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In-situ synthesis and characterization of nano-structured NiAl-Al_2O_3 composite during high energy ball milling

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ABSTRACT

In this work, synthesis of NiAl–Al_2O_3 nanocomposite powders via the mechanosynthesis route and by using Ni, NiO and Al is investigated. Ignition of the reaction inside the ball-mill vial happens after 110 min; NiO is totally finished and NiAl and Al_2O_3 as product phases are formed. After 10 h of ball milling, raw materials are totally used in the reaction and only product phases exist in the vial. By continuing the ball milling process to 60 h, better mixing of the synthesized phases and decrement in their crystallite sizes plus particle size are observed. Crystallite sizes of the product phases are in the nanometer range in all ball milling times. Crystallite sizes of NiAl and Al_2O_3 after 10 h are around 11 nm and 19 nm respectively, and these are reduced to around 8 nm for both phases after 60 h of ball milling.

1. Introduction

Mechanical energy has been proved capable of providing the energy needed to start a reaction as well as thermal energy. It is reported that high energy ball milling provides energy for activation of a chemical reaction [1–4] and also for full occurrence of a chemical reaction [5,6] during milling. The first is defined as mechanical activation and the second is called as mechanochemical synthesis or reactive milling. In such a process, the intensely high mechanical impacts result in repeated welding and fracturing of powder particles. Therefore, the contact area between the reactant powder particles increases and fresh surfaces come into contact in each collision in the ball mill. This matter leads the reaction to proceed without the necessity for diffusion through the product layer. Intense plastic deformation, increment in strain energy and thus high defect density leads to activation/occurrence of a chemical reaction. High defect density accelerates the diffusion process during mechanical milling [7,8].

Hence, it is expected that kinetic and thermodynamic behavior of the aforementioned reactions may be very different from those reactions initiated by thermal energy.

These reactions might undergo two different kinetics based on milling conditions:

1- Gradual reactions or progressive type reactions in which materials transform in a gradual manner and in very small volumes during each collision.

2- A self-propagating combustion reaction when the reaction enthalpy is high enough [8,9].

In the latter type, there is a critical milling time in which the combustion reaction initiates. In the beginning, the temperature of the milling vial shows a slow increase over time. Then, it increases abruptly which implies that the reaction ignition has occurred (ignition time = t_{ig}). After this time, temperature decreases slowly. Measurement of t_{ig} enables definition of the structural and chemical evolution during combustion reaction [10].

In the reactive milling method, there are varied and numerous benefits and these make this process economical. These benefits include the ability to produce solid solutions [11], different volume fractions of different types of submicron reinforcements [12,13] as well as nascent clean interfaces [14]. Researchers have focused on intermetallics such as nickel aluminides. They utilize advantages of this process to improve ductility of such materials by microstructure refinements and to enhance their creep resistance by the reinforced particulates [15]. These goals have led researchers to concentrate on nanostructured composites.

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Alumina has been considered as a promising reinforcement for NiAl by researchers [16,17]. That is because of its thermodynamic compatibility with NiAl and also because its thermal expansion coefficient is relatively close to that of NiAl. And furthermore, alumina has desirable properties such as low density, high specific strength, high modulus and good oxidation resistance [18]. Research has shown that NiAl–Al_2O_3 composite can be utilized for high temperature applications because of improved oxidation [19] and creep resistance [20] and thus is a good candidate for coating purposes [21].

Researchers have reported the formation of NiAl–Al_2O_3 composites by mechanical milling powder mixtures of Ni, Al and Al_2O_3 [22], NiO and Al [23] and $Ni_2(OH)_2CO_3 \cdot 3H_2O$ and Al [24]. Anvari et al. [25] developed NiAl-Al_2O_3 composite by high-energy ball milling of Ni, NiO and Al in a planetary ball mill without any process controlling agent (PCA). Udhayabanu et al. [26] carried out reactive milling of Ni, NiO and Al powder mixture in toluene medium. Then they heated the as-milled powder. Even after the 20 h of ball milling, reaction between raw materials was still incomplete; significant amounts of Ni and NiO remained in the mixture and Al was totally consumed. NiAl-Al_2O_3 composite was gained after the mixture was heated to 1200 °C. Udhayabanu et al. [15] consolidated the as-milled powder containing NiAl, amorphous Al_2O_3 and unreacted NiO by spark plasma sintering and finally gained NiAl-Al_2O_3 composite. Because the above-mentioned researchers have conducted their milling in conditions different from the present work, the phase formation and reaction mechanism are expected to be different in this study.

The present research aims to develop NiAl-Al_2O_3 nano-structured composite by reactive milling of Ni, NiO and Al as raw materials and by completing the reaction totally in the ball mill vial. Ignition time of the reaction is measured. Influence of ball milling time is assessed on phase evolution, crystallite size and lattice strain of phases, microstructure and chemical composition of different phases in the as-milled powder mixture and powder particle size (for milling times higher than 10 h).

2. Experimental

2.1. Characterization

Ball milling was carried out in a Retsch planetary ball mill. The constant ball milling conditions are mentioned in Table 1 and only ball milling time differs for different samples.

Starting powders were weighed into stoichiometric composition corresponding to Eq. (1):

$$3NiO + 8Ni + 13Al = Al_2O_3 + 11NiAl \qquad (1)$$

Stearic acid (1 wt% of the powder mixture) was used as process controlling agent (PCA) to avoid oxidation and excessive cold welding of powders to vial and balls.

Temperature variations of outer wall of the ball mill vial were studied as an indirect indicator of the temperature changes inside the vial. For this purpose, two RoHS Thermochromic Liquid Crystal Reversible Temperature Indicating Strips were attached on the outer wall of the vial. In these strips, temperature ranges are seen in dark brown squares and color change of one square from brown to green indicates temperature change to that range. The temperature range under this survey was 60 °C. This assessment was intended to determine the ignition time of the exothermic reaction inside the ball mill vial.

Table 1
The ball milling conditions.

Vial	Stainless steel vial with volume of 250 ml
Balls	WC balls with approximate weight of 8.4 g/ball
Ball milling speed (rpm)	280
ball-to-powder ratio	10/1
Process controlling agent (PCA)	Stearic acid (1 wt% of the powder mixture)
Raw materials powder mixture weight (g)	Total weight: 5.85 (Ni:2.63, NiO:1.25, Al:1.97)
Ball milling time (h)	1, 2, 3, 4.5, 6, 10, 15, 20, 40, 60
Ball milling atmosphere	Air

The morphologies, microstructures and chemical compositions were studied using a LEO 1530 scanning electron microscope (SEM) with a Gemini column and EDS detector from Oxford Instruments of type 50 mm^2 XMax Silicon Drift Detector (SDD). To prepare samples for powder morphology investigations, powder particles were dispersed in ethanol. To study the microstructure of powder particles and phase investigations, a powder particle cross-section sample was prepared by conventional metallographic techniques. Phase evolution of samples was analyzed by PANalytical X'pert PRO XRD, using Cu Kα radiation with $\lambda = 0.15406$ nm. Using diffraction data of ball milled powder samples, the amount, crystallite size and lattice strain of existing phases were obtained from Rietveld refinement analysis by applying a pseudo-Voigt function and by X'Pert HighScore Plus software. The particle size measurement of raw materials and powder samples was performed using a SHIMADZU SALD-2101 apparatus.

2.2. Materials

Raw-materials used in this work were Al (Merck-art no.1056), Ni (Merck-art no.12277) and NiO (Merck-art no.6723) powders. Particle size measurement showed that d50 of Al, Ni and NiO was 68 ± 0.5, 5 ± 0.1 and 9 ± 0.3 μm, respectively. Fig. 1 shows scanning electron microscopy micrographs of the starting powder particles. The aluminum and nickel powder particles had spherical morphologies while nickel oxide powder particles showed an irregular shape.

3. Results and discussion

3.1. Phase analyses

Fig. 2 presents XRD patterns of the mixed powder mixture (0 h of high energy ball milling) and ball milled ones after different milling times. In the mixed and 1 h ball milled powder, peaks of Ni, Al and NiO are observed, so these were just reactant phases and none of reaction products were formed in powders. While increasing milling time to 2 h led to the disappearance of NiO peaks, NiAl and Al_2O_3 peaks began to appear, which are formed "in-situ" during the milling process. It should be mentioned that in the binary phase diagram of NiO-Al_2O_3, there is no complex oxide composition other than $NiAl_2O_4$ and peaks of this phase were not observed in any of patterns in Fig. 2. Thus, knowing that ball milling is not an equilibrium process, it seems that NiO is not consumed in any complex oxide in Ni-Al-O system and that Al_2O_3 is the product of reduction reaction of NiO and Al. Therefore, within 1 and 2 h of ball milling, the exothermic reaction between starting powders has taken place. With further milling, the intensity of Al and Ni peaks decreases. After 4.5 h of ball milling, Al peaks are not observable in XRD pattern while Ni peaks can still be seen. This has been reported in other references too. Peak broadening is a common phenomenon which is observed as a result of grain refinement and increase in lattice strain [5,27]. Because of the high ductility of aluminum in comparison with Ni, it experiences rapid and severe deformation. Therefore, the broadening and disappearing of peaks happens faster for aluminum, while nickel diffraction lines are observable over longer times because of its greater hardness and so undergoes less deformation than aluminum. Abbasi et al. [28] observed the same phenomenon in milling of nickel and aluminum powder mixture. If solid solution of Ni(Al) forms during ball milling, because of radius difference between nickel and aluminum, it is expected that expansion in the nickel lattice happens and thus Ni diffraction peaks should be detected at lower 2θ. But since such a peak shift is not seen in phase analysis results, it can be concluded that Ni(Al) solid solution has not been formed during