Letter

Mechanical activation on aluminothermic reduction and magnetic properties of NiO powders

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Abstract

We report the mechanically activated aluminothermic reduction of NiO [NiO–Al(x wt.%) with x = 0, 20, 40] into NiO–Ni–Al₂O₃ nanocomposites using high-energy planetary ball milling under dry milling and the resulting structural and magnetic properties. Structural studies reveal that both NiO and NiO–Al powders exhibit a face centered cubic structure with large crystal size reduction. However, the NiO–Al milled powders unveil the process of aluminothermic reaction kinetics, which changes from gradual reaction as a function of milling time for x = 20 powders to self-propagating combustion reaction for x = 40. This allows us to achieve a maximum NiO reduction of 40% and 90% for x = 20 and 40, respectively. The process of NiO reduction by Al is further confirmed through thermal studies. Pure NiO shows an antiferromagnetic (AFM) nature, which transforms into a ferromagnetic (FM) one with the moderate magnetization of about 1 emu g⁻¹ with decreasing crystal size. The formation of FM Ni from AFM NiO matrix in milled NiO–Al powders could be precisely monitored by the change in the magnetization, which increases up to 4 emu g⁻¹ and 28 emu g⁻¹ for the gradual and combustion reactions, respectively. This results in a considerable exchange bias and its magnitude strongly depends on the relative fractions of NiO and Ni phases. Thermomagnetization data confirm the presence of mixed magnetic phases and the component of induced FM phase fades out due to the formation of Ni from the reduction of NiO. The changes in the structural and magnetic properties of milled NiO–Al powders are discussed on the basis of milling time-dependent mechanically activated reduction reaction of NiO into NiO–Ni–Al₂O₃ nanocomposites. The process of mechanical activation on the aluminothermic reduction allows for a controlled reduction of NiO; thus, it is suitable for the applications in catalysis and the ore reduction process.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, the nanostructured transition metal (TM) based oxides have been extensively studied from both applied and fundamental points of view [1]. In particular, the possibility of tuning the properties of nanostructured NiO by a partial reduction process has opened up novel paths for widespread research activities in the nanoscale science. The partial reduction of TM oxides forms composites, which consist of TM nanoparticles embedded in a TM oxide matrix and find applications in various advanced fields such as sensor, supercapacitor, solar cell, microwave, battery, spintronics, solid oxide fuel cell, electrochromic, resistive random access memory, etc [2–6]. Although different synthesis methods such as chemical precipitation [7], electro-deposition [8], solid state [9], micro-emulsion [10], spray pyrolysis [11], sol–gel [12], hydrothermal [13], etc have been employed, the high-energy ball milling [14–16] has been proven as the simplest and inexpensive method for the synthesis of nanosized NiO powders with controlled magnetic properties. The ball milling process is a solid state method producing final materials in powder form with nanosized crystals, which can be tailored in various shapes and dimensions by compaction and giving proper heat treatment for availing commercially. This method is also called as mechanochemical synthesis or reactive milling, as it activates solid–solid and solid–liquid chemical reactions by utilizing the mechanical energy supplied during milling.

The reduction reaction of bulk NiO was first reported by Benton and Emmett in 1924 under hydrogen (H2) atmosphere [17]. Sharma et al [18] showed the complete reduction of NiO using graphite as a reducing agent in both a closed system and in vacuo. Similar reduction reaction was reported by Budarin et al [19] using carbon monoxide as a reducing gas. Kim et al demonstrated the reduction of NiO to Ni using two different reducing gases (N2 and H2) along with carbon and obtained 75% and 100% reduction of NiO, respectively [20]. Recently, Rashidi et al [21] used methane for reducing NiO and Jeangros et al [22] reported that the reduction of NiO by H2 in an environmental transmission electron microscope produces Ni nucleation on NiO either by epitaxial or by the formation of randomly oriented grains. However, the first investigation on the solid-state reaction of NiO–Al using high-energy mechanical alloying to prepare NiAl/Al2O3 nanocomposite was reported by Matteazzi and LeCaer [23] using dry milling condition under argon (Ar) atmosphere. Subsequently, the mechanically activated carbothermal reduction of NiO by graphite was reported by Yang et al using the mechanical alloying process [24]. Later on, Doppiu et al reported that the mechanochemical reduction of NiO in H2 atmosphere is a progressive one, which results in the formation of Ni–NiO nanocomposite through the partial reduction of NiO into Ni [25]. They also reported that a threshold energy is necessary to instigate the reduction. Oleszak [26] and Udhayabanu et al [27] utilized the mechanical activation of aluminothermic reduction of NiO for the development of NiAl/Al2O3 and Ni/Al2O3 nanocomposites under different process controlling agents, respectively. A careful review of literature reveals that (i) the study of maximum NiO reduction and the ability to control the properties of subsequent Ni are the major challenges in the fields of ore reduction, resistive random access memory, catalysis and solid oxide fuel cells [28–30] and (ii) though the process of reduction in NiO has been reported using ball milling, the detailed analyses of the dynamics of the reduction process and the systematic evolutions of magnetic properties as a course of reduction are still missing. Therefore, in this article, we report the systematic investigations on the reduction of NiO by Al in a high-energy planetary ball mill under dry milling in Ar atmosphere as a function of milling period (t0) and Al content and the resulting structural and magnetic properties of novel nanocomposites. In order to compare the results, we have also carried out milling for pure NiO without Al under the similar milling conditions and characterized.

2. Experimental details

Weighed quantities of high purity (>99.9%) NiO and Al powders corresponding to the mixture of NiO–Al (x wt.%) with x = 0, 20 and 40 were taken in a high-energy planetary ball mill filled with high purity Ar gas. The milling process of NiO–Al powders was carried out for different t0 (0–30 h) in a hardened steel vial together with 8 mm diameter hardened steel balls in the mill operated at 500 rotations per minute with a ball-to-powder weight ratio of 10:1. The optimization of milling speed was done mainly by monitoring the variation in the structural and magnetic properties of the resulting nanocomposites in the milled powders. To avoid any excess heat generated during dry milling, the mill was programmed to halt for 15 min after every 15 min of operation.

To understand the evolution of nanostructure in NiO–Al powders, the powders were milled at different t0 and characterized. The phase and structural evolutions were analyzed using x-ray diffraction (XRD) obtained through high-power x-ray diffractometer (Rigaku TTRAX III 18 kW) using Cu-Kα radiation (λ = 1.54056 Å). XRD data were collected at a low scan rate of 0.005° s−1 for quantitative analysis of structural parameters. The microstructural properties of the pure NiO and milled NiO–Al powders were analyzed using transmission electron microscope (TEM, Technai TF20). Differential scanning calorimetry (DSC) was carried out for the as-mixed and milled powders in an Ar atmosphere using LABSYS evo, SETARAM Instrumentation (Caluire, France) and NETZSCH STA 449 F3A00. Magnetic properties were characterized using vibrating sample magnetometer (VSM, LakeShore...
Figure 1 depicts room temperature XRD patterns of pure and milled NiO–Al (x wt.%) powders with x = 0 (a), 20 (b) and 40 (c) at different t_m.

Model 7410) by performing (i) room temperature initial magnetization (M) curves and magnetic hysteresis (M–H) loops and (ii) high-temperature thermomagnetization (M–T) measurements from 300 K to 1200 K performed at 4 °C min⁻¹ heating rate under the applied magnetic field of 2 kOe.

3. Results and discussion

Figure 1 shows room temperature XRD patterns of pure and milled NiO–Al (x wt.%) powders with x = 0 (a), 20 (b) and 40 (c) prepared at different t_m. The pure un-milled and milled NiO powders show Bragg reflections corresponding to face centered cubic (fcc) structure of NiO only. No additional peaks corresponding to any other phases or compounds were observed within the resolution of high-power x-ray diffractometer. However, the broadness of the NiO peaks increases considerably and the peak position shifts to lower angles with increasing t_m. While the first one can well be attributed to effective size reduction, the latter one is mainly due to the change in the lattice parameters in the milled powders. As a result, the color of the pure un-milled NiO powder changes from pale-green into dark green after milling. This could be attributed to the existence of non-stoichiometry in NiO caused by the defects, size reduction [15], oxidation of Ni²⁺ to Ni³⁺ [31] due to breaking of Ni²⁺–O²⁻–Ni²⁺ super-exchange interaction as evident from Raman spectra [16, 32]. On the other hand, the as-mixed NiO–Al powder shows individual Bragg reflections corresponding to fcc structure of NiO and Al. However, the XRD patterns of the milled NiO–Al powders strongly depend on Al content and t_m, and hence the process of milling is described separately.

It is observed for x = 20 powders that (i) after 5 h of milling, the intensity of the Al peaks is decreased largely along with the considerable broadening in NiO peaks. In addition, the formation of new peaks at 2θ = 44.5° and 51.8° is observed. This indicates the commencement of NiO reduction reaction, which results in the materialization of Ni. (ii) With increasing t_m > 5, the intensity of Al peaks decreases further and then disappears eventually for t_m > 10. This could be attributed to its smaller quantity after its utilization for the NiO reduction and its reduced crystal size. (iii) A progressive peak broadening of NiO peak along with a significant shift in the peak position is observed till 30 h. While the peak broadening confirms the refinement of NiO crystals, the peak shift is originated due to atomic disorder induced by dissolution of Al in NiO matrix and the reduction. Furthermore, the intensity of the Ni peaks increases gradually with increasing t_m up to 30 h. This results in substantial changes in the color of the milled NiO–Al powders as follows: The pale-green color of the as-received NiO powder changes into dark green after 5 h of milling mainly due to the non-stoichiometry in NiO and weak reduction of NiO. On further increasing t_m, the dark green color transforms into black one due to the formation of Ni. (iv) Nevertheless, no additional Bragg peaks corresponding to any other phases or compounds were observed. In order to evaluate the percentage of NiO reduction with t_m, we have utilized the change in the integrated intensity of NiO(2 0 0) peak using the relation [33], \[ C = (A - B)/A \times 100 \], where A is the integrated intensity of NiO(2 0 0) peak before milling, B is the integrated intensity of NiO(2 0 0) peak in milled NiO–Al powder at a given t_m and C is the percentage of reduction of NiO. The percentage of NiO reduction increases gradually with increasing t_m and reaches a maximum of about 40% at the end of 30 h milling. This process also decreases the average size of NiO crystals largely into nanoscale regime.

On the other hand, the XRD patterns of the NiO–Al (40 wt.%) powders reveal that (i) the peak intensities of NiO and Al decrease suggestively for 0.5 h of milling. (ii) Interestingly, the process of aluminothermic reduction of NiO starts even by 3 h of milling, which results in the formation of distinct Ni peaks at 2θ = 44.5°, 51.8° and 76.3°. In addition, the development of additional peaks at 2θ = 45.6°, 60.6° and 66.6° corresponding to Al₂O₃ is observed. (iii) With increasing t_m > 3, the NiO(2 0 0) and NiO(3 1 1) peaks at 2θ = 43.35° and 75.46°, diminish progressively and merge into Ni(1 1 1) and Ni(2 2 0) peaks at 2θ = 44.5° and 76.3°, respectively at the end of 30 h of milling. While the NiO(2 2 0) and NiO(2 2 2) peaks disappear completely, the existence of highly strained NiO(1 1 1) peak is still observed after 30 h of milling. (iv) A close observation of Ni(2 0 0) peak at 2θ = 51.8° unveils a considerable peak broadening with increasing t_m from 3 to 30 h. This may be correlated to the refinement of Ni crystals after its formation from NiO reduction. These results suggest that the reduction process for x = 40 powders is quite instantaneous and rapid with...
the maximum reduction of about 90%. This confirms that the reaction process changes from gradual reaction for $x = 20$ to self-propagating combustion reaction for $x = 40$, which needs a typical critical $t_m$ of 3 h for the combustion reaction to be ignited. Therefore, the reduction process clearly relies on $t_m$ and Al content under the present milling conditions.

In a conventional self-propagating high temperature synthesis process, the temperature of the reaction has to be raised at the temperature range of 800–1100 °C under the reactive gas atmosphere [17, 19, 21, 22]. However, the reduction of NiO strongly depends on the types of the reducing gas and the processing conditions. The NiO reduction was also carried out by mixing the NiO with C powders followed by consecutive heating process under different gases [20]. However, the temperature needed for the NiO reduction is still quite high. On the other hand, the reactive milling promotes mechanically activated solid state chemical reactions between oxides and reducing agents such as Na, Mg, Ca and Al for the reduction process, as the milling process creates large number of defects, grain boundaries and sub-grain boundaries, which favors mass transfer and diffusion path length with reduced activation energy [34]. To understand the process of aluminothermic reaction kinetics for the presently investigated samples in correlation with XRD results, we have carried out thermal analysis of the un-milled and milled NiO–Al powders using DSC and the curves are depicted in figure 2. The curves show (i) sharp endothermic peaks at around 650 °C corresponding to Al melting and (i) one exothermic peak at about 1040 °C for $x = 20$ powder corresponding to NiO reduction and two exothermic peaks at 1000 °C and 1070 °C corresponding to two-stage reduction of NiO [24]. On the other hand, the milled NiO–Al powders exhibit a broad exothermic peak at 440 °C indicating the partial reduction of unreacted NiO present in the as-milled powders. However, we observed a significant endothermic Al melting peak at 5 h milled $x = 20$ powder and 0.5 h milled $x = 40$ powder indicating the presence of unreacted Al in the as-milled powders. Similarly, the absence of Al melting peak in DSC curves of other milled samples confirms the solid state reduction of NiO in these milled samples. These results are in good agreement with the XRD patterns (see figures 1(b) and (c)) and strongly support the nature of NiO reduction occurring with different Al content at different $t_m$. Therefore, the observed self-propagating combustion reaction for $x = 40$ powders follows the reaction $3\text{NiO} + 2\text{Al} \rightarrow 3 \text{Ni} + \text{Al}_2\text{O}_3$ since the reduction of NiO by Al is highly exothermic in nature and in agreement with the earlier reports [35, 36]. On the other hand, for $x = 20$ powders, the amount of Al available for the ignition of the above combustion reaction is considerably low and hence promotes only the gradual reduction process. However, a detailed thermal analysis and heat treatment at high temperatures of the as-milled samples at different $t_m$ would elucidate the nature of the reactions more in details.

To study the structural refinement, the lattice constant ($a_{\text{NiO}}$) and crystallite size ($D_{\text{NiO}}$) were calculated after eliminating the contribution from instrumental broadening.

**Figure 2.** DSC curves for un-milled (a) and milled NiO–Al powders with $x = 20$ (b) and $x = 40$ (c) at different $t_m$.

**Figure 3.** The variations of (a) NiO lattice constant, $a_{\text{NiO}}$ and (b) average crystallite size, $D_{\text{NiO}}$ as a function of $t_m$ for NiO–Al ($x$ wt.% ) powders.
Figure 3 displays the variations of $a_{NiO}$ and $D_{NiO}$ as a function of $t_m$ for the milled NiO–Al powders with different Al content. The value of $a_{NiO}$ for pure un-milled NiO powder is 4.176 Å, which increases progressively to 4.179 Å for milled NiO powders after 10 h of milling and then tends to saturate at higher $t_m$. $D_{NiO}$ decreases largely from about 47 nm for the pure un-milled NiO powder to about 13 nm in 5 h of milling. With increasing $t_m > 1$ h, $D_{NiO}$ decreases slowly and reaches to about 11 nm. On the other hand, for $x = 20$ powders, $a_{NiO}$ increases initially to 4.177 Å after 5 h of milling and then decreases gradually to 4.168 Å at a rate of $3.8 \times 10^{-4}$ Å per hour up to 30 h of milling. $D_{NiO}$ decreases largely to about 19 nm in 5 h of milling followed by a gradual variation at higher $t_m$ reaching to about 14 nm at $t_m = 30$ h. With increasing $x$ to 40, the variations of $a_{NiO}$ with $t_m$ exhibit two different slopes: i.e. $19.2 \times 10^{-4}$ Å per hour from 0 to 10 h and $2.65 \times 10^{-4}$ Å per hour from 10 to 30 h of milling. $D_{NiO}$ decreases from 47 nm to 13 nm within 5 h of milling and then reaches to about 11 nm after 30 h of milling. On the other hand, $D_{Ni}$ varies from 7 to 14 nm and from 14 to 23 nm for $x = 20$ and 40 powders, respectively. These changes could be attributed to the time-dependent aluminothermic reduction of NiO, which changes the formation of eventual nanocomposites with different fractions of NiO, Ni and Al$_2$O$_3$.

To understand the evolution of nanocomposites with different Al content, the pure NiO and milled NiO–Al powders were characterized using TEM technique. Figure 4 depicts the bright-field TEM (BF-TEM) and high-resolution TEM (HR-TEM) images, selected area electron diffraction (SAED) patterns and inverse-Fast Fourier transform (i-FFT) images of selected areas of HR-TEM images for pure NiO and milled NiO–Al (x wt.%) powders at different $t_m$ [x = 0, $t_m$ = 3 (c) and (d); x = 0, $t_m$ = 30 (e) and (f); x = 20, $t_m$ = 5 (g) and (h); x = 20, $t_m$ = 20 (i) and (j); x = 40, $t_m$ = 5 (k) and (l); x = 40, $t_m$ = 20 (m) and (n); x = 40, $t_m$ = 30 (o) and (p)].
crystallite size of NiO exhibit almost a similar trend with that of XRD results. Nevertheless, the nanoparticles exhibit irregular shapes with broad size distribution. In order to analyze the lattice parameter prudently, we have carefully resolved the HR-TEM images by the i-FFT method using a GATAN digital micrograph and shown as inset of all HR-TEM images. The i-FFT images help to resolve the lattice fringes with the subsequent determination of interplanar spacing of 0.241 nm corresponding to the NiO(111) lattice plane. With increasing $x = 20$, a similar nanocrystallinity with irregular morphology was observed. The SAED patterns and HR-TEM images evidence the presence of both NiO and Ni phases with fine nanometer sized crystallites of NiO and Ni. The i-FFT images reveal the interplanar spacing of 0.24 nm and 0.20 nm corresponding to the NiO(111) and Ni(111) lattice planes, respectively. $D_{NiO}$ decreases to about 14 nm after 30 h of milling. Diffraction rings of Ni(111) phase is quite continuous and diffusive in nature, which overlaps with the spotty ring from NiO(200) plane for $x = 20$ powders (see figures 4(g) and (i)), while a clear diffraction rings corresponding to Ni and Al$_2$O$_3$ could be observed for $x = 40$ powders milled above 5 h. $D_{Ni}$ calculated from HR-TEM images for $x = 40$ powders is in the range of 14–22 nm, which is in close good agreement with XRD results. These changes in the structural properties are expected to play a major role on the resulting magnetic properties of NiO–Al powders. Hence, we measured room temperature IM curves, $M$–$H$ loops and high-temperature $M$–$T$ curves for pure NiO and milled NiO–Al powders.

Figure 5 displays room temperature IM curves with magnetization in logarithmic scale and $M$–$H$ loops of pure and milled NiO–Al powders at different $t_m$. (a) $x = 0$, (b) $x = 0$, (c) $x = 20$, (d) $x = 20$, (e) $x = 40$, (f) $x = 40$.

Figure 6. The variations of (a) magnetization at 12 kOe field, $M_{12}$ kOe (in logarithmic scale), (b) coercivity, $H_C$ and (c) exchange bias, $H_E$ as a function of $t_m$ for NiO–Al ($x$ wt.%) powders.
un-milled NiO due to its AFM nature, has increased significantly to about 250 Oe after 1 h of milling. On further increasing \( t_m \), \( H_E \) decreases substantially from 250 Oe to about 160 Oe after milling for 20 h and then remains almost constant up to \( t_m = 30 \). (iii) The variation of \( H_E \) with \( t_m \) exhibits almost a similar trend of \( H_C \) versus \( t_m \), i.e., \( H_E \) is observed to be high for the initial period of milling, but decreases with increasing \( t_m \). On the other hand, the shape of the \( M-H \) loops for NiO–Al milled powders changes differently depending on Al content. For \( x = 20 \) powder milled for 5 h, the moment increases noticeably at lower fields followed by a progressive increase at higher fields. This results in a clear \( M-H \) loop with RTFM having \( M_{12\,kOe} \) of 0.88 emu g\(^{-1}\) and \( H_C \) of 155 Oe. With increasing \( t_m > 5 \) h, \( M_{12\,kOe} \) increases substantially and reaches a maximum of about 4.05 emu g\(^{-1}\). However, the rate of increase in \( M_{12\,kOe} \) decreases with increasing \( t_m > 10 \). In contrast to pure milled NiO powder, \( H_C \) of the milled NiO–Al powder increases steadily with increasing \( t_m \) up to 20 h and tends to saturate for 30 h milled powders. Consequently, the value of \( H_E \) also increases up to 30 h. With increasing \( x \) to 40, the nature of \( IM \) curves and \( M-H \) loops is found to be nearly the same for the powders milled up to 1 h and then exhibits a rapid change in magnetization with a maximum of 28.5 emu g\(^{-1}\). Upon increasing \( t_m > 5 \) h, \( M_{12\,kOe} \) decreases almost linearly at a rate of 0.199 emu g\(^{-1}\) per hour and reaches to 23 emu g\(^{-1}\) for 30 h milled powders. \( H_C \) increases largely to 0.59 Oe for 0.5 h milled powder and decreases to 104 Oe for 3 h milled powder. Subsequently, \( H_C \) increases almost linearly at a rate of 4.54 Oe per hour and reaches about 225 Oe for 30 h milled powders. However, \( H_E \) has not increased essentially for \( x = 40 \) powders as compared to \( x = 20 \) powders.

To understand the changes in the magnetic properties of NiO and NiO–Al milled powders, we correlate both the structural and magnetic properties. In pure un-milled NiO (pale green colored) powder, the spins within AFM coupled (111) planes are compensated and hence do not contribute to net magnetic moment [37]. Hence, the \( M-H \) loop of un-milled NiO powder displays a weak response to the applied magnetic field. On the other hand, the milled NiO powders undergo large size reduction and change in the color due to non-stoichiometry [31, 38], which result in a breaking of \( \text{Ni}^{2+}-\text{O}^2-\text{Ni}^{2+} \) super-exchange interaction [16, 31, 32, 39] and increase in the number of uncompensated spins on the surfaces with respect to particle core [40] upon increasing \( t_m \). This leads to an alignment of particles’ net moment in a relatively low field and enhances net moments along with high \( H_C \). Also, the exchange coupling between the induced FM and AFM core instigates the exchange bias effect, which decreases progressively with the size reduction of NiO. Furthermore, the lattice expansion observed in finer crystallites plays a crucial role in controlling the magnetic exchange interaction between the uncompensated surface spins and particle core spins. This is in agreement with the earlier report by Li et al that room temperature magnetic crossover of NiO is due to the lattice expansion [41]. Del Bianco et al [42] reported that saturation magnetization of NiO increases at a rate of 0.62 emu g\(^{-1}\) per Ni wt.\% in hydrogenated NiO. A quantitative comparison with the presently investigated samples indicates that the as-milled NiO powders have about 1.7 wt.\% Ni enriched spatial regions.

In the case of NiO–Al milled powders, the variation of \( M_{12\,kOe} \) strongly depends on the amount of NiO reduction. Considering the AFM nature of NiO and ascribing the increase of the magnetization in the nanocomposite is mainly due to the formation of ferromagnetic (FM) Ni from NiO reduction, the percentage of Ni was estimated by relating the values of \( M_{12\,kOe} \) with respect to saturation magnetization of bulk Ni (~55 emu g\(^{-1}\)) [43]. Figure 7 depicts the variations of NiO reduction determined from XRD analysis and percentage of Ni obtained from magnetic measurements as a function of \( t_m \) for \( x = 20 \) and 40 powders. It can be observed that the percentage of Ni in the nanocomposite increases progressively up to a maximum of 7.5% with increasing \( t_m \) to 30 h. This is in good correlation with respect to the gradual reduction of NiO by Al for \( x = 20 \) powders. As a result, \( H_E \) increases up to 30 h supporting the gradual formation of Ni in NiO matrix, which induces the exchange interaction between FM Ni and AFM NiO. On the other hand, for \( x = 40 \) powders, the intensity of NiO and Al XRD peaks is reduced up to \( t_m = 1 \) due to the dissolution of Al in NiO without any ignition of NiO reduction. As a result, the formation of Ni is not observed. With increasing \( t_m \geq 3 \) h, the self-propagating combustion reaction is ignited suddenly, which reduces 90% of NiO into NiO–Ni–Al2O3 nanocomposite and provides about 52% of Ni after 5 h of milling. On further increasing \( t_m > 5 \) h, a considerable refinement of Ni nanocrystals occurs, which increases \( H_C \) progressively and decreases \( M_{12\,kOe} \). Since larger fraction of NiO is reduced into Ni, \( H_E \) turns out to be low as compared to \( x = 20 \) powders.
It may be noted that the milled NiO–Al powders exhibit RTFM despite having the average size of $D_{Ni}$ in the range below 25 nm, which is significantly below the critical size (~34 nm) of spherical Ni particles for single domain behavior at RT [44]. Hence, Ni nanoparticles will be of single domain but prone to thermal fluctuations [45, 46]. Therefore, the obtained RTFM in the presently investigated samples can be correlated to one or more of the following several origins: (i) The milled powder exhibits quite irregular morphology (see figure 4) and hence the shape anisotropy could play a key role. (ii) Since the milled powders are subjected to severe fracture and cold welding during milling process, the strain anisotropy could contribute to total anisotropy of the nanoparticles. (iii) Surface anisotropy of the nanoparticles may also play an important role [45, 47]. (iv) When the FM nanoparticles are embedded in an AFM matrix, an additional uniaxial type anisotropy is also introduced to the nanoparticles [46, 48].

In order to analyze the effective magnetic anisotropy in the milled NiO–Al powders, we have fitted $IM$ curves using law of approach of the magnetization to saturation (LAS) as defined in equation (1)

$$M(H) = M_S \left(1 - \frac{a}{H} - \frac{b}{H^2} + \ldots\right) + \chi H$$

where $M(H)$ is the magnetization in an applied magnetic field $H$, $M_S$ is the saturation magnetization, $\chi$ is high-field susceptibility, and, $a$ and $b$ are constant coefficients [49]. The constant coefficient $b$ is related to the effective magnetic anisotropy of the cubic crystalline materials as given in equation (2),

$$K_{eff} = \frac{105}{8} b\mu_0 M_S^2.$$

The determined value of $K_{eff}$ as a function of $t_m$ for NiO–Al milled powders are shown in figure 8. For the sake of comparison, $K_{eff}$ of bulk Ni is also shown in the figure. The obtained values of $K_{eff}$ for the milled powders are found to be larger as compared to $K_{eff}$ of the bulk Ni. This could be attributed to the contribution from various anisotropies such as magnetocrystalline anisotropy, shape anisotropy, strain anisotropy and exchange anisotropy for these fine nanosized Ni in nanocomposites prepared by ball milling process. Zhang et al [46] also reported size dependent enhanced $K_{eff}$ of the Ni nanoparticles in the range between $1.2 \times 10^4$ J m$^{-3}$ and $6 \times 10^4$ J m$^{-3}$. High values of $K_{eff}$ have also been reported in other nanocrystalline system [50] prepared by mechanical alloying process. However, in practice, it is impossible to separate these effects individually. Thus, the larger $K_{eff}$ plausibly shifts the blocking temperature of such fine nanoparticles above room temperature and provides thermal stability at room temperature.

In order to study the stability of FM in the milled NiO–Al powders, high-temperature $M$–$T$ measurements were performed under the applied field of 2 kOe. Figure 9 depicts the normalized $M$–$T$ curves for un-milled and milled powders with $x = 0, 20$ and 40 at different $t_m$. The insets display the same data in logarithmic scale for magnetization to demonstrate the relative variation of magnetization close to zero at higher temperatures. The magnetization of the pure un-milled NiO powder increases gradually with increasing temperature up to 525 K and then decreases above 525 K. Since the pure NiO powder exhibits AFM nature at room temperature, the
Néel temperature \( (T_N) \) is determined from the peak in \( M-T \) curve and found to be about 528 K. This is in good agreement with the earlier reports \([51, 52]\). On the other hand, the NiO powders milled for more than 1 h show a continuous decrease in magnetization with increasing temperature and the temperature at which the magnetization becomes zero shifts to higher temperature with increasing \( t_m \) up to 30 h. Although the high temperature magnetic phase transition \( (T_C) \) should be associated with Ni due to the formation of uncompensated surface spin, \( T_C \) is considerably large as compared to its bulk counterpart (~630 K). This can be attributed to the stress induced during the ball milling process or strains due to the Ni and NiO lattice-constant mismatch arising at the interface and competing exchange interaction between the induced FM and AFM core \([53, 54]\). The existence of stress is evident from the non-slow decrease of magnetization in \( M-T \) curves, which acts more like hydrostatic one and hence increases \( T_C \) \([54]\). Such high \( T_C \) has also been reported in Ni/NiO system \([55]\).

In contrast, the magnetization of the milled NiO–Al powders decreases with increasing temperature, but exhibits two different magnetic phase transitions: (i) a large magnetization drop at about 640 K and (ii) a gradual decrease of magnetization at about 640 K and (ii) a gradual decrease of magnetization to a minimum at 300 K. Therefore, these results can be compared to the structural studies. On the other hand, the nature of magnetic phase transition of Ni in \( x = 40 \) powders is quite sharp due to the existence of large fraction of Ni as compared to \( x = 20 \) powders. These results show good correlations between the structural, thermal, magnetic and thermomagnetic properties of milled NiO–Al powders. Furthermore, the process of mechanical activation on the aluminothermic reduction allows for a controlled partial reduction of NiO and hence optimized amount of Ni produced.

4. Conclusions

We have systematically studied the effect of mechanical activation on the aluminothermic reduction reaction of NiO by subjecting the NiO and Al powders with different Al content to high-energy planetary ball milling under dry milling conditions and characterized structural and magnetic properties as a function of milling time and Al content. The milling process in pure NiO powder reduced the crystallite size down to 11 nm without changing the fcc structure. Therefore, the antiferromagnetic (AFM) nature of bulk NiO transformed into FM with a maximum magnetization of about 1 emu g\(^{-1}\) for the powder milled at 30 h. However, in the NiO–Al powders, the reduction of NiO occurred progressively up to a maximum of 40% for NiO–Al (20%) powders with increasing milling time and hence the magnetization increased gradually from 0.12 emu g\(^{-1}\) to 4 emu g\(^{-1}\) due to the increase in Ni content to 7.5%. On the other hand, the increase of Al content [NiO–Al (40%)] changed the reduction process to self-propagated combustion reaction type, which needed a critical time of 3 h to ignite the reaction process. Therefore, the magnetization changed drastically to 28 emu g\(^{-1}\) with a maximum of 90% NiO reduction with the yield of nearly 52% Ni. The microstructural studies revealed that the formation of FM Ni in AFM NiO matrix led to exchange bias effect. However, the magnitude of exchange bias depended on the relative fractions of Ni and NiO phases. High-temperature thermomagnetization data confirmed the presence of mixed magnetic phases in the milled NiO–Al powders and the nature of magnetic phase transition strongly depended on the amount of NiO reduction. The observed results showed a good correlation between structural, thermal and magnetic properties of milled NiO–Al powders. The controlled reduction of NiO in NiO–Al powder mixtures under present milling conditions finds suitable applications in the fields of catalysis and ore reduction.

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