Research Article

Fabrication of Al_2O_3 -Cu Nanocomposites Using Rotary Chemical Vapor Deposition and Spark Plasma Sintering

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Received 15 August 2014; Revised 30 October 2014; Accepted 31 October 2014

Academic Editor: Shaoyun Fu

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A two-step rotary chemical vapor deposition technique was developed to uniformly mix Cu nanoparticles with the $\gamma\text{-Al}_2\text{O}_3$ powders, and then the as-obtained powders were consolidated to Al_2O_3 -Cu nanocomposites by spark plasma sintering. In the RCVD process, the metal-organic precursor of copper dipivaloylmethanate ($\text{Cu}(\text{DPM})_2$) reacted with O_2 and then was reduced by H_2 in order to erase the contamination of carbon. At 1473 K, the relative density of Al_2O_3 -Cu increased with increasing C_{Cu} and the maximum value was 97.7% at $C_{\text{Cu}} = 5.2$ mass%. The maximum fracture toughness of Al_2O_3 -Cu was $4.1 \text{ MPa m}^{1/2}$ at $C_{\text{Cu}} = 3.8$ mass%, and $1 \text{ MPa m}^{1/2}$ higher than that of monolithic Al_2O_3 , validating the beneficial effects of Cu nanoparticles.

1. Introduction

The incorporation of small amounts of metal nanoparticles, such as Cu [1], Ni [2–4], W [5], and Cr [6], has been proved to be beneficial for improving the densification, mechanical properties, and conductivity of Al_2O_3 . Particularly, the incorporation of Cu nanoparticles has attracted much attention due to its high ductility and good electrical conductivity [1, 7, 8]. Kim et al. fabricated Al_2O_3 -Cu nanopowders by ball milling for 30 h and then sintered at 1100–1400°C for 5 min in vacuum under a pressure of 50 MPa by the pulse electric current sintering (PECS) [7]. The composites sintered at 1250°C for 5 min showed a relative density above 97% and enhanced fracture toughness of $4.5 \text{ MPa m}^{1/2}$. Oh and Yoon fabricated Al_2O_3 -Cu nanocomposites by hydrogen reduction and hot pressing of $\text{Al}_2\text{O}_3/\text{CuO}$ powders. The composite prepared from Al_2O_3 -Cu nitrate mixture exhibited maximum strength of 953 MPa [8].

In general, that the wet methods such as coprecipitation usually produces $\gamma\text{-Al}_2\text{O}_3$ phase, which would transform to $\alpha\text{-Al}_2\text{O}_3$ during high temperature sintering. Thus the uniform distribution of Cu would be quite necessary for high mechanical properties. However, the agglomeration of Cu

nanoparticles in sol-gel process and ball milling is usually unavoidable [9]. Compared to the ball milling and wet sol-gel, the dry CVD technique seems more promising due to its easy operation and low pollution to the environments. Fluidized bed CVD (FBCVD) is one of the most efficient CVD techniques to coat each individual particle of a powder from gaseous species [10]. However, the application of FBCVD on powder is limited depending mainly on density and particle size of powder [11, 12]. The use of a novel rotary CVD (RCVD) technique to prepare Ni nanoparticles on ceramic powders has been reported in our previous work. Ni nanoparticles 13.9–84.5 nm and 10–100 nm in diameter were precipitated on the surface of hBN [13] and cBN [14], respectively. The relative density and hardness of hBN were found to be increased by the incorporation of Ni nanoparticles. The hardness of Al_2O_3 -30 vol% cBN/Ni was 27 GPa, about 1 GPa and 5 GPa higher than that of Al_2O_3 -30 vol% cBN and monolithic Al_2O_3 .

In the present study, Cu nanoparticle was precipitated on $\gamma\text{-Al}_2\text{O}_3$ for uniform mixture by RCVD using copper dipivaloylmethanate ($\text{Cu}(\text{DPM})_2$) as a precursor. In order to erase the carbon contamination, the powder was firstly oxidized by oxygen and then reduced by hydrogen into the metal state.

Then the $\gamma\text{Al}_2\text{O}_3$ -Cu powders were consolidated by spark plasma sintering at 1373 to 1573 K for 0.6 ks. The effects of Cu nanoparticles on the sintering behavior, microstructure, and mechanical properties of Al_2O_3 were investigated.

2. Experimental Procedures

The detailed description about RCVD can be found elsewhere [13]. In the present study, Cu nanoparticles were precipitated on $\gamma\text{Al}_2\text{O}_3$ powders by RCVD at 573 to 873 K for 30 min using $\text{Cu}(\text{DPM})_2$ as a precursor. The $\text{Cu}(\text{DPM})_2$ precursor in the evaporator was heated at 393 to 423 K and carried into the reaction zone by Ar at a flow rate of $1.67 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$. The supply rate (R_s) of $\text{Cu}(\text{DPM})_2$ was set at $0.56 \times 10^{-6} \text{ kg} \cdot \text{s}^{-1}$, and O_2 was also filled in to erase the carbon contamination from $\text{Cu}(\text{DPM})_2$. The $\gamma\text{Al}_2\text{O}_3$ powder, <100 nm in average diameter and 2 g in weight, was fed into the reactor and preheated at 793 to 823 K. The total inner pressure of the RCVD apparatus was kept at 800 Pa with a partial pressure of 240 Pa for O_2 and 560 Pa for Ar. The deposition time was fixed at 1.8 ks. After deposition, the O_2 was cut off and H_2 was used to reduce the CuO to Cu. The $\gamma\text{Al}_2\text{O}_3$ -Cu powder was consolidated by spark plasma sintering (SPS, model SPS-210LX, SPS Syntex Inc., Japan) at 1373 to 1673 K for 0.6 ks. The heating rate was $3.3 \text{ K} \cdot \text{s}^{-1}$ and the pressure was 100 MPa loaded in the whole sintering process. The temperature was measured by an optical pyrometer focused on a hole ($\phi 2 \times 5 \text{ mm}$) in the graphite die.

The crystal structure and phase of the $\gamma\text{Al}_2\text{O}_3$ -Cu powder and the sintered bodies were identified by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation. The microstructure was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Cu mass content (hereafter, C_{Cu}) in the Al_2O_3 -Cu powder was estimated by energy-dispersive X-ray spectroscopy (EDS) and was averaged by five measurements at different areas. The specific surface area, a total surface area per unit of mass, was measured by the BET method and calculated using [15]

$$a_{\text{BET}} = \frac{V_m L a_m}{V_L}. \quad (1)$$

Here a_m is the area occupied by a molecule of the adsorbate, L is the Avogadro's number, and V_L is the molar volume of the analysis gas at standard temperature and pressure (STP). V_m is the monolayer adsorbed gas quantity, which could be obtained from

$$\frac{P}{V(P - P_0)} = \frac{1}{V_m} \left(\frac{1}{C} + \frac{C - 1}{C} \times \frac{P}{P_0} \right). \quad (2)$$

Here P and P_0 are the equilibrium and saturation pressure of adsorbates at the temperature of adsorption, V is the adsorbed gas volume quantity, and C is the BET constant.

The bulk density of the sintered body was determined by an Archimedes' method and converted to relative density using the theoretical density of Al_2O_3 ($3.99 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$) [16] and Cu ($8.99 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$) [17]. The hardness of Al_2O_3 -Cu nanocomposites was measured using Vicker's indentation

FIGURE 1: XRD patterns of (a) Al_2O_3 and Cu precipitated Al_2O_3 powders at $T_{\text{SPS}} =$ (b) 573, (c) 673, (d) 773, and (e) 873 K.

test under a load of 19.6 N [18] and the fracture toughness was evaluated by measuring the crack length generated by Vicker's indentation [19]. Ten points were averaged for each value of hardness and fracture toughness.

3. Results and Discussion

Figure 1 shows the effects of precipitation temperature (T_p) on phase structure of the RCVD-treated Al_2O_3 powders. At $T_p = 573 \text{ K}$, no Cu peaks were identified due to the low precipitation temperature. At 673 to 873 K, the diffraction peaks at $2\theta = 43.3^\circ$ (111) and 50.5° (200) were indexed to Cu, and no CuO and C peaks were observed. On the other hand, the intensity of Cu peaks varied with the precipitating temperature and showed the highest at 773 K. Figure 2 shows the TEM image and EDS spectrum of Cu precipitated $\gamma\text{Al}_2\text{O}_3$ powders at 773 K. The EDS spectrum showed clearly the presence of Cu peaks. The Mo peaks were also observed due to the Mo mesh grids used to support the powder for TEM observation. However, it is difficult to distinguish the Cu nanoparticles from Al_2O_3 by the TEM images due to the small grain size of Al_2O_3 and Cu. The presence of carbon and oxygen peaks in the EDS spectra was ascribed to the thin organic film coated on the Mo mesh grid to support the powders for TEM observation. Table 1 shows the specific surface area, Cu grain size, and C_{Cu} of Al_2O_3 and Al_2O_3 -Cu powders. The specific surface area of monolithic $\gamma\text{Al}_2\text{O}_3$ was $49.3 \text{ m}^2 \cdot \text{g}^{-1}$. The addition of Cu decreased the specific surface area of Al_2O_3 slightly from 41.8 to $45.4 \text{ m}^2 \cdot \text{g}^{-1}$ due to the high theoretical density of Cu ($\text{kg} \cdot \text{m}^{-3}$). The crystalline grain size of the Cu nanoparticles was obtained by Scherrer's Formula

FIGURE 2: (a) TEM image and (b) EDS spectrum of Cu precipitated $\gamma\text{Al}_2\text{O}_3$ powders at $T_p = 773$ K.

TABLE 1: Specific surface area, grain size of Cu and content of Cu in Al_2O_3 and Al_2O_3 -Cu powders.

	Precipitation temperature/K	Specific surface area/ $\text{m}^2 \text{g}^{-1}$	Grain size of Cu*/nm	Content of Cu/mass%
Al_2O_3	—	49.3	—	—
Al_2O_3 -Cu	573	41.8	—	1.2
Al_2O_3 -Cu	673	42.3	18	3.8
Al_2O_3 -Cu	773	45.4	25	5.2
Al_2O_3 -Cu	873	43.8	28	2.1

*The crystalline grain size of the Cu nanoparticles was obtained by Scherrer's formula from the XRD patterns.

for the strongest peak using the diffraction angle of the peak and half width of the peak area of Figure 1. The grain size of Cu increased from 18 to 28 nm with increasing the precipitating temperature from 673 to 873 K. The maximum C_{Cu} reached 5.2 mass% at 773 K.

Figure 3 shows the effect of sintering temperature (T_{SPS}) on the phase structure of Cu precipitated $\gamma\text{Al}_2\text{O}_3$ powders at $T_{\text{SPS}} = 773$ K. The phase transformation of $\gamma\text{Al}_2\text{O}_3$ to $\alpha\text{Al}_2\text{O}_3$ started at $T_{\text{SPS}} = 1273$ K, where three $\alpha\text{Al}_2\text{O}_3$ peaks appeared together with $\gamma\text{Al}_2\text{O}_3$ and Cu peaks. At $T_{\text{SPS}} = 1373$ K, the $\gamma\text{Al}_2\text{O}_3$ transformed completely to $\alpha\text{Al}_2\text{O}_3$.

Figure 4 shows the effect of C_{Cu} on the relative density of Al_2O_3 -Cu nanocomposites. At $T_{\text{SPS}} = 1373$, 1473, and 1573 K, the relative density of Al_2O_3 was 93.6%, 98.4%, and 97.6%, respectively. The maximum value of 98.4% at $T_{\text{SPS}} = 1473$ K was a little higher than Kim's results at $T_{\text{SPS}} = 1523$ K for 0.3 ks (97%) [7], indicating that RCVD is better in precipitating Cu nanoparticles for the densification of Al_2O_3 . Hotta and Goto have consolidated $\alpha\text{Al}_2\text{O}_3$ by spark plasma sintering from the raw powder of Al_2O_3 of ~ 200 nm in diameter [20]. The relative density at $T_{\text{SPS}} = 1473$ K reached above 99%.

FIGURE 3: XRD patterns of Al_2O_3 -Cu at $C_{\text{Cu}} = 5.2$ mass% by spark plasma sintering at $T_{\text{SPS}} =$ (a) 1073, (b) 1173, (c) 1273, (d) 1373, (e) 1473, and (f) 1573 K.

In our present work, however, the maximum relative density was only 98.4% at $T_{\text{SPS}} = 1473$ K using the $\gamma\text{Al}_2\text{O}_3$ of 80 nm in grain size, lower than Hotta's result using the $\alpha\text{Al}_2\text{O}_3$ starting powder at the same sintering temperature. This could be attributed to the phase transformation of $\gamma\text{Al}_2\text{O}_3$ to $\alpha\text{Al}_2\text{O}_3$ in the present sintering process, which retarded the densification process slightly. At $T_{\text{SPS}} = 1473$ K, the relative density of Al_2O_3 -Cu increased with increasing C_{Cu} and

FIGURE 4: The effect of Cu content on the relative density of Al_2O_3 -Cu composites at $T_{\text{SPS}} = 1373, 1473$, and 1573 K, respectively.

the maximum value was 97.7% at $C_{\text{Cu}} = 5.2$ mass%. But at $T_{\text{SPS}} = 1373$ and 1573 K, the relative density of C_{Cu} decreased with increasing C_{Cu} . At $T_{\text{SPS}} = 1573$ K and $C_{\text{Cu}} = 5.2$ mass%, the relative density was only 90.6%, about 7% lower than that of monolithic Al_2O_3 at the same sintering temperature. The decrease of the relative density at $T_{\text{SPS}} = 1573$ K was explained from the microstructural observation of Figure 5.

Figure 5 shows SEM images of the fracture surface of Al_2O_3 and Al_2O_3 -Cu sintered at $T_{\text{SPS}} = 1373$ to 1573 K. At $T_{\text{SPS}} = 1373$ K, some pores were observed in Al_2O_3 fracture surfaces. In contrast, almost no pores were identified in Al_2O_3 -Cu at the same sintering temperature, indicating Cu nanoparticles improved the densification of Al_2O_3 . Adding a small amount of nanoparticles could usually inhibit the grain growth of Al_2O_3 . For example, Ji and Yeomans found that 5 vol% Cr apparently decreased the grain growth of Al_2O_3 hot pressed at 1723 K and thus increased the strength and fracture toughness of Al_2O_3 [6]. Zhang et al. also found that Ni could decrease the grain growth of Al_2O_3 [21]. In the present study, however, although the grain size of Al_2O_3 was not apparently inhibited, the relative density was increased due to the decrease of the pores. The reason might be that the Cu was in situ coated on the surface of $\gamma\text{Al}_2\text{O}_3$ (80 nm in grain size) instead of ball-mill mixing. At $T_{\text{SPS}} = 1473$ and 1573 K, the pores were both observed in Al_2O_3 and Al_2O_3 -Cu. By incorporating pores among grains, the grain size increase of Al_2O_3 -Cu at $T_{\text{SPS}} = 1573$ K induced the lower relative density as shown in Figure 4. On the other hand, at 1373 K, the nanocomposite is less porous than monolithic Al_2O_3 , due to the filling of the Cu nanoparticles in the pores of bulk Al_2O_3 . However, the opposite is true at $T_{\text{SPS}} = 1573$ K as Cu

might retard the diffusion of the densification process at a high temperature.

Figure 6 shows the effect of C_{Cu} on the Vickers' hardness and fracture toughness at a load of 19.6 N. The maximum hardness was 20.7 ± 1.4 GPa at 2.1 mass% Cu, whereas the maximum fracture toughness was 4.1 ± 0.3 $\text{MPa m}^{1/2}$ at $C_{\text{Cu}} = 3.8$ mass%. Compared to those values of 19.8 GPa and 3.1 $\text{MPa m}^{1/2}$ of the monolithic Al_2O_3 , the hardness and fracture toughness of Al_2O_3 -Cu nanocomposites were about 4% and 32% higher at 3.8 mass%, respectively. The reason that the hardness and toughness were achieved at different compositions is that the concentration of Cu determined these two quantities differently. The Cu nanoparticle would like to fill the pores of Al_2O_3 and thus increased the relative density and the hardness of Al_2O_3 . But the fracture toughness was increased mainly by crack deflecting and bridging. Thus the maximum hardness and toughness were achieved at different compositions as shown in Figure 6.

The incorporation of second particle phases, such as Cu, Cr, and Ni, would often induce the crack deflection and bridging by absorbing the energy and thus increase the fracture toughness related to the indentation crack length [6, 7, 22]. In the present study, the optimum C_{Cu} was 3.8 mass%, with which the crack length is the lowest and then the fracture toughness was calculated to be the largest value according to the method as described in the experimental part [19]. On the other hand, the Al_2O_3 -Cu nanocomposites in [7] has a fracture toughness of 4.5 $\text{MPa m}^{1/2}$ and 0.4 $\text{MPa m}^{1/2}$ higher than the value in the present study, but the hardness of the nanocomposites was not mentioned [7]. The higher value of the fracture toughness of the nanocomposite in [7] might be due to its lower hardness and the different testing techniques. When the C_{Cu} was higher than 4 mass%, the fracture toughness and hardness of Al_2O_3 -Cu nanocomposites both decreased, which might be due to the agglomeration of Cu nanoparticles at a higher content.

Figure 7 shows a comparison of the hardness and fracture toughness with Al_2O_3 -based nanocomposites in literature mixed by various methods, typically ball milling. The hardness of Al_2O_3 body, Al_2O_3 -Nb, and Al_2O_3 -Nb-CNTs composites ranged from 16 to 22 GPa, with the low fracture toughness of 2.8 – 3.6 $\text{MPa m}^{1/2}$ [6, 23]. The incorporation of soft phases, such as Ti_3SiC_2 , would increase the fracture toughness of Al_2O_3 body with a decrease of hardness [24, 25]. Yao et al. incorporated Ni to increase the fracture toughness of Al_2O_3 to 4.3 $\text{MPa m}^{1/2}$, while the hardness was 14.2 GPa [26]. It is common that the higher hardness, the lower fracture toughness. The reported values ranged in the hatched area in Figure 7. In the present study, the fracture toughness increased to 4.1 $\text{MPa m}^{1/2}$, about 40% higher than that of Al_2O_3 body with the hardness of 20.4 GPa, higher than most of reported values for the Al_2O_3 body and many Al_2O_3 -based composites in literature.

4. Conclusions

Cu nanoparticles were precipitated on $\gamma\text{Al}_2\text{O}_3$ by rotary chemical vapor deposition at $T_{\text{SPS}} = 673$ to 873 K for 30 min,

FIGURE 5: SEM fracture surface images of Al_2O_3 sintered at T_{SPS} = (a) 1373 K, (b) 1473 K, and (c) 1573 K and Al_2O_3 -Cu sintered at T_{SPS} = (d) 1373 K, (e) 1473 K, and (f) 1573 K.

FIGURE 6: The dependence of Vickers hardness and fracture toughness on the mass content of Cu.

and then the as-obtained composite powders were consolidated by spark plasma sintering to get bulk Al_2O_3 -Cu nanocomposites. Although the grain size and C_{Cu} increased with increasing precipitation temperature from $T_{\text{SPS}} = 673$ to 873 K, they were still in the range of nanocomposite powders. The incorporation of Cu enhanced the densification of Al_2O_3 body by SPS at $T_{\text{SPS}} = 1473$ K. The sintered Al_2O_3 -Cu nanocomposites with a fine microstructure showed the maximum hardness and fracture toughness of 20.7 ± 1.4 GPa

at $C_{\text{Cu}} = 2.1$ mass% and $4.1 \pm 0.3 \text{ MPa m}^{1/2}$ at $C_{\text{Cu}} = 3.8$ mass%, respectively. Therefore, the treatment of rotary CVD and spark plasma sintering could be a promising route to obtain high performance ceramic-based nanocomposites.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

FIGURE 7: Comparison of microhardness and fracture toughness of Al_2O_3 -3.8 mass% Cu nanocomposite with those of the Al_2O_3 -based composites reported in literature.

Acknowledgments

The authors appreciate the financial supports from the Fundamental Research Funds for the Central Universities (2013B34414), and the National 973 Plan Project (2015CB057803).

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