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SYNTHESIS OF SiC/Cu COMPOSITE POWDERS FROM POLYCARBOSILANE AND CUPRIC NITRATE TRIHYDRATE

SYNTEZA KOMPOZYTOWYCH PROSZKÓW SiC/Cu Z POLIKARBOSILANU I TRIHYDRATU AZOTANU MIEDZI(II)

SiC/Cu composite powders with the barrier coating of SiC-Al onto SiC powders were synthesized from Al-containing polycarbosilane precursor and Cu-nitrate hydrate. Curing at 200^{o}C and high temperature pyrolysis at 1600^{o}C was used to achieve the crystallization of precursor, forming the SiC-Al coating on the surface of SiC powders. A core-shell structure with the core of SiC and the shell of Cu was constructed by calcination and hydrogen-reduction of Cu nitrate hydrate. XRD and SEM analysis revealed that the β-SiC and 4H-SiC phases were formed on the surface of the initial α-SiC powders. Also, it was observed by EDX mapping that core powders of SiC were homogeneously surrounded with the fine Cu particles on their surface.

Keywords: Cu/SiC composite powders, Polycarbosilane, Cu-nitrate, Microstructure

1. Introduction

Copper exhibits outstanding electrical and thermal conductivities, but its application to thermal management materials is limited because of higher coefficient of thermal expansion (CTE) than the Si substrate. An area of interest may be reinforcement of Cu composites. Among the potential reinforcement materials, SiC is an attractive candidate with relatively high thermal conductivity and low CTE [1]. Thus, SiC-reinforced Cu (Cu/SiC) composites have received considerable attention to meet the challenges of thermal management in the rapidly increased power of advanced electronics [2-4]. They offered a great potential for uses in high-temperature structural applications and electronic packaging due to the superior heat-conductive and heat-releasing natures.

However, the poor wettability between SiC and Cu would lead to flocculation of SiC and segregation from the matrix, and decrease in sinterability and thermal conductivity of the composites [5-7]. In addition, Si in SiC at elevated temperature is partially dissolved in Cu forming a Cu(Si) solid solution, and the dissolved Si reduces the thermal conductivity of Cu/SiC composites [2]. Thus, for the application of Cu/SiC composites in the thermal management, the interface problems between SiC and Cu must be solved.

In order to solve the interface problems, the present study focuses on the barrier coating of SiC-Al onto SiC powders to control the chemical reaction and to enhance the wettability between SiC and Cu. The SiC-Al coating was derived from Al-containing polycarbosilane precursor. A core-shell structure was constructed in the Cu/SiC composite powders with the core of SiC-Al coated SiC and the shell of Cu by calcination and hydrogen-reduction of Cu-nitrate. Microstructural characteristics of Cu/SiC composite powders were analyzed by XRD and SEM. The relationship between synthesis processing and microstructure was discussed.

2. Experimental

SiC powder with an average size of 20 μm was mixed with 2% hexane solution of 1% Al-modified PCS (Al-PCS, TBMTech Co., Korea) [8]. Then the solvent was extracted by a rotary evaporator. The amount of Al-PCS sufficient to coat the powder with the 100 nm thick was determined on the basis of average powder size. The samples were cured at 200°C for 1 h in air and pyrolyzed at 1200°C in a tube furnace. Then, they were heat-treated at 1600°C for the crystallization of amorphous SiOC phase. To synthesis a core-shell structure powders, Cu nitrate hydrate ($CuNO_3{\cdot}3H_2O$, Kojundo Chemical Lab, Co., Japan) powder was used as source material for Cu. Weighted nitrate powder, corresponding to 30 wt% of Cu in the final composite powders, was initially dissolved in ethanol. Subsequently, SiC-Al coated SiC powder was mixed with the solution and ball milled for 10 h with high purity Al_2O_3 balls. Dried mixtures were calcined at 300°C for 1 h in air and reduced at 200°C for 1 h in hydrogen atmosphere. Phase identification was carried out by X-ray diffraction (XRD) analysis. The Microstructure and chemical compositions were characterized by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX).

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3. Results and discussion

Oxidative cross-linking of the PCS was carried out to fabricate infusible prior to pyrolysis. Fig. 1 shows the typical surface morphology of SiC particles mixed with Al-PCS after curing at 200°C in air. It could be found that the PCS coatings were dense and no pore was found. The cured powders were pyrolyzed at 1200°C in Ar atmosphere, and further heat treated at 1600°C for the formation of SiC crystals from amorphous SiOC phase.

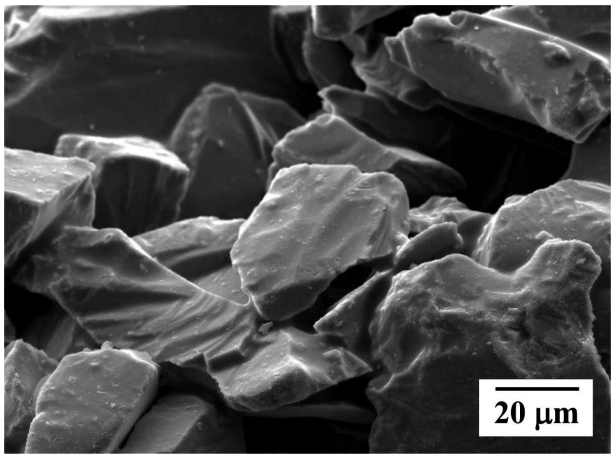


Fig. 1. SEM image of SiC powders mixed with Al-PCS after curing at 200°C in air

The XRD profiles registered for the initial SiC and PCS-coated SiC powders are shown in Fig. 2. In the initial powder, only the lines for α-SiC are found (Fig. 2a). The PCS coated SiC pyrolized at 1600°C shows that the main peaks in the spectrum corresponded to α-SiC phase and the peaks β-SiC and 4H-SiC were visible as minor phases. As reported in literatures [9-11], it is explained that the existence of β-SiC and 4H-SiC phase is attributed to the transformation of cured PCS on the surface of the initial α-SiC powders.

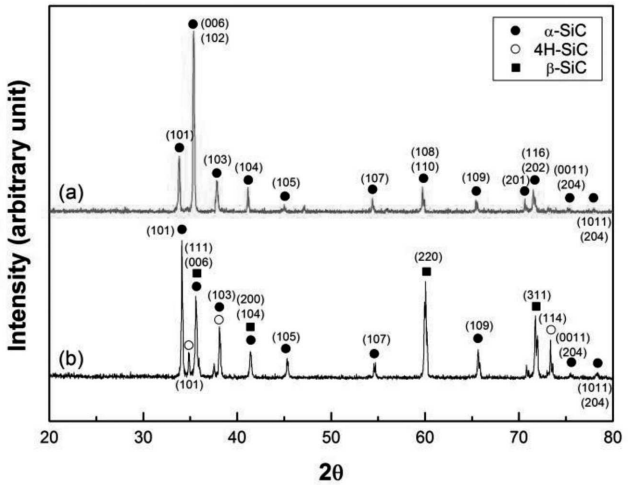


Fig. 2. XRD profiles of (a) the initial SiC powder and (b) PCS-coated SiC powder heat-treated at 1600°C

To fabricate a core-shell structure powders as the core of PCS-coated SiC and shell of Cu particles, chemical solution method using Cu nitrate hydrate as source materials for Cu was applied. Fig. 3 shows typical SEM image of the PCS-coated SiC with Cu-nitrate powder mixture after calcination for 1 h at 300°C in air. The micrograph clearly shows a homogeneous dispersion of the fine particles with an average size of 4 μm on the surface of SiC powders. Considering that Cu-nitrate is converted to CuO by calcination [12], these fine particles in this microstructure are considered as CuO phase.

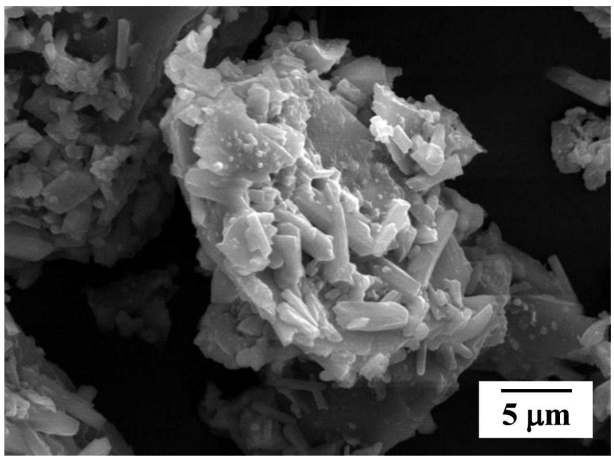


Fig. 3. SEM micrograph of PCS-coated SiC and Cu-nitrate powder mixture after calcination at 300°C

The calcined powder mixture was heat-treated for 1 h at 200°C in hydrogen atmosphere. As shown in the XRD patterns (Fig. 4), the observed peaks in the reduced powder mixture were registered as α-SiC, β-SiC and Cu phase without any reaction phase. As reported in the literature [13,14], the CuO is reduced to elemental Cu phase at the temperature of about 200°C under hydrogen atmosphere. Thus, it suggested that CuO powders can be completely transformed to elemental Cu powders by the hydrogen reduction process.

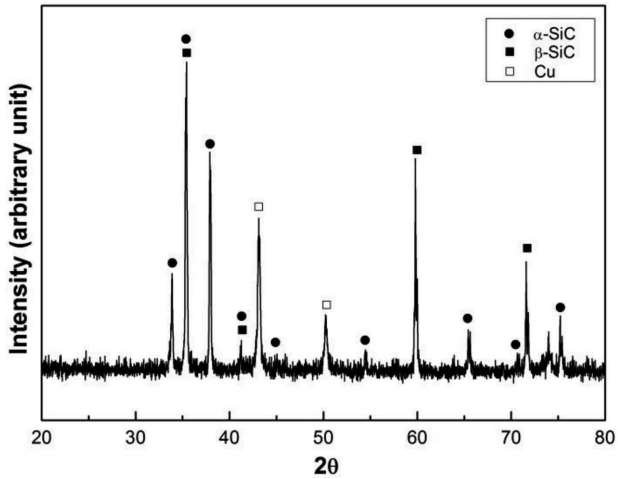


Fig. 4. XRD pattern of the powder mixture reduced at 200°C in hydrogen atmosphere

For further microstructural characterization of hydrogen-reduced composite powders, SEM-EDX analysis was performed. As clearly seen in Fig. 5, core particles were surrounded with the fine particles on their surface, forming core-shell structure. Also, the phase of shell structure as determined by EDX mapping is presented in Fig. 5, in which the elemental mapping images obtained for Si and Cu match with

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that of the corresponding SEM image. This result indicated that Cu/SiC composite powders with the core of SiC-Al coated SiC and the shell of Cu can be successfully fabricated from Al-containing polycarbosilane and Cu-nitrate.

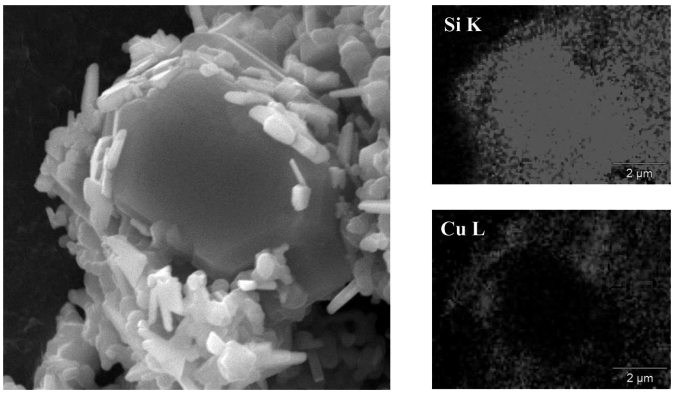


Fig. 5. SEM microstructure and EDX mapping of SiC/Cu composite powder

4. Conclusions

This work has demonstrated the synthesis of Cu/SiC composite powders with barrier coating of SiC-Al onto SiC powders to control the interface problems between Cu and SiC phases. The SiC-Al coating was derived from Al-containing PCS precursor. Cu-coated SiC powders were prepared by calcination and hydrogen-reduction of Cu-nitrate. XRD analysis revealed that the β-SiC and 4H-SiC phases were formed by the transformation of cured PCS on the surface of the initial α-SiC powders. A core-shell structure powders as the core of PCS-coated SiC and shell of Cu particles can be successfully fabricated by calcination and hydrogen reduction of Cu-nitrate powders.

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