Fabrication of Al$_2$O$_3$–Ni–CNTs nanocomposites by co-precipitation of CNTs and Ni nanoparticle on Al$_2$O$_3$ powder and spark plasma sintering

Huiyang CAO,*,** Jianfeng ZHANG,**,* Chunlong ZHAO,* Gaile LI,* Xin ZHANG* and Takashi GOTO***

*College of Mechanics and Materials, Hohai University, Nanjing 210098, China
**State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Shanghai 200050, China
***Institute for Materials Research, Tohoku University, Sendai 980–8577, Japan

Due to the unique properties of low dimension, large specific surface area, high strength and good thermal conductivity, carbon nanotubes (CNTs) have been widely used as a dispersoid reinforcing various ceramic-based composites, most typically Al$_2$O$_3$-based ones.1–3 The Al$_2$O$_3$–CNTs composites have generally been fabricated by mixing Al$_2$O$_3$ powders and CNTs and consolidating by pressureless sintering, hot pressing or spark plasma sintering.4–7 However, because of the large aspect ratio (100–10,000),8–10 CNTs are hardly dispersed uniformly in a ceramic matrix by milling, which would degrade the mechanical and thermal properties of the Al$_2$O$_3$–CNTs composites.

Instead of the mechanical mixing of the powders, a catalytic chemical vapor deposition (CCVD) method has been proposed to grow CNTs directly on the surface of Al$_2$O$_3$ powders.11–13 This technique involves three main steps: (1) mixing the metal or metal-oxide catalysts with Al$_2$O$_3$ powder, (2) selective reduction of the metal oxide into metal phase, and (3) decomposition of carbon source to form CNTs on metal phase. Peigney et al. produced CNTs–Fe–Al$_2$O$_3$ nanocomposite powders based on a catalytic chemical vapor deposition (CCVD) route involving the reduction of Al$_2$O$_3$–Fe$_2$O$_3$ solid solutions in H$_2$–CH$_4$.14 Piao et al. fabricated CNTs on Ni–Al$_2$O$_3$ powders at 575°C in CH$_4$–N$_2$.15 However, this process takes a long time with a high energy cost. Furthermore, at a high reduction temperature, metal nanoparticle catalysts would agglomerate and grow easily, inducing the agglomeration of CNTs.

In the present study, rotary CVD (RCVD)[16,17] was adopted to prepare CNTs on Al$_2$O$_3$ powder using nickelocene (NiCp$_2$) as a source for both Ni and carbon. Thus, CNTs were synthesized simultaneously catalyzed by Ni nanoparticles on the surface of Al$_2$O$_3$ powders. Then the Al$_2$O$_3$–Ni–CNTs nanopowder was consolidated by spark plasma sintering (SPS). Compared with hot pressure sintering and pressureless sintering, SPS has more advantages, such as accelerating the sintering speed, avoiding the loss of CNTs and so on. Due to the hard texture and good corrosion resistance of Ni, two dimension and large specific surface area of CNTs, the chemical corrosion resistance and high thermal conductivity of α-Al$_2$O$_3$, this kind of nanocomposites based on α-Al$_2$O$_3$ has excellent physical and chemical properties, so it can be widely used in the surface protective layer material, refractory material, optical material, catalyst and carrier, ceramic and other aspects. Research on this material is crucial to our scientific progress. The microstructure and mechanical properties of the Al$_2$O$_3$–Ni–CNTs composite were investigated to show the effects of Ni and CNTs.

1. Introduction

Carbon nanotubes (CNTs)-dispersed ceramics were usually obtained by simple mixing, or firstly dispersing the metal catalysts inside ceramic powders, and then growing CNTs from the thermal decomposition of hydrocarbon gas. In the present study, a novel route for the fabrication of Al$_2$O$_3$–Ni–CNTs nanocomposites was proposed by co-precipitation of CNTs and Ni nanoparticle on Al$_2$O$_3$ powder using nickelocene as a precursor in a rotary CVD reactor. Fine Ni nanoparticles (10–50 nm in diameter) and CNTs (20–50 nm in diameter and as long as 1 μm in length) were uniformly dispersed on agitated Al$_2$O$_3$ powders. After spark plasma sintering at 1923 K for 0.6 ks, the Al$_2$O$_3$–Ni–CNTs nanocomposites showed uniform microstructure and enhanced mechanical properties. Carbon incorporated in nickel changed from amorphous to crystalline phase state after the high temperature treatment. No other impurities were identified, and the incorporation of CNTs and Ni was also found to enhance the relative density and mechanical properties of Al$_2$O$_3$. Thus the present method is promising for fabrication of high performance CNTs-ceramic composites.

2. Experimental procedures

Al$_2$O$_3$–Ni–CNTs nanopowder was prepared by RCVD via thermal decomposition of NiCp$_2$ on alpha-Al$_2$O$_3$ powders (ICPDS No. 10-173, 10–20μm in diameter). The details of the RCVD apparatus can be found elsewhere.17 The NiCp$_2$ precursor in the evaporator was heated at 393 to 423 K, and carried into the reaction zone by H$_2$ at a flow rate of 0.83 × 10$^{-6}$ m$^3$ s$^{-1}$. The supply rate of NiCp$_2$ (Rs) was fixed at 0.56 × 10$^{-6}$ kg s$^{-1}$. The Al$_2$O$_3$ powder, 10–20μm in diameter and 4g in weight, was fed into the reactor and preheated at 823 K. The deposition time was fixed at
1.8 ks. The total inner gas pressure was varied to adjust the Ni and CNTs in the final products.

The RCVD-treated \( \text{Al}_2\text{O}_3 \) powders were collected and consolidated by spark plasma sintering (SPS, model SPS-210LX, SPS Syntex, Japan) at 1923 K. The heating rate was 3.3 ks\(^{-1}\) and the sintering time was 0.6 ks. A pressure of 100 MPa was loaded from the beginning and kept until the end of the sintering process. The temperature was measured by an optical pyrometer focused on a hole (\( 62 \times 5 \) mm) in the graphite die. The crystal structure of the powders and the sintered bodies was identified by X-ray diffraction (XRD) with Cu K\( \alpha \) radiation (XRD; Geigerflex, Rigaku Corp.).

The microstructure was observed by scanning electron microscopy (SEM; Hitachi: S-3100H) and transmission electron microscopy (TEM; JEOL: JEM-2000EX). The Ni content (\( C_{\text{n}} \)) and Carbon content (\( C_{\text{c}} \)) in the sintered \( \text{Al}_2\text{O}_3-Ni-CNTs \) was estimated by energy-dispersive X-ray spectroscopy (EDS, equipped with SEM) averaged from five measurements at different areas, and the \( C_{\text{c}} \) was corrected by wiping off the carbon content of \( \text{Al}_2\text{O}_3 \) raw powder tested by EDS. The bulk density of the sintered body was determined by an Archimedes’ method and converted to relative density using the theoretical density of \( \text{Al}_2\text{O}_3 \) (3.99 \( \times \) 10\(^3\) kg m\(^{-3}\)\(^{18}) \) Ni (8.91 \( \times \) 10\(^3\) kg m\(^{-3}\)\(^{19} \) and carbon (2.28 \( \times \) 10\(^3\) kg m\(^{-3}\)\(^{20}) \). The hardness of \( \text{Al}_2\text{O}_3-Ni-CNTs \) nanocomposite was measured using Vicker’s indentation test (HM-221, Mitutoyo, Japan) under a load of 1.96 N and the fracture toughness was evaluated by measuring the crack length generated by Vicker’s indentation at a load of 19.6 N.\(^{21)} \) Ten points were averaged for each value of hardness and fracture toughness.

3. Results and discussion

Nickelocene, or \( \text{Ni}((\text{C}_5\text{H}_5)\text{H})_2 \) is a common precursor for Ni due to its high volatility, quite low expense and toxicity. Nickelocene is prone to occur hydrogen desorption reaction, which should be attributed to the function of catalytic hydrogenation of nickel. Nickelocene is a kind of metalloocene, having ample chemical reaction properties. Due to the aromatic properties of the cyclopentadienyl ring and its derivatives, some reactions similar to benzene can occur in the cyclopentadienyl ring, and others can also react on the metal atoms. Although carbon incorporation usually accompanies the formation of Ni due to the two cyclopentadienyl ligands, it was utilized as a carbon source of CNT and/or graphite, which provides a novel idea by combining the formation of CNTs and dispersion of Ni catalysts into one step.\(^{22–24)} \)

\[
\begin{align*}
\text{Ni}((\text{C}_5\text{H}_5)\text{H})_2 + \text{nH}_2 & \rightarrow \text{Ni}(\text{H})_n + 2((\text{C}_5\text{H}_5)\text{H}) \quad (1) \\
\text{C}_2\text{H}_2 + (n+m)\text{H}_2 & \rightarrow \text{C}_2\text{H}_{2n+m} + \text{m} \quad (2) \\
\text{C}_5\text{H}_{5n} & \rightarrow \text{C}(\text{s}) \text{ or C}(\text{Ni}) \quad (3) \\
\text{C}(\text{Ni}) + 2\text{H}_2 & \rightarrow \text{CH}_4(\text{g}) \quad (4)
\end{align*}
\]

Figure 1 shows the XRD patterns of (a) raw \( \text{Al}_2\text{O}_3 \) and RCVD-treated \( \text{Al}_2\text{O}_3 \) powders at \( P_{\text{gas}} = \) (a, b) 5000, (c, d) 10000 and (e, f) 20000 Pa. The RCVD-treated \( \text{Al}_2\text{O}_3 \) powders consisted of \( \alpha-\text{Al}_2\text{O}_3 \) and Ni peaks, indicating that nickelocene has decomposed to Ni and the two cyclopentadienyl ligand \[ (2((\text{C}_5\text{H}_5)\text{H})) \] according to Eqs. (1) and (2). The intensity of Ni increased with increasing \( P_{\text{gas}} \), indicating that Ni content increased correspondingly. The diffraction peaks of carbon were not detected from XRD patterns, which could be attributed to the amorphous state or solid solution into Ni.\(^{25)} \)

Figure 2 shows the FESEM images of RCVD-treated \( \text{Al}_2\text{O}_3 \) powders at \( P_{\text{gas}} = \) (a, b) 5000, (c, d) 10000 and (e, f) 20000 Pa. At \( P_{\text{gas}} = 5000 \) Pa, fine Ni nanoparticles about 20 nm in diameter partly covered the \( \text{Al}_2\text{O}_3 \) powder surface. A short CNT was observed on the surface of \( \text{Al}_2\text{O}_3 \) powder catalyzed by the Ni nanoparticles. With increasing \( P_{\text{gas}} \) further, some agglomerates of Ni and CNTs formed around the \( \text{Al}_2\text{O}_3 \) powders. At \( P_{\text{gas}} = 10000 \) Pa, Ni nanoparticles and CNTs were uniformly distributed on the surface of \( \text{Al}_2\text{O}_3 \) powders. But at \( P_{\text{gas}} = 20000 \) Pa, the alumina surface seems to be “cracked” and this morphology could be attributed to the aggregation of the Ni and CNTs. Figure 3 shows typical TEM images of the CNTs formed...
on the surface of Al₂O₃ powder at \( P_{\text{gas}} = 20000 \text{ Pa} \). CNTs were about 20–100 nm in outer diameter, 200 nm in length and curled on the surface of Al₂O₃. [Fig. 3(a)], and longer CNTs were also observed, about 1 μm in length, and 20 nm in diameter [Fig. 3(b)], from the decomposition of nickelocene and catalytic action of Ni nanoparticles. Govindaraj et al. have proposed that multi-walled as well as single-walled CNTs could be prepared by pyrolysis of organometallic precursors, such as metallocones and phthalocyanines in a reducing atmosphere, and enhanced yields could be obtained with a mixture with hydrocarbons. The present work has validated that, without using hydrocarbon gas, the synthesis of Al₄C₃ could be prepared by them. Figure 6 shows the mirror surface images of (a) Al₂O₃ and the Al₂O₃–Ni–CNTs nanocomposites consolidated by SPS using RCVD-treated Al₂O₃ powder at \( P_{\text{gas}} = \) (b) 800 Pa, (c) 2000 Pa, (d) 5000 Pa, (e) 10000 Pa map and (f) 20000 Pa. The pores in Al₂O₃ were apparently filled by the Ni and CNTs, which was believed to enhance the fracture toughness of the Al₂O₃. However, although deletion of the pores was beneficial for increasing the hardness, its value was still decreased as Ni and CNTs are soft phases. Figure 7 shows the fracture surface images of (a) Al₂O₃ and the Al₂O₃–Ni–CNTs nanocomposites consolidated by SPS using RCVD-treated Al₂O₃ powder at \( P_{\text{gas}} = \) (b) 800 Pa, (c) 2000 Pa, (d) 5000 Pa, (e) 10000 Pa map and (f) 20000 Pa. The pores in Al₂O₃ were apparently filled by them.
sintering rate and short holding time. The Ni nanoparticles and CNTs content increased with increasing the $P_{\text{gas}}$, and effectively enhanced the relative density of $\text{Al}_2\text{O}_3$ by filling in the pores. The maximum density was as high as 98.2%, about 6% higher than that of the monolithic $\text{Al}_2\text{O}_3$, as shown in Fig. 8.

Figure 9 shows the hardness and fracture toughness of the $\text{Al}_2\text{O}_3$–Ni–CNTs nanocomposites. The amount of Ni incorporation into CNTs at 823 K is about 0.2 wt%. Ni itself is a ductile metal phase and its toughness can be improved by crack deflection. In addition, Ni and CNT content were calculated from the mass gain after the RCVD process. Generally speaking, the toughening mechanism is that, the higher the content of Ni and CNT, the greater the toughness. Ni itself is a ductile metal phase, so the toughness of $\text{Al}_2\text{O}_3$ can be improved by means of crack deflection. The hardness of $\text{Al}_2\text{O}_3$–Ni–CNTs nanocomposites decreased from 12.6 to 4.7 GPa with increasing $C_{\text{Ni}+\text{C}}$ from 0 to 22 wt%. The reason that the hardness decreased to less than half value of the monolithic $\text{Al}_2\text{O}_3$ might be due to the formation of soft Ni phases and CNTs. The fracture toughness increased from 2.8 to 3.8 MPa m$^{1/2}$ at $C_{\text{Ni}+\text{C}} = 15$ wt% and then decreased to 3.3 with increasing $C_{\text{Ni}+\text{C}}$ to 22 wt%. Because both Ni and CNTs have been reported to improve the toughness of the ceramics. However, the toughening mechanisms are not the same. Ni itself is a ductile metal phase, so the toughness of $\text{Al}_2\text{O}_3$ can be improved by means of crack deflection. While due to the nano-whisker or fiber of CNTs, the toughness can be improved not only by deflection mechanism of crack, but also by the grain size, dislocation density, twinning and slip system. In literature, Ahmad et al. fabricated $\text{Al}_2\text{O}_3$–CNTs (multi-walled) nanocomposites by hot pressing, and the good dispersion of CNTs within the matrix was proposed to contribute to improved fracture toughness. In addition, aluminum oxy-carbide was found to be the main interfacial phase via a localized carbothermal reduction process, which enhanced the connections with CNTs and the matrix. Thus the incorporation of CNTs may improve the brittleness of ceramics in essence, and the maximum fracture toughness was about 36% higher than that of the monolithic $\text{Al}_2\text{O}_3$. Figure 10 shows the indentation morphologies of (a, b) $\text{Al}_2\text{O}_3$ and (c, d) $\text{Al}_2\text{O}_3$–Ni–CNTs nanocomposites using RCVD-treated $\text{Al}_2\text{O}_3$ powder at $P_{\text{gas}} = 10000 \text{ Pa}$. Consolidated by SPS at 1923 K for 0.6 ks. The microstructural collapse was observed both in $\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$–Ni–CNTs composites, but the indentation mark shape of $\text{Al}_2\text{O}_3$–Ni–CNTs was much more integrated, indicating that the damage tolerance was enhanced with the incorporation of Ni and CNTs.29–31
4. Conclusions

CNTs and Ni nanoparticles were co-precipitated on Al$_2$O$_3$ powders from the thermal decomposition of nickelocene at 823 K by rotary CVD. Although CNTs were observed in the obtained powders, the XRD patterns indicated that carbon should exist in the form of amorphous or solid solution in Ni. It transformed to the crystalline carbon phase after spark plasma sintering at 1923 K for 0.6 ks, and no intermediate phases were identified. CNTs were well remained after high temperature treatment due to the rapid temperature increasing/decreasing rate and short sintering time of SPS technique. The relative density of Al$_2$O$_3$–Ni–CNTs composites was increased to a maximum value 98% and the fracture toughness to 3.8 MPa m$^{1/2}$. The microstructure observation also indicated that the damage tolerance of Al$_2$O$_3$ was also enhanced with the incorporation of Ni and CNTs.

Acknowledgements The authors would like to acknowledge the financial supports from Fundamental Research Funds for the Central Universities (2015B01914), National Natural Science Foundation of China (51301059), Natural Key Foundation of Jiangsu Province (BK2011025) and National 973 Plan Project (2015CB057803) and the Opening Project of State Key Laboratory of High Performance Ceramics and Superfine Microstructure (SKL201401SIC).

References
18) Al$_2$O$_3$, JCPDS, International Centre for Diffraction Data, No. 41-142.