



Effect of high energy ball milling on the reduction of nickel oxide by zinc powder



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ABSTRACT

The effect of high energy ball milling on the NiO reduction by zinc powder has been studied. XRD analysis on the as-milled mixtures of NiO–Zn with stoichiometric composition indicated that the traces of nickel phase observed after 30 min milling and the NiO reduction reaction by Zn progressed gradually during milling procedure. DTA analysis on the raw mixture (un-milled sample) with stoichiometric ratio under high pure argon atmosphere showed that the reduction of NiO by Zn occurred at about 630 °C. The final products in both as-milled and isothermally heated of un-milled samples were mainly the mixtures of ZnO and Ni_{0.6}Zn_{0.4}O phases.

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1. Introduction

High energy ball milling has been known to activate the solid–solid chemical reactions during milling. Since the mechanical energy supplied during milling is utilized for the chemical reactions it has been called mechanochemical synthesis [1,2]. Depending on milling conditions and nature of raw materials the mechanochemical reaction fall into two categories, namely those which occur during the mechanical activation process and those which occur during subsequent thermal treatment. The first type of reactions takes place in two different modes, i.e., either self-propagation combustion reaction or a progressive (gradual) reaction. The reaction enthalpies in both modes of first type of reactions are highly negative [2,3]. If a reaction is highly exothermic, the impact of the milling balls can initiate a mechanically induced self sustaining reaction (MSR). It has been shown that a reaction can propagate in form of a self-sustaining process, if the $\frac{-\Delta H_{298}}{C_{p298}}$ ratio, where $-\Delta H_{298}$ is the reaction enthalpy and C_{p298} is the total heat capacity of the products at 298 K respectively, is higher than about 2000 K [4,5]. In recent years, high energy ball milling and mechanical milling procedures can be used to induce chemical reactions (displacement reactions) during milling at much lower temperatures than normally required.

Those procedures have been widely used to reduce most of the oxides and sulphates by solid-metallic reducing agent (such as aluminium and magnesium) [6–11].

The solid state reaction of nickel oxide and a solid-metallic reducing agent has been studied before. Matteazzi and Le Care have initially investigated the solid state reaction of NiO–Al using planetary ball mill to produce Ni/Al₂O₃ nanocomposite [12]. Li et al. [13] studied the preparation of Ni/Al₂O₃ nanocomposite powder by high-energy ball milling. Self-propagation reactions did not occur during their milling processes because they use the diluents alumina in raw mixtures [13].

In another research paper, the effect of mechanical activation on NiO–Al reaction using toluene as a process controlling agent has been studied. The reduction reaction progress gradually during milling process and after heating the milled samples at 1000 °C the amorphous alumina transformed to stable α -Al₂O₃ [2].

NiAl–Al₂O₃ nanocomposite has been synthesised using ball milling of mixture of NiO, Al and nickel powders [3]. Although Al and NiO with stoichiometric composition react during ball milling in highly exothermic, dilution of reactants with Ni phase increases the ignition temperature and therefore the reaction mode is changed to gradual [3].

Zinc oxide (ZnO) has the particular properties including specific electrical, optical and mechanical properties, high thermal stability and large Seebeck coefficient [14,15]. Zinc oxide is n-type semiconducting oxide with a wide band gap semiconductor (3.37 eV) and

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has a large excitation binding energy (60 meV) [15,16]. The optical band gaps of bulk NiO is 4.00 eV. Furthermore nickel oxide films are suitable for magneto-resistance sensors, chemical sensors, electrochromic devices and transport p-type semiconducting layer, smart windows and dye sensitized photocathode [14,17]. Recent investigations on ZnO ceramics show that their thermoelectric properties can be improved by substitution with aluminium, titanium, antimony or nickel [15]. The Ni-doped ZnO ceramics and composite material with $\text{Ni}_x\text{Zn}_{1-x}\text{O}$ structure have been synthesized previously and the physical properties, magnetic and optical properties have been studied [14–16,18].

There is no report about effect of ball milling on the reduction reaction of nickel oxide by zinc powder. It is however interesting to study the mechanochemical reaction of NiO–Zn system with high-energy ball milling in order to elucidate the products of the reaction and the mode of the reaction (self-propagation combustion reaction or gradual reaction). In the present approach, the solid state reduction reaction of NiO by Zn with stoichiometric composition has been investigated in a planetary ball mill and the phase transformations in milling have been studied. The unmilled mixtures of NiO–Zn with stoichiometric composition were also prepared and the results have been compared with milled samples. The results were examined using differential thermal analysis (DTA), X-ray diffraction (XRD) and thermodynamic analysis.

2. Experimental

Mixtures of nickel oxide (Merck, 100782) and zinc powder (Merck, 108774) with stoichiometric composition were prepared based on reaction (1).



XRD analysis on the raw materials showed that they are included mainly NiO (JCPDS No.47-1049) and Zn (JCPDS No. 004-0831) but few sodium nitrate peaks with low intensity were also observed in XRD pattern of nickel oxide.

All mixtures of raw materials (based on reaction 1) were milled under vacuum in a planetary ball mill (Farapazhouhesh, Iran, FP2 model) for different times. Preliminary experiments indicated that the following conditions were suitable: 600 rpm, five 20 mm diameter high Cr-Steel balls in a high Cr-Steel milling chamber giving a ball-to-sample weight ratio of 40:1.

Differential thermal analysis (DTA) were carried out for both un-milled (Raw mixture) and milled mixtures at the heating rate of 10 K/min up to 1100 °C under a flowing high pure argon atmosphere using thermo-gravimetric analyser (Netzsch STA 409 PC/PG).

Isothermal runs were undertaken in a tube furnace (Lenton, LFT, 16–180) with the sample being held at different temperatures for one hour and then allowed to cool to room temperature all under a flow of high pure argon atmosphere.

The phases present in the products were analysed using X-ray diffraction (XRD, Philips Analytical, Co K α radiation, 40 kV, 40 mA, XPert MPD) was performed over a range of 15–90° 2 θ , using a step size of 0.05° and one second count time per step.

3. Results

Thermodynamic calculations [19] show that $\Delta H_{298\text{K}}^0$ for reaction (1) is negative at room temperature ($\Delta H_{298\text{K}}^0 = -110.759\text{kJ}$), also the amount of $\frac{-\Delta H_{298}^0}{C_{p,298}}$ ratio is about 1718 K. Therefore, the initiation of MSR is not anticipated when ball milling is carried out on a stoichiometric mixture of nickel oxide and zinc powder (reaction 1). However, the reaction (1) can thermodynamically occur during ball milling the mixture of Zn and NiO in room temperature due to its negative free energy change ($\Delta G_{298\text{K}}^0 = -108.938\text{kJ}$) [19].

Fig. 1 shows the XRD patterns of NiO–Zn powder mixture with stoichiometric composition as a function of milling time (the as-milled samples). The decrease in reactants peak intensities (NiO and Zn) and the presence of new peaks corresponding to nickel phase (JCPDS No. 004-0850) indicates that nickel oxide reduction reaction starts after 30 min milling. The intensity of zinc peak at $2\theta = 42.4^\circ$ is decreased in one hour milled sample. After 3 h milling the traces of NiO and Zn peaks have disappeared and the intensity

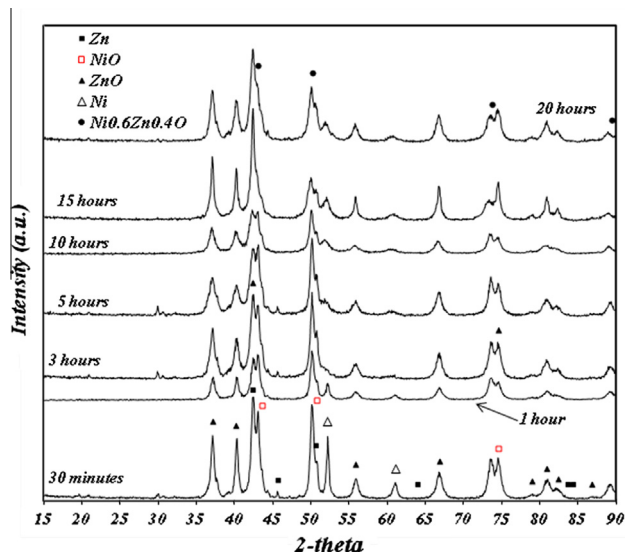


Fig. 1. The XRD patterns of the as-milled samples for Zn–NiO mixtures with stoichiometric composition at different milling time.

of ZnO peak (JCPDS No. 036–1451) at $2\theta = 42.357^\circ$ has increased. The intensities of nickel peaks decrease with milling time and they have disappeared in 3 h milled sample. The decrease in nickel peak intensities after one hour milling indicates that a reaction should take place with increasing milling time. Nickel oxide peak at $2\theta = 50.7^\circ$ has gradually shifted to lower degrees with increasing milling time and its integrated intensity increases and reaches to highest amount after 5 h milling. The traces of ZnO (JCPDS No. 036-1451) and nickel zinc oxide phase, $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{O}$ (JCPDS No. 075-0273), are clear after 5 h milling and increases the milling time up to 20 h has no effect in the final products. Therefore the products of reaction (1) during mechanochemical reaction at room temperature are mainly mixtures of ZnO and $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{O}$ after 5 h milling. Therefore XRD patterns of as-milled samples indicate that it is possible to obtain nickel zinc oxide structures using high energy ball milling of NiO–Zn mixtures.

$\text{Ni}_{0.6}\text{Zn}_{0.4}\text{O}$ phase is related to the nickel zinc oxide ($\text{Ni}_x\text{Zn}_{1-x}\text{O}$) structures, while x value varies from 0 to 1, and it is observed that the related complex structures depend on the x values. It was previously established that NiO and ZnO monoxides form solid solutions $\text{Ni}_x\text{Zn}_{1-x}\text{O}$ for $x > 0.40$ [18,20]. The nickel zinc oxide ($\text{Ni}_x\text{Zn}_{1-x}\text{O}$) structures were prepared previously using solid stated reaction of ZnO and NiO and the samples were fired in air at different temperatures up to 1250 °C for about five hours [20]. The Ni–Zn–O films and $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ nanorod arrays have been also prepared previously [14,16]. In the works about NiZnO, in general, small amounts of Ni were incorporated to ZnO in the $\text{Ni}_x\text{Zn}_{1-x}\text{O}$ structure and the structural, morphological and physical properties of these films were investigated [14,16].

The crystallite size of ZnO in the final products of the as-milled samples (The XRD patterns of Fig. 1) was calculated using the well-known Scherrer's formula (Eq. (1)):

$$D = \frac{k\lambda}{D \cos \theta} \quad (1)$$

In Eq. (1), k is a constant (0.9), λ is the wavelength of X-rays (for Co radiation is 1.78901 Å), D is the full width-at-half-maximum (FWHM) and is θ the angle of diffraction. The crystallite size values were evaluated according to the one of the main highest peak belonging to the ZnO phase (e.g. $2\theta = 40.192^\circ$, $d = 2.6033\text{Å}$) in the products of the as-milled samples. The final results are given in Fig. 2

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