CONSOLIDATION OF Si_3N_4/Cu COMPOSITE POWDERS FABRICATED BY ELECTROLESS DEPOSITION TECHNIQUE

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Abstract

Copper/Si_3N_4 composites have been produced by powder metallurgy rout. Particle coated with Cu metal is an appropriate solution to enhance the interfacial bonding as well as physical and mechanical properties of the Cu/Si_3N_4composites. Electroless Cu coating of Si_3N_4 particles with different weight % were achieved. The produced Si_3N_4 /Cu composite powders underwent cold compaction and sintering at 850^{o}C. The prepared Si_3N_4 /Cu powders as well as the consolidated composites were investigated by SEM. It was observed that the Si_3N_4 particles were encapsulated by copper metal and the microstructures of the consolidated compacts show homogeneous distribution of Si_3N_4 in the copper matrix. The density and microhardness of the produced Si_3N_4 /Cu composites were measured. The relative green and the sintered densities were decreased but the hardness was increased by increasing the Si_3N_4 weight percent.

1. Introduction

Metal matrix composites offer the possibility to tailor the properties of a metal by adding an appropriate reinforcement phase and to meet the demands in physical and mechanical management. Copper base composites can offer excellent strength properties in several applications and it currently produced by mixing the constituents, cold compaction and/or hot pressing at high temperature and high pressure during sintering is necessary because the compacts expand during sintering leads to form pores and weakening of the bond between the ceramic powder and the metal matrix [1-4]. Copper is one of the most important materials for thermal and electronic applications. It has higher electrical and thermal conductivities and a lower CTE than aluminum. Unfortunately, the thermal expansion of copper is about four times higher than that of the semiconductor silicon. The use of Si_3N_4 particles as reinforcements in copper based composites is considered very attractive to meet the increasing demands for high performance heat sink materials and packages. When the ceramic particles are embedded in a copper matrix, the interface plays a crucial role in determining the thermal conductivity, the CTE and also the mechanical properties of the composite. An ideal interface should provide good adhesion and minimum thermal boundary resistance.

It is known that the bonding between ceramic particles like SiC, diamond, Si_3N_4 and Cu is very weak [5-9]. One of a reasonable solution of this problem is coating of the reinforcement ceramic particles with copper. Electroless coating technique has been widely used to prepare the composite coatings. As the advancement of this technique, electroless nanometer composite coatings, in which ultra fine particles are used as reinforcing phase and metals were deposited on its surfaces.

The purpose of the present work to improve the homogeneity and the distribution of silicon nitride reinforcement particles in copper matrix by using electroless Cu coating process as a kind of nonbonding between Cu and Si_3N_4 particles. Silicon nitride/copper composites with different silicon nitride weight percent were prepared using powder coating technique followed by cold compaction and sintering. The composite powders as well as the sintered materials were underwent investigations by SEM for metallographic characterizations. The mechanical properties were evaluated by measuring the hardness test.

2. Materials

Silicon nitride powder grade of particle size less than 1µm were used as reinforcement. Figure 1a shows the SEM micrograph for the silicon nitride raw materials has cubic particle shape. Highly pure chemicals of Copper (II) sulphate pentahydrate was used as the Cu metal source, potassium-sodium tartarate was used as a complexing agent, (38vol.%) formaldehyde solution was used as a reducing agent.

3. Methods

Previous published work was occurred for determining the optimum chemical composition and conditions of electroless metal depositions on different powder reinforcements [10-14]. The silicon nitride particles were coated with copper by a chemical method. The known weight were dispersed in an aqueous solution which consisted of 70 gm $CuSO_4.5H_2O$, 170 gm $KNaC_4H_4O_6.4H_2O$ and 50 gm NaOH dissolved in one liter of distilled water. A suitable amount of 37 wt.% formaldehyde solution were added. By controlling the concentration, the pH value and the temperature of the solution, the coating process started spontaneously and finished within 30 minutes. The coated powders were washed with distilled water, dried and weight. The above mentioned chemical bath composition was used for preparing six Si_3N_4/Cu composite powders contains 0 (pure copper), 1, 2, 3, 4 and 5 wt.% of Si_3N_4. The Cu-coating was estimated from the differences in weight of Si_3N_4 before and after coating.

The produced Si_3N_4/Cu composite powders underwent cold compaction under pressure of 600 MPa in a uniaxial die of 12 mm diameter. The compacted samples were sintered in a closed tube furnace at 850^{o}C for 90 min.

The sintered samples underwent mounting and grinding using 2000, 4000 grade SiC papers respectively. The grinding samples were polished down to 3 µm diamond baste of 3 µm particle size. The microstructures of the polished composites were investigated by SEM. Extensive metallographic and image analysis investigations were carried out for the consolidated bulk materials to calculate the equivalent reinforcement (Si_3N_4) volume percent for each weight percent.

The density of the bulk materials was measured using water as a floating liquid and the sintered density (ρ) were calculated by the Archimedes method using the following equation;

$$\rho = W_{air} / (W_{air} - W_{water}) \qquad (1)$$

Where, W_{air} and W_{water} are the weight of the specimen in air and water respectively.

The hardness was measured by applying a 100 gm load using the Microhardness-Vickers tester. The test was repeated five times at different points in each sample, and the values were compiled by calculating the average of the reported values of five sets of indentation tests.

4 Results and Discussion

4.1 Powder Coating Process

Figure 1b shows SEM image of the prepared nanosized copper powder by electroless deposition technique. It was observed that the prepared copper powder has 200 nm particle sized with a spherical particle shape. Figure 1c shows SEM image of the coated silicon nitride particles with copper metal. The silicon nitride particles were coated with copper as implanted type and the copper metal covers the surface of the particles by a homogeneous layer.

4.2 Compaction and Sintering Process

The produced Si_3N_4/Cu composite powders were cold compacted at 600 MPa in a uniaxial die using hydraulic pressing machine. The compacts were sintered at 850^{o}C. Figure 2 shows the dilatometer shrinkage curve of the 5wt.%Si_3N_4/Cu composites. Our finding indicated that Cu-coated powders sinter like pure copper due to the existence of Cu/Cu contacts. Accordingly, a rapid rate of shrinkage is observed. The sintering mechanism of this system is mainly by grain shape accommodation [15].

4.3 Microstructure Investigations and Density Measurements

Figure 3 shows SEM micrographs of the prepared 1wt.% Si_3N_4/Cu composite and 5wt.% Si_3N_4/Cu composite. It was observed from the microstructure that, the silicon nitride particles are homogenously distributed in the copper matrix and a good adhesion between Si_3N_4 and Cu-matrix is observed.

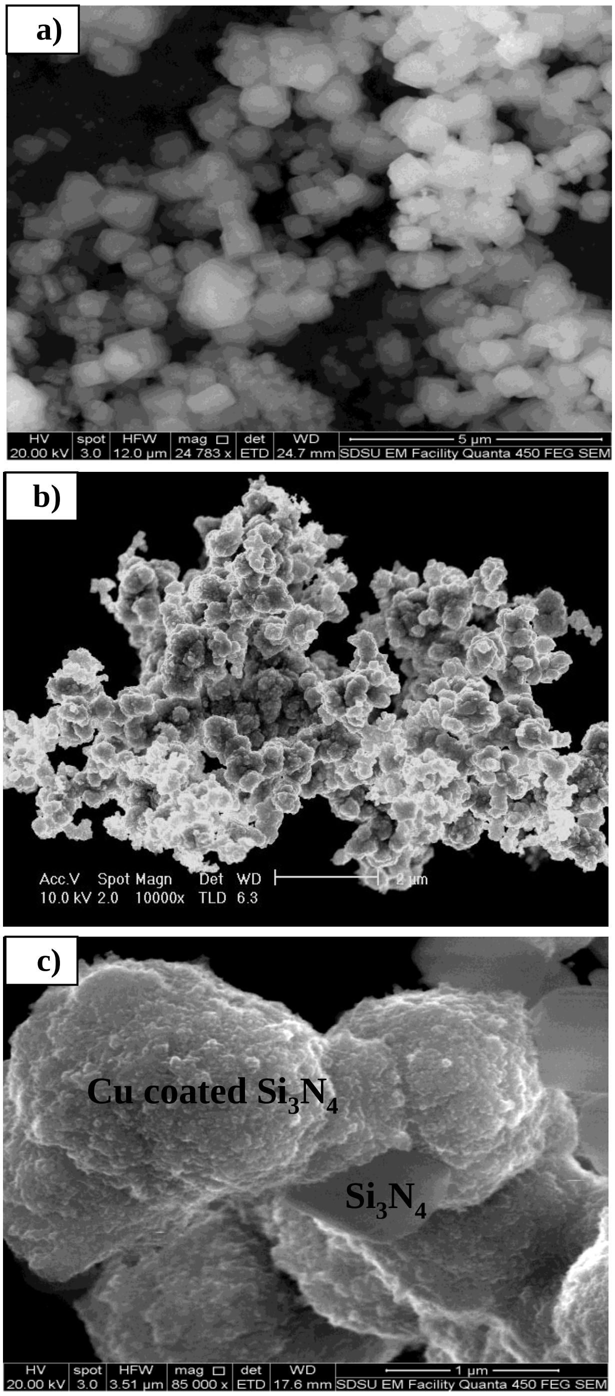

Figure 1 SEM Images of a) the investigated Si_3N_4 particles, b) the prepared copper powder and c) the copper coated Si_3N_4 composite powders by electroless deposition technique.

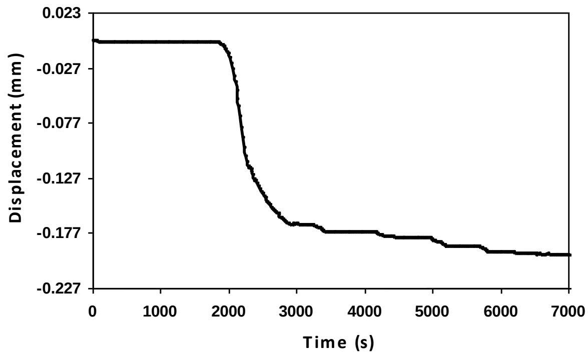

Figure 2 Dimensional changes of 5wt. % Si_3N_4/Cu composite as a function of sintering time.

Figure 4 shows the relationship between the dispersed reinforcements phase (Si_3N_4) volume fractions on a two-dimensional cross-section measured by means of an image analysis and the Si_3N_4 weight %. It was deduced that by increase the weight percent of the reinforcement phase (Si_3N_4) the volume fraction increased.

The theoretical densities of the produced composites were calculated by using the rule of mixtures (equation 2) which is a method of approach to approximate estimation of composite material properties, based on an assumption that a composite property is the volume weighed average of the phases (matrix and dispersed phase) properties.

$$\mathbf{d_c = d_m \cdot V_m + d_f \cdot V_f} \qquad (2)$$

Where $\mathbf{d_c}$, $\mathbf{d_m}$, $\mathbf{d_f}$ densities of the composite, matrix and dispersed phase respectively and $\mathbf{V_m}$, $\mathbf{V_f}$ volume fraction of the matrix and dispersed phase respectively.

The relative density (actual density by a theoretical one) of the investigated sintered composites were measured using a method based on Archimedes' rule. Figure 5 shows the relative sintered densities in comparing with the relative green densities of the prepared Si_3N_4/Cu sintered materials with different weight percent of Si_3N_4. It was observed that by increasing the weight percent of Si_3N_4 the green and sintered densities decreased.

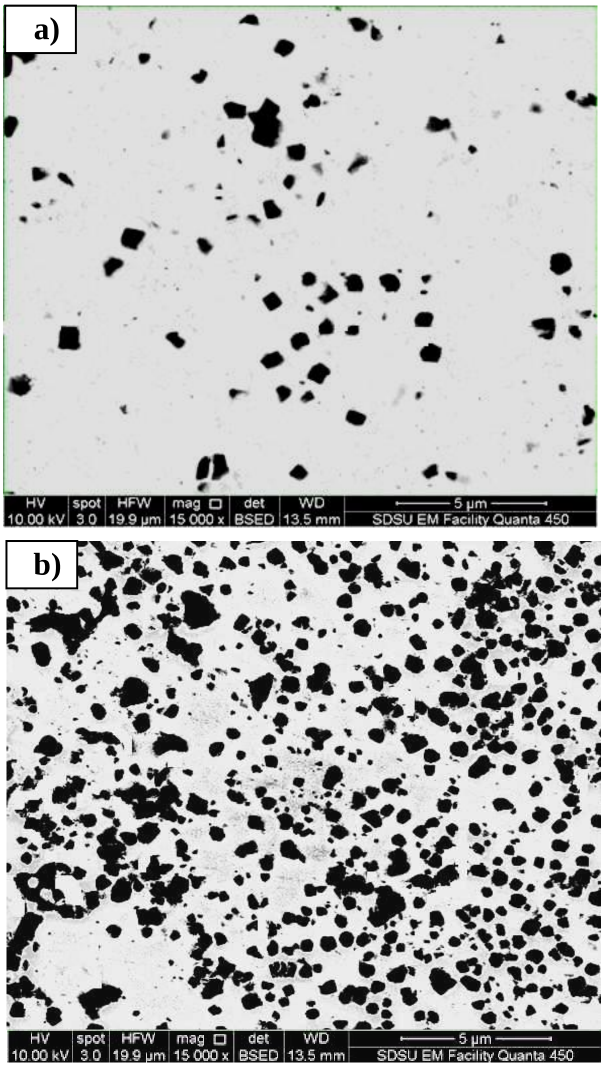

Figure 3 SEM micrographs of a) 1wt. % Si_3N_4/Cu composite and b) 5wt. % Si_3N_4/Cu composite fabricated by cold compaction at 600 MPa followed by sintering at 850°C in Argon atmosphere.

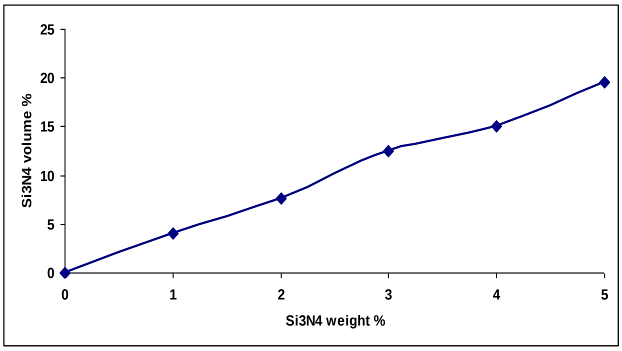

Figure 4 The relationship between Si_3N_4 volume fraction and the Si_3N_4 weight % measured by image analysis.

Figure 6a shows SEM micrograph with high magnification of the interface between the dispersed reinforcement phase (Si_3N_4) and the copper matrix. It was observed that the dispersed phase (Si_3N_4) interact with the matrix phase (Cu) due to the dissolution of the silicon metal in the matrix phase. And it can be determined by EDAX analysis of the interface between Si_3N_4 and copper matrix as shown in Figure 6b. It was expected due to the dissolution of silicon content from the Si_3N_4 dispersed phase in the copper matrix and formation of the solid solution between silicon and copper.

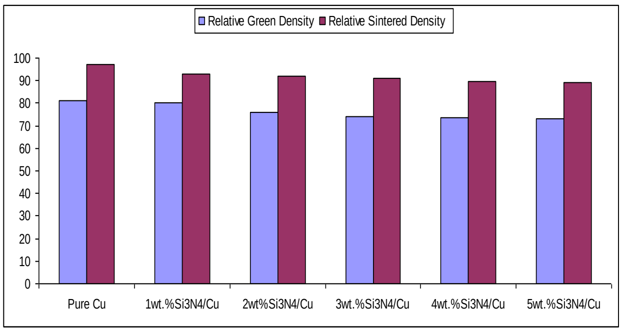

Figure 5 The relative green and sintered densities of the produced Si_3N_4/Cu composites.

4.4 Hardness Measurements

The mechanical properties of the prepared Si_3N_4/Cu composites was evaluated by measuring the hardness test. It was observed from the results of the hardness values in Figure 7 that by increasing the weight percent of the Si_3N_4 hard phase the hardness of the composite increased. It was due to the contribution of the Si_3N_4 hard phase in the copper matrix and the tight adhesion between the Si_3N_4 reinforcement particles and Cu-matrix as well as to the higher relative density and low porosity of the produced composites. However the hardness values are not increased so much by increasing the Si_3N_4 hard phase. This result can be discussed due to the copper matrix effect. By increasing the matrix content which has lower hardness than the reinforcement phase (Si_3N_4), the thickness of the matrix phase around the reinforcement phase was increased and the total composite hardness of the cemented carbide increased by moderate extent due to the contribution of the low hardness for the copper matrix phase [16].

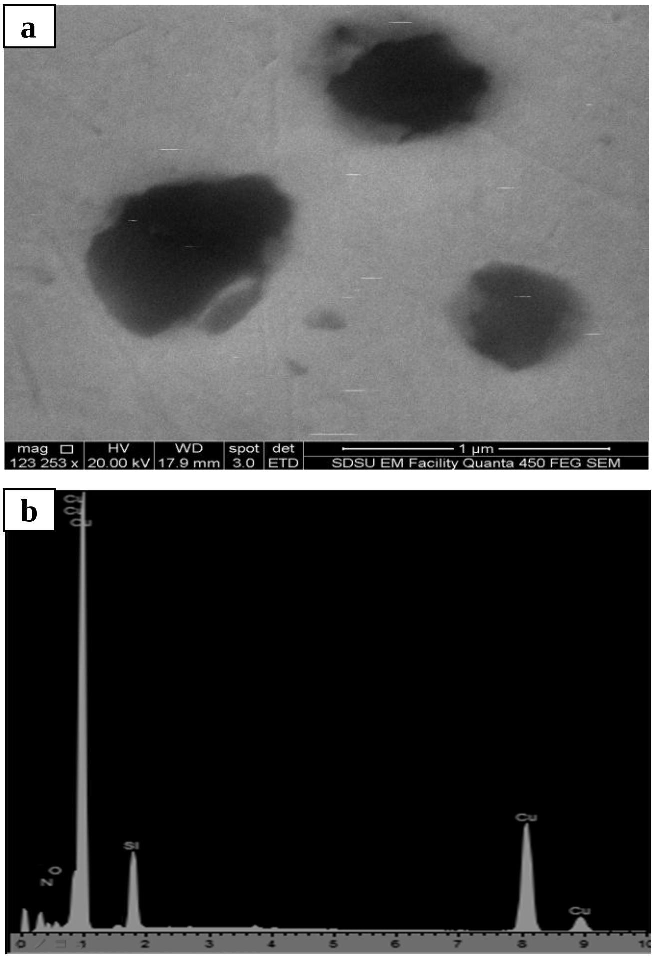

Figure 6 a) SEM image with high magnification of Si_3N_4/Cu composite and b) EDAX semi-quantitative analysis of Si_3N_4-Cu interface.

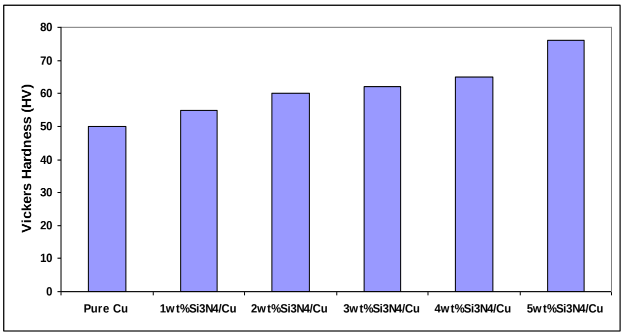

Figure 7 The effect of the Si_3N_4 weight percent on the hardness of the produced Si_3N_4/Cu composites.

5. Conclusions

1. Uniform coating of copper can be formed on the surface of the Si_3N_4 powders by electroless copper deposition.
2. The copper composites made from coated type Si_3N_4/Cu powders shrink during sintering.
3. The volume fraction of the dispersed phase increased by increasing the weight percent of the Si_3N_4 reinforcement phase.
4. A solid solution formed in the interface between the dispersed phase (Si_3N_4) and the copper matrix due to the formation of the copper-silicon solid solution.
5. The relative green density as well as the sintered density decreased by increasing the reinforcement phase (Si_3N_4) in the copper matrix.
6. The hardness of the Si_3N_4/Cu composites increased by increasing the reinforcement Si_3N_4 phase.

5. References

[1] S. Moustafa, W. Daoush, E. El- Shereafy, Canadian Metall., 40, 4 (2001) 533.
[2] J. Groza, J. Gibeling, Mater. Sci Eng.A, 171 (1993) 115.
[3] S. Ho, E. Lavernia, Metall.Trans., 27A(1996) 3241.
[4] A. Yeoh, C. Persad, Z.Eliezer, Scripta Mater., 37, 3(1997) 271.
[5] T. Weißg¨arber, G. Lefranc, J. Schulz-Harder, H. Meyer, O. St¨ocker (Eds.), Advances in Powder Metallurgy & Particulate Materials, part 6, Metal Powder Industries Federation, Princeton, NJ, 2003, pp. 33–40.
[6] G. Sundberg, Adv. Microelectron. Nov.Dec. (2004) 8.
[7] G. Sundberg, P. Paul, Ch. Sung, Th. Vasilos, J. Mater. Sci. 40 (2005) 3383.
[8] Q. Sun, O. Inal, Mater. Sci. Res. B 41 (1996) 261.
[9] A. Robin, J. Pinheiro de Santana, A. Sartori, J Appl. Electrochem. 40(2010) 507.
[10] S. Moustafa, S. El-Badry, A. Sanad, B. Kieback, Wear, 253, 7(2002) .699.
[11] W. Daoush, S. Moustafa, S. Kayetbay, Powder Metall. Prog., 6(2006) 164.
[12] S. Moustafa, W. Daoush, Mater. Processing Tec. 181(2007)59.
[13] W. Daoush, S. Moustafa, Met. Powder Rep., 62, 1(2007) 30.
[14] W. Daoush, B. Lim, C. Mo, D. Nam, S. Hong, J. of Mat. Sci. & Engine. A, 213-214 (2009)247.
[15] J. Johnson, R. German, Metall. Trans., 23A(1996) 1455.
[16] W. Daoush, K. Lee, H. Park, S. Hong, Int. J. of Refractory Metals & Hard Materials 27 (2009) 83.