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Effects of titania films on the oxidation resistance and dispersibility of ultrafine diamond

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ABSTRACT

Titania-coated ultrafine diamond (UFD/TiO_2) composites had been prepared successfully, which were the core/shell structures with amorphous titania shells of approximately 4 nm thickness using tetrabutyl titanate (TBOT) as the precursor of titania in acidic condition via sol–gel process. It had a great influence on the synthesis of UFD/TiO_2 composites to control the hydrolysis and polymerization of TBOT. Contrasting to the pristine ultrafine diamond powders (UFDs), the coated UFDs could be kept dispersed in the multi-component inorganic salts aqueous solution at least 12 h without aggregation. More importantly, the oxidation resistance temperature of the coated UFDs was enhanced nearly 150 °C than the pristine, improving greatly the sintering temperature of UFD-vitrified bond composite powers obtained by polyacrylamide gel (P–G) method.

1. Introduction

The ultrafine diamond (UFD) is widely used in a variety of areas such as electroless metal plating, magnetic resonance imaging, ultra-precision grinding etc [1–3]. Especially in the field of ultra-precision grinding, it could effectively reduce the roughness of the materials using the ultrafine and superhard properties of UFD [4,5]. The P–G method has been used as a technology for preparing UFD-vitrified composites as ultra-precision grinding tools in our work [3,6]. However, there have been some problems about the oxidation resistance and dispersibility of UFDs when preparing and sintering the UFD-vitrified bond composite powders by P–G method. UFDs aggregated badly when introduced in the multi-component inorganic salts aqueous solution, and the multi-component inorganic salts were the precursors of the chemical component of ceramic matrix; the oxidation resistance of UFDs was relatively poor and the mass loss temperature was about 450 °C, it reduced the strength of UFDs easily because the sintering temperature of UFD-vitrified bond composite powders exceeded 550 °C generally. Nowadays, there are many methods to improve the oxidation resistance and dispersibility of UFDs, such as chemical plating and ultrasonic treatment [7,8]. But it only keeps good dispersibility of UFDs in aqueous solution and doesn't work in the multi-component inorganic salts aqueous solution by ultrasonic treatment; the impurities are easily introduced by the chemical plating, resulting in the corrosion, although improving the oxidation resistance temperature of UFDs.

In this study, the titania-coated method was attempted to improve the oxidation resistance temperature and dispersibility of UFDs. Quite a few researchers had also reported that some colloids were coated with titania successfully via sol–gel process, such as Au, Ag, ZnO, Fe_3O_4, a-Fe_2O_3 [9–13]. However, the difficulties in titania coating were mostly caused by fast and aggressive reaction kinetics of titania precursors, making it difficult to control their precipitation and causing the particles to aggregate or the titania to form separate particles [14]. Then in this paper, using nonionic surfactant polyvinylpyrrolidine (PVP) as a coupling agent, UFD/TiO_2 composites were prepared with TBOT as the precursor of titania in acidic condition via sol–gel process. The oxidation resistance and the dispersibility of UFD/TiO_2 composites were further investigated and discussed.

2. Experimental

Preparation of UFD/TiO_2 composites: All of chemical reagents were used as-prepared without further purification. UFDs (100–200 nm in size) were the ultrafine powders obtained by mechanical crushing method from Henan Huifeng Co. Ltd (China). Specifically,

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80 mg UFDs and 50 mg PVP were charged into 60 ml absolute ethanol by ultrasonication of the solution for 0.5 h, then the mixture was stirred vigorously for 10 h at room temperature. Subsequently, 20 ml absolute ethanol including TBOT (200 μl) was added slowly into the above mixed solution, then deionized water (50 μl) dissolved in absolute ethanol (10 ml) was added dropwise into the mixed solution, the pH value of which was adjusted to 4, using a 1.0 M HCl. Finally the reaction mixture was stirred for another 6 h at room temperature. The resultant products were separated and collected, followed by washing with absolute ethanol for 3 times and then dried at 100 °C for 3 h. In addition, the fractional samples were calcined to improve crystallinity at 400 °C in air for 2 h.

Characterization: Transmission electron microscope (TEM, JEM-2010F), and thermogravimetric and differential scanning calorimeter (TG–DSC, STA-449C) were used to characterize morphologies and anti-oxidation behaviors of UFD/TiO_2 composites and pristine UFDs. X-ray diffractometer with a Cu $K\alpha$ line (XRD, D/max-rB) and Fourier transform infrared spectrometer (FTIR, E55+FRA106) were performed to show phase composites and functional groups of UFD/TiO_2 composites and pristine UFDs. Besides, the differential settlements of pristine UFDs and UFD/TiO_2 composites in the multi-component inorganic salts aqueous solution over time were used to verify their dispersibility.

3. Results and discussion

The TEM images of the pristine UFDs and the UFD/TiO_2 composites were shown in Fig. 1a and b. From Fig. 1a, the pristine UFDs were obscure and cross-linked each other, appearing serious aggregation. However, the UFD/TiO_2 composites were well dispersed, defined without adhesion in Fig. 1b. The HRTEM images of the UFD/TiO_2 composites shown in Fig. 1c explained that the UFDs were coated uniformly with approximately 4 nm thickness titania forming the core/shell structures. This was due to the fact that the hydrolyzation of TBOT was a multiple-step electrophilic reaction in acidic condition. First, it was easy that H^+ combined with C_4H_9O- to form hydrogen bond under the effect of lone-pairs, which led to break the $\equiv Ti{-}OH_9C_4$ bond and form the $\equiv Ti{-}OH$ bond by the following reaction.

$$Ti(\ddot{O}H_9C_4)_4 + H^+ \rightarrow (C_4H_9\ddot{O})_3Ti - \ddot{O}HH_9C_4 \overset{OH^-}{\rightarrow} (C_4H_9\ddot{O})_3Ti - OH + C_4H_9OH$$

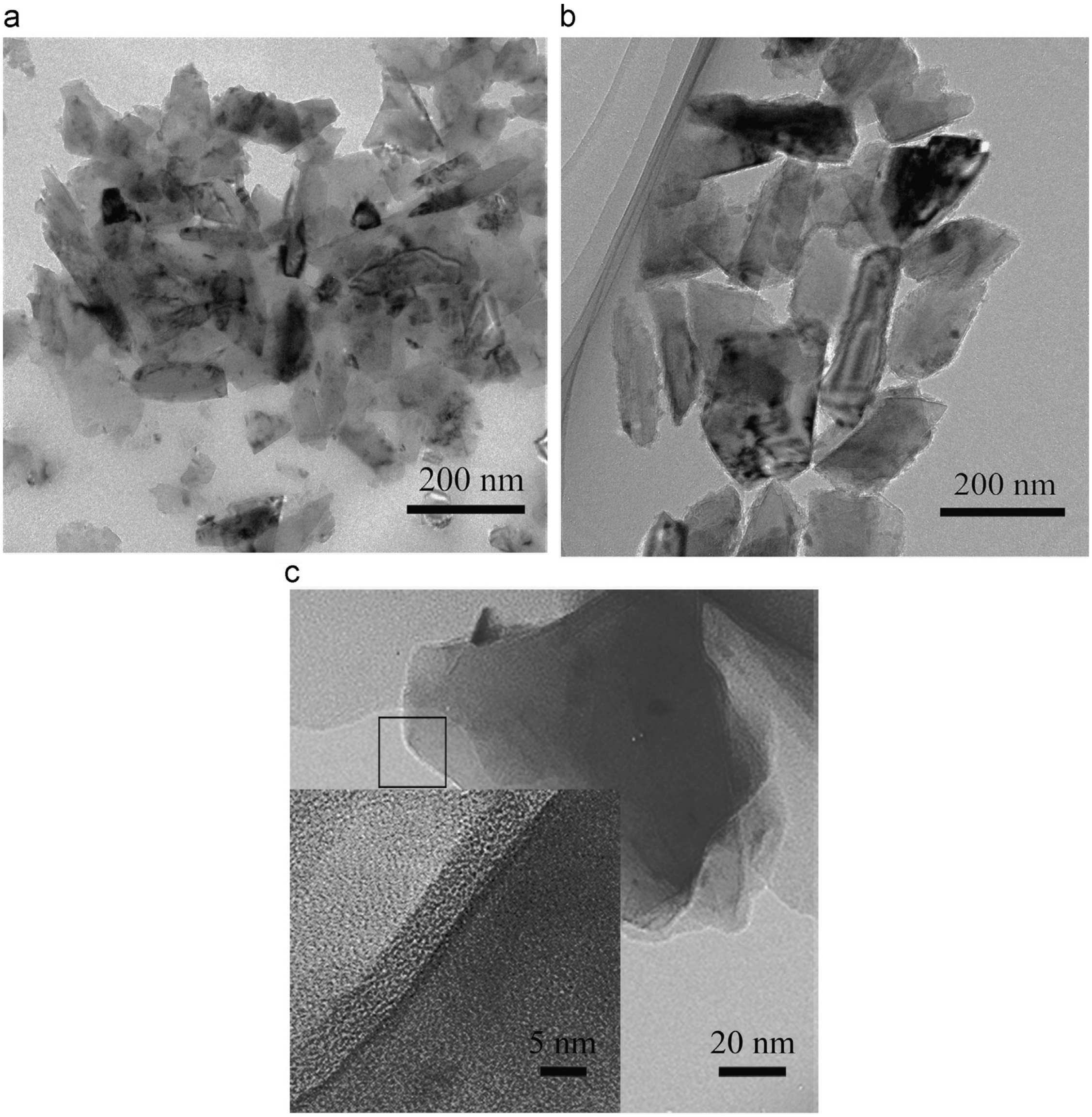

Fig. 1. TEM images of (a) the pristine UFDs, (b) the UFD/TiO_2 composites. HRTEM images of (c) the UFD/TiO_2 composites (inset: partial enlargement details (the black frame)).