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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.

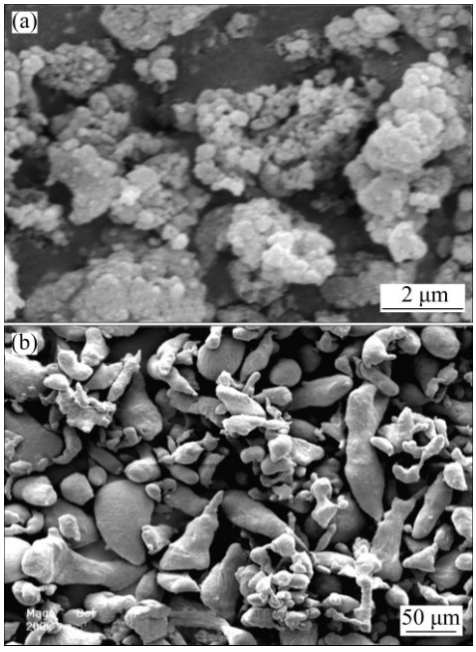

Fig. 1 Morphologies of initial materials: (a) $NiCO_3$; (b) Al

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

pattern of powders milled for 15 min, only the diffraction peaks of the pure Al are evident. $NiCO_3$ peaks are not observed because of its amorphous structure. The broadening of the Al peaks and a remarkable decrease in their intensities are observed after 3 h of milling, indicating grain refinement and straining during the milling [16]. Meanwhile, small peaks of Al_2O_3 appeared in the XRD pattern, indicating the gradual oxidation of Al according to the following reaction:

$$2Al(s)+(3/2)O_2(s)\rightarrow Al_2O_3(s) \quad (2)$$

The oxygen comes from the air. After 5 h of milling, the diffraction peaks of Al completely vanish and only diffraction peaks of crystalline Al_2O_3 are observed in the XRD pattern, indicating that all the Al powders in the vial were transformed to Al_2O_3 via the solid state oxidation reaction. The crystallite size of Al_2O_3 in this sample was ~12 nm. Further milling up to 10 h has no effect on the phase composition.

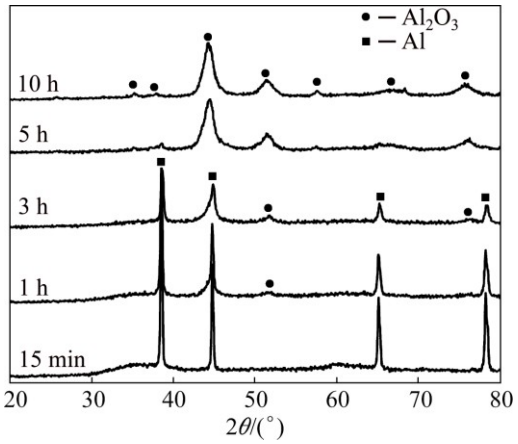

Fig. 2 XRD patterns of initial powders after milling for different times

The DSC and TG curves of the powders after 15 min and 5 h of milling are illustrated in Fig. 3. In the DSC curve of sample milled for 15 min (Fig. 3(a)), three endothermic peaks are observed at 140, 310 and 661 °C, which are attributed to the dehydration, $NiCO_3$ decomposition (removal of CO_2) and the melting of Al. Two exothermic peaks are also observed in this figure: one small peak at 820 °C associated with the formation of $NiAl_2O_4$ spinel by reaction between Al_2O_3 and NiO, and a highly exothermic peak at 944 °C which is attributed to the oxidation of liquid Al (ΔH^{Θ} ~1675.7 kJ/mol [25]). The TG curve of sample milled for 15 min has three stages. The first stage (~25% of mass loss) occurred at temperatures below 300 °C due to the dehydration and $NiCO_3$ decomposition (removal of CO_2). The second stage is between 300 and 900 °C, which shows no significant mass change. Finally, the third stage (~20% mass gain) occurred at temperatures higher than 900 °C owing to the oxidation of Al.

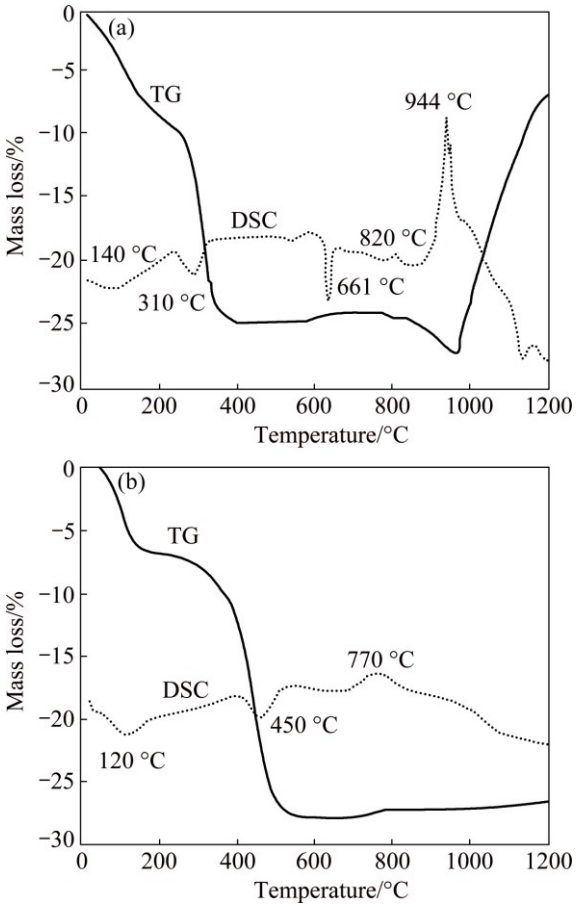

Fig. 3 DSC and TG curves of samples milled for 15 min (a) and 5 h (b)

The DSC curve related to the 5 h-milled sample in Fig. 3(b) shows three peaks: two endothermic peaks at 120 and 450 °C, and one broad exothermic peak at 770 °C. The endothermic peaks at 120 and 450 °C are attributed to the dehydration and $NiCO_3$ decomposition, respectively. The broad exothermic peak at 770 °C is due to the formation of spinel phase. The mass loss of this sample occurred in two stages. The first stage (~7% of mass loss) occurred at a temperature below 300 °C due to the dehydration. The second stage (~20% of mass loss) took place below 500 °C owing to the decomposition of $NiCO_3$. According to the DSC and TG results, the temperature of $NiCO_3$ decomposition in the sample milled for 5 h is higher than that for the sample milled for 15 min. This is due to the enhancement of the thermal stability of $NiCO_3$ by milling, in agreement with previous studies [26].

Based on the DSC results, the milled powders were annealed at 900 °C for 2 h. Figure 4 shows the XRD patterns of the annealed samples. In the sample milled for 15 min, Al peaks disappeared after annealing and peaks corresponding to Al_2O_3, NiO and $NiAl_2O_4$ spinel

are observed. The relative intensities of spinel peaks increase and those for Al_2O_3 and NiO decrease by increasing the milling time to 3 h. This indicates that milling process promotes the formation of $NiAl_2O_4$ spinel during the subsequent annealing. According to the XRD results, the $NiAl_2O_4$ single phase compound is obtained from the sample milled for 5 h after annealing at 900 °C for 2 h. The average crystallite size of $NiAl_2O_4$ spinel in the sample with 5 h of milling was calculated to be ~30 nm, using the Williamson−Hall method.

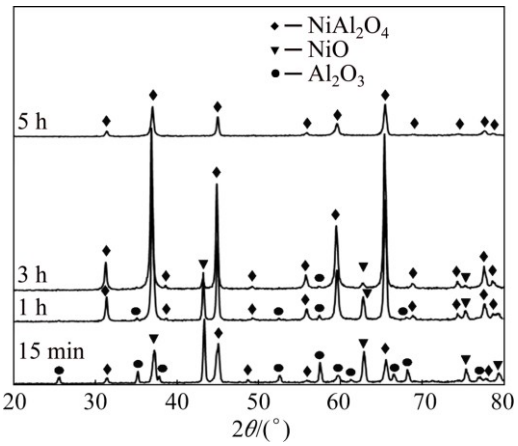

Fig. 4 XRD patterns of milled powder mixtures after annealing at 900 °C for 2 h

According to the XRD and DSC results, the first step in the formation of $NiAl_2O_4$ compound from the Al and $NiCO_3$ powders is the oxidation of Al to Al_2O_3 according to reaction 1. This step can be done during the milling or subsequent heat treatment. During the heat treatment, $NiCO_3$ is decomposed according to the following reaction:

$$NiCO_3(s)\rightarrow NiO(s)+CO_2(g) \quad (3)$$

The CO_2 is released to the atmosphere and the NiO is remained in the form of a porous powder. The produced NiO has a high reactivity and reacts with Al_2O_3 to form $NiAl_2O_4$:

$$NiO(s)+Al_2O_3(s)\rightarrow NiAl_2O_4(s) \quad (4)$$

It is well understood that formation of $NiAl_2O_4$ spinel by solid state reaction between Al_2O_3 and NiO involves counter diffusion of Ni and Al ions through the spinel layer and requires high temperatures between 1200 and 1500 °C for long period of time [5]. PEELAMEDU et al [27] reported that microwave-assisted reaction sintering of NiO−Al_2O_3 powder mixture at 1400 °C for 15 min leads to the formation of $NiAl_2O_4$ spinel. It was also reported by NAZEMI et al [23] that the formation of $NiAl_2O_4$ spinel from NiO and Al_2O_3 requires 15 h of milling with subsequent heat treatment at 1100 °C for 2 h. However, in the present study, formation of single phase $NiAl_2O_4$ spinel occurred after 5 h of milling with subsequent heat treatment at 900 °C for 2 h, which is ~500 °C lower than the temperatures used in the traditional solid state methods. This is due to the increase in kinetics of reaction between NiO and Al_2O_3 as a result of creation of high diffusivity paths for Al and Ni ions such as free surfaces, grain boundaries, dislocations and point defects during the milling process [16]. Moreover, fine particle size of ball-milled powders reduces the diffusion distances for atoms and therefore facilitates the formation of $NiAl_2O_4$ spinel compound during the subsequent heat treatment. The temperature for the formation of $NiAl_2O_4$ spinel in the current study is also ~200 °C lower than that reported by NAZEMI et al [23]. This can be attributed to the different raw materials used in the present study. As mentioned earlier, the release of CO_2 during the thermal decomposition of $NiCO_3$ leads to the formation of a porous NiO powder with high surface area. This increases the contact between Al_2O_3 and NiO powders and provides shorter diffusion paths for the ions involving in the chemical reaction, enhancing the kinetics of $NiAl_2O_4$ spinel formation.

Figure 5 shows the SEM images of the powders milled for 5 h before and after heat treatment. As can be seen in Fig. 5(a), the powder milled for 5 h consists of very small and highly agglomerated particles with a nearly spherical shape. The SEM image of the powder milled for 5 h and heat treated at 900 °C (Fig. 5(b)) shows very small and agglomerated particles of $NiAl_2O_4$ spinel phase which have sizes less than 200 nm.

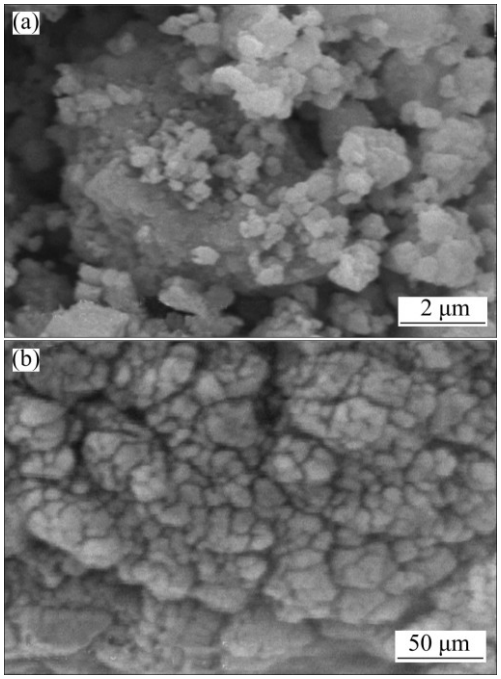

Fig. 5 SEM images of initial powders after 5 h of milling (a) and 5 h of milling with subsequent heat treatment at 900 °C for 2 h (b)

The details of powder agglomerates in Fig. 5(b) were investigated using TEM. The bright field electron micrograph of the $NiAl_2O_4$ powders produced at 900 °C is shown in Fig. 6. It is observed that the $NiAl_2O_4$ spinel powders have spherical shapes with diameters less than 100 nm, which is in agreement with the Williamson−Hall results.

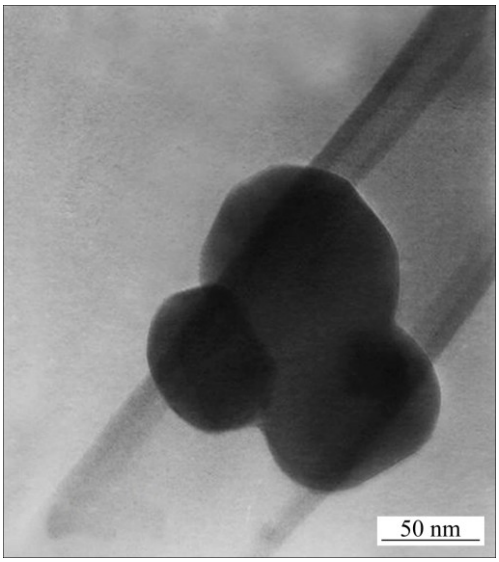

Fig. 6 Bright field TEM images of single phase $NiAl_2O_4$ spinel compound obtained after 5 h of milling with subsequent heat treatment at 900 °C for 1 h

4 Conclusions

1) The ball milling process applied on $NiCO_3$ and Al powder mixture for 5 h in air atmosphere results in the oxidation of Al to Al_2O_3 with a crystallite size of ~12 nm. Further milling up to 10 h has no effect on phase composition.

2) DSC and TG analyses of samples milled for 15 min showed that $NiCO_3$ decomposes to NiO and CO_2 during the heating of the milled powders. The temperature of $NiCO_3$ decomposition increased after 5 h of milling.

3) Formation of $NiAl_2O_4$ spinel compound from $NiCO_3$ and Al powders takes 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.

4) Based on DSC and XRD results, formation of single phase $NiAl_2O_4$ spinel in the sample milled for 5 h is completed after 2 h of heat treatment at 900 °C, which is ~500 °C lower than the temperatures used in the traditional solid state methods. This temperature is also ~200 °C lower than the temperature needed for the formation of single phase $NiAl_2O_4$ spinel compound from the mechanically milled NiO and Al_2O_3 powders.

5) The average crystallite size of spinel phase in the sample milled for 5 h and annealed at 900 °C for 2 h was ~30 nm. TEM study showed that the particle diameter of the prepared spinel compound is less than 100 nm.

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以铝和碳酸镍为原料机械合金化及后续退火制备铝酸镍纳米陶瓷

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摘　要：通过高能球磨 $NiCO_3$ 和 Al 粉后退火制备纯 $NiAl_2O_4$。采用 X 射线衍射、差热扫描、热重分析、扫描电子显微镜和透射电子显微镜研究粉末样品的相组成、热学行为、形貌和组织。从 $NiCO_3$ 和 Al 粉中合成尖晶石结构 $NiAl_2O_4$ 分为三步：Al 氧化成 Al_2O_3，碳酸镍分解为 NiO 和 CO_2，最后 Al_2O_3 与 NiO 发生固相反应。$NiCO_3$/Al 混合物经 5 h 机械球磨后于 900 °C 退火 2 h 即可形成 $NiAl_2O_4$ 单相，退火温度比传统固相方法低约 500 °C。透射电子显微镜结果表明，所得尖晶石结构的 $NiAl_2O_4$ 化合物的粒径小于 100 nm。

关键词：铝酸镍；纳米陶瓷；球磨；退火

(Edited by Xiang-qun LI)