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Microstructure and mechanical properties of $NiFe_2O_4$ ceramics reinforced with ZrO_2 particles with different sintering temperatures

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ABSTRACT

$NiFe_2O_4$ ceramics reinforced with ZrO_2 particle was fabricated by conventional high-temperature solid state reaction. Effect of the sintering temperature (1100–1500 °C) on the microstructure and mechanical properties of the $ZrO_2/NiFe_2O_4$ composite ceramics was investigated in detail. The fracture surfaces of $NiFe_2O_4$ composite ceramics were observed by scanning electron microscopy (SEM). Elemental analysis of micro-structural phases was performed using energy dispersive spectroscopy (EDS), attached with SEM. Flexural strength by three-point bending techniques and fracture toughness were measured. It was indicated that when the sintering temperature was above 1400 °C, phase transformation causing crack can directly lead to the strength degradation. The grain size of ZrO_2 increases with increasing of the sintering temperature. The samples sintering at 1400 °C had the highest flexural strength of 192 ± 10 MPa and fracture toughness of 3.38 ± 0.05 MPa $m^{1/2}$ due to densification, phase transformation.

1. Introduction

In conventional aluminum electrolysis, using carbon anodes has many disadvantages such as the consumption of carbon anode and the emission of greenhouse gases (CO_2), fluorocarbons (CF_4, C_2F_6) and sulfurous gases (SO_2, CS_2, H_2S), so the novel techniques of aluminum electrolysis with inert anodes have been an important item in aluminum electrolysis area for many years [1,2]. At present, inert anode can be divided into three kinds, i.e. metals, ceramic oxides and cermets [3–5]. Compared with metals and oxides, cermets have become one of the most promising inert anode materials because of metallic conductivity and its high ceramic corrosive resistance. $NiFe_2O_4$ is the first choice as ceramic matrix for cermets inert anode because it shows a good combination on physical and chemical properties such as high melting-point, good thermal stability and strong resistance to molten cryolite as the preferred materials for ceramics inert anode [6–8]. Nonetheless, we all know that its low fracture toughness and bad thermal shock resistance is still the obstacle preventing ceramic matrix composites from being widely used. Its poor toughness and inability to withstand heat shocks make the anode crack, and the purity of the electrolytic Al is influenced negatively when this kind of anode materials were used in aluminum electrolysis. In 2001, Alcoa Company announced that an experiment on the inert anode was delayed due to its cracking in aluminum electrolysis [9]. Hence, thermal shock resistance is especially important for industrialized application of inert anode. In order to reduce the brittleness and to increase the strength and toughness, a great deal of research work has been done. Zhang [10] found that the fracture toughness increases from 1.22 MPa $m^{1/2}$ to 2.80 MPa $m^{1/2}$ with increasing metallic (85Cu–15Ni) content from 0% to 20%. Zhang et al. [11] found a gradual improvement of mechanical properties of $NiFe_2O_4$ by adding SiC_w, but she pointed that SiC_w can easily react with the ceramic matrix at a high sintering temperature. Ma et al. [12] reported the bending strength of samples is improved by about 22% with 3 wt.% copper-coated carbon fiber compared to that of $NiFe_2O_4$ composite ceramics. Hua et al. [13,14] investigated the best preparation technique on synthesis of $ZrO_{2(f)}/NiFe_2O_4$ composite ceramics, and also studied corrosion behavior of $ZrO_{2(f)}/NiFe_2O_4$ inert anode in cryolite molten salt. The results shows the electrolytic corrosion rate of anode samples containing 3 wt.% $ZrO_{2(f)}$ is 2.2 mg/(cm^2 h), which is much lower than its static thermal corrosion rate. So it is very clear that the additions have great influence on the fracture toughness of composite ceramic. Whereas there are few reports on ZrO_2 particle reinforced $NiFe_2O_4$ composite ceramics according to present literatures.

In this work, powder metallurgy methods were adopted to prepare $ZrO_2/NiFe_2O_4$ composite ceramics. In order to improve the mechanical properties of $NiFe_2O_4$ ceramics, the major approach is to introduce ZrO_2 particle into the ceramic matrix to form

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composite ceramics. It is interesting to know that ZrO_2 undergoes at least three crystallographic transformations (monoclinic, tetragonal and cubic) when it cools from high temperature to room temperature.

It is reported that yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) possess superior fracture toughness because of phase transformation [15,16]. While the temperature was the key influencing factor of phase transformation, it was necessary to investigate the effect of different sintering temperatures on microstructure and mechanical properties of the $ZrO_2/NiFe_2O_4$ composite ceramics. The purpose of this work was to find the optimal sintering temperature for the $ZrO_2/NiFe_2O_4$ composite ceramics.

2. Experimental procedure

2.1. Synthesis

Commercially available Fe_2O_3 powder, its average grain size and purity are 0.5–1.0 μm and 99.3 wt.%, was used as the raw material. The average grain size and purity of NiO (excessive 15 wt.%) are 0.5–1.0 μm and 99.98 wt.%, respectively. The mixture of the two powders ground in distilled water by ball-milling for 24 h, and then the mixture was dried thoroughly and sieved by a 100-mesh sieve. The sieved mixture was calcined at 1200 °C in air for 6 h to produce the $NiFe_2O_4$ spinel matrix material. The calcined ceramic matrix was crushed and screened, and then the powders with particle size under 100 meshes were milled with 5 wt.% ZrO_2 particle in distilled water for 6 h. The slurries with ZrO_2 particle were dried thoroughly and were ground with 4 vol.% polyvinyl alcohol (PVA) binder and pressed into blocks (60 mm × 15 mm × 8 mm) at 200 MPa. The green samples were sintered in air at 1100, 1200, 1300, 1400, and 1500 °C for 6 h, respectively, and then cooled in a furnace.

2.2. Characterization

Microstructure of fracture surfaces of $ZrO_2/NiFe_2O_4$ composite ceramics and fracture sections of samples after three-point bending tests were observed by scanning electron microscopy (SEM, SSX-550, Japan) with simultaneous chemical analysis by energy dispersive spectroscopy. The phase composition was determined by X-ray diffraction (XRD, Rigaku, Dmax-rb, Cu Ka = 1.5418 Å). The bulk density of the samples was determined using the Archimedes technique with water as the immersing medium. Flexural strength in a three-point configuration was tested using an electron omnipotence machine NSTRON-4206 on a 60 mm × 15 mm × 8 mm chambered bar with a span of 30 mm and crosshead speed of 0.05 mm/min. Peak load was obtained when the sample was fractured and the average value of six samples was obtained. The fracture toughness (K_{IC}) was evaluated with a span of 30 mm and a crosshead speed of 0.05 mm/min using a single-edge notched beam test on 60 mm × 15 mm × 8 mm test bars on the same jig used for the flexural strength.

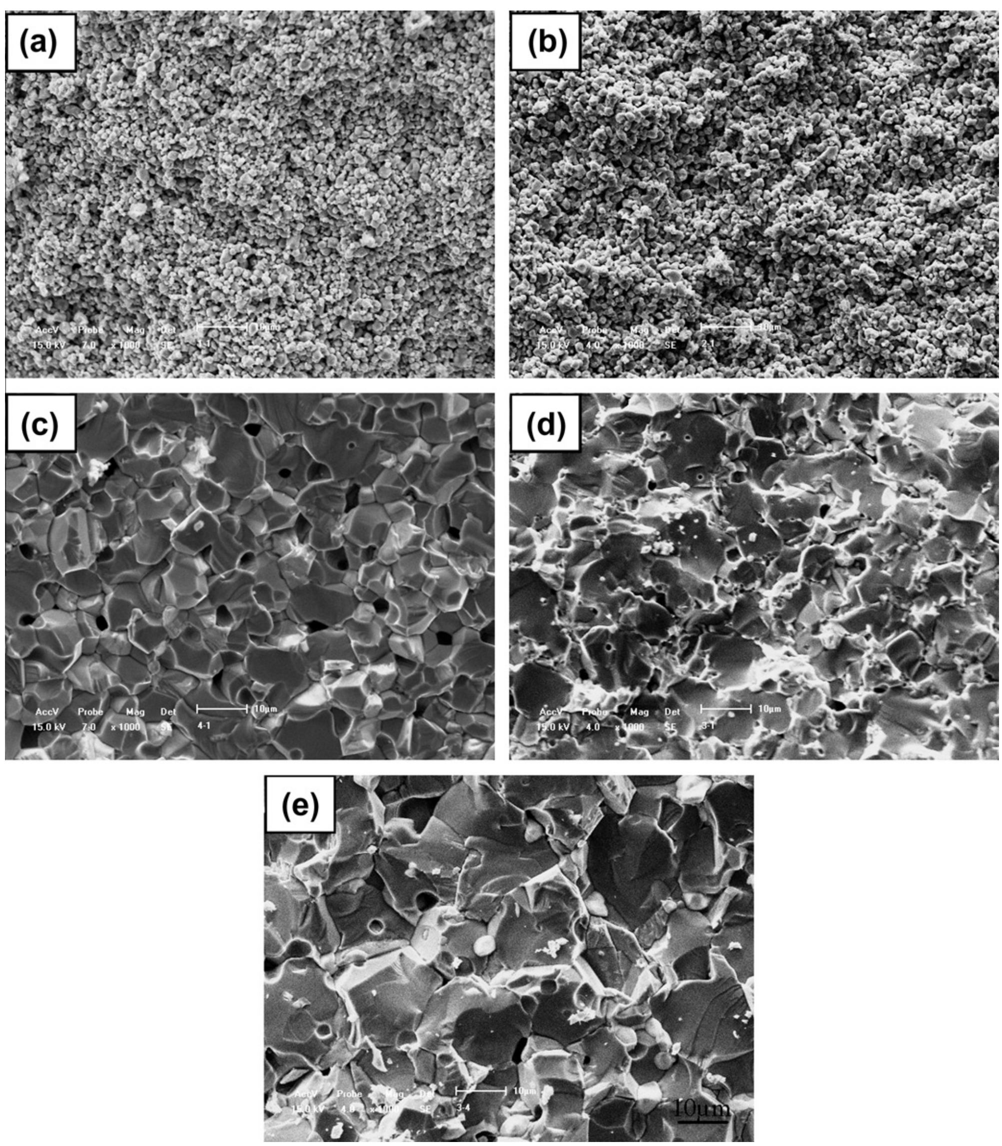

Fig. 1. SEM micrographs of fracture surfaces of $ZrO_2/NiFe_2O_4$ composite ceramics: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, (d) 1400 °C and (e) 1500 °C.