Fabrication and characterization of Copper/Silicon Nitride composites

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Abstract. Copper/silicon nitride (Cu/Si_3N_4) composites are fabricated by powder technology process. Copper is used as metal matrix and very fine Si_3N_4 particles (less than 1 micron) as reinforcement material. The investigated powder were used to prepare homogenous (Cu/Si_3N_4) composite mixtures with different Si_3N_4 weight percentage (2, 4, 6, 8 and10). The produced mixtures were cold pressed and sintered at different temperatures (850, 950, 1000, 1050℃). The microstructure and the chemical composition of the produced Cu/Si_3N_4 composites were investigated by (SEM) and XRD. It was observed that the Si_3N_4 particles were homogeneously distributed in the Cu matrix. The density, electrical conductivity and coefficient of thermal expansion of the produced Cu/Si_3N_4 composites were measured. The relative green density, sintered density, electrical conductivity as well as coefficient of thermal expansion were decreased by increasing the reinforcement phase (Si_3N_4) content in the copper matrix. It is also founded that the sintered density and electrical conductivity of the Cu/Si_3N_4 composites were increased by increase the sintering temperature.

Keywords: Copper; Silicon Nitrides; powder metallurgy; sintering; electrical conductivity; coefficient of thermal expansion

1. Introduction

Heat sinks are the most common and cost-effective hardware employed for the thermal management of microelectronic circuits and microelectro-mechanical systems (MEMS) devices. The function of heat sinks is the efficiently transferring thermal energy (heat) from an object at a relatively high temperature to a second object at a lower temperature with a much greater heat capacity (Ashby and Jones 1996). This quickly rapid transfer of thermal energy brings the first object into thermal equilibrium with the second and lowering the temperature of the first object, fulfilling the heat sink's role as a cooling device as described by Gilleo and Dennis (2005). Heat sinks find wide applications in microelectronics and have become almost essential to modern

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integrated circuits like microprocessors, digital signal processors (DSP), graphics processing units (Madou 2002). Integrated circuits such as computer central processing units (CPUs) often produce a lot of heat which should be dissipated as quickly as possible since failure of integrated circuits increases with their working temperature. Since integrated circuits often work in a Boolean manner, switching on and off, thermal loads are often transient state. This gives rise to thermal fatigue which also reduces the lifetime of integrated circuits. Therefore, the design of heat sinks is very important. The ideal material for heat sink applications combines a high thermal conductivity with a high heat capacity to absorb thermal spikes. Metals have a high thermal conductivity and hence are commonly used as heat sinks, but their heat capacity is low. Therefore, recently new heat sinks were designed which combine metals with phase change materials (PCMs) (Gauché P. and Xu 2000). Heat dissipating systems like micro- and power electronic devices, LEDs and CPUs require an efficient heat removal to avoid possible damage or de-lamination due to thermal stresses. Therefore effective heat removal is in need for materials with high thermal conductivity and low coefficient of thermal expansion tailored to the substrates. Composites containing fillers with highest intrinsic thermal conductivity and concomitantly a very low coefficient of thermal expansion CTE could fulfil the requirements as described by Baughman *et al*. (2002).

Copper is one of the most important materials for thermal and electronic applications. Compared with Al, Cu has higher electrical and thermal conductivities and a lower CTE. However, the thermal expansion of Cu is high (200-300W/mK) with a CTE of 4.5×10^{-6} K^{-1}. It is available with low price and good machinability. Diamond has exceptional thermal properties with a very low CTE of about 1.0×10^{-6} K^{-1}. The thermal conductivity of synthetic diamonds is in the range 1500-2000 W/mK. Therefore, the use of SiC or diamond particles as reinforcement in copper based composites is considered very attractive to meet the increasing demands for high performance of heat sink materials. When SiC or diamond particles are embedded in a copper matrix, the interface plays a crucial role in determining thermal conductivity, CTE and the mechanical properties of the composite. An ideal interface should provide good adhesion and minimum thermal boundary resistance. Silicon carbide reinforced copper composite is the subject of several investigations (Weißgaerber *et al*. 2003, Sundberg 2004). Many different particles such as hard oxides Al_2O_3 (Terzieva *et al*. 2000, Allahkaram *et al*. 2011), SiO_2 (Li *et al*. 2009), TiO_2 (Medeline *et al*. 2004, Ramalingam *et al*. 2009), ZrO_2 (Benea *et al*. 2000), CeO_2 (Mangam *et al*. 2010), carbides SiC (Zhu *et al*. 2007, Lekka *et al*. 2009), and WC (Medeliene and Kosenko 2008), nitrides Si_3N_4 (Robin *et al*. 2011), polymeric materials, graphite (Stankovic and Gojo 1996), and multi-wall carbon nanotubes (Arai *et al*. 2010) are used with copper to enhance its physical, chemical and mechanical properties.

Silicon nitride (Si_3N_4) and silicon oxy-nitride (Si_2N_2O) are strong candidates for producing porous materials because of their attractive properties. The former has an exceptional wear, corrosion resistance and high-temperature mechanical properties. Due to its low coefficient of thermal expansion and high thermal conductivity, Si_3N_4 has excellent thermal shock resistance [28]. Silicon nitride is most promising engineering material for high temperature applications, due to its excellent thermal shock resistance, good mechanical properties, and chemical stability at both room and high temperatures (Jang et al. 1996).

The aim of present work is to improve the distribution of Si_3N_4 reinforcement particles in copper matrix. The effect of addition of different Si_3N_4 particles content, and the change in sintering temperature on the density, thermal and electrical properties of Cu/Si_3N_4 composites were studied.
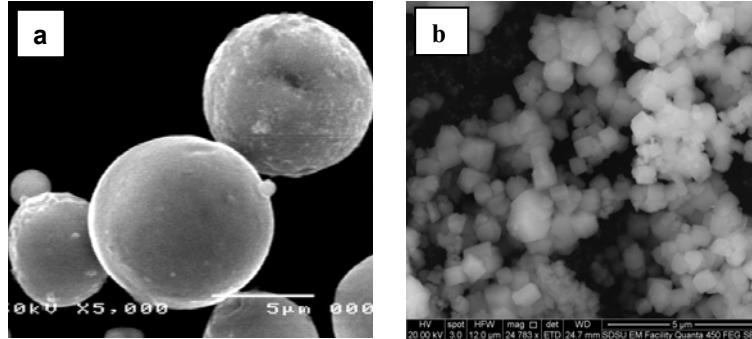
Fig. 1 SEM Images of: (a) Water atomized Cu powder, and (b) Si_3N_4 particles

2. Materials

Powder of Cu are prepared by the atomization technique at the Central Metallurgical Research and Development Institute, Cairo, Egypt using water atomizer model PSI; UK. Copper powders are prepared by induction melting in silicon carbide crucibles in air. The Cu ingot is superheated to1300°C. After complete melting bottom pouring is carried out through a ceramic melt delivery nozzle of 6 mm diameter into a confined water atomizer operating at a pressure of 20 MPa. The high pressure water jets were directed against the molten stream. The melt flow rate, estimated from the operating time and weight of the atomized melt, is about 4 kg/min. The water flow rate, calculated from the water consumption rate, was about 200 l/min. Sieved powders with a specific size range of 100 μm are used for present investigation. Silicon nitride powder with an average particle size of 500 nm~1 micron is purchased from (ILGIN Co. LTD- South Korea). Fig. 1 shows SEM micrographs of the investigated copper and silicon nitride powders.

3. Methods

Six groups of Cu and Si_3N_4 powder mixtures are prepared consists of 0.0, 2.0, 4.0, 6.0, 8.0, and 10.0 wt% Si_3N_4 powder and the rest is Cu powder. Each group is subdivided into four quantities of mixed powders, from which test specimens are prepared and cold compacted at 400 MPa in a uniaxial die 8.85mm long and 7.45mm diameter using a hydraulic press. Compacted samples are then sintered at 850, 950, 1000 or 1050°C under controlled atmosphere ($C/CO_2/CO$ mixture) for 120 min. Sintered samples are cross-sectioned and mounted in a cold resin. The mounted specimens are grounded using SiC papers grit 1000, 1200, 2000 followed by polishing, then investigated by SEM.

The theoretical densities of the produced composites were calculated by using the rule of mixtures using Eq. (1) which is a method of approach to approximate estimation of composite material properties

$$d_c = d_m . V_m + d_f . V_f \qquad (1)$$

Where d_c, d_m, d_f densities of the composite, matrix and dispersed phase respectively and V_m, V_f volume fraction of the matrix and dispersed phase respectively.

The density of the bulk materials is measured using water as a floating liquid and the sintered

density ρ is calculated by Archimedes method using Eq. (2) as follows

$$\rho = W_{air}/(W_{air} - W_{water})$$ (2)

where, W_{air} and W_{water} are the weight of specimen in air and in water, respectively. The relative density ρ $_{relative}$ is estimated by calculating the ratio of actual composite density ρ_r to the theoretical density ρ $_{th}$ by using Eq. (3) follows equation

$$\rho_{relative} = \rho_r/\rho_{th}$$ (3)

The coefficient of thermal expansion is measured using a dilatometer on each sample at 50, 100, 150, 200, 250, 300 and 350°C respectively for 15 min and 17°C/min heating rate. The linear CTE is measured in accordance with the Eq. (4)

$$\alpha = (1/\Delta T)\varepsilon = (1/L_o)(\Delta L/\Delta T)$$ (4)

where, α is the coefficient of thermal expansion, $\Delta T = T - T_o$ is the temperature interval, and $T_o = 293K$, $\varepsilon = \Delta L/L_o$ is the relative length change, and ΔL is the expansion, $\Delta L = L - L_o$, and L_o is the original length.

The theoretical electrical conductivity of the produced composites is calculated by using the rule of mixtures by using Eq. (5) as follows

$$E_c = P_m \cdot V_m + P_f \cdot V_f$$ (5)

The electrical resistivity of sintered material is measured by a digital Multi-meter GDM-6145 device. The resistivity ρ is determined using Eq (6), while the electrical conductivity σ is determined by Ohm's law as follows

$$\rho = (R. A)/L$$ (6)

Where, R is the resistance in $\mu \Omega$, L is the length measured in cm, A is the cross section area in cm^2, ρ is the resistivity in $\mu \Omega$ cm and the electrical conductivity σ is the reciprocal of the electrical resistivity σ=1/ρ.

4. Results and discussion

4.1 Microstructure investigations and density measurements

Fig. 2 shows the SEM images of the prepared Si_3N_4/Cu composites at 1050°C with 2, 4, 6, 8 and 10 wt. % Si_3N_4 content. It was observed from the microstructure that the Si_3N_4 reinforcement particles are distributed into Cu matrix. It was also observed that by increasing the silicon nitride content the particles were agglomerated on the grain boundaries specially in case of 4 wt. % Si_3N_4/Cu as compared to 2 wt. %. Some of the Si_3N_4 particles are distributed in the copper matrix homogeneously and the remained is distributed on the grain boundaries. It may be due to two reasons. The first is the low wettability of silicon nitride and the copper matrix. The second is the high volume fraction of the ultrafine silicon nitride particles in the copper matrix.

Fig. 3 shows the relationship between volume fractions of the dispersed phase (Si_3N_4) determined by image analysis and its weight percent on a two-dimensional cross-section. As expected, by increasing the weight percent of Si_3N_4 linearly increases its volume fraction. The volume fraction for each composition is used to calculate the physical and mechanical properties

using the rule of mixture.

The theoretical density of the produced composites is calculated by using the rule of mixtures in Eq. (7), which is based on an assumption that, a composite property is the volume weighed average of the phases (matrix and dispersed phase) properties

$$d_c = d_m.V_m + d_f.V_f \tag{7}$$

Where, d_c, d_m and d_f are the densities of the composite, matrix and dispersed phase, respectively. Also, V_m and V_f are the volume fraction of the matrix and dispersed phase, respectively.
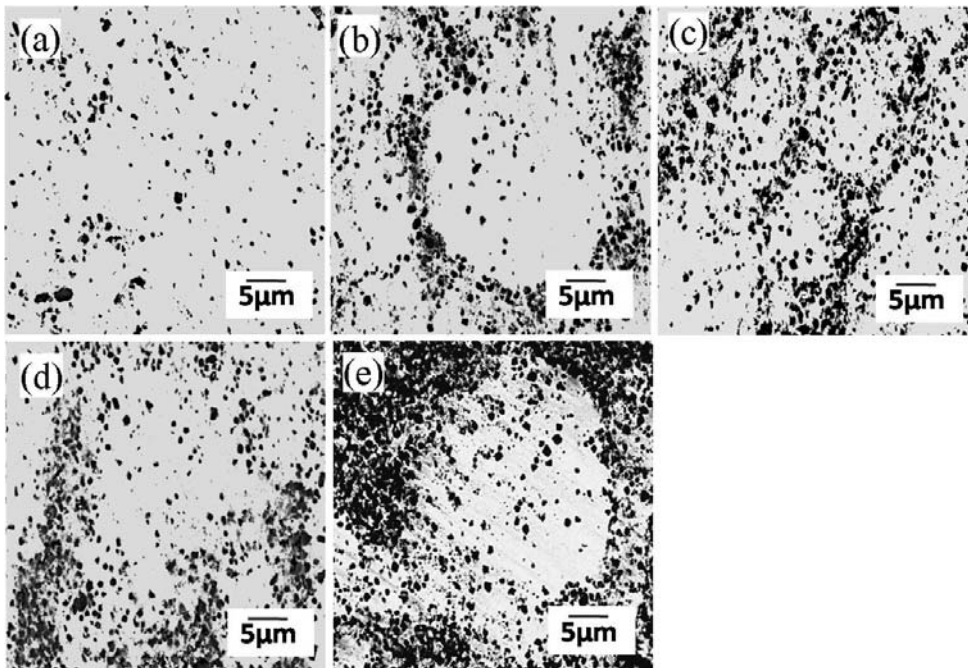
Fig. 2 SEM micrographs of a) 2 wt. % Si_3N_4/Cu, b) 4 wt. % Si_3N_4/Cu, c) 6 wt. % Si_3N_4/Cu, d) 8 wt. % Si_3N_4/Cu and e) 10 wt. % Si_3N_4/Cu composites
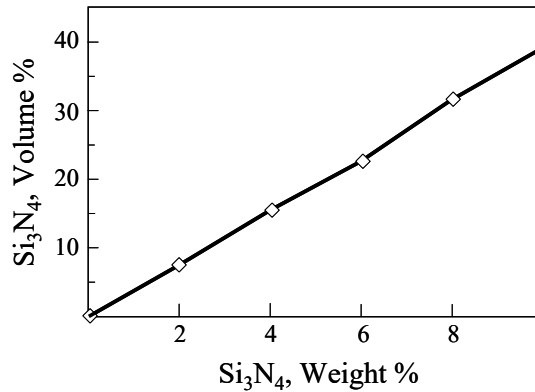

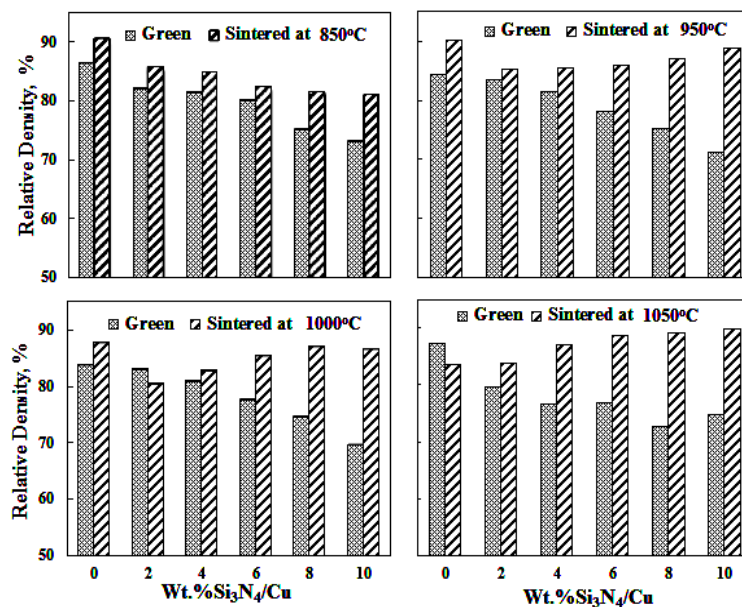Fig. 3 The relationship between Si_3N_4 volume % and the Si_3N_4 weight %

Fig. 4 The relative green and sintered density of the prepared Si_3N_4/Cu composites

The relative densities (measured/theoretical) of the produced Si_3N_4/Cu composites were calculated using the measured Archimedes' densities and the theoretical densities of copper and silicon nitride. Fig. 4 shows the relative sintered densities in comparison with the relative green densities of the produced Si_3N_4/Cu composites with different weight percent of Si_3N_4. It was observed that, by increasing Si_3N_4 content the relative green density is decreased and the density of sintered specimens at 850°C were decreased. On the other hand, by increasing the Si_3N_4 content the sintered density of specimens sintered at 950°C, 1000°C and 1050°C were increased. It may be due to the lower sintering temperature of 850°C but in case of 950°C, 1000°C and 1050°C the sintering temperature is enough to consolidate the compacts. However in some samples the sintering density was decreased by increasing the sintering temperature too high nearby the melting temperature of copper. As we can see in 2wt% Si_3N_4/Cu sintered at 1000°C and Cu sample sintered at 1050°C. It is maybe due to increase the sintering temperature nearby the melting point of copper can cause partially melting of the copper metal matrix in some samples and swelling in the sintered samples were appeared as well as the sintered density is lower than the green density.

4.2 X-Ray Diffraction Analysis

Fig. 5 shows XRD spectrum of four samples (10 wt. %Si_3N_4/Cu) sintered at 850, 950, 1000 and 1050°C for 2h. XRD spectrum shows presence of strong peak of Cu.

4.3 Coefficient of Thermal Expansion

Fig. 6 shows the influence of the Si_3N_4 content in the prepared Si_3N_4/Cu composites on the coefficient of thermal expansion (CTE) with the variation of the temperature. It was observed from
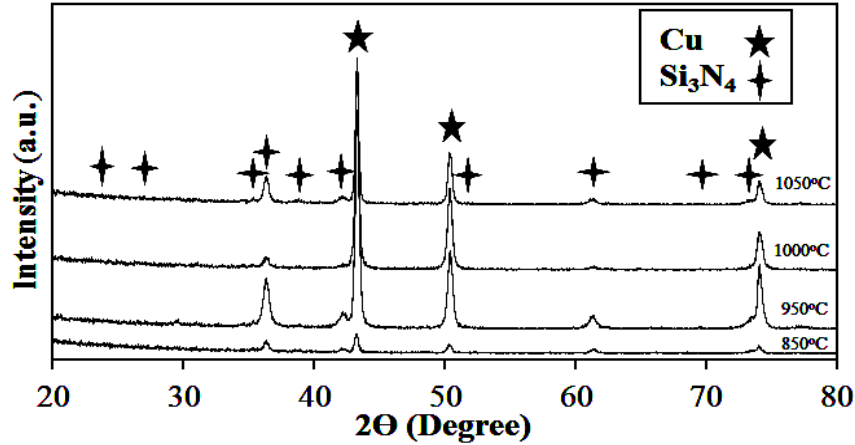
Fig. 5 XRD spectra at different sintering temperatures of 10 wt. % Si_3N_4/Cu matrix composites

the results that, the CTE increases by increasing the temperature, and decreases with the increase of Si_3N_4 reinforcement. Also, the thermal expansion of copper is about four times higher than that of the semiconductor silicon, and CTE of Cu can be tailored for a specific application by using reinforcement with a lower CTE (Massalski et al. 1995). Moreover, silicon nitride (Si_3N_4) is of low thermal expansion coefficient and high thermal conductivity, and has excellent thermal shock resistance (Lee and Rainforth 1994).
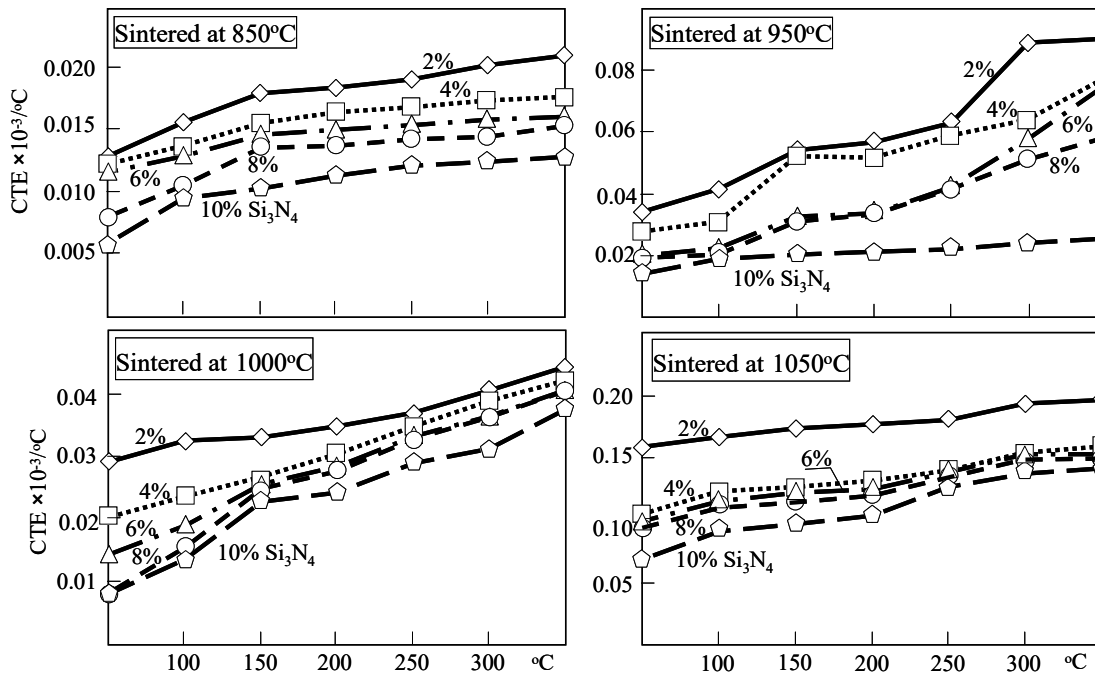
Fig. 6 the effect of Si_3N_4/Cu composition on the CTE at different temperatures

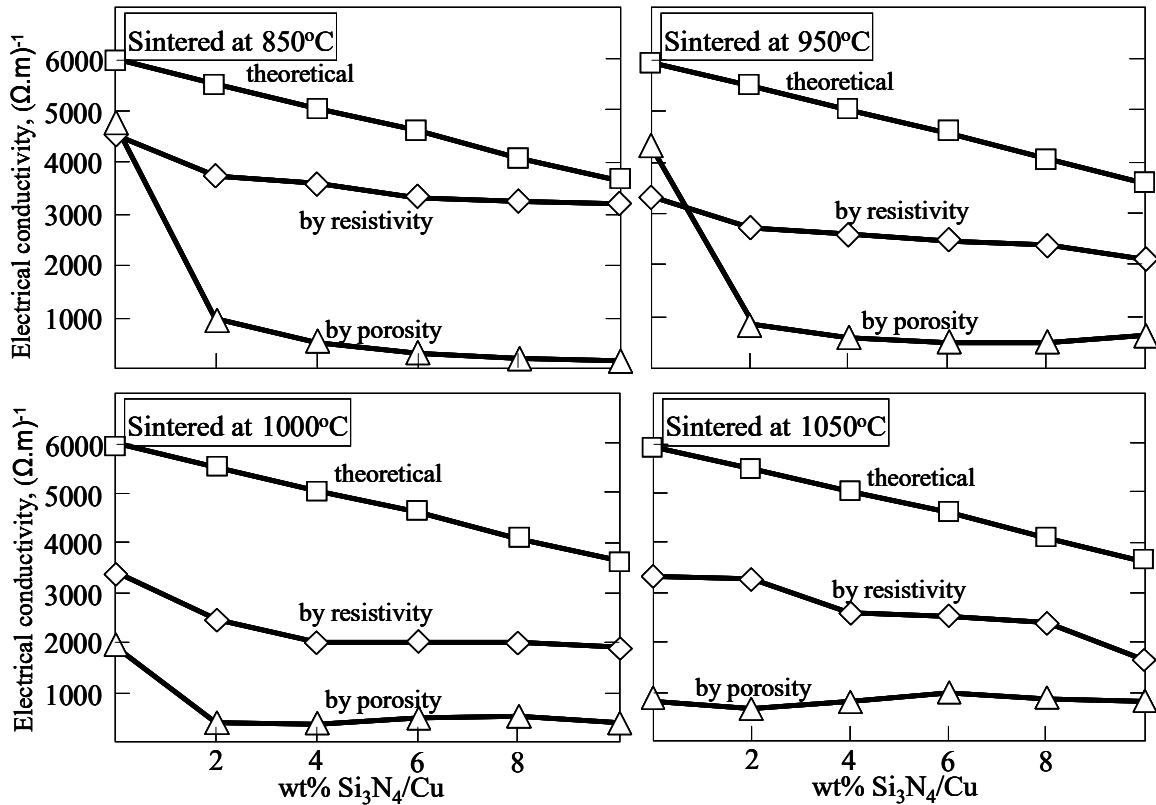Fig. 7 The effect of Si$_3$N$_4$/Cu composition on the Electrical conductivity.

4.4 Electrical conductivity

Fig. 7 shows the effect of Si$_3$N$_4$ content on the electrical conductivity of Si$_3$N$_4$/Cu composites. It is obvious that, the electrical conductivity decreases with increasing Si$_3$N$_4$ content. Electrical conductivity of metals is basically influenced by electron motion in the structure. Increasing Si$_3$N$_4$ content in metal matrix composites causes some impediment to free electron motion. As a result, electrical conductivity of composites is reduced with increasing Si$_3$N$_4$ content.

Besides, Electrical conductivity is directly affected by porosity; the greater the void content, the lower is the electrical conductivity. Since the conductivity of a pore is zero, the relation between porosity and conductivity is described by Montes *et al.* (2003) as given by Eq. (8)

$$\rho_E = \rho_o / [1 - (\theta / \theta_T)]^2 \tag{8}$$

where, ρ_E=Thermal or electrical conductivity of actual material, ρ_o=Intrinsic thermal or electrical conductivity of the massive metal, θ=porosity and θ_T=Tap density.

5. Conclusions

Copper/silicon nitride (Cu/Si$_3$N$_4$) composites are fabricated by powder technology process. The

physical and mechanical properties were measured to evaluate the produced composites in this study.

• The relative green density as well as density of specimens sintered at 850°C decrease and the density of specimens sintered at (950°C, 1000°C, 1050°C) increases by increasing the reinforcement phase (Si_3N_4) in the copper matrix.

• The hardness of Si_3N_4/Cu composites increases with increasing the Si_3N_4 phase content.

• The coefficient of thermal expansion was increased with temperature, and decreases by increasing the Si_3N_4 content.

• However the electrical conductivity of Si_3N_4/Cu composites decreases by increasing the Si_3N_4 content.

Acknowledgements

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