

EFFECT OF DEFORMATION ON DENSIFICATION AND CORROSION BEHAVIOR OF Al-ZrB₂ COMPOSITE

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Abstract

In the present investigation, aluminium based metal matrix composites (MMCs) were produced through powder metallurgical route. Different composites were processed by adding different amount of ZrB₂ (0, 2, 4 and 6 wt. %) at three aspect ratios of 0.35, 0.5, and 0.65, respectively. The powder mixture was compacted and pressureless sintered at 550 °C for 1 h in controlled atmosphere (argon gas). The relative density of the sintered preforms was found to be 90%, approximately. Sintered preforms are used as workpiece materials for deformation study at different temperatures in order to find the effect of temperature on the densification behaviour. Potentio-dynamic polarization studies were performed on the deformed preforms to find the effect of mechanical working. The corrosion rate was found to decrease with increase in deformation.

Keywords: *Pure Al; Al-ZrB₂ composites; densification; deformation; hardness; potentio-dynamic polarization.*

Introduction

Aluminium being durable, lightweight, ductile, malleable metal and nonmagnetic gives a great opportunity over for a wide range of applications. Aluminium is known for its low density and its ability to resist corrosion. It has about one-third the density and stiffness of steel which made aluminium a replacement in various applications. Aluminium and its alloys can be machined, cast, drawn and extruded. Alloying and composite preparation with the combination of aluminium metal improved the material properties for wide range of applications [1].

Aluminium metal matrix composites are gaining great scope for applications within aerospace, defense, automotive industries and various other fields. The continuous increase in demand for lightweight, fuel efficiency and comfort in auto

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industries lead to the development of advanced materials such as metal matrix composites (MMCs). Aluminium MMCs have a great application potential in automotive engineering components, i.e. braking systems, piston rods, piston pins, pistons, structural frames, valve spring caps, brake discs, disc brake caliper, brake pads, cardan shaft, engine heads etc. Axle tubes, reinforcements, blade, gear box casing, turbine, fan and compressor blades are some other significant applications in military and civil aviation for aluminium MMCs. MMCs and alloys are extensively used over metals as they offer higher specific properties (properties/unit weight) of strength, stiffness, higher specific modulus, thermal stability, tribological properties and various other mechanical properties which enhances the product performance [1, 2].

Powder metallurgical (PM) components have better properties than components produced through conventional manufacturing processes. Production through powder metallurgy process is rapid, economical suitable for high volume production with less contamination of parts from powders. Products with high strength, wear resistance, homogenous composition with close dimensional tolerance are possible to process with this route [3].

PM comprises of powder mixing or blending for homogenous mixture, compaction followed by pressureless sintering. The density levels obtained after sintering are always lower than the theoretical densities. This is because of the difficulty in elimination of pores completely. Presence of such micropores is always deleterious for the performance of the material. This may be because the pores may act as the sites of origination of cracks during operating conditions. Elimination of these micropores in sintered components are necessary for subsequent deformation processing of performs, such as forging, extrusion etc. Among these processes forging is economic and effective method to improve density with enhanced mechanical properties with homogenous structure [4].

Some limitations during hot working are oxidation, surface decarburization of billets, excess die wear, poor surface finish and appearance of thermal stresses. Due to all these disadvantages cold working has been gaining great importance in recent times [5-7]. The deformation behaviour of MMCs has been widely studied during compression upsetting test. Narayanasamy et al. [8-11] have done significant amount of research work on Al-SiC composites during cold upsetting. They reported the effect of particle size and percentage addition of SiC on workability of Al-SiC composites.

Kumar et.al [12, 13] studied the effect of glass and SiC particles on the workability and strain hardening behaviour of composites. Density increased with the addition of glass particles decreasing the strain hardening behavior.

Desalegn et al. [3] reported the densification behavior of Al-Cu powder metallurgy preforms. Hassani et al. [14] investigated the influence of pores and the size of pores on the workability and densification behavior of the Al-SiC preforms. Appa Rao et al. [15] investigated the deformation and workability behavior of pure copper and reported the effect of aspect ratio on the workability. Composites with borides exhibit better performance than other ceramic reinforcements.

Borides have properties such as high chemical stability, high hardness and good thermo-electric properties. Titanium diboride (TiB₂) and zirconium diboride (ZrB₂) are significant boride ceramics which exhibit superior properties like high melting point, extremely high hardness and wear resistance, low specific gravity, magnetic, electrical properties, with high mechanical properties and chemical inertness at elevated

temperatures. The ZrB₂ based materials exhibit great dimensional stability which was of prominent importance in automobile functioning. The ZrB₂ powder can be used in order to manufacture ceramic reinforced composites such as Cu-ZrB₂, Al-ZrB₂ etc. The powder metallurgy appears to be an ideal way to disperse the reinforcement in the matrix in order to produce composites.

The objective of the present study is to develop more densified aluminium MMCs by hot and cold deformation and to study the effect of aspect ratio on the densification behavior during cold and hot deformation. In view of the importance of Al-MMCs and Al alloy-MMCs in automotive and marine industries, corrosion studies are necessary to evaluate the performance and life of material. Therefore, potentiodynamic polarizations studies are performed on deformed Al-ZrB₂ preforms.

Experimental procedures

Raw materials

Al and ZrB₂ were used as the precursors for the preparation of Al-ZrB₂ composites: Al (> 99% pure and the particle size < 44 µm, Sisco Research Laboratories, India). ZrB₂ (> 99 % pure and the particle size < 4 µm. H.C Starck, Germany).

Mixing and compaction

Al and ZrB₂ powders were mixed in proper weight proportions to yield Al, Al-2% ZrB₂, Al-4% ZrB₂ and Al-6% ZrB₂ composites. Powder compaction was done by using 25 ton capacity manual pellet press (Kimaya Enterprises, Mumbai, India). All the compositions were milled for sufficient time period to ensure homogeneous composition. Al-composite mixture was compacted in 20mm diameter high strength tool steel die, where the punch moved freely in axial direction. Al-composite compacts were made in three aspect ratios: 0.35, 0.5, and 0.65. The effect of aspect ratio (ratio of height to diameter) on densification could be studied by varying the height of the composite during compaction of compacts and then by analyzing the results.

Sintering

The prepared green preforms were placed in stainless steel crucible in the tube furnace. The same preforms were then subjected to a heating cycle in the presence of continuous flowing argon gas. Preforms were sintered in a tubular furnace (Swamequip, Chennai, India). During sintering, the green compacts were heated up to 550°C at the rate 10°C/min and allowed to sinter at this temperature for 1 h prior to furnace cooling. Flow of argon gas was maintained at a constant rate during the sintering process till the composite preforms reached the room temperature. The densities of the composites were measured using Archimedes principle with an accuracy of ±1%.

Microstructural characterization and hardness

Microstructure of sintered preforms were studied by scanning electron microscope (SEM), whereas for identification of present phases in composites X-ray diffraction (XRD) analysis was applied. Vickers hardness of preforms was also measured.

Deformation study

The sintered composite preforms of different compositions and aspect ratios were used as raw materials for deformation study. Six samples of each composition and each

aspect ratio were used for deformation. The intention was to evaluate the effect of compositional changes and aspect ratio on the densification behaviour during the process of deformation. Deformation process was progressed up to an evolution of visual crack on the bulge, which was considered to be finally densified preform. To evaluate the effect of temperature, temperature during deformation process was varied. Deformation of composite preforms were performed in a 40 ton hydraulic press (SVS hydraulics, Hyderabad, India) at three different temperatures, 25 °C (room temperature), 400 °C and 500 °C. The dimensional measurements were noted down after each deformation step to calculate the strain behaviour. The densities of the composite preforms were measured again after every deformation step, to plot the densification behaviour during deformation process.

Potentio-dynamic polarization study

Three out of each set of sample preforms used during deformation process were used as samples for polarization studies. The surfaces of the samples were polished to mirror surface finish for polarization studies. Sample of the deformed composite preform was fixed in a 3 electrode cell unit as shown in Fig. 1. Potentio-dynamic polarization experiments were performed by using EIS analyzer (AMETEK, Parstat 4000, USA).

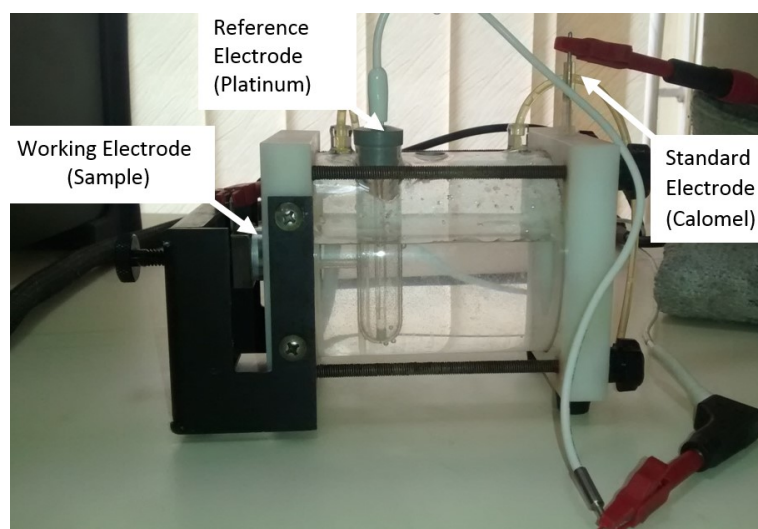


Fig. 1. Experimental setup for polarization study.

Preform was exposed to electrolytic solution with constant surface area. As the electrolyte, 3.5% NaCl aqueous solution was used. Among the three electrodes, the deformed composite preform was placed as the working electrode; Platinum acted as a counter electrode. Open circuit potential (OCP) was performed for 30 min to stabilize the flow of electrons followed by tafel polarization between -0.5V to $+0.5\text{V}$ with a scan rate of 0.166 mV/s as a standard. I_{Corr} and E_{Corr} were extracted from the tafel extrapolation. Corrosion rate was calculated by using the I_{Corr} extracted from tafel extrapolation.

Results and discussion

Fig. 2(a) and 2(b) are the SEM micrographs of pure aluminum and zirconium diboride (ZrB₂) powders which were used to prepare Al-ZrB₂ composites. SEM micrographs of Al powder show that the particles are of irregular shape and average size of 40-50 μm . Similarly, SEM micrograph of ZrB₂ shows particles are of 4 μm . Fig. 3 shows the X-ray analysis of the elemental powders.

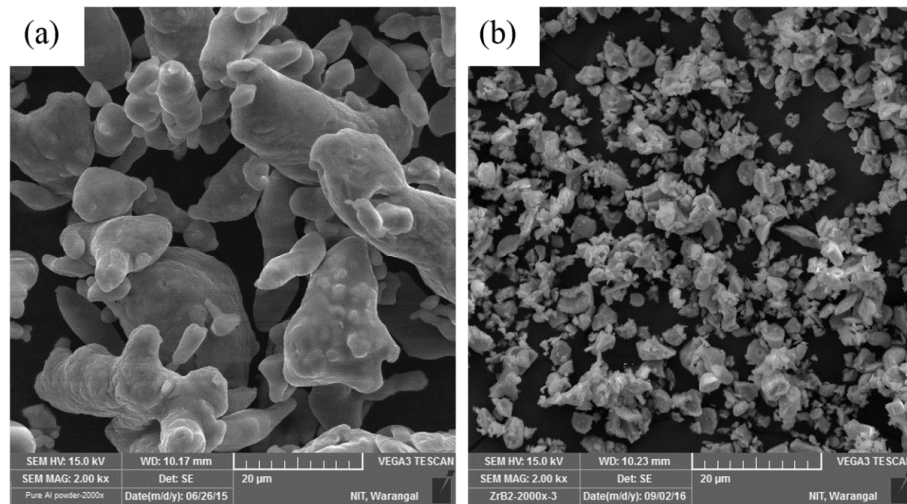


Fig. 2. SEM micrographs of (a) Al and (b) ZrB₂ powders.

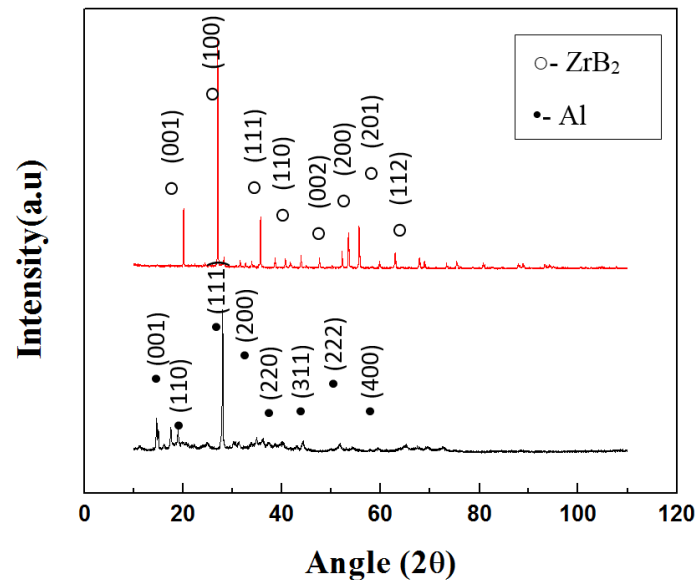


Fig. 3. XRD patterns of elemental powders.

The sintering of the samples was done over a range of 450-600 °C to optimize the sintering condition (Fig. 4). The highest density of all composites was obtained after sintering at 550 °C for 1 h. Fig. 5(a) and 5(b) are the SEM micrographs of pure aluminum and Al-6%ZrB₂. Presence of pores in the Al could not be seen while in case of Al-6%ZrB₂ there are pores around the ZrB₂ particles. In Fig. 6 X-ray analysis of preformed Al and Al-6%ZrB₂ did not reveal the presence of chemical bond between Al and ZrB₂.

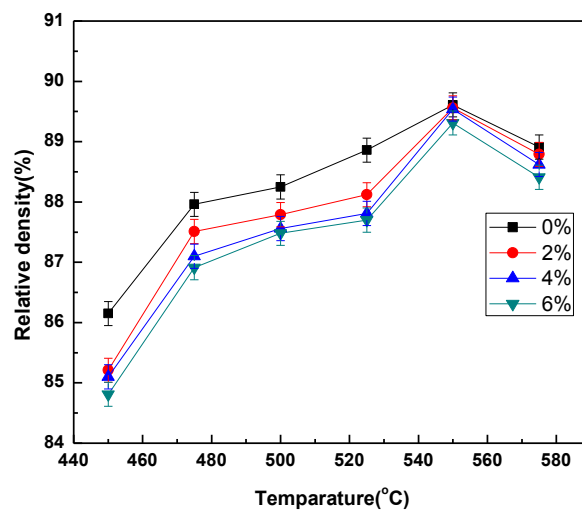


Fig. 4. Change of relative density of samples with the sintering temperature.

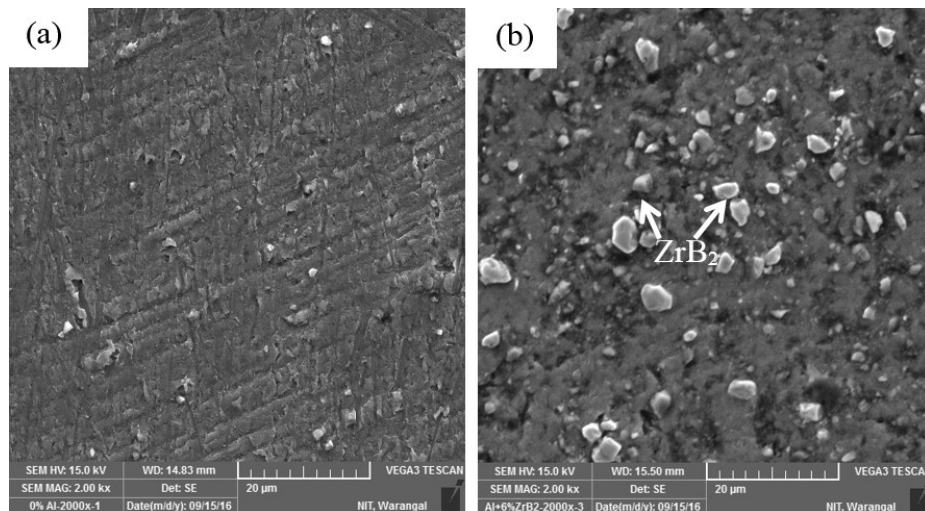


Fig. 5. SEM micrographs of (a) Al and (b) Al-6%ZrB₂ sintered preforms.

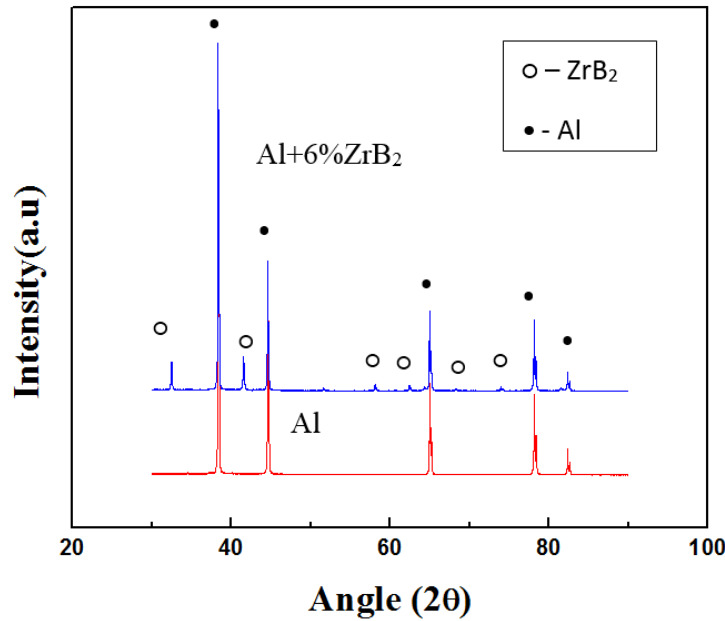


Fig. 6. XRD patterns of Al and Al-6%ZrB₂ sintered preforms.

Fig. 7(a), 7(b), 7(c) and 7(d) show the plots of relative density versus load applied during deformation process of pure Al, Al-2%ZrB₂, Al-4%ZrB₂ and Al-6%ZrB₂, respectively. Approximately 90% of relative density was maintained for all compositions for better comparison. Each plot shows the densification behavior of respective composition with three aspect ratios (ASPR) namely 0.35, 0.5, and 0.65. All the preforms were deformed at three different temperatures during deformation. It is observed that density is improved with the extent of deformation. Composite appeared to be highly densified when deformed at 500 °C with lower aspect ratio of 0.35 for all compositions. Densification increases with the temperature during deformation. Similarly, at the same time as aspect ratio increases the densification decreases which is almost observed in all compositions. Under both hot and cold deformation modes, 96% of relative density is the maximum attained during deformation of Al at 500 °C at 0.35 ASPR.

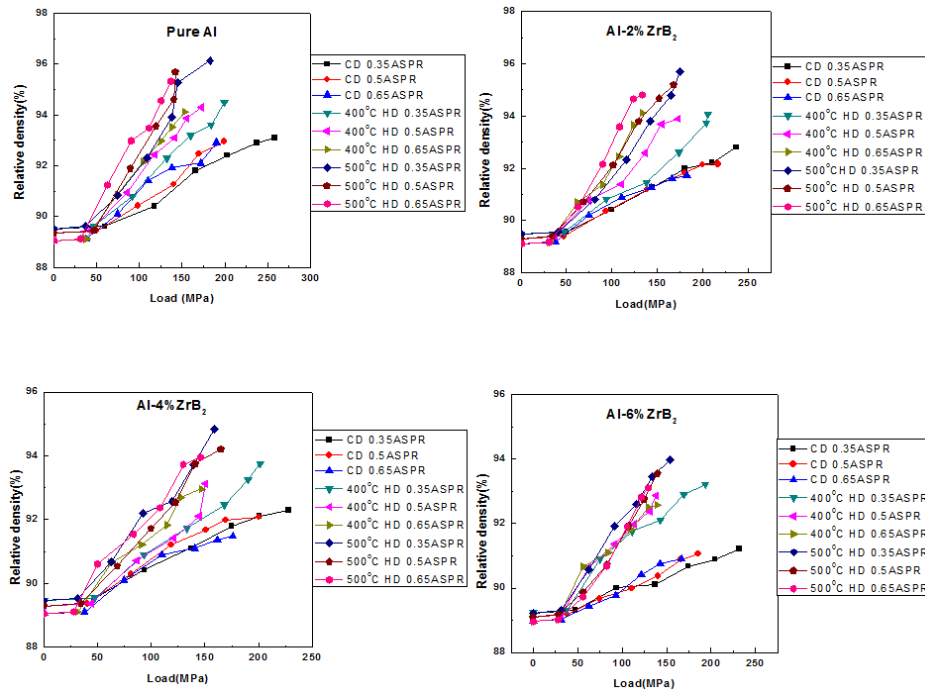


Fig. 7. Relationship between the relative density and deformation load of samples: (a) Al, (b) Al-2% ZrB₂ (c) Al-4% ZrB₂ and (d) Al-6% ZrB₂

Fig. 8 shows the plots of comparison between all the compositions which are deformed at 25 °C (room temperature), 400 °C and 500 °C, respectively. In all conditions, pure Al appeared to be highly densified than other compositions. Al-2%ZrB₂ is densified to an extent where the difference with pure Al is almost negligible. The relative density difference between Al and Al-6%ZrB₂ after deformation is never higher than 3% at the maximum. When compared between different compositions, composites deformed at 500 °C appeared to be highly densified than others.

The effect of deformation on hardness of the composites is shown in Fig. 9. Hardness increases with the increase of amount of ZrB₂. Hardness of composites increases with the increase in the relative density. The composites deformed at 500 °C exhibited maximum hardness than composites deformed at 25 °C and 400 °C. This is due to the extent of deformation.

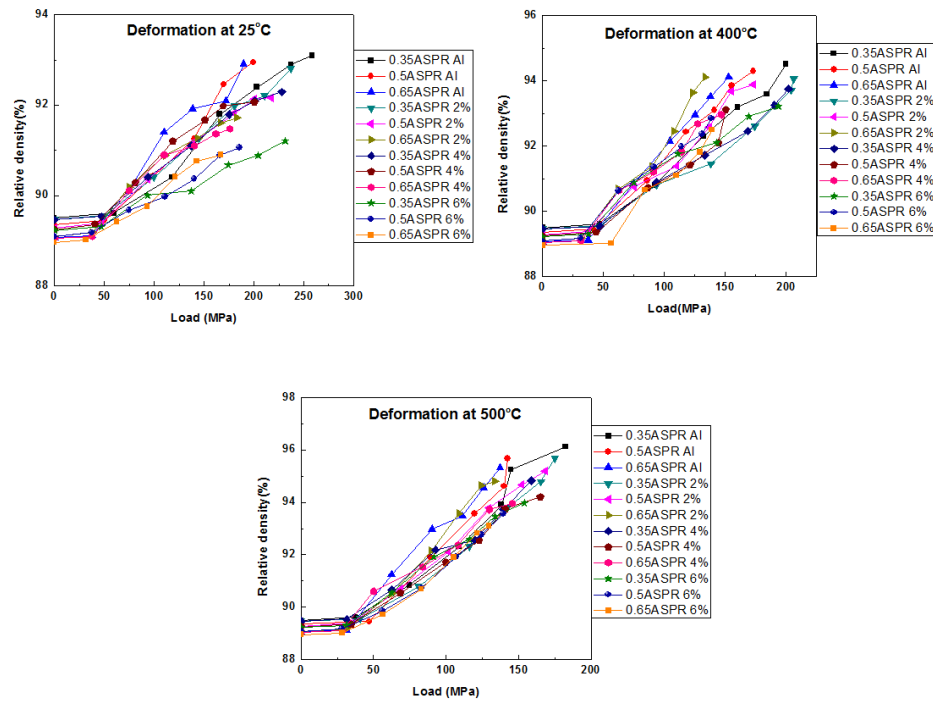


Fig. 8. Relationship between the relative density and deformation load of samples deformed at three different temperatures.

As shown in Figs. 10-12 potentiodynamic polarization Tafel extrapolation curves of all compositions are plotted and indexed separately according to the temperature used during deformation. Samples densified during deformation are observed to be of more cathodic behaviour, which is similar for all compositions and temperatures of deformation.

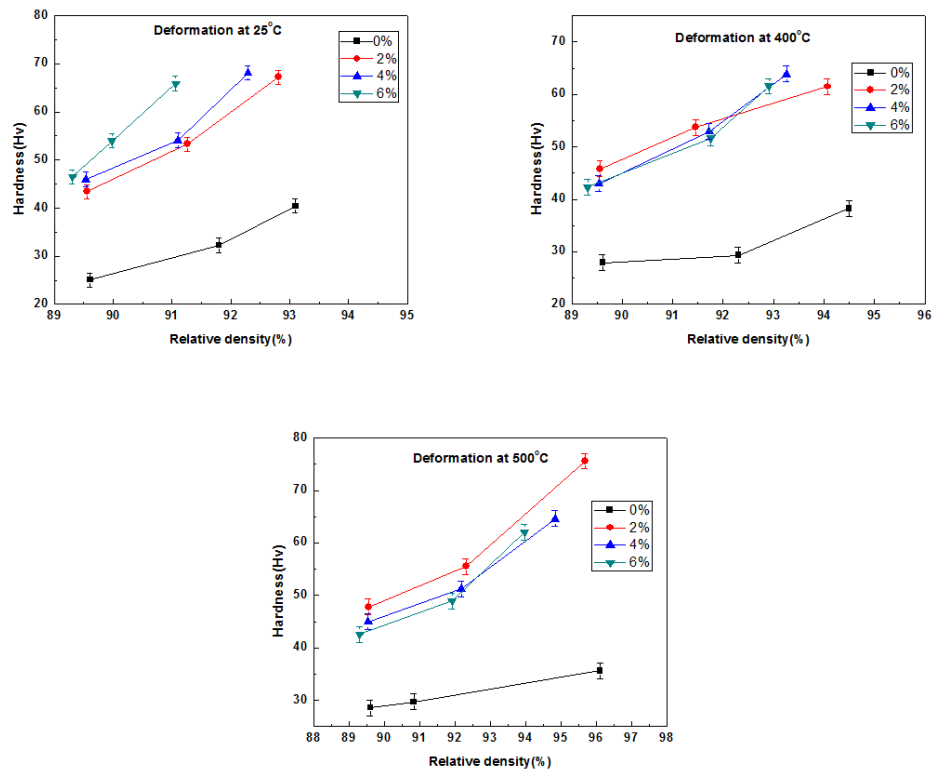


Fig. 9. Relationship between the relative density and hardness of samples deformed at three different temperatures.

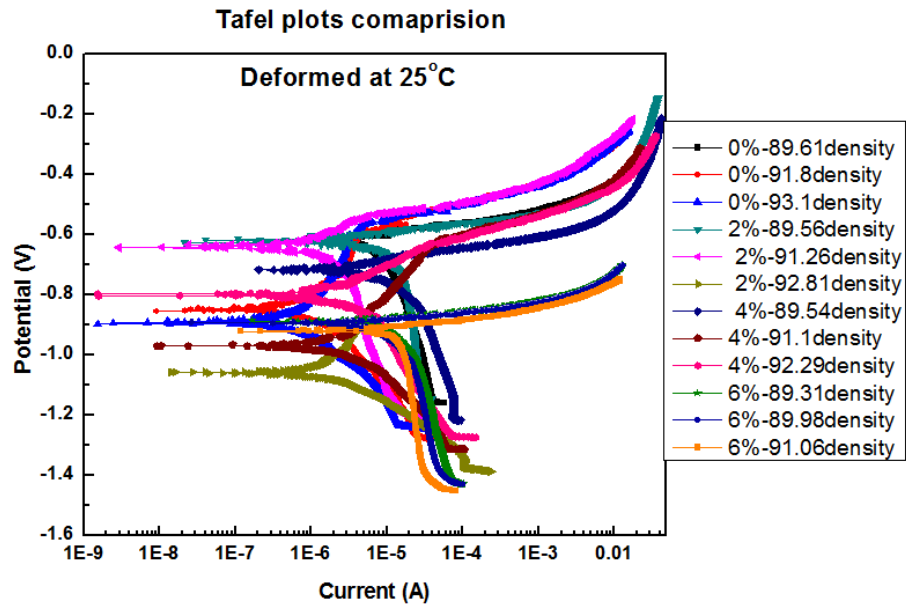


Fig. 10. Comparision of Tafel extrapolation plots of composites deformed at 25 °C.

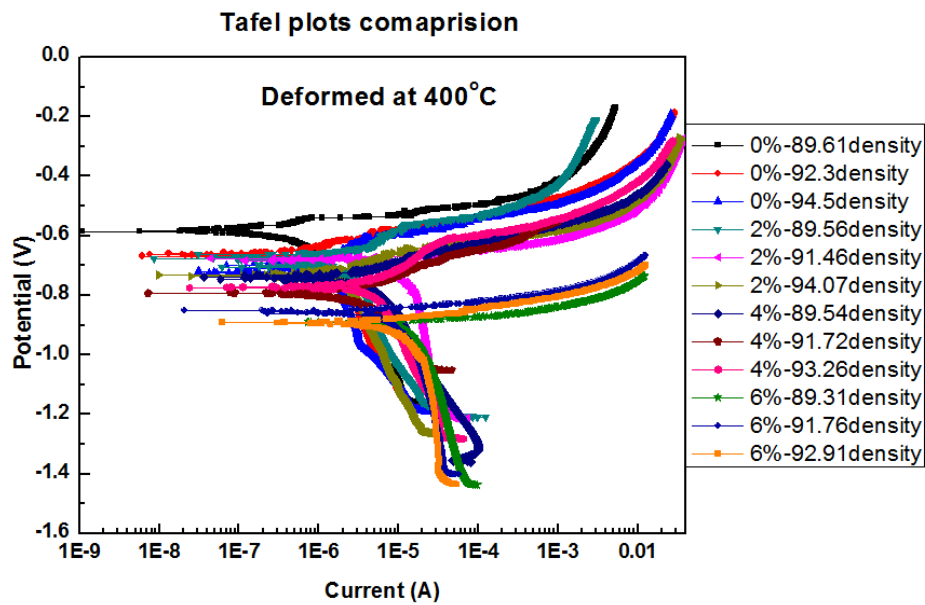


Fig. 11. Comparision of Tafel extrapolation plots of composites deformed at 400 °C.

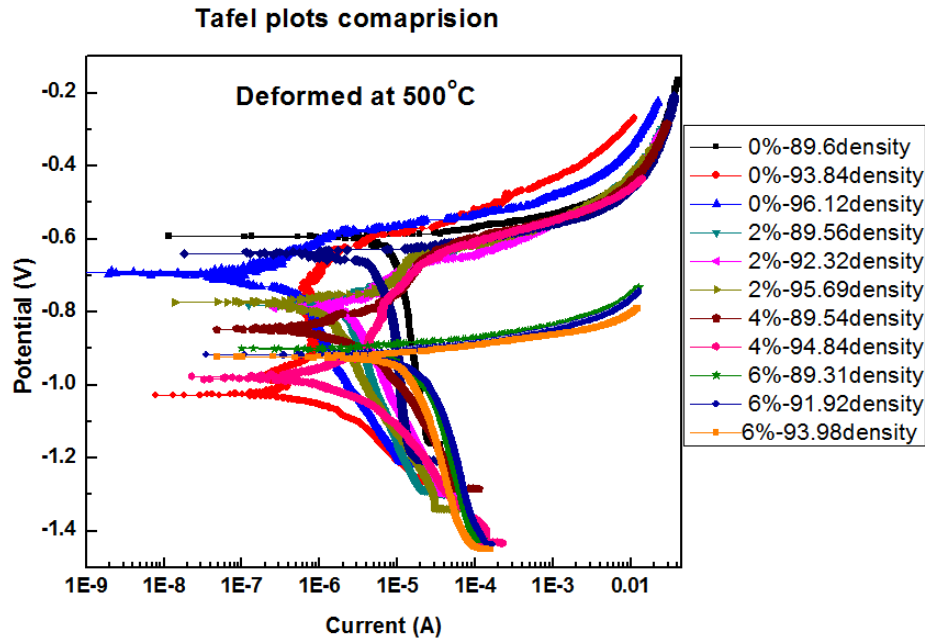


Fig. 12. Comparision of Tafel extrapolation plots of composites deformed at 500 °C.

From Fig. 13-16 Tafel extrapolation curves of the same composition are compared. Samples deformed at 500°C are more cathodic in nature which resulted in less corrosion rate. Corrosion rate is calculated from the corrosion current (I_{Corr}) value obtained from the interception of anodic and cathodic tangents of tafel extrapolation curve. Corrosion rate is increased with the increase in the amount of ZrB_2 in the composite. The increase in the corrosion rate is due to the galvanic effect between the ZrB_2 particle which is highly corrosion resistant and the aluminium matrix which is comparatively anodic in nature. This trend of increase in corrosion rate with ~~an~~ increase in the amount of ZrB_2 is also correlated to the densification of samples after deformation.

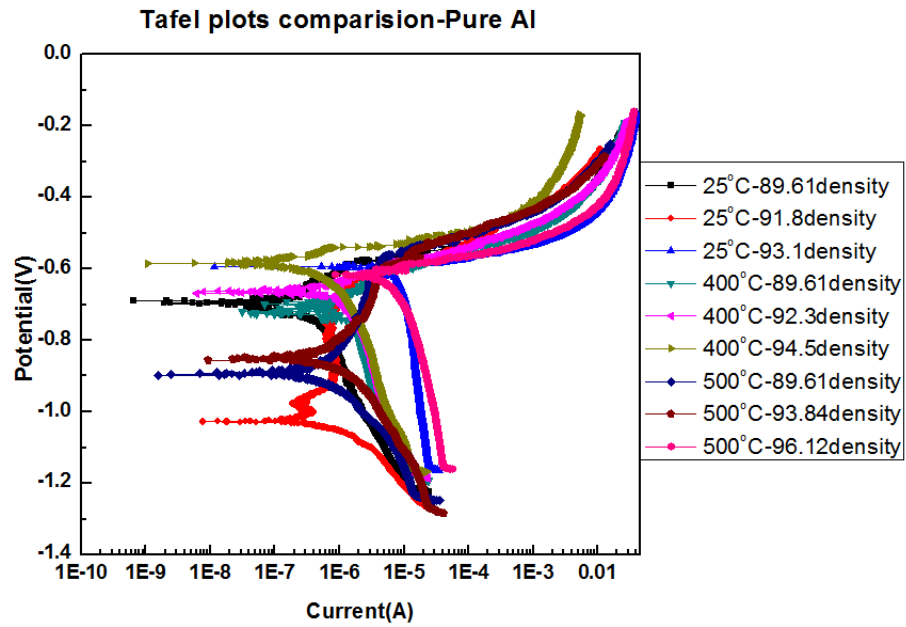


Fig. 13. Comparison of Tafel extrapolation plots of pure Al composites deformed at 25 °C, 400 °C and 500 °C.

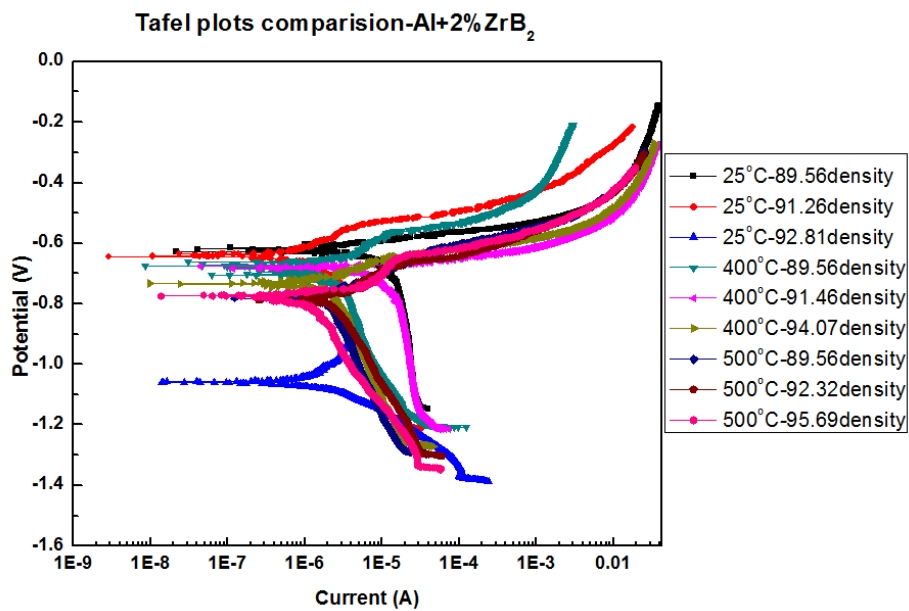


Fig. 14. Comparison of Tafel extrapolation plots of Al+2%ZrB₂ composites deformed at 25 °C, 400 °C and 500 °C.

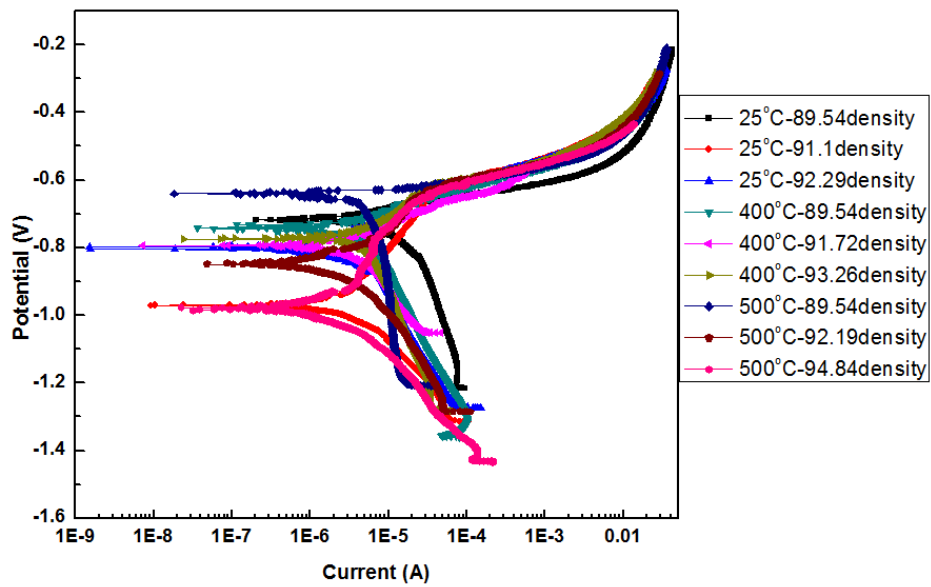


Fig. 15. Comparison of Tafel extrapolation plots of $Al+4\%ZrB_2$ composites deformed at 25 °C, 400 °C and 500 °C.

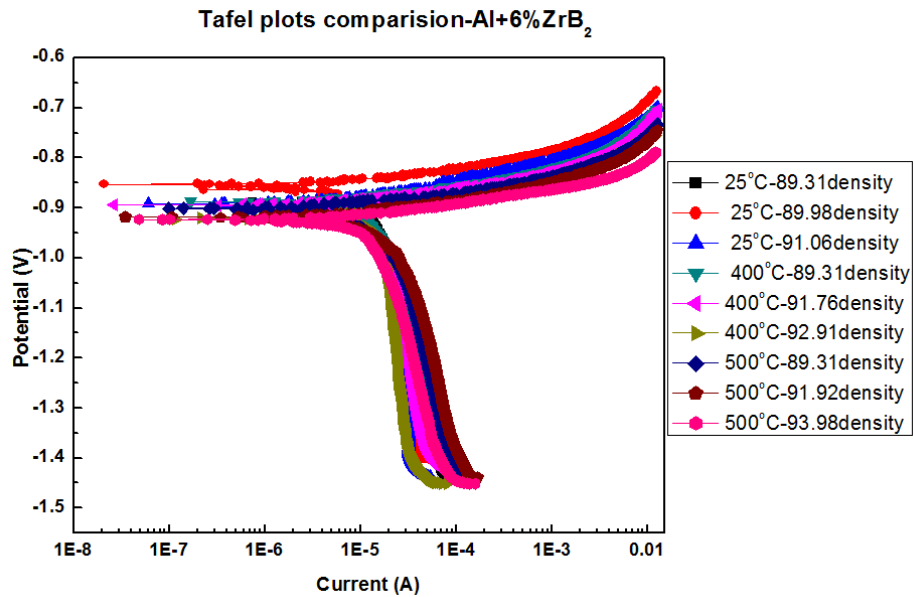


Fig. 16. Comparison of Tafel extrapolation plots of $Al+6\%ZrB_2$ composites deformed at 25 °C, 400 °C, and 500 °C.

As aluminium and Al+2%ZrB₂ are highly densified, they exhibited minimum corrosion rate. The galvanic couple effect is also at minimum in the case of Al+2%ZrB₂ which is the reason for low corrosion rate when compared with Al+4%ZrB₂ and Al+6%ZrB₂. Fig. 17 represents the plot of corrosion rates versus relative density of composites after deformation of pure Al, Al-2%ZrB₂, Al-4%ZrB₂ and Al-6%ZrB₂, respectively. Each plot exhibits the corrosion rate versus relative density during three different temperature modes of deformation processes. The three different deformation conditions are as follows: 25 °C (room temperature) cold deformation and 400 °C, 500 °C hot deformation. Corrosion rate decreases with extent of deformation, as densification is improved with the extent of deformation. Similar trend is observed in all the compositions. When compared within the composites deformed at three different temperature modes of deformation, composites hot-deformed at 500 °C showed minimum corrosion rate since they are highly densified.

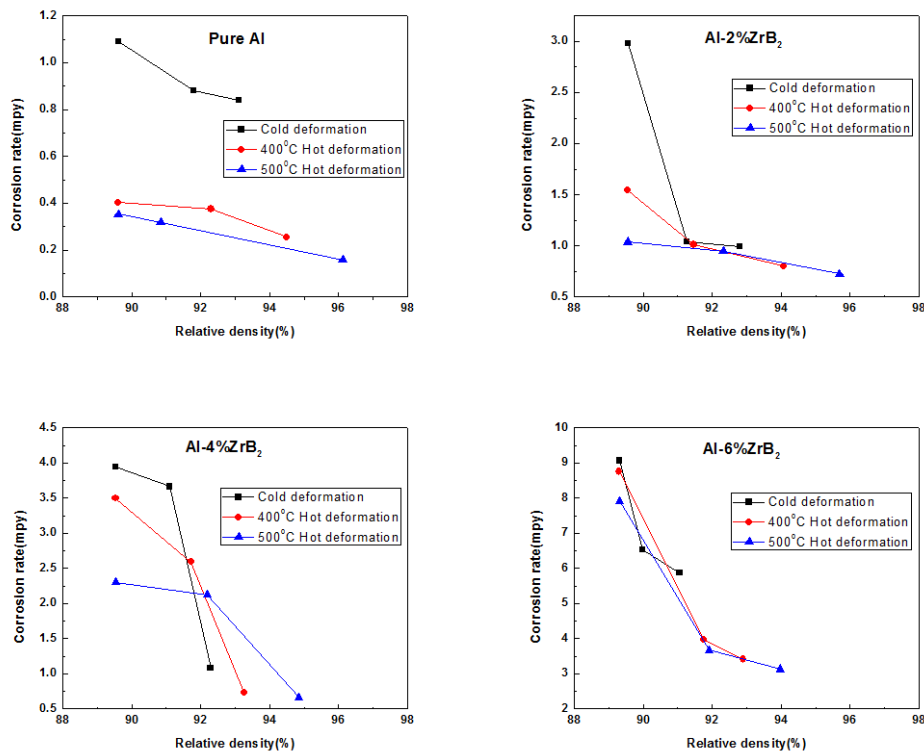


Fig. 17. Effect of relative density on the corrosion behaviour of Al- 0, 2, 4, 6 wt% ZrB₂.

Fig. 18 shows the individual plots of corrosion rate versus relative density of all composites deformed at three different temperatures. Corrosion rate appeared to increase with increase of ZrB₂ content in the composite. However, with the extent of deformation, corrosion rate is decreased as an effect of deformation. Pure Al which is highly densified during deformation at 500 °C appeared to have lowest corrosion rate

followed by Al-2%ZrB₂ composites with same corrosion rates, but with enhanced properties.

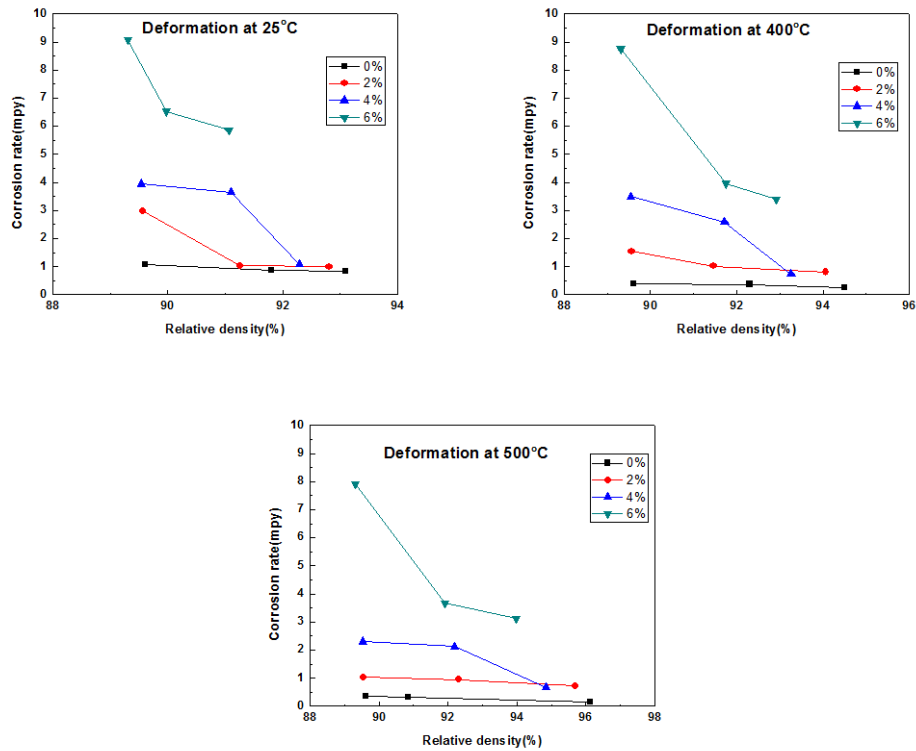


Fig. 18. Corrosion rate versus relative density(%) of samples deformed at three different temperatures.

Conclusions

- Densification is improved with the increase in temperature during deformation process.
- Lower the aspect ratio higher the densification after deformation.
- Hardness of the composites increases with densification.
- Hardness is increased with increase in the amount of ZrB₂ in the composite.
- Corrosion rate decreases with the extent of densification. This is due to the closure of pores after deformation which results in higher densification.
- Al+2%ZrB₂ with enhanced properties is equally densified as pure Al and possesses approximately equal corrosion rate as pure Al.

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