Journal of Alloys and Compounds 581 (2013) 11–15

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

# Preparation and performance of ZnO nanowires modified carbon fibers reinforced $NiFe_2O_4$ ceramic matrix composite

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ARTICLE INFO

*Article history:*
Received 26 April 2013
Received in revised form 24 June 2013
Accepted 26 June 2013
Available online 3 July 2013

*Keywords:*
Nickel ferrite
Ceramic matrix composite
Carbon fiber
Zinc oxide nanowire
Liquid growth

ABSTRACT

The surface of carbon fibers was modified by ZnO nanowires using the liquid growth method. $NiFe_2O_4$ ceramic matrix composites reinforced by the modified carbon fibers were prepared by a high-temperature solid-state reaction method at 1300 °C for 5 h in $N_2$ atmosphere. The influences of modified carbon fibers on the mechanical performances of $NiFe_2O_4$ composites were investigated. The crystal structure of modified carbon fibers and the morphology of modified carbon fibers surface and the $NiFe_2O_4$ composites fracture cross-section were observed by meaning of X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. The results showed that hexagonal wurtzite ZnO nanowires array grew from the surface of carbon fibers vertically, with nanowires diameters ranging from 170 nm to 380 nm and lengths up to 2.8 μm. Unlike existing chemical modification and high temperature oxidation method, the liquid growth allowed morphology control and maintained the single fiber tensile strength substantially unchanged under certain growth procedures. Compared to pure $NiFe_2O_4$ ceramic and bare carbon fibers reinforced $NiFe_2O_4$ composite, the bending strength of $NiFe_2O_4$ composite reinforced with ZnO nanowires surface modified carbon fibers was shown to increase by up to 70% and 45%, respectively. The development of an interphase offering control over the morphology will provide a means to produce multifunctional composites.

## 1. Introduction

Since the Hall–Héroult process was brought into aluminum production, various researches have been carried out to explore an novel material serving as inert anode to instead of traditional carbon anode, so as to decrease the consumption of massive carbon resources and eliminate the emission of green house gases ($CO_2$), fluorocarbons ($CF_4$, $C_2F_6$) and sulfurous gases ($SO_2$, $CS_2$, $H_2S$). Recently, most researchers have concentrated on $NiFe_2O_4$ ceramic matrix composite (CMC), because of whose excellent properties, such as high resistance against fluoride melts and oxygen produced by electrolysis, adequate strength at high temperature and high thermal stability, etc. [1–4]. A phenomenon found from electrolysis experimentation results was that oxygen produced by electrolysis formed a protective membrane to decrease inert anode corrosion of cryolite fused salt. Nonetheless, the low fracture toughness and inability to withstand heat shocks make the $NiFe_2O_4$ based inert anode crack, thus the purity of the electrolytic aluminum should be influenced negatively as long as fine fragments of anode material come off [5,6]. So the low fracture toughness is still the obstacle preventing this kind of ceramic matrix composites from being widely used. Therefore, how to improve the mechanical performances of $NiFe_2O_4$ CMC has become a challenging study.

Now, rapid growth has occurred in the field of fiber reinforced CMC due to high specific strength and high elastic modulus they provide with respect to other engineering materials [7–9], but studies have seldom been carried out to improve the mechanical properties of $NiFe_2O_4$ CMC reinforced by carbon fibers. Ma et al. [10] reported that the bending strength of $NiFe_2O_4$ CMC reinforced with 3 wt% copper-coated carbon fibers was up to 25.64 MPa and increased about 22% compared to pure $NiFe_2O_4$ ceramics. Long et al. [11] investigated the effect of carbon fibers (CFs) and nickel-coated carbon fibers (NiCFs) on the toughness of $NiFe_2O_4$ CMC and found that it was sub-optimal owing to the poor wetting among metal coating, carbon fiber and $NiFe_2O_4$ ceramics. In addition, the chemical modification and atmospheric oxidation can modify the morphology of carbon fiber surface to obtain increased adhesion with the matrix; however, these treatments have all seen to improve interfacial properties at the cost of the fiber strength, because of the high-temperature processing (350–400 °C) required. Hua et al. [12] reported that $ZrO_2$ fibers could serve as a potential toughening agent for $NiFe_2O_4$ CMC, and the $ZrO_2$ fibers doped $NiFe_2O_4$ composite had an improved fracture toughness of $3.05 \pm 0.1\ \mathrm{MPa\ m^{1/2}}$ compared with $NiFe_2O_4$ CMC of $1.91 \pm 0.2\ \mathrm{MPa\ m^{1/2}}$ due to fiber debonding, fiber pulling-out and fiber bridging as well as microcrack toughening. An alternative

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http://dx.doi.org/10.1016/j.jallcom.2013.06.157

interphase approach is to grow nanowires, nanorods, nanotubes or microscale whiskers on the surface of carbon fiber, which can protrude into the matrix and lead to contact area increasing, so the bonding force and the load transfer between fiber and matrix should be strengthened. ZnO nanowires array growing on the surface of carbon fibers was developed by Galan et al. [13]. It was shown that the interfacial shear strength increased from 45.72 MPa to 154.64 MPa with nanowires diameter increasing from 50 nm to 200 nm. The morphology of ZnO nanowires could be controlled through the adjusting the properties of growth solution and consequently, this method should offer new opportunities for researchers to improve the interface strength.

The aim of the present work was to exploit liquid growth method for the preparation of ZnO nanowires array on carbon fibers (ZnO/CFs) and to explore the effect of ZnO/CFs with controlled diameter and length on the microstructure and mechanical properties of $NiFe_2O_4$ CMC. The resulting techniques should provide a means to design the interphase to maximize load transfer from the matrix to the fiber efficiently.

## 2. Experimental procedure

### 2.1. Preparation of ZnO nanowires array on carbon fibers surface

To synthesize ZnO colloid solution as quantum dot seeds, 0.0125 M (40 ml) of zinc acetate ethanol solution and 0.02 M (40 ml) of sodium hydroxide ethanol solution was stirred vigorously for 5 min at 50 °C, separately. These two solutions were added into 500 ml of ethanol solution with vigorous stirring. Then the mixed solution was heated at 65 °C for 30 min to prepare ZnO colloid solution. Carbon fibers were pretreated in concentrated nitric acid for 5 min to change hydroxyl organic compounds into carboxylic acid groups. Subsequently, the treated carbon fibers were rinsed with distilled water and dried at 100 °C for 10 min. Then the dried carbon fibers dipped into the ZnO colloid solution for 10 min and finally annealed at 120 °C for 10 min for a total of three times to obtain ZnO crystal seeds layer on the surface of carbon fibers.

For the synthesis of ZnO nanowires array growth solution, 0.0125 mol of zinc nitrate hexahydrate and 0.0125 mol of hexamethylenetetramine (HMTA) were dissolved in 500 ml of distilled water, and the solution was heated with vigorous stirring until the temperature of water bath reached 90 °C. The carbon fibers coated with ZnO crystal seeds layer were immersed into the growth solution for 2, 4 and 10 h, respectively, then taken out and rinsed with distilled water to remove most of the large prisms adhered on the surface of the ZnO nanowires. Finally, the treated carbon fibers were annealed at 80 °C to obtain ZnO/CFs, signed as ZnO/CFs-2, ZnO/CFs-4 and ZnO/CFs-10, respectively. The resulting continuous carbon fibers were cut into 2 mm pieces.

### 2.2. Synthesis of modified carbon fibers reinforced $NiFe_2O_4$ ceramic matrix composite

Powders of $Fe_2O_3$ (0.05–0.10 mm, purity >99.4 wt%) and $Ni_2O_3$ (0.05–0.10 mm, purity >99.5 wt%,) used as the raw materials, with the molar ratio of 4–3, were wet ground by vertical planetary mill for 20 min. The mixture was dried thoroughly and calcined at 1000 °C in air for 6 h to synthesize $NiFe_2O_4$ spinel phase, then crushed to obtain the $NiFe_2O_4$ ceramic powders of the fineness of 200 mesh sieve. $NiFe_2O_4$ ceramic powders were mixed with 2 wt% short carbon fibers by vertical planetary mill for 10 min in absent of abrasive media to avoid the fibers being damaged during milling. The milled powders were pressed into blocks (70 mm × 15 mm × 5 ± 1 mm) at 40 MPa, and the composite green bodies were sintered in $N_2$ atmosphere at 1300 °C for 5 h, with an average heating rate of 4 °C/min, to synthesize ZnO/CFs reinforced $NiFe_2O_4$ CMC.

### 2.3. Characterization

The crystal structure of ZnO/CFs was characterized by an X-ray diffractometer (XRD) (model: D/max-RB with an accelerating voltage 40 kV) with Cu K$\alpha$ radiation ($\lambda$ = 1.54059 nm) and a scan rate of 8 °/min at room temperature. The morphologies of ZnO/CFs surface and ZnO/CFs reinforced $NiFe_2O_4$ CMC fracture cross-section were scanned using a FEI Sirion 200 scanning electron microscopy (SEM). The single fiber tensile strength was determined using a YG/B/003A electronic single fiber strength tester. Single carbon fiber was separated and clipped at both ends of the fiber to ensure fiber in verticality, leaving a 20 mm fiber segment for testing. The peak load was obtained when the fiber was fractured and the average value of ten or twelve samples was obtained. The mechanical performances of ZnO/CFs-4 reinforced $NiFe_2O_4$ CMC (abbreviated as S-ZC4) and ZnO/CFs-10 reinforced $NiFe_2O_4$ CMC (abbreviated as S-ZC10) were investigated compared with pure $NiFe_2O_4$ CMC (abbreviated as S0) and bare CFs reinforced $NiFe_2O_4$ CMC (abbreviated as S-CF). The bulk density of the sample was determined using the Archimedes technique. Bending strength was tested using a WDW1020 electron omnipotence machine. The as-sintered specimens were ground to final size of 50 mm × 10 mm × 3 mm for three point bending strength tests conduced with supports spans of 30 mm at a loading speed of 0.5 mm/min. The peak load was obtained when the sample was fractured and the average value of five samples was obtained.

## 3. Results and discusses

### 3.1. Microstructure of ZnO nanowires array on carbon fiber surface

The XRD patterns of bare CFs and ZnO/CFs-10 are shown as Fig. 1. From pattern b, the characteristic peaks at 32.06°, 34.68°, 36.6°, 47.9°, 56.85°, 63.24°, 68.4° and 69.4° are found, which presents the hexagonal wurtzite ZnO phase corresponding to the reflecting planes of (100), (002), (101), (102), (110), (103), (112) and (201), respectively; other characteristic peaks are corresponding to those of carbon fiber, without any impurity phase. But compared to standard ZnO patterns (JCPDS No: 79-0205), the diffraction peak intensity of (002) plane is higher than that of (101) plane, which indicates that ZnO crystals growth had priority on (002) lattice plane in our experiment condition. Thus, inner stress raised from *c*-axis oriented ZnO crystal caused lattice distortion, which made all characteristic peaks show shifting right slightly.

The morphology of ZnO nanowires array on surface of carbon fibers scanned by SEM can be seen in Fig. 2. The ZnO nanowires array with exact hexagon cross section presents vertically on the surface of carbon fibers; in addition, the ZnO nanowires are well-distributed throughout the entire fiber and relatively uniform in length and diameter; however, we also found some of the large prisms remain on the surface of the ZnO nanowires. When the time of liquid growth was less than 2 h, ZnO nanowires were of irregular boundary of hexagon cross section, inhomogeneous diameters and step-like ends, shown in Fig. 2(a), inset, which indicates that the degree of ZnO crystallization was imperfect. While the liquid growth time was prolonged to 4 h, the highly crystalline ZnO nanowires were of hexagonal columnar-like structure in large-scale drawing as shown in Fig. 2(b), inset. From Fig. 2(d), it is shown that the structure of ZnO nanowires array coating changed with the distance from the carbon fiber surface; ZnO quantum dot seeds layer synthesized by dipping the carbon fibers into ZnO colloid solution repeatedly, as compact layer, adhered to the surface of carbon fibers and consequently, the ZnO nanowires grew from the ZnO seed layer with vertical alignment.

The mechanism of ZnO nanowires grown on the surface of carbon fibers has been reported [14,15]. To alleviate poor adhesion

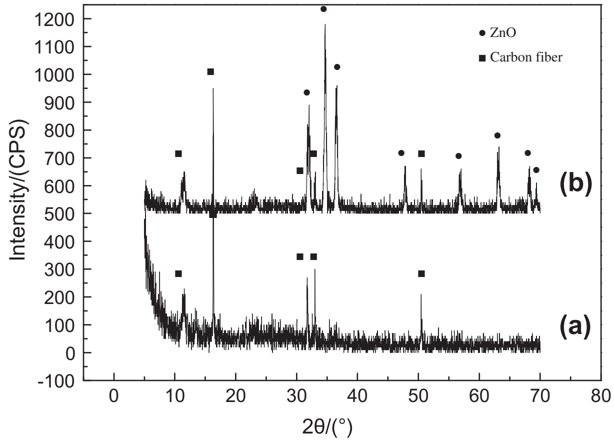

**Fig. 1.** X-ray diffraction patterns of samples (a) bare carbon fiber and (b) ZnO nanorods modified carbon fiber.