Review Article

Synthesis, microstructural and mechanical properties of ex situ zircon particles (ZrSiO$_4$) reinforced Metal Matrix Composites (MMCs): a review

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Metal Matrix Composites (MMCs) are playing an increasingly important role in engineering applications and are in the forefront of significant research today because of their scientific and technological advantages. Particle or discontinuously reinforced MMCs are relatively inexpensive and are found to possess isotropic properties compared to fiber reinforced MMCs. Among the various types of particulate reinforcements such as boron, silicon nitride, boron nitride, silicon carbide, titanium carbide and alumina, extensive research has been directed toward the development of zircon particle reinforcement. Zircon reinforced composites are preferred as these composites exhibit relatively high refactoriness, excellent resistance to abrasion, thermal shock and chemical attack compared to composites reinforced with many other reinforcements.

This review article details the current development on the synthesis, microstructure and mechanical properties of zircon reinforced MMCs, with specific attention on the abrasive wear behavior of the composites. This review also summarizes the work done by various research groups on zircon reinforced MMCs in achieving higher hardness and wear resistance in these composites.

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1. Introduction

Conventional monolithic materials have limitations in achieving good combination of strength, stiffness, toughness and ductility. To overcome these shortcomings and to meet the ever increasing property demands, composites are being increasingly used as the most promising candidate materials [1].

Metal Matrix Composites (MMCs) have attractive combination of properties like high specific modulus and strength, enhanced elevated temperature properties, wear resistance, good abrasion resistance properties [1,2]. Due to these attractive properties, MMCs are being considered for a wide range of applications in space shuttles, commercial airliners, electronic substrates, bicycles, automobiles and golf clubs [3]. MMCs have been in existence for the past 30 years and a wide range of MMCs has been studied [4]. However, majority of MMCs are still in their development stage of production, and whose manufacturing processes are not well established. A major drawback of MMCs is their high cost of fabrication, which has placed limitations on their actual applications [5]. Generally, low density metals are advantageous for the fabrication of MMCs and metals like aluminum, magnesium and titanium are the popular matrix materials of current interest.

MMCs have been fabricated using a variety of methods such as stir casting [6–20], squeeze casting [21], compocasting [22], powder metallurgy [23,24], spray forming [25], liquid metal infiltration [26], mechanical alloying [27] and in situ methods [1,2]. Composites fabricated by ex situ method suffer from limitations such as poor wettability and subsequent interfacial reactions between matrix and reinforcement in comparison to in situ composites [1]. In spite of the above drawbacks, ex situ fabricated composites exhibit isotropic properties and hence are widely preferred over in situ fabricated one due to their low cost and ease of fabrication [8]. In ex situ processes, reinforcement size ranges from few microns to nano sizes and the resultant properties greatly depend on the volume fraction of the reinforcement [1]. To improve the mechanical properties of MMCs, many researchers have prepared composites by ex situ method with various particulate reinforcement such as boron, silicon nitride, silica sand, magnesium oxide, mica, glass beads, boron nitride [8], silicon carbide, titanium carbide, alumina, titanium boride and boron carbide [8,9].

Among these reinforcements, zircon has been found to be a very promising reinforcement owing to its high refractoriness and resistance to sudden volume changes at elevated temperatures. In addition to being a high melting point material, zircon also exhibits properties such as resistance to abrasion, impact and chemical attack [7,28,29].

Many researchers have fabricated zircon reinforced MMCs using different techniques and reported their microstructural and mechanical properties [6–25]. Though, a significant amount of work has been done on zircon composites, review articles are limited. Hence, a detailed review consolidating all the various aspects including possible fabrication methods for the production of zircon reinforced MMCs, their microstructure as well mechanical property characterization such as hardness and wear has been attempted.

2. Fabrication of zircon reinforced MMCs

Table 1 – Different alloys used in the fabrication of zircon reinforced MMCs.

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>Alloy designation</th>
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<tbody>
<tr>
<td>Al–11Si–1.5Ni–1Mg–1Cu</td>
<td>LM 13 alloy</td>
</tr>
<tr>
<td>Al–7Si–0.3Fe</td>
<td>Al 356.1 alloy</td>
</tr>
<tr>
<td>Al–0.45–0.9Mg, 0.2–0.6 Si</td>
<td>Al 6063 alloy</td>
</tr>
<tr>
<td>Al–0.8–1.2Mg, 0.4–0.8 Si, 0.15–0.40 Cu</td>
<td>Al 6061 alloy</td>
</tr>
<tr>
<td>Zn–4Al–3Cu</td>
<td>ZAS alloy</td>
</tr>
<tr>
<td>Al–4.5 wt. % Cu</td>
<td>Al 2024 alloy</td>
</tr>
</tbody>
</table>

Until date, various processing methods have been employed for the fabrication of zircon reinforced MMCs. Various fabrication techniques have been used for zircon reinforced MMCs (Fig. 1).

Table 1 summarizes the composition of all the matrix alloys that are reviewed in this article.

Both cast and wrought alloys have been used as matrix and from Table 1 it can be concluded that investigations have been carried out mainly on Al alloys because of their low density and zinc alloy have also been used for fabricating zircon reinforced MMCs.
2.1. Stir casting

Stir casting technique has been widely adopted for the fabrication of MMCs due to its simplicity, flexibility and applicability of the technique to large scale production of commercial components [30]. Composites fabricated by this technique involve melting of the matrix material followed by the addition of reinforcement to the melt with simultaneous stirring, followed by casting in a mold. The schematic diagram of stir casting process is shown in Fig. 2. This technique has been used by many research groups to fabricate and to study the different combinations of Al-based alloys with zircon reinforcement [6–18,20–25].

Banerji et al. [6] fabricated LM 13 alloy (refer Table 1), castings with zircon reinforcement by stir casting. Composites were prepared in an induction furnace by melting aluminum at ≈800 °C along with stirring and then adding zircon particles, which was preheated to 450 °C. It was suggested that, with the addition of 3 wt.% Mg, up to 25–30 wt.% of zircon could be dispersed, while with addition of 5% Mg, up to 60 wt.% zircon could be dispersed in the melt. These melts were cast using a horizontal die casting machine under an injection pressure of 100 MPa.

Table 2 shows the classification of the developed composites containing zircon particles of different sizes.

Table 3 shows the classification of the developed composites reinforced with coarse and fine size particles.

This alloy was also used by different authors [10,11,15,16,20] for reinforcing zircon along with silicon carbide [10,16], zircon particles [11], different sizes and proportion of zircon particles with, coarse particles (SSR-1), fine particles (SSR-2) and both coarse and fine particles (DSR) [15] (refer Table 2). Different combinations of zircon particles as single particle size (SPS) and dual particle size (DSP) (refer Table 3) have also been used to fabricate MMCs [20]. Similarly, Al 356.1 alloy (refer Table 1) was reinforced with zircon or titanium boride particles at three different temperatures namely 750 °C, 850 °C and 950 °C [17].

Das et al. [7] have reported the incorporation of zircon particles of different sizes and amount into Al-4.5 wt.% Cu alloy melt using stir casting process. It was observed that, up to 30 wt.% of coarser particles of sizes 90 and135 μm were dispersed, whereas finer particles of sizes 15 and 65 μm could be dispersed only up to 20 wt.%. Very little settling was observed when the composite was reinforced with 65 μm particles in comparison to coarser zircon particles. This was attributed to the ability of the finer particle to be in suspension for longer time compared to coarser particles. This approach was adopted by several other authors [8,9,12,13] to incorporate alumina and zircon particles [8], silicon carbide and zircon

![Fabrication Techniques](Image)

![Schematic diagram of Stir casting technique for the fabrication MMCs.](Image)
particles [9], graphite and zircon particles [12], and zircon particles [13] in Al-4.5 wt.% Cu alloy.

Similar to the fabrication process reported by Banerji and his co-workers [6], zircon reinforced composites were fabricated by employing Aluminum (6063) alloy (refer Table 1) [14] and ZAS alloy (refer Table 1) [19] as matrix materials. Pillai et al. [18] have investigated aluminum/zircon composites both in as cast and forged conditions. Cylindrical castings were cast and then soaked at 475 °C for 2 h followed by forging in a hydraulic press. The strength and fracture toughness of these composites were compared with cast and forged Al/graphite composites and regions of optimum performance were identified.

2.2. Squeeze casting/compocasting

Squeeze casting is a process which involves combination of both casting and forging to produce a near net shape component. A schematic diagram of the process illustrating the sequence of steps involved is shown in Fig. 3. It consists of two dies, in which the upper die is movable and the lower die is fixed. The melt containing the reinforcement is poured in to the lower die, which is preheated and as the metal starts solidifying, the upper die and the lower die are closed and pressure is applied until the melt gets completely solidified. In the case of compocasting process, the liquid metal along with reinforcement will be forced in to the die [31]. The advantages of squeeze casting/compocasting are low shrinkage, gas porosity, and enhanced mechanical properties due to fine grain structure caused by rapid solidification as well as good surface quality. This process is most commonly used for processing aluminum and magnesium alloy based MMCs.

Okafor et al. [21] have used squeeze casting route to prepare Al-4.5 Cu/ZrSiO₄ composites by varying the percentage of the reinforcement in the range of 5–25 wt.%. The composites were prepared using a graphite crucible using an electrical resistance furnace. 0.01 wt.% of NaNO₃ powder was used as a cover for melting the alloy and for creating a protective atmosphere inside the furnace. The furnace temperature was raised to 800 °C and ZrSiO₄ particulates (2–15 μm) preheated to 1200 °C, were added to the molten aluminum alloy, stirred thoroughly and poured in to a die. A squeeze casting machine with a press capacity 10 MPa, approach speed of 50 m/s, return force of 5 MPa, pressing speed of between 1 and 10 mm/s, die length of 0.18 m and die diameter of 0.02 m was used to prepare the samples. A similar procedure was adopted by Sharma et al. [22] to prepare zinc-aluminum alloy composites reinforced with zircon particles of size 30-50 mm.

2.3. Powder metallurgy

Powder metallurgy is a conventional route used commonly for the synthesis of ceramic reinforced MMCs. MMCs fabricated by this method involves elemental blending and mixing of matrix powders and reinforcements, pressing it into green compacts of desired shape and size, followed by sintering under a controlled atmosphere at suitable temperatures [23,24].

Ejiofo et al. [23] have developed a conventional low-cost, double-compaction powder metallurgy route for the synthesis of Al–13.5Si–2.5Mg alloy reinforced with zircon particles. In this case, the tensile bar specimens were produced at pressure levels 200–450 MPa in steps of 50 MPa with stearic acid as the lubricant. A double-action hardened steel mold and punch was used to prepare the green compacts followed by liquid phase sintering at 615 °C in vacuum for 20 min. A similar procedure was accepted for the fabrication of aluminum matrix reinforced with different volume percentages (2.5, 3.5, 5, 10, 15, and 20) of zircon particles by Abdizadeh et al. [24]. Here, the green compacts were obtained by pressing at 400 MPa and were sintered at two different temperatures, 600 °C and 650 °C for 65 min with a heating rate of 20 °C/min.

2.4. Spray forming

Spray forming technique is a near net shape casting process, which involves melting of an alloy in a furnace, forcing...
the melt through a small orifice, passing a stream of compressed inert gas, forcing reinforcement or powder through the jet and breaking the liquid metal into fine semi solid droplets. These semi solid droplets are deposited over a stationary substrate to form solid perform. Fabrication of composite by spray forming process is shown schematically in Fig. 4.

Kaur et al. [25] fabricated zircon reinforced LM13 alloy (refer Table 1), by spray forming technique. The alloy was melted at 800 °C in a resistance furnace with nitrogen atmosphere. High pressure nitrogen gas was passed and the alloy was poured into a pre-heated crucible. Two external powder injectors were used to feed the preheated zircon particles (106–125 μm). The atomized droplets were collected on the stationary copper substrate to obtain a solid preform.

3. Microstructural characteristics of zircon particle reinforced MMCs produced by various techniques

A detailed review of microstructural characterization of zircon particle reinforced MMCs is represented in the following sections.

3.1. Stir casting

Investigation on microstructures of Al–11.8% Si alloy composites fabricated by stir casting technique revealed a distinct zone at the periphery of zircon particles [6]. Segregation of Mg and Si was observed at the particle–matrix interface, and

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Fig. 4 – Schematic diagram of spray forming process.

Fig. 5 – SEM images of composite showing (a) uniform distribution of particles and (b) presence of intermetallic phase [13].
confirmed by EPMA analysis. Micrographs of cast Al–11.8\% Si alloy and composites containing 10 and 30 wt.\% zinc showed considerable refinement in the eutectic silicon structure due to the presence of dispersed zircon particles that acted as heterogeneous nucleation sites. As the percentage of zircon increased, the size of the proeutectic Al became finer and a frequent nucleation of eutectic silicon was observed near zircon particles. Pressure die cast composite containing 60 wt.\% zircon particles of size 40–100 \( \mu \)m also exhibited uniform dispersion of particles in the cast aluminum alloy matrix.

According to Panwar et al. [11], Al–12\% Si alloy composite reinforced with zircon particles showed a uniform distribution of particles exhibiting good bonding between the matrix and the reinforcement. Morphology of Al–4.5 wt.\% Cu alloy composites revealed a cellular structure with uniform distribution of ZrSiO\(_4\) particulate throughout the matrix (Fig. 5a) along with the presence of a copper rich secondary phase (CuAl\(_2\)) in the vicinity of the particle–matrix interface (Fig. 5b) [7,13]. Li et al. [19] reported on the microstructure of ZAS alloy (refer Table 1), that clearly revealed a hypoeutectic dendritic phase, consisting of zinc-rich primary \( \eta \) phase dendrites and a thin layer of eutectic phase at the interface of zircon and Zn–Al eutectic matrix (Fig. 6).

Aluminum alloy hybrid composites have also been produced by incorporating zircon with other reinforcements such as alumina, graphite, and silicon carbide into aluminum alloy to improve the hardness, wear and abrasion resistance of the composite. Microstructures of Al–4.5 wt.\% Cu alloy prepared by stir casting technique with zircon particles as reinforcement were found to reveal uniform distribution of particles with better bonding compared to alumina particles reinforced composite [8].

Graphite and zircon reinforced Al 6061 alloy (refer Table 1), hybrid composites revealed the presence of coarse acicular intermetallic particles along the primary aluminum dendrite boundaries of the as-cast specimen [12]. Gopi et al. [12] reported a refined grain structure with additions of different percentage of zircon and graphite into Al 6061 alloy along with the heat treatment. Similar to the results obtained by other researchers [7,13], formation of secondary phase (Al\(_2\)Cu) at the interdendritic regions in the microstructure was reported by Das et al. [9] during incorporation of zircon and silicon carbide particles in Al–4.5 wt.\% Cu alloy. Similarly, incorporation of the above mentioned reinforcements in LM13 alloy (refer Table 1) resulted in the presence of globular and finely distributed eutectic silicon in the vicinity of the reinforced particles [10,16].

Similarly, the effect of coarse and fine size particle reinforcement of zircon into LM13 alloy (refer Table 1) was investigated by Kumar et al. [20]. Though the uniform distribution of particles was observed, SPS1 composite (refer Table 3) revealed particle clustering along with porosity, which was confirmed from micrograph of this composite. In addition, coarse dendrites and presence of silicon in between dendrite arm were observed. Homogeneous distribution of coarse and fine particles with eutectic silicon morphology changing from acicular to dense globular structure in the vicinity of zircon was also observed from the optical micrograph of DPS1 (refer Table 3) composites (Fig. 7a).

Fig. 6 – Optical micrographs of ZAS alloy showing the distribution of hypoeutectic, zinc-rich primary \( \eta \) phase dendrites [19].

![Zircon particle](image)

![Globular phase dendrites](image)

![100 \( \mu \)m](image)

Fig. 7 – (a) Optical micrograph of DPS1 composites containing 12\% coarse and 3\% fine particles showing eutectic silicon morphology changes from acicular to globular in vicinity to particle and (b) optical micrograph of DPS2 composites containing 12\% fine and 3\% coarse particles shows clustering of fine particles [20].
DPS2 composites (refer Table 3) exhibited good bonding between zircon particle and alloy matrix with clustering of fine particles (Fig. 7b), similarly to those of SPS2 composites.

Abdizadeh et al. [17] tried a new approach for incorporating ZrSiO₄ and TiB₂ particles in A 356.1 alloy (refer Table 1) and the microstructure revealed homogeneous dispersion of ceramic particles with better wettability for Al–5% TiB₂ composite. However, agglomeration of ceramic particles was observed in the case of Al–5% ZrSiO₄ composite. According to Pillai et al. [18], the microstructure of cast Al/zircon particulate composites revealed a dendritic network structure whereas, the microstructure of forged Al/zircon particulate composites revealed a mixture of structure containing broken dendrites and fine grained structure.

3.2. Squeeze casting/compocasting

Microstructure of Al–4.5 Cu/ZrSiO₄ composite [21] prepared by squeeze casting revealed uniform distribution of ZrSiO₄ particles up to additions of 15% of ZrSiO₄. However, addition of ZrSiO₄ particles in excess of 15% led to segregation along the grain boundaries, resulting in a decrease in the degree of bonding.

3.3. Powder metallurgy

Microstructural analysis of zircon particle reinforced Al-Si alloy [23] revealed a good distribution of the dispersed zircon particulates in the matrix alloy. From the SEM images (Fig. 8a and b) of Al matrix composite reinforced with 5 vol.% and 15 vol.% of zircon particles [24], the zircon particles were found to be well dispersed in Al matrix with internal porosity (black spots). In addition, an increase in the amount of zircon particles led to agglomeration and clustering of zircon particles. This in turn was found to increase the porosity thereby, preventing the densification of the composite.

3.4. Spray forming process

From the optical micrograph studies [25], it was seen that as cast LM13 alloy showed the dendritic growth of α-Al grains of size 25–50 μm (Fig. 9a) and a eutectic phase in between the interdendritic arms (Fig. 9b). Presence of nearly 3–10 μm sized globular Si particles along the vicinity of the embedded zircon particle was observed while elongated Si needles were observed at region away from the interface. This was attributed to localized chilling effect produced by zircon particle around its environs. SEM micrographs revealed (Fig. 10a

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Fig. 8 – SEM micrographs of composites sintered at 600 °C containing: (a) 5 and (b) 15 vol.% zircon [24].

Fig. 9 – Optical micrographs of as cast LM13 alloy at (a) low and (b) high magnification showing dendritic morphology [25].
and b) a distribution of about 15 vol.% of reinforced particles in the middle of the preform and about 5% of reinforced particles at the periphery of the preform. It was concluded that the particles were well embedded in the matrix with good interfacial bonding, showing no porosity at the interface of zircon particle and the matrix.

### 4. Mechanical properties of zircon particle reinforced MMCs produced by various techniques

Any composite material should be homogeneous in order to be effectively used as a candidate in engineering applications such as automotive and aircraft [1]. Effective load-bearing capacity of the reinforcement can only be achieved if the composite possess uniform distribution of reinforcement, as non-uniform distribution of reinforcement leads to poor mechanical properties.

#### 4.1. Stir casting

Various mechanical properties of MMCs produced by stir casting technique is detailed below.

##### 4.1.1. Tensile properties

Strength of a composite depends on the reinforcement and a strong reinforcement–matrix interface. Strength of the composite generally increases on increasing the volume fraction of reinforcement. However, because of processing difficulties, strength of the composite sometimes found to decrease at higher levels of reinforcement [31]. Tensile properties of zircon particles reinforced composite are detailed in the following section.

Mechanical properties such as elastic modulus, 0.2% proof stress and ultimate tensile strength (UTS) of cast Al–11.8% Si–3% Mg alloy were found to improve with dispersions of zircon particles (Fig. 11) [6]. With additions of 25 wt.% of zircon particles, the elastic modulus, 0.2% proof stress and UTS were found to increase by 43%, 11% and 10% respectively. However, increase in additions of zircon was found to decrease the percentage elongation of composite. Composite containing 25 wt.% zircon exhibited only about 4% of elongation in the as-cast condition.

Variation in maximum tensile strength of Al 356.1 alloy reinforced with zircon and titanium boride particles is shown in Fig. 12 [17]. The highest tensile strength for Al–ZrSiO₄ and Al–5% TiB₂ was achieved at 750 °C and 950 °C respectively. In conclusion, the improvement of hardness and tensile strength of aluminum by incorporation of TiB₂ particles was attributed to the better wettability of TiB₂ by aluminum, as well as due to high work hardening at low strain in the composite system. It was observed that, the wettability of TiB₂ was better than that of ZrSiO₄ and a larger fraction of TiB₂ particulates will be incorporated in the matrix causing large value of hardness and tensile strength.

With reference to the particulate size highest values of mechanical properties such as yield strength, tensile strength, % reduction in area and % elongation were obtained for cast Al/zircon particulate composites with particle size in the range
of 180–250 μm with 6% addition of zircon particles. The values of yield strength, tensile strength, % reduction in area and % elongation were respectively 70 MPa, 87 MPa, 9.5% and 9.3%. Similarly in the case of these forged composites, the highest values reported for yield strength, tensile strength, % reduction in area and % elongation were 87 MPa, 112 MPa, 10% and 9.9% respectively [18]. The Young’s modulus, ultimate tensile stress (UTS), and 0.08% yield stress of the ZAS alloy (refer Table 1) reinforced with zircon particles showed a decrease with increase in particle volume fraction, as shown in Fig. 13 [19].

4.1.2. Fracture toughness
Fracture toughness is the ability of a material containing flaws to resist fracture and is one of the most important material properties that are used in many structural applications. Fracture toughness of particle reinforced composites can be improved by various mechanisms like crack bowing, crack deflection and debonding [31].

Fracture toughness evaluation was carried out for the aluminum/zircon composites by Pillai et al. [18] and the Crack Tip Opening Displacement (CTOD) and toughness values of cast zircon composites were reported to decrease continuously with increasing volume fraction of zircon. However, in the case of cast and forged composites, toughness was found to increase with increasing the zircon content from 6 to 12 vol.%. A decrease in toughness with increasing particle size was observed in both as cast and forged zircon composites. The fracture toughness was found to increase with increasing tensile strength in the case of as cast composites. Maximum toughness for a strength value of 80 MPa was observed for forged composites, beyond which the toughness started to decrease.

The highest fracture toughness value for as cast composites with 125–180 μm and 6 vol.% of zircon particle reinforcement was found to be as 15.2 kJ/m² while in the case of forged composites, the highest fracture toughness value was 15.6 kJ/m² for composites reinforced with 125–180 μm and 12 vol.% of zircon particle. It was also observed that forged graphite composites exhibited better toughness than forged zircon composites. Decohesion at the particle–matrix interface, as well as matrix cracking, was responsible for the cracking of the cast zircon composites. The particulate phase in forged composites tends to deflect the crack from its main path and was reported to be the main reason for the observed increase in toughness values.

4.1.3. Hardness, room temperature and high temperature wear behavior
Generally, metal matrix materials, such as aluminum alloy, exhibit poor seizure and wear resistance during sliding owing to its softness. This acts as a limitation restricting the use of these alloys in tribological environments. Hence, ceramic reinforcing phases in the form of fibers, whiskers and particles, can be employed as reinforcements into the matrix to

Fig. 12 – Maximum tensile strength variation of composite samples in different thermal conditions (a) zircon and (b) TiB₂ [17].

Fig. 13 – Tensile properties of the composite reinforced with different zircon volume fractions [19].
improve the wear resistance of aluminum alloys [1]. The wear behavior of zircon particle reinforced composites is discussed below.

Hardness and abrasive wear resistance of cast Al–11.8% Si–3% Mg alloy were found to increase with increase in weight percentages of zircon particles (Fig. 14). With dispersions of 25 wt.% of zircon, the respective increases were found to be 142% and 72%. Whereas with 5 wt.% addition, the wear resistance of composite and the alloy were found to be similar [6].

Mechanical properties of Al–4.5 wt.% Cu alloy with zircon as reinforcement was studied by Das et al. [7]. The abrasive wear resistance of the composite was reported to improve with an increase in the amount, as well as a decrease in size of zircon particles. Wear volume loss of composites reinforced with 65 or 90 μm size zircon particle was found to decrease as the amount of reinforcement increased from 10 to 15 wt.%. Similarly, the composite reinforced with 135 μm size zircon particle exhibited a decrease in wear volume loss on increasing the amount of reinforcement from 10 to 20 wt.%. This decrease in wear volume loss was attributed to the increase in the amount of reinforcement of zircon particles.

Das et al. [8] has carried out a comparative study on abrasive wear behavior of Al–4.5 wt.% Cu alloy reinforced with alumina and zircon sand particles. The hardness of alumina reinforced composites was reported to be higher than that of composites reinforced with zircon, which resulted from the higher hardness of alumina particles. Size of the particle was found to have a significant impact on the hardness and wear resistance of the composite since both hardness and wear resistance increased with decrease in particle size of both alumina and zircon particles. Further, the wear resistance of alumina particle reinforced composite was observed to be poor compared to zircon reinforced composite, which was attributed to the excellent bonding between the zircon particle and the matrix.

In addition, some researchers reported the mechanical properties of hybrid Al–Cu alloy composite with silicon carbide [9] and graphite [12] particles along with zircon particles as reinforcement. Similarly, for composites with silicon carbide and zircon as reinforcement, the abrasive wear resistance of silicon carbide reinforced composites was reported to be dependent on the size and morphology of the reinforcement particles [9]. According to Das et al. [9], maximum bulk hardness and minimum wear rate was observed for composite containing both zircon and silicon carbide with average particle size of 65 μm and 7.5 vol.% of zircon. In case of graphite reinforced composites, the maximum hardness value reported was 73.5 BHN with addition of 2 wt.% graphite to 4 and 6 wt.% of zircon particles [12]. A 13% increase in the hardness value was reported for composites in heat treated condition compared to that of as-cast condition. However, in the case of wear resistance, an average increase of 35% was observed at a test speed of 400 rpm and 28–30% of increase in wear resistance at 800 rpm.

Incorporation of zircon into Zn–4Al–3Cu (ZAS) alloy was first attempted by Li et al. [19], who reported an increase in sliding wear resistance of the composites with an increase in the amount of reinforcement. Similar result was obtained by Suchitharan et al. [14] for zircon particle reinforced Al 6063 alloy (refer Table 1). LM 13 alloy reinforced with zircon [11,15,20] along with silicon carbide and zircon [10,16] was investigated for its mechanical properties. Hardness and wear resistance of LM 13 alloy reinforced with zircon was found to increase with an increase in the amount of reinforcement [11,15] and a dispersion of fine size particles was also reported [15].

According to Kumar et al. [20], composite incorporated with 3 wt.% of fine zircon particles (20–32 μm) and 12 wt.% of coarser zircon particles (106–125 μm) in LM 13 alloy exhibited higher wear rate at different loads. Fig. 14 shows the wear rate of composites SPS1, SPS2, DPS1, and DPS2 (refer Table 3) at different loads. From Fig. 15, wear rate was found to follow a near linear relationship with increasing load that portrays Archard’s law of adhesive wear. It was reported that the SPS1 exhibited better wear resistance compared to all other composites.
Silicon carbide and zircon particles have also been incorporated into LM 13 alloy to study the mechanical properties of such hybrid composites [16]. Composites with 3.75% zircon particles and 11.25% silicon carbide particles were found to exhibit higher microhardness value, which was achieved by good interfacial bonding and microstructure refinement [16]. The hardness of the samples reinforced with ZrSiO₄ and TiB₂/A 356.1 alloy, investigated by Abdizadeh et al. [17] was found to increase with increase in temperature. Hardness value for Al–ZrSiO₄ composites synthesized at 850 °C was reported to be 75 BHN and the hardness value for Al–TiB₂ samples synthesized at 950 °C was reported to be 83 BHN.

The role of temperature is important in determining the wear behavior of a composite. Generally, increase in temperature can cause wear damage to all the metallic components and increases the severity of wear leading to the plastic deformation of matrix material [11]. The effect of temperature on the wear behavior of zircon reinforced composites is detailed here.

High temperature wear of LM 13 alloy reinforced with zircon was studied by Panwar et al. [15]. Finer particles and coarser particles in the ratio of 1:4 were found to enhance the hardness, wear resistance and provide better load transfer from the matrix to reinforcement materials [15]. Wear rate of both matrix and composite was found to increase with applied load, but the wear rate was found to remain constant in composites containing 15–20 wt.% of zircon particles. Fig. 16 shows a comparison of wear rate against temperature for base alloy and composites at 9.8 N and 49 N. It was observed that DSR-10D (refer Table 2) composites were found to exhibit better wear resistance under all conditions compared to other DSR composites.

The wear rate of the composite increased with increase in temperature from 50 to 150 °C, which was attributed to the wedging of particles in softened matrix providing better wear resistance at both loads. At 200 °C, formation of oxide layer decreased the wear rate of all the DSR composites, as the oxide layer prevent contact between the sliding surfaces of specimen and steel disk.

All the composites were tested at 200 °C as well as 250 °C at a load of 49 N, to study their wear behavior. From the topographical study of the worn surface, it was found that all the composites exhibited better wear resistance both at higher loads and at higher temperatures. The effect of temperature on wear was also studied by Panwar et al. [11,15] at different loads and with various concentrations of zircon particles. Increasing the concentration of the reinforcement led to an increase in wear resistance and thermal stability of the composites. Surface morphological studies revealed mild to severe wear transition at high temperatures and at high loads.

Table 4 tabulates the combination of zircon particles and silicon carbide reinforcement in LM13 alloy composites.

Kumar et al. [10] investigated the wear nature of the composites reinforced with different wt.% of zircon and silicon carbide particles (refer Table 4). Fig. 17a and b shows the variation of wear rate as a function of temperature for DRP and SRP composites. At low load of 1 kg, the wear rate of both DRP and SRP composites was found to decrease with increase in temperature from 50 °C to 200 °C (Fig. 17a). After 200 °C (critical temperature), the wear rate was found to increase with increase in temperature. This was attributed to the thermally activated deformation process that leads to softening of the

<table>
<thead>
<tr>
<th>Composite</th>
<th>Total 15 wt.% reinforcement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZrSiO₄</td>
</tr>
<tr>
<td>A</td>
<td>15</td>
</tr>
<tr>
<td>B</td>
<td>3.75</td>
</tr>
<tr>
<td>C</td>
<td>7.5</td>
</tr>
<tr>
<td>D</td>
<td>11.5</td>
</tr>
<tr>
<td>E</td>
<td>–</td>
</tr>
</tbody>
</table>
material adjacent to the contact surfaces. The wear rate of all composites at a load of 5 kg with variation in temperature from 50 °C to 300 °C is shown in Fig. 17b. The wear rate was found to increase slightly from 50 °C to 150 °C and thereafter decreased at 200 °C for both DRP and SRP composites due to strain hardening of the composite. The decrease in wear rate between 150 °C and 200 °C was due to the formation of oxide layer on the surface of pin. Above 200 °C, wear transition occurs from mild to severe causing breaking of the oxide layer because of delamination. The combination of zircon particles and silicon carbide particle in a ratio of 1:3 was reported to exhibit a better wear resistance at all temperatures, as well as for both loads.

The effect of temperature under oxidative environment on wear for LM13/Zr composite was studied at different temperatures from 50 °C to 300 °C and for varying loads between 9.8 N and 49 N. It was concluded better wear resistance and thermal stability was exhibited by composites with higher concentration of zircon particles. Addition of zircon sand was found to improve the critical transition temperature of alloy from 100 °C to 200 °C [11].

4.2. Squeeze casting/compocasting

From the result of the investigation on Al–4.5Cu alloy zircon reinforced MMC [21], it was reported that, addition of ZrSiO₄ particles increased the hardness value and apparent porosity by 107.65 and 34.23%, respectively. Likewise, addition of ZrSiO₄ particles decreased the impact energy by 43.16%. The yield strength and UTS was found to reach up to a maximum of 168.10 and 231.48 N/mm², respectively, at 15% of ZrSiO₄ addition and increased further with increase in the % of ZrSiO₄.

According to Sharma et al. [22], the wear rate of the composites was reported to be lower than that of matrix alloy and was found to decrease further with increase in zircon content. However, in the case of both the composites and alloy, the material loss in terms of wear rate and the wear volume increased with an increase in load and sliding distance. Fig. 18 clearly shows the presence of a transition load at which there is a sudden increase in the wear rate of both the reinforced and as cast materials. It was also further reported that, as the load increased and reached a transition value where the severity of the wear increases, a change in the wear mechanism from abrasion to particle cracking induced delamination wear was observed.

4.3. Powder Metallurgy

Mechanical properties of Al-Si alloy with 15 vol.% zircon were investigated by Ejobor et al. [23]. It was found that the UTS increased by 4%, 0.2% yield strength (YS) by 12.8% and hardness by 88%. In addition, consistent increase in these properties was observed with further addition of zircon into the alloy, which was attributed to the load – bearing ability and intrinsic hardness of zircon. An additional 1 wt.%
Mg was then added into the matrix alloy (Al–13.5Si–2.5Mg) resulting in a slightly reduced effect on the measured mechanical properties. The presence of magnesium was found to increase the reactions at the interfaces enhancing the dispersion of the zircon in the matrix. The mechanical properties of Al–13.5Si–2.5Mg and Al–13.5Si–3.5Mg are tabulated in Table 5.

<table>
<thead>
<tr>
<th>Property</th>
<th>Al–13.5Si–2.5Mg+</th>
<th>Al–13.5Si–3.5Mg+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 vol.% zircon</td>
<td>15 vol.% zircon</td>
</tr>
<tr>
<td>UTS, MPa</td>
<td>86</td>
<td>85.1</td>
</tr>
<tr>
<td>0.2% YS, MPa</td>
<td>50.5</td>
<td>46.7</td>
</tr>
<tr>
<td>Hardness, HVI</td>
<td>106.6</td>
<td>95.4</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Sintered density, %</td>
<td>88</td>
<td>90</td>
</tr>
<tr>
<td>theoretical</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.4. **Spray forming process**

Bulk hardness of the base LM13 alloy was found to increase from 76.3 BHN to 83.7 BHN with addition of zircon particles, which was attributed to the microstructural refinement of the composite by rapid solidification [25]. Kaur et al. [25] investigated the linear expansion coefficient (LEC), which for base alloy was found to be $8.67 \times 10^{-6} \, K^{-1}$ and for spray formed composite it was found as $8.38 \times 10^{-6} \, K^{-1}$ (5% $V_f$ of zircon) and $9.11 \times 10^{-6} \, K^{-1}$ (15% $V_f$ of zircon) in 25–465°C temperature limit, indicating good interfacial bonding.

5. **SEM analysis of the worn surfaces of zircon particle reinforced MMCs produced by various techniques**

Topographical analysis of the worn surface of the composites using SEM helps in understanding the wear mechanism as well as the mechanism involved during the wear test [15]. The wear mechanism of the fracture and abraded Al–3% Mg–25 wt.% zircon composite surfaces were studied by Banerji et al. [6]. It was reported that the SEM images (Fig. 19) of these surfaces revealed good bonding with no evidence of debonding at the particle–matrix interface.

Similarly, the wear surfaces of the Al–4.5 wt.% Cu alloy reinforced with alumina and zircon particles was studied by Das et al. [8]. From the worn out surface of the alloy and composites, it was concluded that the predominant wear mechanism was due to the plowing of the surface by the SiC abrading particles. The same conclusion was also drawn by Das et al. [9] on studying the abrasive wear behavior of Al–4.5 wt.% Cu/zircon sand and silicon carbide hybrid composite.

The room temperature wear behavior of LM 13 alloy reinforced with zircon and silicon carbide particles was investigated by Sharma et al. [16]. From the results, the delamination of matrix material by propagation of crack was found as the primary mechanism in determining the wear of these composites. Similar to room temperature wear behavior, at high temperature, these composites, exhibited the presence of large amount of flake type debris suggesting delamination as the predominating mechanism of wear due to high pressure at high temperature [10].

The effect of temperature under oxidative environment on wear for LM13/Zr composite was studied at different temperatures by Panwar et al. [11]. Both the adhesive and abrasive wear mechanisms were found to be responsible for the wear of the composites. Non-lubricated wear behavior of LM 13 alloy reinforced with different ratios of coarse and fine size zircon sand particles, at different ambient temperatures was studied by Panwar et al. [15]. From the analysis, the worn surface of the entire composite tested at 200°C showed formation of continuous abrasive grooves along with delamination (Fig. 20a), while composites tested at 250°C showed the formation of deeper and continuous abrasive grooves along with extensive delamination (Fig. 20b) exhibiting higher wear rate. Similar to the result obtained by Panwar et al. [11], in this case, both abrasive and adhesive wear mechanisms were found to contribute to the wear nature of the composites.

In order to study the wear behavior of dual particle size (DPS) zircon sand reinforced aluminum alloy, the composites were tested at 1–5 kg loads and at 1.6 m/s speed. The SEM images revealed the formation of grooves and ridges running parallel to the sliding direction. This was observed as one of the features at both lower and higher loads. In addition, finer wear grooves appeared on the worn pin surface of composite that were subjected to low load compared to higher load [20]. In the case of zinc–aluminum alloy reinforced with 5% of zircon particles, the wear surface revealed parallel and continuous grooves, resulting in abrasive wear at lower loads (Fig. 21a) and delamination wear at higher loads (Fig. 21b). This was also confirmed by the presence of worn surfaces and the subsurface cracks in the composites as well as the base alloy [22].
6. **Summary**

In this review article, current development on fabrication, microstructural characterization and mechanical property evaluation of MMCs with zircon reinforcement have been discussed. With regard to processing of zircon reinforced MMCs, a review of available literature shows that these processing techniques can be classified as casting (stir casting, squeeze casting, compocasting), solid state processing (powder metallurgy) and semi-solid processing (spray deposition). Among these processes, the stir casting process is extensively adopted because of its simplicity, flexibility and low cost for the fabrication of large size components. Though this method offers several advantages, it leads to porosity in the fabricated composites. However, composites produced by squeeze casting, compocasting and powder metallurgy exhibit lesser porosity compared to the composites produced by stir casting technique. Spray forming technique, though advantageous in producing a dense near net shape product, is limited to small sized components.

Microstructural evaluation showed the uniform distribution of zircon particles in the metal matrix, as well as strong bonding between the particle and matrix at the interface. Mechanical properties such as hardness, abrasive wear resistance, elastic modulus and tensile strength were reported to improve with the dispersions of zircon particles. In particular, the abrasive wear resistance of the composite was found to improve significantly with increase in amount of zircon as well as a decrease in the size of zircon particles. In conclusion, considering from technical and economic factors, zircon particles appear to be promising reinforcement especially for aluminum Metal Matrix Composite.

**Conflict of interests**

The authors declare that they have no direct financial, personal or other relation with the commercial identities mentioned in this paper that might lead to a conflict of interests for any of them.
REFERENCES


