

Characterisation of powder metallurgy Cu-ZrO₂ composites

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ABSTRACT

Cu-ZrO₂ composites can be used as electrical contact materials in relays, contactors, switches, circuit breakers, electronic packaging requiring good electrical and thermal conductivity as well as welding or brazing properties. In the presented work copper matrix composites reinforced with 8 mol % yttria-stabilised 1 wt. %, 2 wt. %, 3 wt. %, 4 wt. %, and 5 wt. % zirconia (8-YSZ) particles were fabricated by the powder metallurgy method. Cu and Cu-ZrO₂ powder mixtures were compacted with a compressive force of 500 MPa and sintered at 900 °C for 2 h within an argon atmosphere. The results of the study on the mechanical properties of the composites showed that with increasing content of ZrO₂, the micro-hardness and compressive strength increase. The relative densities of the composites decreased from 96.1 % to 92.0 % with increasing zirconia content up to 5 wt. %. The results of the electrical test on the composites indicated that electrical conductivity reduced gradually with increase in reinforcement content. SEM and EDS studies showed that Cu-ZrO₂ composites have a uniform microstructure in which zirconia particles are distributed uniformly in the Cu matrix.

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ARTICLE INFO

Keywords:

Powder metallurgy
Cu-ZrO₂ composites
Mechanical properties
Electrical conductivity

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Article history:

Received 29 July 2013
Revised 16 November 2013
Accepted 20 November 2013

1. Introduction

Metal matrix composites (MMCs) reinforced with various hard ceramic particles, (such as SiC, Al₂O₃) have emerged extensive development in the last decades. Because of their improved specific properties, their potential application in the aerospace, automotive, army equipment, electronic industry, nuclear and other industries seems encouraging [1]. The reinforcement may improve specific stiffness, specific strength, abrasion resistance, creep resistance, thermal conductivity, and dimensional stability [2].

Due to low mechanical strength, a highly conductive copper matrix needs to be dispersion strengthened and new composite materials with superior characteristics have been developed [3, 4]. Among copper-based composites, high strength, high conductivity, resistance to high temperatures, and wear are very important and necessary qualities for electric contact materials, resistant electrodes, and many other industrial applications as compared to pure copper and copper alloys [5-8]. Copper matrix composites (CMCs) consisting of a metallic matrix (Cu) with high thermal conductivity and a ceramic reinforcement (SiC, AlN, TiB₂, and β -eucryptite [9]) with low coefficient thermal expansion (CTE) provide exceptional freedom in tailoring these two properties to specific application [10]. For example, application for thermal management systems in electronics (e.g., expansion matched to substrate while maximizing conductivity for electronic heat sinks) [11].

Yttria-stabilised zirconia particles can be used as reinforcement material to enhance the strength of copper matrix. Zirconia as a ceramic material finds many applications as piezoelectric devices, ceramic condensers and oxygen sensors due to some of its unique properties such as

high hardness, low coefficient of friction, high elastic modulus, chemical inertness and high melting point [12].

Various techniques are employed in the fabrication of MMCs, which can be broadly classified into two major groups, namely liquid metallurgy (LM) and powder metallurgy (PM). LM route is one of the many production processes under investigation for the manufacture of metal matrix composites. The main argument against them is usually the claim of high reactivity of melt / filler systems [13]. Powder metallurgy is one of the near net shape processing methods commonly used for fabricating engineering components based on metal-based materials. The PM method usually involves mixing of powders, compaction and solid-state sintering. Sintering can be done in a number of ways using radiant, plasma, induction and microwave heating sources [14, 15].

In this work, Cu-ZrO₂ composites are fabricated by means of PM process. The effects of yttria-stabilised zirconia on the microstructure, mechanical and electrical properties of the Cu matrix are studied.

2. Experimental

Commercial copper powder (< 50 µm) and 8 mol % yttria-stabilised zirconia (8-YSZ) powder (< 35 µm) in a range of composition of 100 %, 99 %, 98 %, 97 %, 96 %, and 95 % of Cu and 1 %, 2 %, 3 %, 4 %, and 5 % of ZrO₂ were mixed mechanically. Milling was carried out at room temperature using a planetary high energy ball mill (Union Process Co, Akron, OH, USA). High hardened cup (60 mm diameter and 80 mm height) containing the powders and the Al₂O₃ balls is fixed onto a rotating disc and rotates in the opposite direction to that of the larger platform. In order to obtain the proper mixing, rotational speed was controlled to 250 rpm for 16 h. The mass of powder charge was 45 g and the weight ratio between Al₂O₃ balls and the powder charge was controlled about 15 : 1 and Al₂O₃ balls with the charge ratio of 20 : 1 were used in all cases. The powders and milling balls were loaded into the cup which was filled with purified argon gas to avoid air contamination.

Prior of sintering, the mixed powders were compacted in a hydraulic press at a pressure of 500 MPa in a steel mold to obtain cylindrical shaped specimens having 10 mm diameter and 18 mm height. Compacted samples were sintered at 900 °C for 2 h within an argon atmosphere. Since yttria-stabilised zirconia reinforcement particles were well wetted by Cu matrix, there was no need to use wetting agent.

The relative density of the specimens was measured using Archimedes' method (ASTM B 311). Micro-hardness measurements were performed on the polished samples using a HVS-1000A automatic digital micro-hardness tester under a test load of 50 g and a dwell time of 10 s in accordance with the ASTM standard E 92. The compression tests were performed over an initial strain rate of 10⁻⁴ s⁻¹ at room temperature using Instron 8516 machine in compliance with ASTM E9-89a standard for measuring the compressive response of the matrix and composite materials [16]. Microstructures of polished and chemically etched (40 % HNO₃-H₂O solution) samples were observed by scanning electron microscopy with energy dispersive spectrometer. The samples for 4 probe conductivity measurements were 10 mm height and had a diameter of 9-10 mm after cutting and grinding. The two end faces of the specimens were ground flat, cleaned and painted with platinum paste (Hanovia Liquid Gold 6082 or Johnson Matthey Metal Ltd. N758). Platinum foil contacts for passing current were attached to these paste electrodes later on. A constant current of 0.5-200 µA (depending upon the specimens' resistances) was supplied by a Keithley constant current source model 227. All the current ranges were pre-calibrated and correction was applied during calculation of the conductivity.

3. Results and discussion

3.1 Microstructure

Fig. 1 illustrates the SEM microstructures of ZrO₂ reinforcement agent and Cu powder. Pure ZrO₂ has monoclinic crystal structure at room temperature. At high temperatures the crystal structure converts to tetragonal and cubic. Volumetric shrinkage caused by the structure conversions

leads to severe stress and results in cracking of the zirconia structure. To avoid this, stabilising oxides like MgO, Y_2O_3 , Ce_2O_3 , and CaO can be added to pure zirconia. The oxides stabilise tetragonal and cubic structure and lead to improve mechanical, thermal and electrical properties of pure zirconia.

Microstructural studies conducted on the composites revealed homogeneous distribution of the zirconia particles in the copper matrix. To achieve optimised mechanical and electrical properties of the composite materials, it is significant to obtain uniform distribution of reinforcement in the matrix. If reinforcement particles in the composites do not disperse uniformly, this affects mechanical and electrical properties of composites negatively [17].

Microstructural morphology and distribution of the components in the Cu-ZrO₂ composites sintered at 900 °C for 2 h, as a function of ZrO₂ content are shown in Fig. 2. Grey regions imply Cu matrix and light and cornered particles imply the reinforcement component of ZrO₂. The composite samples had also been examined in energy dispersive spectrum (EDS). EDS analyses of the composites show (Table 1) that O and Zr content increase with increasing weight percentage of the ZrO₂. As shown in Fig. 2, it is noted that reinforcement of the composites was located at the copper particle boundaries. The particle sizes seemed to be slightly decreased as contents of zirconia are increased from 1 wt. % to 5 wt. %. Due to ductile nature of copper, with increasing of ceramic content in the composites, the ceramic particles permeated into the metal matrix particles. The presence of agglomeration as well as nodular individual particles is seen in the structures. SEM images verified that by powder metallurgy technique, the Cu-ZrO₂ composites with high density are developed.

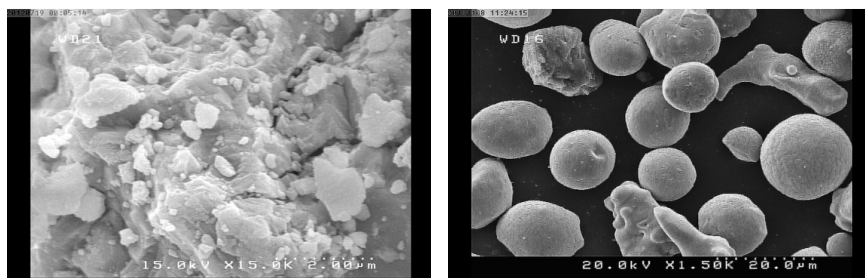


Fig. 1 SEM micrographs of starting powders of yttria-stabilised zirconia (left), and copper (right)

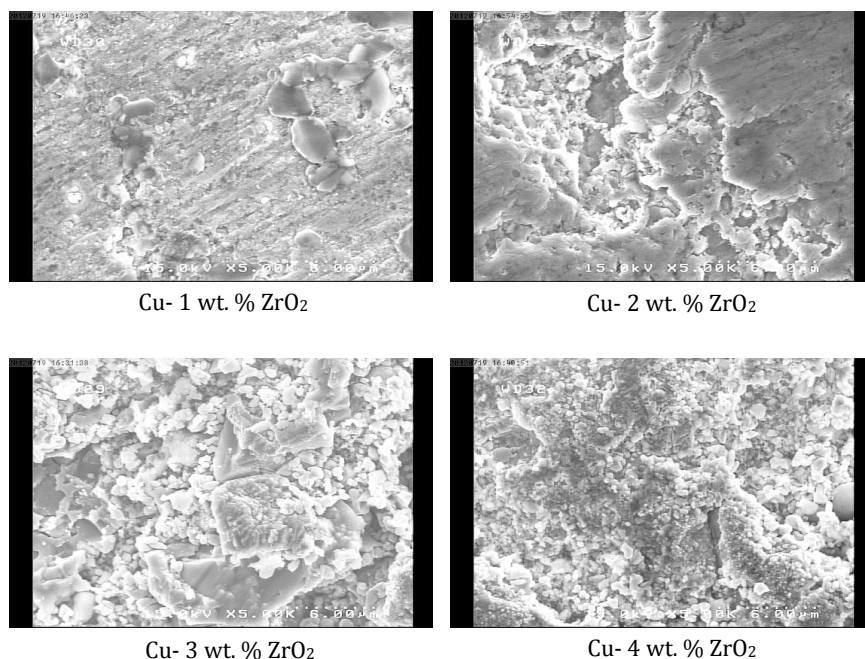


Fig. 2 SEM micrographs of Cu-ZrO₂ composites reinforced with different content of ZrO₂

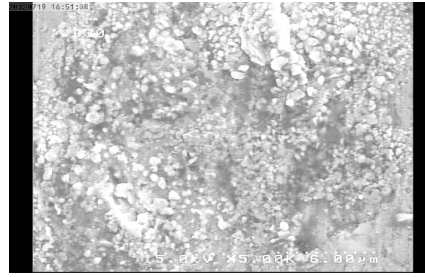

 Cu- 5 wt. % ZrO₂

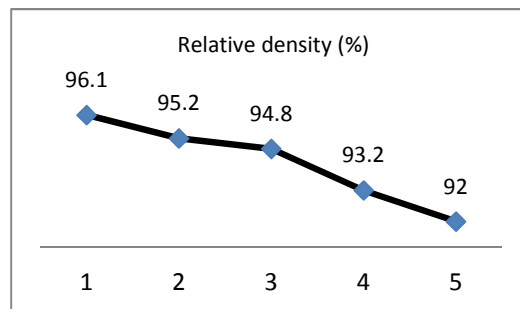
Fig. 2 (Continued)

Table 1 EDS surface scanning of Cu-ZrO₂ composites reinforced with different content of ZrO₂

ZrO ₂ , wt. %	Cu, wt. %	Zr, wt. %	O, wt. %
1	99.02	0.66	0.31
2	97.55	1.43	1.01
3	93.72	3.66	2.61
4	91.68	5.08	3.19
5	88.70	6.25	4.49

3.2 Relative density

Relative densities of the Cu-ZrO₂ composites at various zirconia content determined by using Archimede's principle were shown in Fig. 3. The relative density of pure copper was determined as 97.1 %. The densities of composite samples decreased from 96.1 % to 92.0 % with increasing the amount of ZrO₂ up to 5 wt. %. This is due to the density of zirconia particles being much lower than that of Cu. In the composite with low ZrO₂ volume fraction, less Cu-ZrO₂ interface means less copper atom diffusion barrier, copper atoms can diffuse easily and spread between the ZrO₂ particles, thus leading to a higher densification of the composites. Preparing techniques and sintering were combined in the process the compact green density directly influenced the properties of composites [18].


Fig. 3 Effect of zirconia content (wt. %) on the relative density of Cu-ZrO₂ composites

3.3 Mechanical properties (micro-hardness and compressive strength)

In order to obtain optimum results, micro-hardness values were determined by taking the average of six different measurements on each sample. Micro-hardness of the composites reinforced with different content of ZrO₂ that measurements were performed on the regions including the Cu grains and zirconia particles uniformly were shown in Fig. 4. The micro-hardness of the pure copper (59.7 HV) was increased to 121.6 HV with increasing zirconia content up to 5 wt. %. With regard to Fig. 4, it is revealed with increasing hard reinforcement content in the ductile copper up to 5 wt. %, micro-hardness can be improved up to 50 %. Increasing of micro-hardness can be attributed to: the presence of harder ceramic particulates in the metal matrix, decreased grain size (Fig. 2) and dislocations that are created by ceramic particles in the metal matrix.

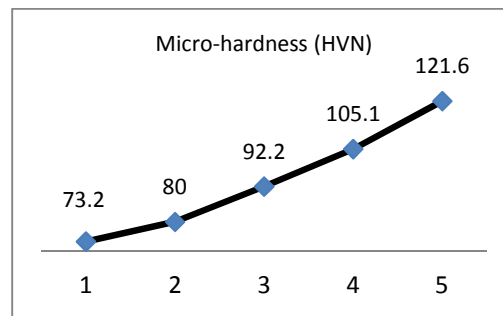


Fig. 4 Effect of zirconia content (wt. %) on the micro-hardness of Cu-ZrO₂ composites

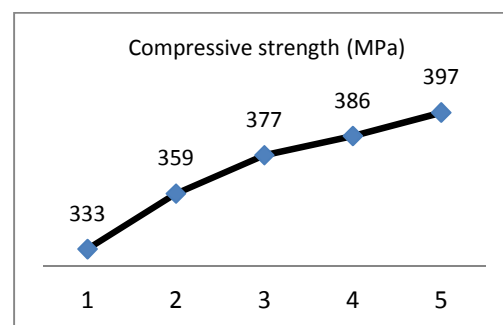


Fig. 5 Effect of zirconia content (wt. %) on the compressive strength of Cu-ZrO₂ composites

Compressive strength values of the copper matrix composites reinforced with yttria-stabilised 1 wt. %, 2 wt. %, 3 wt. %, 4 wt. % and 5 wt. % zirconia (8-YSZ) particles were shown in Fig. 5. Five measurements were performed and averaged to obtain the accurate compressive strength of the specimen. Compressive strength of pure copper was determined as 322 MPa. Strength of the composites increased up to 18 % with increasing ZrO₂ content up to 5 wt. %.

Two strengthening mechanisms were proposed for high hardness and compression strength of the materials, i.e., grain size and dispersion hardening effects [19]. The main strengthening of metallic materials is based on preventing dislocation motion and propagation. Under the applied stress, increasing the amount of grain boundaries acts as obstacle to the dislocation movement and end up with dislocation pile up at the grain boundary region [20]. Again, multi-directional thermal stress induced during processing easily starts multi-gliding system under applied stress so that dislocations were found developing and moving in several directions. These multi-glide planes agglomerate under the applied stress forms grain boundary ledges. As applied load increases, these ledges act as obstacle to dislocation movement resulting in pile-ups. The coupled effect of these two obstacles leads to increase in the strength of the composite [21].

3.4 Electrical conductivity

Fig. 6 illustrates electrical conductivity values of the copper-zirconia composites, varying depending on the rate of reinforcement component. It is obvious that electrical conductivity of the samples decreased with increasing the concentration of ZrO₂. Electrical property of metals basically is influenced by the electron motion in the structure. Increasing of ZrO₂ content in metal matrix composites, structure distorts and causes some impediment for metal electrons. As a result, electrical conductivities of the composites reduced with increasing ZrO₂ percentage. In addition, zirconia particles form a great number of interfaces considered as a possible source of additional electron scatter, which is a significant factor in reducing conductivity. The electrical conductivity of two-phase composites is determined by many factors, such as: 1) the volume fractions and distributions of the constituent phases, 2) the size, shape, orientation, and spacing of the phases, 3) the electrical conductivities of the constituent phases, 4) the preparation method, and 5) interaction between phases.

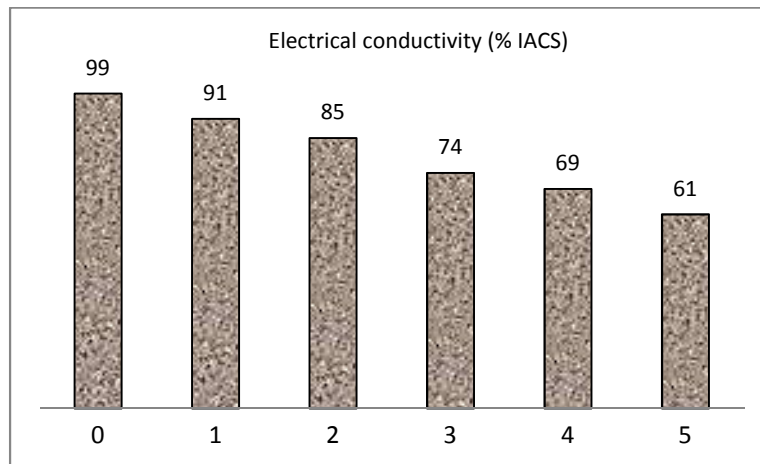


Fig. 6 Electrical conductivity of Cu and Cu-ZrO₂ composites as a function of zirconia content (wt. %)

4. Conclusion

From fabricating of Cu-8 mol % yttria-stabilised 1 wt. %, 2 wt. %, 3 wt. %, 4 wt. % and 5 wt. % zirconia (8-YSZ) composites by powder metallurgy technique, the following results can be concluded:

- the microstructural studies verified that the Cu-ZrO₂ composites involving good reinforcement-matrix interfacial integrity with the least porosity are developed,
- increment in the weight percentage of ZrO₂ reinforcement particles up to 5 wt. % caused the slight reduction in the densification of the composites,
- the results of the electrical test on the Cu-ZrO₂ composites indicated that electrical conductivity reduced gradually with the increase in reinforcement content up to 5 wt. %,
- the highest micro-hardness and compressive strength of the composites is related to the Cu-5 wt. % ZrO₂ which shows increment in the ZrO₂ content up to 5 wt. %, mechanical properties of the metal matrix increase significantly,
- the obtained results show that adding ZrO₂ particles into copper matrix not only enhances the mechanical performance, but also keeps its desirable electrical conductivity, thus application scope of copper and copper-based materials is extended in industry.

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