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Preparation of Ni-coated Si_3N_4 powders via electroless plating method

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Abstract

The Ni/Si_3N_4 coated powders were successfully prepared via electroless plating method by using hydrazine hydrate ($N_2H_4{\cdot}H_2O$) as a reducing agent. The coated powders were characterized with several techniques such as scanning electron microscope, energy dispersive spectrometer, Transmission electron microscopy, high-resolution transmission electron microscopy and X-ray diffraction to determine particle size, composition, phase and morphology. It indicated that the core–shell structure of Ni/Si_3N_4 has been constructed in the present method, the Ni layer on the surface of Si_3N_4 particles was relatively continuous and uniform, but it is inevitable that only in very small area occurred the aggregation of Ni particles. In principle, the coated process was successful and expectable.
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Keywords: A. Powders: chemical preparation; B. Composites; C. Microstructure; D. Si_3N_4

1. Introduction

Silicon nitride (Si_3N_4) ceramics have been investigated for many years for their potential application as structural materials because of their excellent mechanical properties at room and elevated temperatures. The wide use of Si_3N_4, however, is still limited due to its catastrophic fracture. By combining ceramic with metal homogeneously, materials with high fracture toughness can be achieved. Nickel (Ni), with excellent corrosion-resistance and wear-resistance properties, could be used as a ductile phase to improve toughness of brittle Si_3N_4. In recent years, various coating methods [1–4] have been developed to substitute the admixture method, by which the uniformity of the components can be improved, leading to the improvements of the sintering property and the stability of materials [5,6]. The electroless plating is one of the most effective coating techniques and could be applied on almost all material surfaces, such as plastic [7], ceramic [8–11], alloy [12] and powders [13,14]. In the present work, the Ni-coated Si_3N_4 powders were prepared via the electroless plating.

2. Experimental procedure

2.1. Preparation of the Si_3N_4

The Si_3N_4 powders (SN-E10, UBE, Japan, $d_{50} = 0.3$ μm) were used in the present study. Non-metallic material surface must have pretreatment process before electroless plating. In this work, the Si_3N_4 powders were processed as follows.

Surface cleaning: to eliminate the impurities on original surface, the powers were immersed in hydrochloric acid for 10 min. Powers were then rinsed in deionized (DI) water until pH 7, then rinsed in ethanol.

Etching: chemical roughening provides areas into which the deposited nickel became anchored and, therefore, roughening the surface typically improved adhesion. The coarse surface was gained at room temperature for 20 min by immersing in a solution of HF (concentration: 40% 20 ml/L), NH_4F (2 g/L) and DI water.

Activation: the Si_3N_4 powders surface was non-conducting, so the activation was necessary to improve its catalytic nature. Traditional palladium activation was introduced in this work. The etched powders were immersed at room temperature for 20 min in a palladium activation solution consisting of palladium chloride, $PdCl_2$ (0.5 g/L), stannous chloride, $SnCl_2{\cdot}2H_2O$ (30 g/L), sodium chloride, NaCl (160 g/L) and hydrochloric acid, HCl (60 ml/L).

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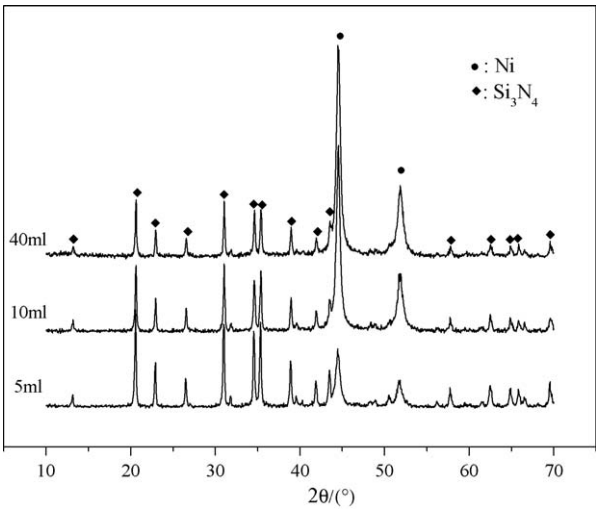

Fig. 1. XRD patterns of the Ni/Si_3N_4 coated powders obtained at the different contents of $NiCl_2$.

2.2. Electroless plating process

The Si_3N_4 powders were then dispersed in DI water to form a Si_3N_4 suspension (Si_3N_4 concentration of 0.045 mol/l) via a 12 h stirring, and adjust pH value to 11 by adding NaOH solution. Then the coating was done with constant temperature baths (70 °C) having nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) as the source of nickel and hydrazine hydrate ($N_2H_4{\cdot}H_2O$) as the reducing agent. The $NiCl_2$ solution and N_2H_4 solution were dropped into the suspension (the ratio of N_2H_4 to $NiCl_2$ kept to be 7:1) and a 5 min stirring was performed. During the reaction process, the pH value of the system was kept constant by adding NaOH solution. After coating, the powers were centrifugalized, rinsed and dried.

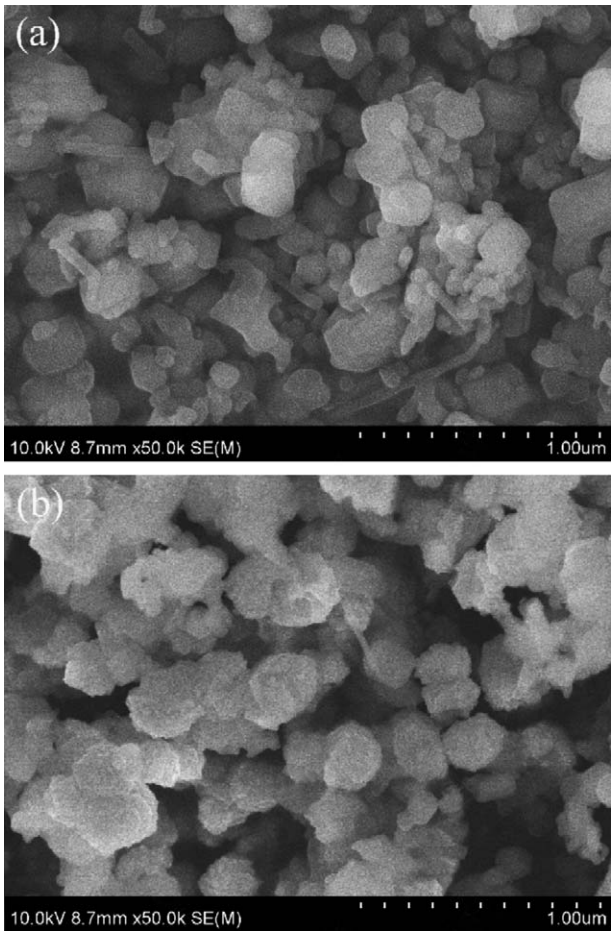

Fig. 2. SEM morphologies of the (a) as-received Si_3N_4 powders, and (b) the Ni/Si_3N_4 coated powders.

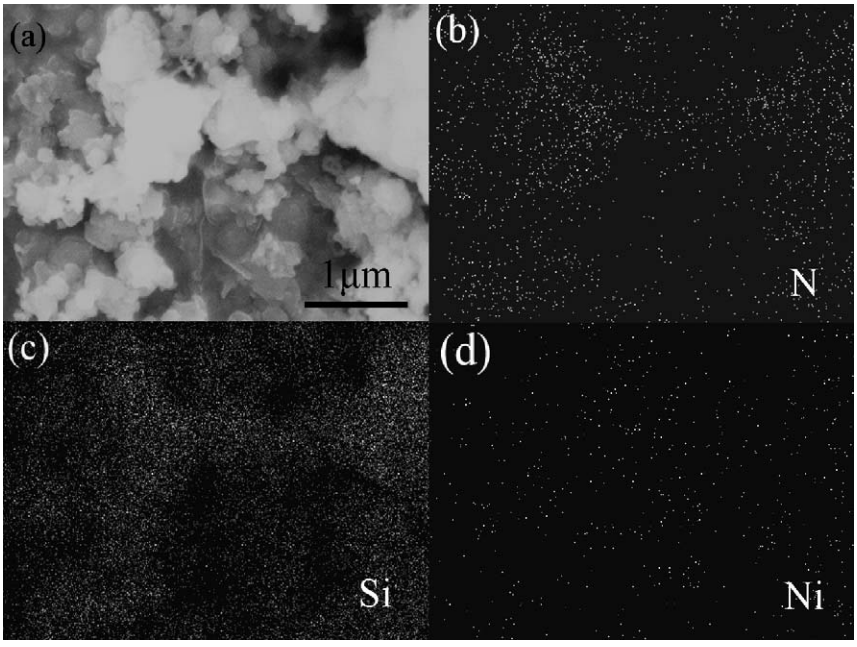

Fig. 3. SEM morphologies of the coated powders and element distribution of the surface from EDS: (b) N, (c) Si and (d) Ni.

2.3. Characterization

The phase composition was determined by X-ray diffraction (XRD). The morphology and composition of the coated powders were characterized by scanning electron microscope (SEM), Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectrometer (EDS).

3. Results and discussion

The phase composition of the coated powders was showed in Fig. 1. Only the two phases of Ni and Si_3N_4 were present in this experiment, indicating we can get Ni in the bath, and the quantity of Ni can be controlled through the quantity of $NiCl_2$, so we can control the thickness of coated layer through the quantity of $NiCl_2$ theoretically too.

SEM micrographs of as-received Si_3N_4 powders and the Ni-coated Si_3N_4 powders were presented in Fig. 2. The morphology seen in Fig. 2(a) was as-received Si_3N_4 powders with irregular shape, the surface was smooth in principle. In Fig. 2(b), all the Si_3N_4 powders were observed to be uniformly coated by the present electroless method and the coated Si_3N_4 powers retain their original high aspect ratio by this technique. In connection with the XRD analysis (Fig. 1), the layer is identified as Ni.

In order to clarify the Ni and Si_3N_4 distribution in the coated powders, Si, N and Ni element distribution maps were obtained via EDS surface analysis and shown in Fig. 3 from the maps, it can be seen that the Ni element distribution was similar to that of the coated Si_3N_4 powders, indicating a successful coating process of Ni onto the Si_3N_4 particle surface.

The Ni/Si_3N_4 composite microspheres were further investigated by TEM. Fig. 4 showed the TEM image of the microsphere. It is obviously shown that the Ni particles could be dispersed on the surface of Si_3N_4 uniformly basically. However, a small darker area could be seen in Fig. 4, indicating Ni particles were aggregated in this area. As we know, segregation in small area in bath was inevitable.

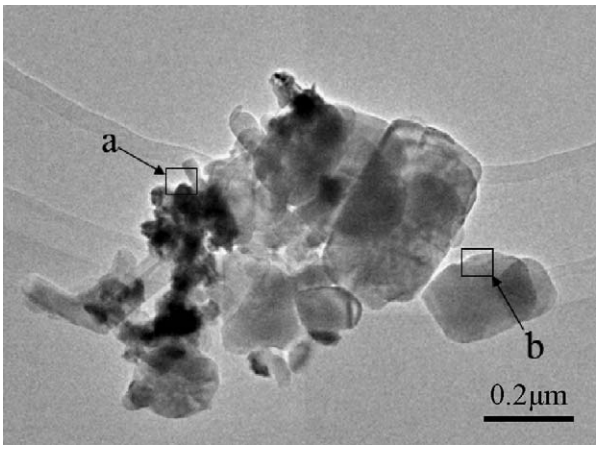

Fig. 4. TEM morphologies of the coated powders.

To identify the microstructure between the dark area and other area, HRTEM images which were taken of Fig. 4 as marked with boxes-and-arrow were observed. Fig. 5 shows the HRTEM of (a) dark area, (b) other area, and EDS profiles of (c) dark area and (d) other area. The EDS data in Fig. 5(c) and (d) confirmed that the elements of the selected area were Ni, N and Si without any other impurities. The singlet of O is probably from unavoidable surface-adsorption of oxygen on to the sample from exposure to air during sample processing. The atomic concentration of Ni in (c) and (d) was 5.28% and 1.83%. It confirmed that the concentration of Ni in dark area is higher than that of other area. Meanwhile, from the HRTEM image shown in Fig. 5(a) and (b), it was confirmed the core–shell

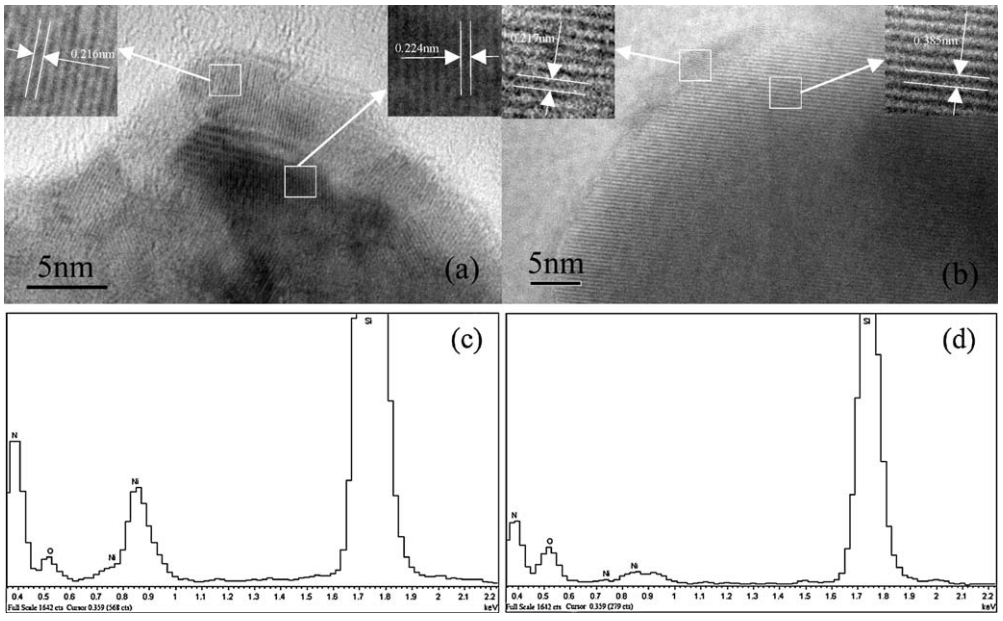

Fig. 5. HRTEM images of (a), (b), the (a), and (b) area in Fig. 4 and (c), and (d) their corresponding EDS profiles respectively.

structure of the composites. On the particles surface of (a) and (b), the lattice spacing of 0.216 nm and 0.217 nm is observed respectively and this value is assigned to the (1 1 1) plane of Ni; in particles inner, the spacing of 0.224 (a) and 0.385 (b) corresponds to the (2 1 1) plane and (1 0 2) plane of Si_3N_4. The thickness of Ni shell in (a) and (b) is about 5 nm and 2 nm respectively, indicating the difference between these two areas.

4. Conclusion

Through the processes of Surface cleaning, etching and activation, nickel film via electroless plating was deposited on the surface of Si_3N_4 successfully. The core–shell structure with shell of Ni and core of Si_3N_4 has been constructed. The Ni layer on the surface of Si_3N_4 particles was relatively continuous and uniform, only in very small area occurred the concentration of Ni particles. The thickness of Ni shell is about 2–5 nm. The preferable pH value is 11 and temperature is 70 °C for the reaction system.

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