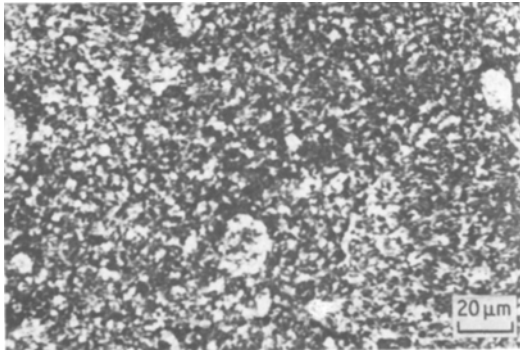
Figure 2 Scanning electron micrograph of untreated TiO_2 powder.

medium to defloculate and disperse the agglomerates into fine oxide particles. Recoveries of the order of 40% were obtained with the additions of ultrasonically-pretreated powders in Al—Si melts. Castings prepared with ultrasonically-pretreated powders in acetone were found to be generally free from agglomerates of particles and blow holes.

Further improvement in recoveries (up to 80%) were obtained by adding 1 wt% Mg to the surface of the melts at the same time as the ultrasonically-pretreated powders were added. It was found that the recoveries of the TiO_2 particles were greater (80%) than the recoveries of the ZrO_2 particles (60%), both with 1 wt% Mg additions, under similar conditions. Fig. 3a and b show the photomicrographs of composites prepared with ultrasonically-pretreated powders in the presence of magnesium in the melt. These micrographs were taken in selected regions where only coarse particles were present since fine particles would not be readily visible in the optical microscope. A possible reaction zone could be seen around the oxide particles.

The reaction zone around a TiO_2 particle (Fig. 3a) is more prominent and consistent than that around a ZrO_2 particle (Fig. 3b). Fig. 4a and b show the SEM pictures of composites prepared with ultrasonically-pretreated TiO_2 and ZrO_2 particles, respectively. It can be seen that the individual titania particles are well dispersed among the silicon particles in the last freezing eutectic region (see Fig. 4a).

EPMA and X-ray elemental line analysis of Al-alloy—TiO_2 (see Fig. 5) and Al-alloy—ZrO_2 (see Fig. 6) composites across the oxide particles (dispersed in cast Al-alloys) and their surroundings confirmed the presence of both the oxide particles themselves and the reaction-zone containing magnesium around the periphery of the oxide particles. The reaction-zone of Al-alloy—TiO_2 composite has a different appearance in the electron image from either TiO_2 particle or matrix and is found to be rich in magnesium (see Fig. 5a). The concentration of magnesium in the reaction-zone around a ZrO_2 particle (see Fig. 6a) is less than that around a TiO_2 particle. Relative peak intensity values of magnesium also varied along the periphery of the particles (see Figs 5b and 6b).

Table II shows the mechanical properties of cast Al—11.8 wt% Si—1 wt% Mg and its composites containing 1 to 4 wt% TiO_2 and 3 wt% ZrO_2 particles. The hardness of the composites was found to increase with increasing weight fractions of the dispersoids, whereas, UTS values were comparable with that of the base alloy. However, percentage elongations of the composites decreased due to the dispersions of TiO_2 and ZrO_2 particles.
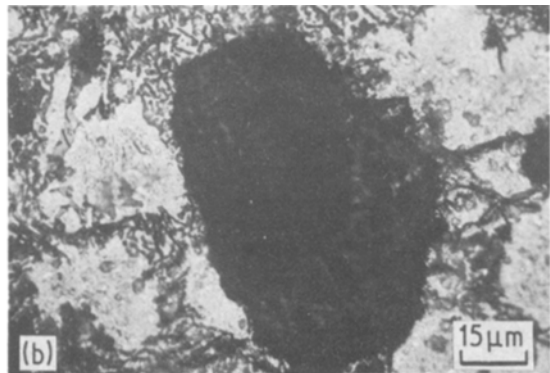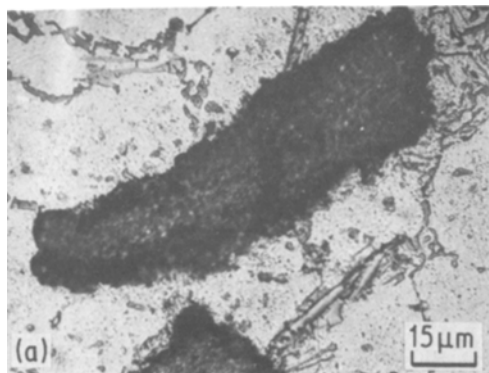

Figure 3 Photomicrographs showing (a) TiO_2 particles and (b) ZrO_2 particles, in cast Al—11.8 wt% Si—1 wt% Mg matrix.
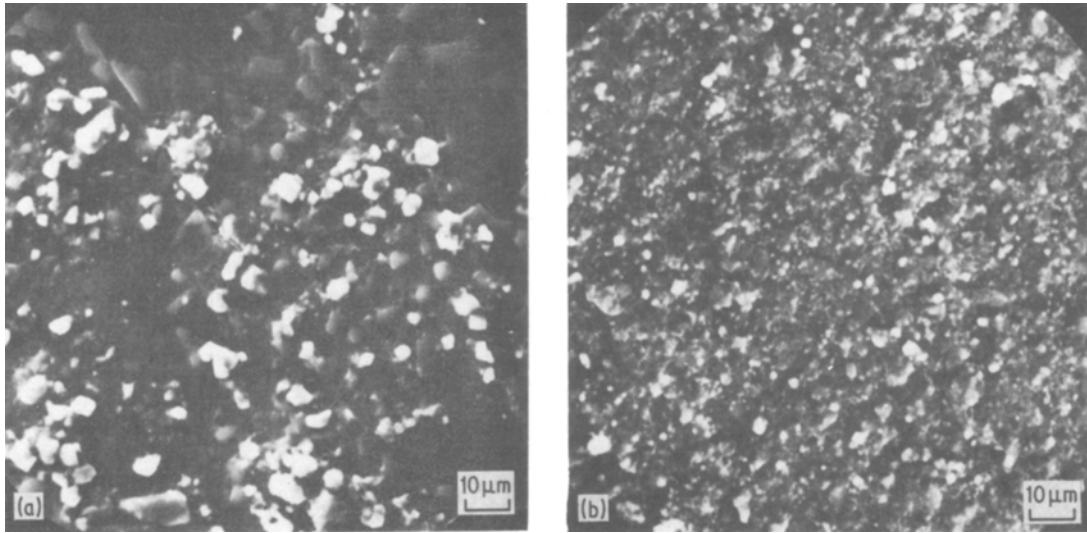
Figure 4 (a) Scanning electron micrograph of cast Al–11.8 wt% Si–1 wt% Mg–4 wt% TiO$_2$ composite showing dispersed TiO$_2$ particles, (b) Scanning electron micrograph of cast Al–11.8 wt% Si–1 wt% Mg–3 wt% ZrO$_2$ composite showing dispersed ZrO$_2$ particles.

4. Discussion
4.1. The role of pretreatment of TiO$_2$ and ZrO$_2$ particles

The rejection of untreated TiO$_2$ and ZrO$_2$ particles by the Al–Si melt could be due to:

(a) the adsorbed water molecules covering these particles; or

(b) non-wetting of these particles by molten aluminium. Similar observations have been made on the rejection of untreated silica particles by molten aluminium [9]. The surfaces of metal oxides are generally covered with chemisorbed water, in the form of surface hydroxyls. These surface hydroxyls further physisorb some additional water molecules through hydrogen bonding. The physisorbed water layer can be desorbed by evacuating samples at room temperature while surface hydroxyls start being removed at a temperature of about 373 K and remain attached to some extent to the surfaces of oxides even after treatments at 1273 K [14].

The volume of adsorbed water molecules increases with increasing surface area of the particles. The presence of adsorbed water on oxide surfaces could be detected from analysis of the infra-red (i.r.) spectra of the as-received titania and zirconia powders which show a broad OH-stretching peak at 3500 cm^{-1} and a weak peak at 1620 cm^{-1} due to molecular water. Presumably, these water molecules led to blow holes in the castings when untreated particles were added into

the melt. On the other hand, these bands were absent in the i.r. spectra of ultrasonically-treated powders in acetone showing that ultrasonic vibrations in acetone caused desorption of water from oxide surfaces. Interestingly, acetone was not, in turn, adsorbed on the oxide surfaces, as was evident by the absence of any band in the carbonyl-stretching region (1580 to 1900 cm^{-1}) of the i.r. spectra of treated powders.

It was observed that both untreated and heat-treated titania and zirconia particles had a tendency to float on the melt surface, although their densities are higher than that of liquid aluminium alloy. In contrast, when the acetone-pretreated particles were added to the surface of the melt, they settled to the bottom of the crucible soon after stirring was stopped.

The flotation of untreated and heat-treated particles is attributed either to the presence of adsorbed water molecules or clustering of particles or a combined effect of both. The water molecules present in the oxide surfaces react with molten aluminium and give rise to hydrogen gas-bubbles inside the melt: a particle might go inside the melt with the gas envelope when it is stirred in, and rise to the surface of the melt along with the gas bubble when stirring is stopped. The replacement of the gas–particle interface by a liquid–particle interface may not be energetically favourable enough to cause the particle to get transferred from the gas-bubble into the melt [6].
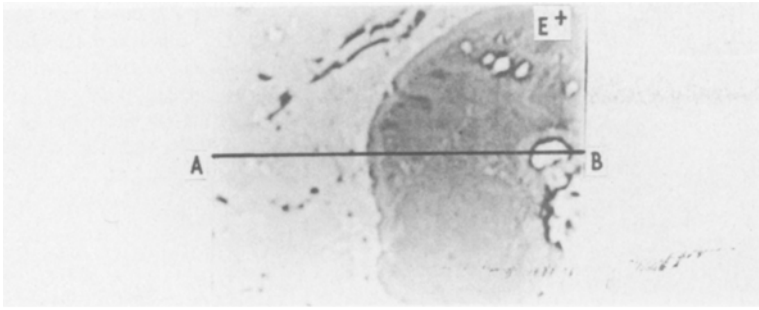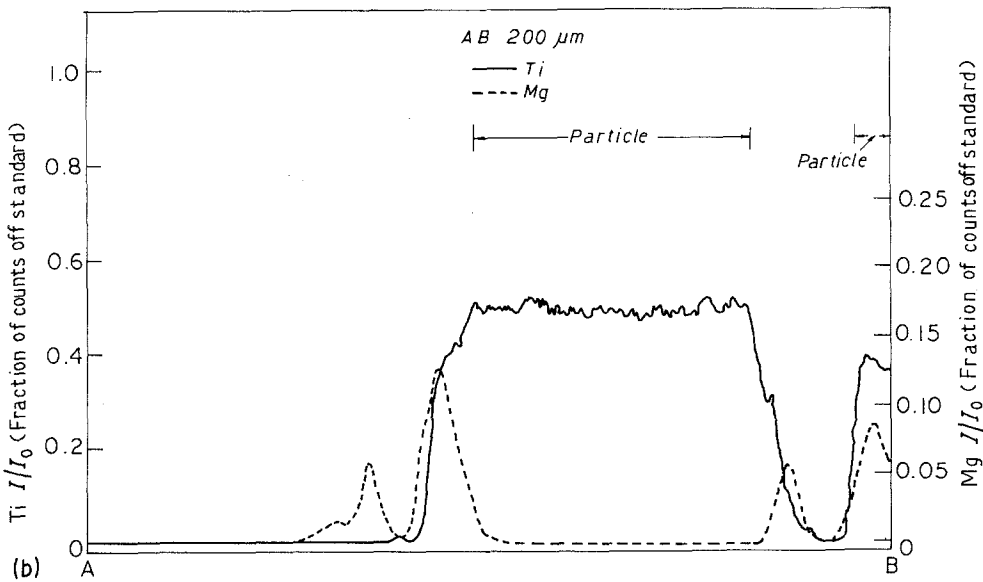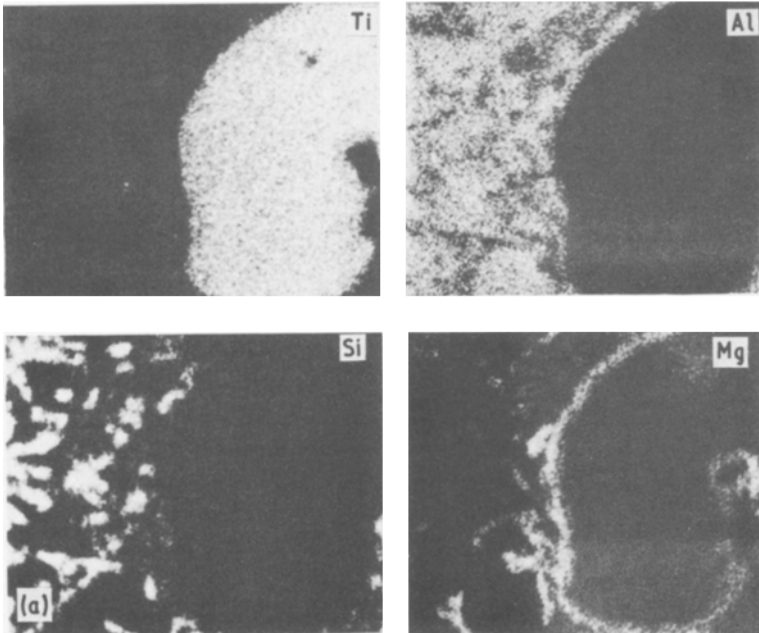
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Figure 5 (a) EPMA of cast Al-alloy–TiO$_2$ composite showing electron image of a region and corresponding X-ray images of Ti, Al, Si and Mg. (b) X-ray elemental line analysis of Ti and Mg across AB. AB = 200 µm.
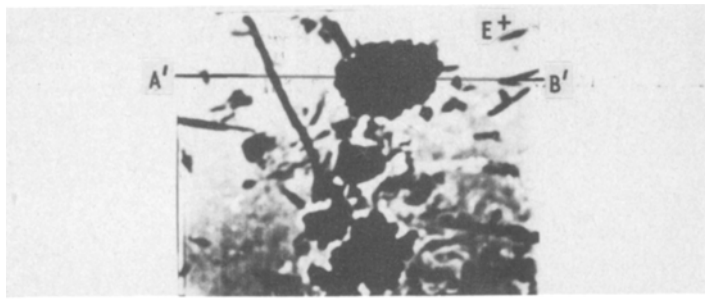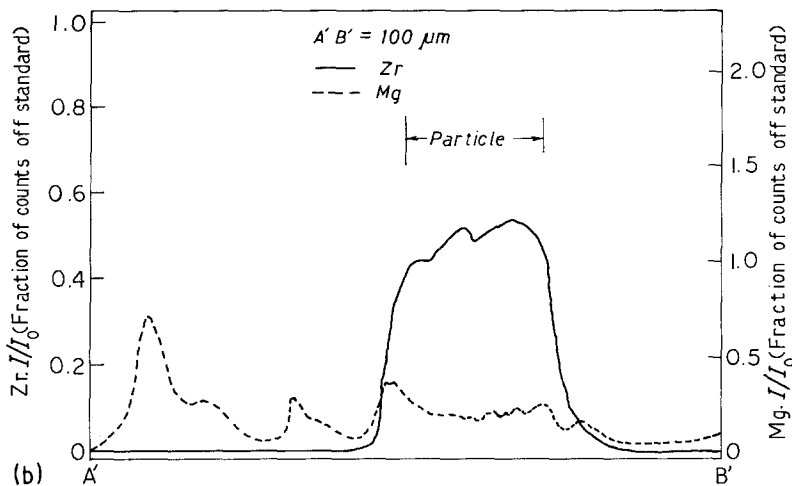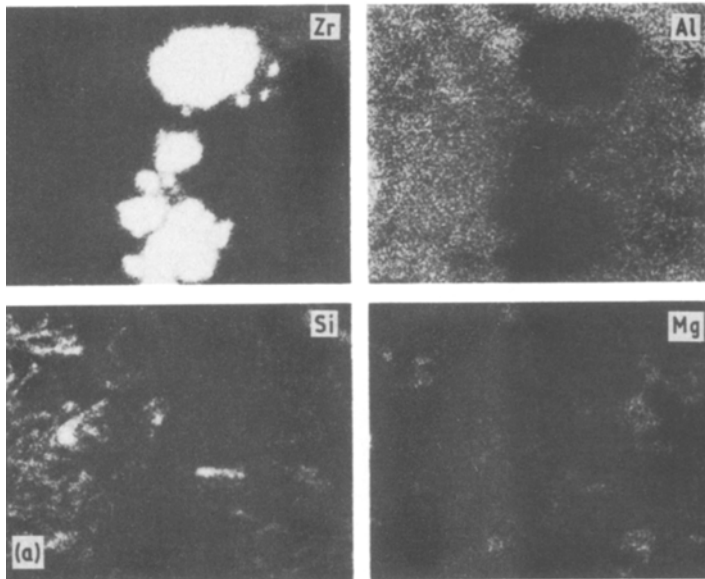
Figure 6 (a) EPMA of cast Al-alloy–ZrO_2 composite showing electron image and corresponding Z-ray images of Zr, Al, Si and Mg. (b) X-ray elemental line analysis of Zr and Mg across A'B'. A'B' = 100 μm.

In case of an agglomerate of particles, its apparent density may be less than that of aluminium melt and so the agglomerate is likely to float. However, particles ultrasonically-pretreated in acetone hardly contained any agglomerates. Since acetone is highly volatile and inflammable (flash point: 293 K), acetone-treated particles might loose ace-tone through vaporization before entering the melt. This would result in clean surfaces on the particles leading to their apparent densities being very close to the true densities.

Adsorbed gases on the surfaces of particles decrease their surface energy according to

$$\gamma_{SV} = \gamma_{SO} - p, \qquad (1)$$

TABLE II Mechanical properties of cast Al–11.8 wt% Si–1 wt% Mg alloy and its composites containing TiO_2 and ZrO_2 particles.

Material	Hardness (BHN)	UTS (kg mm^{-2})	Elongation (%)
Cast Al–11.8 wt% Si–1 wt% Mg	72	16.8	5
Cast Al–11.8 wt% Si–1 wt% Mg–2 wt% TiO_2	85	17.0	4
Cast Al–11.8 wt% Si–1 wt% Mg–3 wt% TiO_2	91	17.4	3
Cast Al–11.8 wt% Si–1 wt% Mg–4 wt% TiO_2	99	18.8	2
Cast Al–11.8 wt% Si–1 wt% Mg–3 wt% ZrO_2	90	18.0	3

where γ_{SV} and γ_{SO} are the surface energies of the solid particles in vapour phase and vacuum, respectively, and p is the surface pressure of adsorbed vapour. Murase et al. [15] found that adsorbed water on the surfaces of zirconia particles decrease their surface energy. Therefore, desorption of water from oxide surfaces by ultrasonic vibrations in acetone is expected to lead to an increase in surface free-energy. Ultrasonic vibrations have been reported to increase the surface energy of zirconia particles [16]. An increase in the surface free-energy of oxide particles will improve wetting by liquid-Al according the the equation of Young:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta, \qquad (2)$$

where γ_{SV}, γ_{SL} and γ_{LV} denote the interfacial tensions between the solid and vapour, the solid and liquid and the liquid and vapour, respectively, and θ is the contact angle.

4.2. The role of magnesium additions

Higher recoveries of TiO_2 and ZrO_2 particles in the castings in the presence of Mg in the melt may be due to the preferential concentration of magnesium at the periphery of the oxide particles, causing a decrease in the interfacial tension, γ_{SL}, in a manner similar to that reported in the Al–Al_2O_3 system [17]. Magnesium also substantially reduces the surface tension, γ_{LV}, of molten aluminium [18, 19]. Reductions in γ_{SL} and γ_{LV} would decrease the contact angle, θ, thereby improving wetting of the oxide particles by the molten aluminium and facilitating transfer of the particles in the melt. In addition, Mg might impart chemical-reaction-induced wettability.

Due to higher free-energies of formation of TiO_2 and ZrO_2 compared with that of MgO at the molten aluminium temperatures, magnesium is expected to reduce the surfaces of these oxide particles. Magnesium has been reported to reduce TiO_2 to Ti containing 2.5 wt% oxygen at 1273 K and at lower temperatures the reduction yielded Ti_3O_4 and TiO [20]. Mg was also found to reduce

ZrO_2 into Zr-metal containing some oxygen [21]. Preferential concentrations of magnesium around TiO_2 and ZrO_2 particles in the composites, as were found in the EPMA (Figs 5 and 6) results of the composites, indicate the possibility of such chemical reactions. The concentration of Mg found around TiO_2 particles was higher than that found around ZrO_2 particles. This may be due to the higher free-energy of formation and higher surface energy of TiO_2, indicating that the former is more likely to react with magnesium which might have resulted in the higher recoveries of TiO_2 particles as compared with ZrO_2 particles. The observations of this preliminary study and the analysis, as above, will facilitate the determination of suitable pretreatments for other oxides to be dispersed in metals.

5. Conclusions

(a) A liquid metallurgy technique has been developed to disperse up to 4 wt% of TiO_2 and 3 wt% of ZrO_2 particles, of average size 5 μm, in cast Al–11.8 wt% Si–1 wt% Mg alloy.

(b) Ultrasonic pretreatment of TiO_2 and ZrO_2 powders in acetone medium and the addition of 1 wt% Mg, in small pieces, to the surface of the melt were necessary for the dispersion of the oxide particles in aluminium alloy castings. This pretreatment also produced composite castings free from gas blow-holes, presumably due to desorption of water molecules from the oxide surfaces.

(c) Electron probe microanalysis studies showed that magnesium added to the melt surface segregated around the TiO_2 and ZrO_2 particles in the castings thereby increasing wettability between the oxide particles and molten-Al. The concentration of magnesium around the TiO_2 particles was greater than that around the ZrO_2 particles.

(d) Cast Al-alloy–TiO_2 and Al-alloy–ZrO_2 composites possessed higher hardness than the base alloy, whereas their UTS values were comparable to that of the base alloy.

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