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Synthesis of nickel aluminate nanoceramic compound from aluminum and nickel carbonate by mechanical alloying with subsequent annealing

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Abstract: The aim of present work was to produce pure nickel aluminate ($NiAl_2O_4$) nanoceramic compound by high energy milling of nickel carbonate ($NiCO_3$) and aluminum (Al) powders followed by annealing. Phase composition, thermal behavior, morphology and microstructure of powder samples were characterized by means of X-ray diffraction, differential scanning calorimeter, thermogravimetric analysis, scanning electron microscopy and transmission electron microscopy. The results showed that formation of $NiAl_2O_4$ spinel compound from $NiCO_3$ and Al powders took place in three steps: oxidation of Al to Al_2O_3, decomposition of $NiCO_3$ to NiO and CO_2, and finally the solid state reaction between Al_2O_3 and NiO. It was also demonstrated that single phase $NiAl_2O_4$ spinel compound can be produced by 5 h of mechanical milling with subsequent annealing of $NiCO_3$/Al mixture at 900 °C for 2 h, which is ~500 °C lower than the temperatures used in the traditional solid state methods. The particle diameter of the produced $NiAl_2O_4$ spinel compound was found to be less than 100 nm as measured by transmission electron microscopy.
Key words: nickel aluminate; nanoceramic; ball-milling; annealing

1 Introduction

Nickel aluminate ($NiAl_2O_4$) is a mixed cation oxide with normal spinel structure, where aluminum (Al) occupies the octahedral sites and nickel (Ni) occupies the tetrahedral sites [1]. Due to its high thermal stability and chemical inertia, $NiAl_2O_4$ has been used in the catalytic applications ranging from methane/steam and methanol reforming to hydrocarbon cracking, dehydrogenation, hydrodesulfurization, and hydrodenitrogenation [2,3]. Other applications include anode electrode material for internal reforming solid oxide fuel cells [4].

Different methods such as solid state reaction [5], impregnation, co-precipitation [6], sol−gel [7], microwave [8,9] and combustion [10] have been suggested for the preparation of $NiAl_2O_4$ spinel. Solid state reaction of metal oxides needs high temperatures of calcination and long reaction time, resulting in a $NiAl_2O_4$ spinel with low surface area [11]. Co-precipitation method requires enormous efforts to ensure a homogeneous material with uniform particle size and composition [12]. Sol−gel route presents the disadvantages of the relatively high costs of the metal alkoxides and the release of large amounts of alcohol during the calcination step which requires safety considerations [13]. Microwave heating is limited by the low tendency of some materials to absorb microwave radiation [8].

Mechanical alloying is a solid state processing route which is simply capable of producing nanostructured materials and powders in the nanometer size range [14,15]. This process involves repeated fracturing and cold welding of raw materials, which lead to particle size reduction [16,17]. This fine particle size with high density of crystalline defects induced during the milling provides high diffusivity paths for atoms which enhances the kinetics of chemical reactions at room temperature [18]. This process can also enhance the reactivity of milled powders and hence, reduce the temperature of chemical reactions during subsequent thermal treatment, called mechanical activation [19,20]. Mechanical activation and mechanochemical synthesis have been used to produce spinel compounds. SHIRI et al [21] produced the single phase monocalcium aluminate ($CaAl_2O_4$) spinel compound by 100 h of mechanical activation of oxide powders followed by annealing at 1200 °C for 2 h. HAN et al [22] produced the single phase $NiAl_2O_4$ spinel compound through 168 h of mechanical alloying of alumina (Al_2O_3) and nickel oxide (NiO) powders followed by sintering at 1300 °C for 2 h. NAZEMI et al [23] prepared the nanostructured $NiAl_2O_4$ spinel powder from spent NiO/Al_2O_3 catalyst

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using mechanochemical synthesis. Their results showed that single phase $NiAl_2O_4$ compound can be synthesized by 60 h of mechanical alloying. They also found that milling for 15 h with subsequent heat treatment at 1100 °C for 2 h is enough to produce $NiAl_2O_4$ spinel.

Although synthesis of $NiAl_2O_4$ spinel by mechanical alloying of Al_2O_3 and NiO powders was previously investigated, the milling time used was very long (over 60 h). Also, when mechanical activation with subsequent heat treatment was employed to synthesize $NiAl_2O_4$ spinel, a high annealing temperature (above 1100 °C) was required. Therefore, the aim of the present work was to develop an easy method for producing pure nanocrystalline $NiAl_2O_4$ spinel powder. In this study, $NiCO_3$ and Al powders, which are cheaper than oxide powders (NiO, Al_2O_3), were used as starting materials.

2 Experimental

The materials used in this study were $NiCO_3$ (98% purity, Sigma-Aldrich) and Al (99.5% purity, Khorasan Powder Metallurgy) powders. Figure 1 shows the morphologies of the initial powders. The $NiCO_3$ powder had an angular morphology with a mean agglomerates size of 3 μm. The Al powders had an irregular shape with particle sizes between 20 and 100 μm.

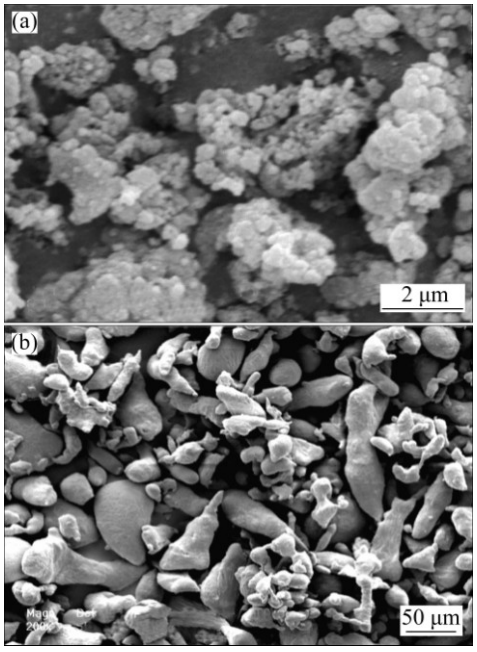

Fig. 1 Morphologies of initial materials: (a) $NiCO_3$; (b) Al

The $NiCO_3$ and Al powders were mixed at a 1:2 molar ratio (5.57 g $NiCO_3$ and 2.43 g Al) and then the mixture was mechanically milled in air atmosphere at room temperature for 15 min, 1, 3, 5 and 10 h. The milling process was carried out in a planetary ball mill (Retsch PM400 type). Table 1 presents the processing parameters of milling operation.

Table 1 Processing parameters of milling operation

Parameter	Value
Rotation speed of vial/(r·min^{-1})	250
Rotation speed of disk/(r·min^{-1})	350
Diameter of vial/mm	90
Diameter of disk/mm	350
Vial material	Zirconia
Capacity of vial/mL	120
Ball material	Zirconia
Diameter of balls/mm	10
Number of balls	5
Ball to powder mass ratio	20:1
Total powder mass/g	8
Atmosphere	Air

Structural changes during the milling were determined by X-ray diffraction (XRD- Philips X'PERT MPD X-ray diffractometer) with Cu K_α radiation (λ=0.15406 nm). The XRD patterns were recorded in the 2θ range of 20°−80° (step size 0.05°, time per step 1 s). Morphology of milled powders was investigated by scanning electron microscopy (SEM- Philips XL30) at an accelerating voltage of 30 kV. Thermal behavior of milled powders was studied by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis (Setaram DSC-TG calorimeter) at a constant heating rate of 10 °C/min in air.

The milled powders were annealed at 900 °C for 2 h in air atmosphere. The phase compositions of heat treated samples were characterized by XRD. The crystallite size of spinel powder was determined based on the XRD line broadening by the Williamson−Hall method [24]:

$$B\cos\theta=(K\lambda)/D+2\varepsilon\sin\theta \quad (1)$$

where β is peak breath at half maxima intensity, θ is the Bragg angle, λ is the wavelength of the radiation used (λ=0.15406 nm), D is the mean crystallite size, ε is the average internal strain and K is the Scherrer constant (~0.9). Microstructure of annealed powders was studied using SEM and transmission electron microscopy (TEM-model 120 kV LEO 912AB). The TEM sample was prepared by suspending the powder in methanol using ultrasonic vibration. A drop of the suspension was placed on a carbon-coated copper grid and dried. The sample was then investigated using TEM.

3 Results and discussion

Figure 2 shows the XRD patterns of the initial powder mixture after different milling time. In the XRD