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Materials and Design 24 (2003) 281-286

www.elsevier.com/locate/matdes

Materials

& Design

Structure and properties of Zn–Al–Cu alloy reinforced with alumina particles

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Received 8 July 2002; received in revised form 13 January 2003; accepted 16 January 2003

Abstract

Metal matrix composites were prepared using Zn–21Al–2Cu (zinalco) as base alloy, by means of powder metallurgy techniques. Alumina particles were used as reinforcement in concentrations of 7, 14 and 27% in volume. The composites prepared using this technique exhibit good consolidation even before sintering. Samples of the base alloy and of the different composites were sintered in air at 473 K in periods of 10, 20, 40 and 80 h. Measurements of density, hardness and yield strength in compression were performed in green and sintered materials. A decrease of 30% in density is achieved for the 27 vol.% alumina composite compared with the unreinforced base alloy. An improvement of 13% in the values of conventional yield strength and hardness is shown for the composite with 7 vol.% alumina deformed at a strain rate of 10^{-3} s^{-1} and after 20 h of sintering time. At higher strain rates, the ductility of unreinforced and composite materials is reduced for all alumina concentrations. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Metal matrix composites; Particulates and powders; Powder metallurgy; Plastic behavior

1. Introduction

Metal matrix/ceramic composite materials have been of interest in the past decade because the addition of ceramics in the form of whiskers or particulates into matrices such as aluminum enhances the wear resistance, elastic modulus, and yield strength [1-4].

The zinc–aluminum-rich family of alloys has been particularly popular during recent years. They offer several advantages, are inexpensive high strength alloys, have good corrosion resistance and are low melting point materials. A particular case of this family of alloys is the Zn–Al eutectoid alloy, modified with 2–3 wt.% copper (zinalco alloy). This alloy has many advantages due to its high strength, good machinability and toughness. Zinalco alloy has been widely studied in order to determine the characteristic parameters of production and physical properties of casting, rolling, extrusion, and forging materials [5,6]. This alloy shows at room temperature the presence of the intermetallic compound $\text{CuZn}_4(\varepsilon)$, which is stable above 540 K, and decomposes during prolonged aging (≈ 9 h at 450 K) [7] into the stable form at room temperature, the ternary ordered Al rich τ' phase. This intermetallic phase increases the mechanical properties of the alloy.

The powder metallurgy method to produce parts made from metal powder alloy can be used to create materials with highly useful characteristics. For example, high strain rate superplasticity, porous parts or production of intricate shapes that can be easily processed and sintered. This investigation examines the properties of zinalco– base metal/ceramic composites fabricated by conventional cold powder pressing and hot solid state sintering techniques.

2. Experimental procedure

Powdered zinalco was prepared by grinding filings of extruded zinalco alloy (Zn-21wt.%Al-2wt.%Cu) in an agate ball mill for a minimum of 24 h. A sieve classification of this powder was made to obtain a

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Fig. 1. Fine grain microstructure inside the metal particles, produced by the milling process: (a) unreinforced green material; (b) welded particles in the base alloy, after 80 h sintering at 473 K. The grain size inside of these particles increased in size for (c) zinalco-7 vol.%, unsintered; whereas for (d) zinalco-7 vol.%, sintered 80 h at 473 K, the grain size did not grow.

distribution of particle sizes in the range of $40-90 \ \mu m$. Fine particles of alumina with a particle size of 0.05 μm , were used as reinforcement material. Zinalco and zinalco–alumina compact cylinders were prepared by compacting the milled filings at room temperature in a stainless steel die using a mechanical press at 580 MPa for 15 min. The resultant cylinders (10 mm diameter, 8 mm height) were sintered in an electrical furnace under air atmosphere at 473 K for 10, 20, 40 and 80 h, respectively, in order to observe the variation in properties as a function of sintering time.

Green and sintered materials were tested in compression. These tests were carried out at room temperature, in a Universal Instron 1125 machine, using different strain rates: 10^{-4} , 5×10^{-4} , 2.5×10^{-3} , 10^{-2} and 10^{-1} s⁻¹. The specimens were tested for each condition probe.

3. Results

3.1. Microstructural observations

The internal structure of the particles of zinalco is composed of fine grains (Fig. 1a) and a few zones of fine pearlite. These fine grains are produced in the material after the milling process of a material with an initial stable pearlite structure as has been observed before [3].

During the sintering process, the fine grains inside the metal particles grow in the pure zinalco and at the same time, the metal particles are bonded by diffusion (Fig. 1b), leaving some porosity between the particles. This process is completed in 20 h.

In the reinforced material with alumina, the grains grow very slowly as a function of the amount of alumina. Fig. 1c shows 7 vol.% of alumina green composite microstructure, the grain grows slightly after the sintering process (Fig. 1d). In the material with 27 vol.% alumina, the grains remain fine even after 80 h of sintering time. It was established by microanalysis (EDXS) that the alumina is accommodated around the big metal particles producing some sort of thermal insulation for the metal grains, and with higher amounts of alumina the effect of insulation is bigger, resulting in a retardation of grain growth inside the metal particles.

In the composite zinalco-7 vol.% alumina, the ceramic distributes homogeneously around them (Fig. 2a), refilling the original roughness of the metal particle surfaces. When the amount of alumina is increased to 14 and 27 vol.%, wide black regions of alumina are found in between the metal particles (Fig. 2b).

3.2. Density

An advantage of adding ceramic particles into a metallic matrix is to diminish the density of the resulting material. Table 1 shows the results of density changes that occur after sintering pure and reinforced alloy. The theoretical values were calculated using the rule of mixture. The actual density of the composites prepared





Fig. 2. Distribution of the alumina (black regions) around the metal particles. (a) Zinalco-7 vol.% alumina, unsintered; (b) zinalco-27 vol.% alumina, unsintered.

under conditions of this work, was obtained measuring the weight and volume of cylinders, these values change from 5.00 g/cm³ (unreinforced material) to 3.83 g/cm³ (27 vol.% alumina). This observed large change in density is due to porosity as well as the larger amounts of alumina.

No appreciable volume changes were observed during the sintering of the composite. Fig. 3 shows that density remains almost constant for all compositions and sintering time. At the sintering temperature used in this work (473 K), it is not expected that bonding occurs between alumina particles.

3.3. Mechanical properties

The base alloy yield stress in compression was measured in both green and sintered material. The compressive properties of the composites tested as a function of sintering time are shown in Fig. 4.

The results clearly indicate that the addition of 7 vol.% alumina particles into the zinalco matrix resulted

Table 1 Density values of particle reinforced zinalco-alumina composites

Material	Density (g/cm ³) Theoretical Actual		Porosity (%)
Zinalco	5.40	5.00 ± 0.02	7.41
Zinalco-7 vol.% alumina	5.27	4.73 ± 0.01	10.25
Zinalco-14 vol.% alumina	5.15	4.44 ± 0.01	13.79
Zinalco-27 vol.% alumina	4.91	3.83 ± 0.01	22.00



Fig. 3. Effect of sintering time on the density of zinalco and zinalcoalumina composites.



Fig. 5. Effect of sintering time on hardness of zinalco and zinalcoalumina composites.

in an improvement of the yield strength after sintering, reaching a maximum improvement of 13%, after 20 h. Higher sintering times keep the strength of both materials almost constant. The composites with 14 and 27 vol.% alumina, fracture without yielding.

Alumina increases the hardness of the green compacts up to a content of 14 vol.% (Fig. 5). This value diminishes when the alumina content is 27 vol.% because the particles separate very easily when the force is applied. Sintering increases the hardness of the unreinforced and zinalco-7 vol.% alumina composite, reaching a maximum after 20 h of sintering time, and the hardness remains almost constant for a longer sintering time.



Fig. 4. Effect of sintering time on yield strength of zinalco and zinalco-alumina composites. Test was performed at a strain rate of 10^{-3} s⁻¹.



Fig. 6. Effect of strain rate on (a) yield strength and (b) true strain of zinalco and zinalco-alumina green composites.

Fig. 6 shows that the green unreinforced material increases its plastic deformation and yield stress with strain rate. The reinforced material with 7 vol.% alumina, increases its ductility up to 10^{-3} /s and then starts to fail in a brittle manner.

The behavior of the green unreinforced zinalco is similar to that of high strain rate superplastic metals [4], reaching 113% at 10^{-1} /s and will possibly reach higher values at higher strain rates, not measured in this work.

Sintering changes this behavior completely; the composites with 14 and 27 vol.% alumina tested at 10^{-4} /s behave like unreinforced zinalco as shown in Fig. 6a. The green and sintered composite materials behave as being brittle when the strain rate increases. For longer sintering times both unreinforced and reinforced zinalco behaves in a brittle manner when tested in compression at any strain rate.

Fig. 7 shows the microstructure of the compression deformed (113%) green composite with 7 vol.% alumina. It is possible to observe that deformation took place by plastic deformation of the particles, which are elongated by the effect of stress. We can say that the particles slip one over the other because the alumina interface has been broken into small rounded pieces. Sintering causes welding of the metal particles and impedes the slip of one particle over the other, reducing the ductility of the material.

4. Discussion

The present study shows that the incorporation of alumina particles in the zinalco alloy affects the density and mechanical properties of the unreinforced alloy. The low sintering temperature (473 K) used in this work, is not enough to produce sintering of the alumina, so under these experimental conditions, large amounts of alumina produces brittle behavior, and impedes the grain growth inside the metal particles. During mixing and compaction operations, the fine alumina particles infiltrate to the irregularities of the zinalco fillings surface, making a smoother interface resulting in better accommodation of the distorted particles during deformation at low strain rates ($<10^{-3}$ s⁻¹) in the 7 vol.% alumina unsintered composite, increasing the total strain (Fig. 6b) with respect to the unreinforced green zinalco alloy.

In the green base alloy an almost linear dependence of yield stress with strain rate was observed (Fig. 6a), and this value increases as a function of strain rate. This behavior changes with the sintering process in the reinforced and unreinforced materials. In the sintered ones, yield stress was observed only when the strain rate was below 10^{-3} s⁻¹, for higher strain rates (> 10^{-3} s⁻¹) fracture occurs without yielding in both sintered materials, possibly due to diffusion bonding between metal particles, which obstructs the free accommodation of these particles, one over the other. Yield strength in the unreinforced material achieves a maximum after 20 h of sintering, and then the stress remains constant with longer sintering time. In the reinforced material with 7 vol.% alumina the yield stress increases up to 20 h. The initial increase of the yield stress in both reinforced and unreinforced materials is probably due to diffusion bonding of the metal particles that obstructs the free accommodation of the deformed metal particles. A bigger yield stress is observed in the case when the alumina is present, probably due to the fact that the metal particles remain as a microstructure of fine grains.

Increases in alumina volume fraction (14 and 27 vol.%), results in a poor contact between metal particles, reducing the possibility that diffusion bonding occurs between them, and so the material behaves in a very brittle manner because particle/alumina decohesion occurs.

5. Conclusions

The mechanical properties of Zn-21Al-2Cu prepared by powder metallurgy techniques are improved with the



Fig. 7. Zinalco-7 vol.% alumina green composite deformed by 113% in compression at 10^{-3} s⁻¹. The arrows show how the alumina powder compact was broken.

addition of 7 vol.% alumina and sintering. This composite reaches 380 MPa after 20 h of sintering at 473 K in air when the strain rate is below 10^{-3} s⁻¹.

Green materials with and without alumina shows that its deformation proceeds principally as plastic deformation of the metal particles. The main effect of the sintering process in the composite material with 7 vol.% alumina and pure zinalco, is to produce diffusion bonding between the metal particles and grain growth inside them. Alumina reduces the grow rate of the grains of the metal particles.

The behavior of the green base alloy as a function of strain rate is similar to that of high strain rate superplastic metals reaching 115% true strain at 10^{-1} s⁻¹, and possibly this alloy will reach higher values at higher strain rate.

The composite with 7 vol.% alumina unsintered also shows changes in its mechanical deformation as a function of strain rate, at low strain rate it behaves in a ductile manner, and for values of strain rate higher than 10^{-3} s⁻¹ behaves as a brittle material.

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