Research Article

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Electrical conductivity anisotropy of copper matrix composites reinforced with SiC whiskers

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Abstract: Copper matrix composites reinforced with 1, 3, 5, 7 vol.% Cu-coated SiC whiskers of consistent orientation (SiC_w/Cu) were prepared by powder metallurgy and hot extrusion. The microstructure of composites was investigated by scanning electron microscopy. The SiC whiskers were arranged along the direction of hot extrusion and distributed uniformly. The composites were fabricated into specimens with different whisker orientations, and their electrical conductivity was tested. The effects of SiC whiskers orientation and content on the electrical conductivity of composites were investigated through experiment. Results show that the SiC whiskers content was the major factor affecting the electrical conductivity of the composites. With increasing SiC whisker orientations angel, the electrical conductivity of composites is improved. The electrical conductivity model has been established by taking into account the SiC whiskers content, whisker orientation and microstructure parameters, and the results were in good agreement with experimental data.

Keywords: Copper matrix composites; SiC whiskers; Electrical conductivity anisotropy; Electrical conductivity model

1 Introduction

Copper matrix composites have high strength at the room, and the electrical and thermal conductivity close

Graphical abstract: Copper matrix composites reinforced with SiC whiskers of consistent orientation were prepared. The orientation of SiC whiskers changes from 0° to 90°, resulting in electrical conductivity anisotropy of composites.

to pure copper, which are widely used as high voltage dynamic/static contact, electromagnetic gun orbit, electric resistance welding electrodes, etc. [1–5]. Ceramic particles and whiskers with excellent thermal stability and strength are used for reinforcing copper matrix composites [6–8]. However, ceramic particles can improve the strength while reduce the plasticity of metal matrix composites [9]; Whiskers can enhance plasticity of copper matrix composites, especially at high temperatures [10], which is beneficial to the durability-damage tolerance design of composites [11]. This is due to the fact that whisker has less defects (voids, dislocations, grain boundaries, etc.), so that their strength are close to the theoretical value of intact crystals. Furthermore, whisker has high aspect ratio characteristics, which can effectively enhance the strength of metal matrix composite [12–14].

At present, most of the reported literature on whisker/fiber reinforced composites is about the effect of whisker/fiber types and interface optimization on its mechanical properties and conductivity [15–18]. Results show that the strength and ductility of composites are greatly improved with SiC whiskers of consistent orientation [19]. The surface modifying can evidently enhance strength

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Figure 1: SEM morphology of (a) Cu power, (b) uncoated SiC whiskers, (c) Cu-coated SiC whiskers, (d) XRD diffraction patterns of SiC_w coated before and after

and conductivity of copper matrix composites reinforced with whiskers [12, 20]. In fact, the orientation of whiskers also can affect the electrical conductivity greatly. Klinski-Wetzel had found that the Cr particles (aspect ratio > 1) alignment leads to the electrical conductivity anisotropy of Cu-Cr composites [4]. It was further supported by Yang [21] with finding that the electrical conductivity parallel along the CNTs length direction was higher than that of vertical to CNTs length direction. However, there is few literatures reported on electrical conductivity of copper matrix composite reinforce with different orientation whiskers. Besides, the established models on electrical conductivity of copper matrix composite are mostly based on various simplifying assumptions, which just consider parameters of volume fraction, electrical conductivity of each phase [22, 23]. And electrical conductivity models are applicable to isotropic composites. Therefore, value of prediction is greatly deviated from the experimental data. It is necessary to establish an anisotropic conductivity model for copper matrix composites.

In the paper, we investigated the effects of different SiC whiskers orientation on the microstructure, electrical conductivity of SiC_w/Cu composites reinforced with SiC

whiskers. SiC whiskers consistent orientation of SiC_w/Cu composites was fabricated by powder metallurgy and hot extrusion. The composites were fabricated into specimens with different whisker orientations, and their electrical conductivity was tested. Considering the effects of orientation and volume fraction of SiC whiskers on the electrical conductivity, a model for predicting the electrical conductivity of SiC_w/Cu composites was established. The results show that electrical conductivity of SiC_w/Cu composites can be predicted by the model.

2 Experiment

2.1 Raw powders

Commercially available SiC whiskers (purity 99.0 wt. %, average diameter and length is 0.5 μm, 10 μm, respectively) and Cu powder (purity 99.8 wt. %, with a mean size of 75 μm). The SEM morphologies of SiC_w and Cu powder are shown in Figure 1.

Figure 2: Schematic diagram: (a) the extrusion process experimental set-up, (b) extruded billet and samples, (c) electrical conductivity measurement method

Table 1: Electroless deposition chemical composition

Chemical composition	Quantity
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (g/L)	12
$\text{C}_4\text{O}_6\text{H}_4\text{KNa}$ (g/L)	35
Formaldehyde (ml/L)	18
Activated SiC_w (g/L)	4
pH	11.5-12.5
Temperature ($^\circ\text{C}$)	55-60

2.2 Preparation of Cu coated SiC whiskers and composite powders

The Cu coated SiC whiskers were fabricated using an electroless deposition (ED) method [24]. Table 1 shows electroless deposition chemical composition. Firstly, the cleaned SiC whiskers were put into sensitizing solution (SnCl_2 20 g/L, HCl 25 mL/L) with electromagnetic stirring for 30 min. And secondly, the sensitized SiC whiskers were added into the Tollens' reagent with electromagnetic stirring for 30 min. After then, the activated SiC whiskers were added into the ED bath with stirring. The formaldehyde and NaOH were added into the solution, and the pH of solution was maintained at 11.5-12.5 during the reaction. After the deposition was completed, the Cu-coated SiC_w were washed to neutral with deionized water as shown in Figure 1c. The improvement of the wettability and density of SiC whiskers were beneficial to the homogeneously dispersion of SiC whiskers.

In order to obtain mixed powders with different SiC whiskers contents, the powders were placed into an ethanol solution with heating and stirring. Then, the suspensions become slurry, which dried in vacuum dryer for 4 h at 60°C . Mixing was carried out on a QQM/B light ball

mill for 24 h and a ball-to-batch ratio of 1:1. The mixed powders with SiC whiskers content of 1, 3, 5, 7 vol.% were prepared, respectively.

2.3 Fabrication of SiC_w/Cu composites

The mixed powders were compacted by cold isostatic press at the pressure of 210 MPa, the sample was $\varnothing 50$ mm $\times$ 50 mm block. After then, the samples were sintered at 950°C for 90 minutes under hydrogen atmosphere in the tube furnace, and frozen to room temperature in the furnace. The sintered samples were hot extruded into $\varnothing 14.5$ mm rods at 900°C .

2.4 Characterization tests

The density of SiC_w/Cu composites was measured by Archimedes drainage method, and the relative density was calculated. Phase analysis was characterized by X-ray diffraction. The microstructures of the powders and SiC_w/Cu composite were observed by Scanning electron microscope. Figure 2a shows the hot extrusion schematic diagram. The orientation of SiC whiskers was parallel to the extrusion direction by hot extrusion. This is a unique method to study the influence of whiskers orientation on the electrical conductivity of the SiC_w/Cu composites, sampling as shown in Figure 2b, and the samples were $\varnothing 13$ mm $\times$ 3 mm. Measurements of the electrical conductivity were used by the eddy current test instrument with a $\varnothing 8$ mm measuring sensor at a frequency of 60 KHz.

Figure 3: SEM morphology of the extruded SiC_w/Cu composite with different volume fraction: (a) 1 vol.%, (b) 3 vol.%, (c) 5 vol.%, (c) 7 vol.%. ED, ND, TD is extruding direction, normal direction, and transverse direction, respectively

3 Results and discussion

3.1 Microstructures and density of SiC_w/Cu composition

Figure 1 shows the morphologies and the XRD diffraction patterns of SiC whiskers before and after coating Cu. It is noted that the surface of the uncoated SiC whiskers are clean and smooth (Figure 1b) and the surface of the Cu-coated SiC whiskers is rough (Figure 1c). Figure 1d shows the XRD diffraction patterns of SiC whiskers before and after coating Cu. The peaks of Cu can be clearly detected from the XRD patterns of Cu-coated SiC whiskers. The results show that required Cu-coated has been deposited on SiC whiskers, and without formation of Cu_2O and other byproducts.

Figure 3 shows the microstructure of SiC_w/Cu composites with different volume fraction in all directions after hot extrusion. The black long rod is SiC whisker with parallel to the hot extrusion direction. The SiC_w/Cu composites have a compact microstructure without defects such as pores. However, when the SiC whiskers are more than 5 Vol.%, the SiC whiskers agglomeration phenomenon can be observed. Therefore, the higher the content of SiC whiskers, the easier it is to agglomerate and the worse the performance of the composites.

The relative density of the SiC_w/Cu composites before and after hot extrusion is shown in Figure 4. The relative density of the sintered SiC_w/Cu composites decreases from 91.5% to 81.0% with increasing the SiC whiskers content. After hot extrusion, the relative density of SiC_w/Cu composites is greater than 96.2%, which is consistent with the law of that of sintered samples in Figure 4. The rel-

Figure 4: Relative density of SiC_w/Cu composites

ative density of SiC_w/Cu composites has been increased 8.6%~18.7% compared with that of sintered state. In the hot extrusion process, the agglomerate SiC whiskers can be dispersed uniformly due to the rapid flow of copper matrix, and voids left after sintering can also be filled rapidly, which greatly improves the SiC_w/Cu composites density. Additionally, the copper atomic are deposited on the surface of SiC whiskers in the ED process, which fills the pores between copper powder and SiC whiskers that can not be filled. It also helps to improve the density of composite materials.

SiC whiskers are added to the copper matrix composite as a second phase, which are distributed around or gaps between the copper particles in the mixing process. During the densification process, they hinder the movement of copper phase to fill pores, and weaken the deformation, diffusion and rearrangement between copper particles, especially in the case of high SiC whiskers content [25, 26].

3.2 Electrical conductivity anisotropy of composites

Figure 5 displays the electrical conductivity of SiC_w/Cu composites with different SiC whiskers content. As seen from Figure 5, the electrical conductivity of the SiC_w/Cu composites decreases with increasing SiC whiskers content, but they are higher than 76.5 %IACS. In general, the electrical conductivity of copper matrix composites is related to the microstructure, density and content of the composites, etc. There are two main factors affecting the electrical conductivity of SiC_w/Cu composites. On the one hand, the electrical conductivity of SiC whiskers is lower than

Figure 5: The electrical conductivity of cross and longitudinal sections of SiC_w/Cu composites with different SiC whiskers content

that of copper. With the increase of SiC whiskers volume fraction, the copper matrix participating in conductivity decreases. The electrical conductivity of the SiC_w/Cu composites decreases. On the other hand, the aspect ratio of SiC whiskers leads to the microstructure and electrical conductivity anisotropy of the composites, as shown in Figures 3 and 5.

During hot extrusion process, the SiC whiskers changes from a random arrangement to align along the axial direction, as shown in Figure 3. It is conducive to study the influence of SiC whiskers orientation on electrical conductivity anisotropy of composites. The electrical conductivity of the cross section ($\theta=0^\circ$) and the longitudinal section ($\theta=90^\circ$) was investigated. The results show that the electrical conductivity of longitudinal section is higher than that of cross section, that is, when the current direction is parallel to SiC whiskers, the electrical conductivity is higher, as shown in Figure 5. The aligned CNTs reinforced ceramic composites also leads to electrical conductivity anisotropy, and the values of electrical conductivity along the length direction of the CNTs is higher [21]. The results are consistent with those of SiC_w/Cu composites. For composites with different SiC whiskers volume fractions, the electrical conductivity increases with increasing the angle θ , as shown in Figure 6. Therefore, the knowledge of conductive mechanism can be used to prepare copper matrix composites, which can achieve a good match between electrical conductivity and mechanical properties.

Figure 7 displays a schematic diagram of the electronic path through the SiC_w/Cu composite conductor under the action of electric field. We assume that the resistance in the material is caused by the interaction of drifting electrons

Figure 6: Relationship among electrical conductivity, SiC whiskers spatial distribution and volume fraction in the SiC_w/Cu composites

Figure 7: Schematic representation of the electron path through the SiC_w/Cu composite conductor under the action of an electric field

with some defects in the material. (Such as impurity atoms, second phase, grain boundaries, etc.).

The electrical conductivity σ of metal can be deduced by classical electronic theory [27].

$$\sigma = \frac{ne^2\tau_F}{m} \quad (1)$$

Where, τ_F is a relaxation time (the average time between two consecutive collisions), n is the number of electron (per unit volume), e is the elementary electric charge, m is the mass of an electron. As shown in Figure 7, the volume fraction and spatial distribution of SiC whiskers affect τ_F . When content of SiC whiskers is fixed, the aligned SiC whiskers are parallel to axial direction. It is conducive to reduce the consecutive collisions between electrons and SiC whiskers, so the electron relaxation time is large, and the

Figure 8: The calculated electrical conductivity of SiC_w/Cu composites in comparison with the experimental data

electrical conductivity increases. On the contrary, when the aligned SiC whiskers is vertical to axial direction, the consecutive collisions between electrons and SiC whiskers increase, so the electron relaxation time decreases, and the electrical conductivity decreases. Figure 7 and Eq. 1 show that the electrical conductivity is large for a large relaxation time τ_F .

3.3 Establishment of the electrical conductivity model

The electrical conductivity of metal materials mainly depends primarily on the composition, structure and defects of the materials. The resistivity of copper matrix composites mainly comes from electron scattering, including phonon scattering, impurity/reinforced phase scattering, dislocation scattering and interface scattering [28–31]. If the content is constant, the electron scattering effect caused by the reinforced phase is much lower than that of atoms (impurities) in solid solution, which can be neglected [5]. The effects of phonon scattering and dislocation scattering on the resistivity of composites are also minimal [28, 30]. However, the interface scattering is a main factor affecting resistivity of composites. It is related to the volume fraction, size, shape and distribution of reinforced phases and microstructure.

The classical rule of mixture (ROM) (Eq. 2) [32] and Maxwell's equation (Eq. 3) [33] predicted that the electrical conductivity of SiC_w/Cu composites is larger than the experimental data, as shown in Figure 8. They only consider the electrical conductivity and volume fraction of each phase. Maxwell model is applicable to isotropic compos-

ites. Therefore, the models are not enough to accurately predict the electrical conductivity. Besides the electrical conductivity and volume fraction of the each phase, the microstructure parameter (n_p) is very important for predicting the electrical conductivity of copper matrix composites. It is assumed that the microstructure parameter is the characteristic parameters and arrangement of phases.

$$\sigma_c(\text{ROM}) = (1 - v_w) \cdot \sigma_m + v_w \cdot \sigma_w \quad (2)$$

$$\sigma_c(\text{Maxwell}) = \frac{\sigma_w + 2 \cdot \sigma_m + 2 \cdot v_w \cdot (\sigma_w - \sigma_m)}{\sigma_w + 2 \cdot \sigma_m - v_w \cdot (\sigma_w - \sigma_m)} \cdot \sigma_m \quad (3)$$

Where v_m is the volume fraction of SiC whiskers, σ_w (about 0 %IACS) and σ_m (100 %IACS) are the electrical conductivity of SiC whiskers and copper.

Fan [34] proposed an electrical conductivity model based on topological microstructure of composites and the equivalent electrical circuit analysis technique. The electrical conductivity of composites can be predicted by combining the electrical conductivity, volume fraction of each phases and microstructure parameter (n_p). The electrical conductivity of SiC whiskers is significantly less than that of copper, which is almost zero. The electrical conductivity model of SiC_w/Cu composite the can be expressed as:

$$\sigma_c = \sigma_m \cdot (1 - v_w)^{n_p} \quad (4)$$

Where σ_c is the electrical conductivity of composites, n_p is the microstructure parameter. The smaller the value of n_p ($n_p \geq 1$), the more continuous of the matrix. It should be emphasized that in order to accurately predict the electrical conductivity of composites, the n_p must be measured experimentally. The experimental data are substituted into Eq. 4, and the n_p value obtained can be expressed by Eq. 5, the n_p is given as:

$$n_p = 2.5 + \cos \theta \quad (5)$$

Where, θ ($0^\circ \leq \theta \leq 90^\circ$) is the angle between whisker orientation and vertical direction. When $n_p(0^\circ)=3.5$ and $n_p(90^\circ)=2.5$, can describe two extreme cases distribution of whiskers in copper matrix, as shown in Figure 8. The model can well reflect the relationship among electrical conductivity, microstructure and volume fraction of SiC_w/Cu composites.

The electrical conductivity of composites with different orientation angles (0° , 30° , 45° , 60° , 90°) were calculated and compared with experimental data in Figure 9. The electrical conductivity of composites is between two extreme cases, and its mathematical expression predicts the electrical conductivity of composites more accurately than Eq. 2 and 3.

Figure 9: The electrical conductivity of composites with different SiC whiskers orientation angles was calculated and compared with experimental data

4 Conclusions

SiC_w/Cu composites with volume fraction of 1~7% were prepared by powder metallurgy and hot extrusion. The microstructure and electrical conductivity were investigated. The density and electrical conductivity of composites are closely related to the SiC whiskers volume fraction. They decrease with the increase SiC whiskers volume fraction. The consistent orientation of SiC whiskers leads to microstructure and electrical conductivity anisotropy of the composites. The electrical conductivity of the longitudinal section is higher than that of the cross section. Based on the microstructure parameters and volume fraction, a simple SiC whiskers reinforced copper matrix composite electrical conductive model was established, and the results were in good agreement with experimental data.

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