Journal of Alloys and Compounds 509 (2011) 1020–1024

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

The effect of heat treatment on the structure and magnetic properties of mechanically alloyed Fe–45%Ni nanostructured powders

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ARTICLE INFO

Article history:
Received 8 July 2010
Received in revised form
20 September 2010
Accepted 26 September 2010
Available online 20 October 2010

Keywords:
Permalloy
Nanostructure
Mechanical alloying
Heat treatment
Magnetic properties

ABSTRACT

Magnetic iron–nickel alloys generally called permalloys are of great interest due to their magnetic properties. Fe–45%Ni alloy is one of the major iron–nickel compositions, well-known for high flux density, low coercivity and their responsiveness to the magnetic annealing. In this study, nanocrystalline Fe–45%Ni alloy powders were prepared by mechanical alloying process using a planetary high-energy ball mill under an argon atmosphere. The synthesized powders were heat treated at different temperatures using a vacuum furnace. The structural properties of the as-milled and the post-heat treated powders were studied by means of X-ray diffraction (XRD) technique and transmission electron microscopy (TEM). The magnetic measurements on the powders were carried out using a vibrating sample magnetometer (VSM). The results showed that the lattice strain decreases and the crystallite size increases with annealing temperature. It was also found that the variation of coercivity is dominated by the removal of residual stress at low annealing temperatures, whereas the value of coercivity depends on the crystallite size at higher annealing temperatures.

1. Introduction

It has been known that large-grained polycrystalline ferromagnetic materials (grain sizes D typically ranging from $\sim 10\,\mu m$ to 1 mm) can be magnetically soft, with coercivity below approximately 1 Oe. When a grain is large enough to contain multidomain, friction to domain motion (domain pinning) arises from inclusions and residual stresses rather than from grain boundaries. As the grain size decreases, the main contribution to the coercivity arises from grain boundaries. Thus, fine-grained materials are usually magnetically harder than coarse-grained materials of the same composition [1]. As a consequence, the coercivity decreases when the grain size increases according to the well known $1/D$ law [2].

Nanocrystalline soft magnetic materials do not follow the above mentioned domain pinning model in such away soft ferromagnetism with as low as possible coercivity was found in nanocrystalline alloys. This phenomenon has been described by random anisotropy model (RAM). The random anisotropy model was originally developed by Alben et al. [3] to describe the soft-magnetic properties of amorphous ferromagnets. Herzer [4] modified this model to explain the soft magnetic properties of nanocrystalline alloys. According to the Herzer's random anisotropy model, whenever grain size is smaller than the magnetic exchange length $L_{exch} \approx 40–50\,nm$ [5], the coercivity of nanocrystalline soft magnetic materials can be expressed as [2]:

$$H_c = \frac{{K_1}^4 D^6}{J_s A^3} \tag{1}$$

where K_1 is the anisotropy constant, D is the average crystallite size, A is the exchange constant and J_s is the saturation polarization as an intrinsic characteristic of the material.

Mechanical alloying is a powerful and relatively simple technique which allows the preparation of nanostructured Fe–Ni based alloys [6]. In spite of this fact that the grain size of the mechanically alloyed Fe–Ni nanostructure powders is smaller than the magnetic exchange length, their coercivity does not follow the random anisotropy model [7,8] because of the high level of structural defects such as residual strain [1].

In this study, nanostructured Fe–45%Ni powders were synthesized by the mechanical alloying process. The effect of heat treatment at elevated temperatures on the structure and magnetic properties is examined. The magnetic properties are discussed with respect to the internal strain and the grain growth behavior of the material.

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doi:10.1016/j.jallcom.2010.09.159

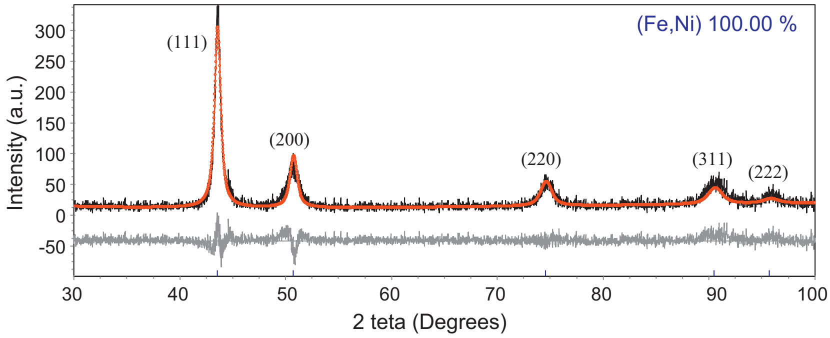

Fig. 1. X-ray diffraction pattern of the as-milled Fe–45%Ni powder. Experimental data are shown as continuous black line and refined simulated patterns are shown as red dots. The difference between experimental data and fitted simulated pattern is shown as continuous gray line under the diffraction pattern. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental method

The initial powders of Fe and Ni (purity >99%, average particle size <100 μm) were weighed and mixed to give the composition of Fe–45%Ni, and then introduced into a cylindrical tempered steel vial of the capacity of 100 ml. The ball-to-powder ratio was 15:1. In order to minimize oxidation, the entire operation was performed in a dry argon atmosphere, and the vial was sealed with a Teflon O-ring. The mechanical alloying process was carried out at ambient temperature by a planetary ball mill at the vial rotation speed and milling time of 350 rpm and 24 h, respectively. The synthesized powders were heat treated at different temperatures varying from 250 °C to 550 °C for 60 min followed by furnace cooling to the room temperature. The annealing process was performed in a vacuum of 10^{-5} Pa.

The phase analysis and structural parameters were characterized with X-ray diffraction (XRD, Shimadzu XRD-6000 diffractometer Cu Kalpha-1 radiation). The structural parameters were determined from Rietveld's powder structure refinement analysis of the X-ray powder diffraction data. The Rietveld calculations were performed by TOPAS 3 software (from Bruker AXS). In the TOPAS software, the Double–Voigt approach [9] is used for obtaining the crystallite size and strain components. This method is based on the broadening of the diffraction lines. In addition to the crystallite size and lattice strain, diffraction line broadening includes an instrumental broadening which is caused for different reasons [6]. For instrumental broadening correction, a specially processed Si standard was used. Correction coefficients were estimated and incorporated in the TOPAS software as instrumental broadening. The crystallographic model of FCC FeNi ($Fm{-}3m$, $a = 0.35975$ nm) was used as a starting model for the refinements. For each refinement, the following variations were applied: the background parameter, scale factor, cell parameter, zero point correction, Lorentzian crystal size and Gaussian lattice strain. In order to judge the quality of fitting on the structure model, the Bragg reliability factor (R_{Bragg}) was used. The refinements resulted in accurate fits to the experimental data and the average R_{Bragg} value was less than 5%.

Transmission electron microscopy (TEM, JEOL-JEM 2010) was used to study the microstructure of the powder particles. Magnetic measurements were obtained at the room temperature with a vibrating sample magnetometer (VSM, Lakeshore 7404) with a saturating field of ±10 kOe, field increment of 404 Oe and a field ramp rate of 40.4 Oe/s. The average value of saturation magnetization and coercivity was determined by an accuracy of ±3 emu/g and ±2 Oe after three times of measurement.

3. Results and discussion

3.1. Structure

The XRD diffraction pattern of the as-milled powder after 24 h of milling time is shown in Fig. 1. To estimate structural parameters such as crystallite size and lattice strain, the XRD pattern is analyzed by employing Rietveld's powder structure refinement analysis. In the Rietveld method, the least squares refinements are carried out until the best fit is obtained between the calculated patterns, which is based on the refined structure models and the observed diffraction patterns [9,10]. It is shown from this figure that the observed diffraction pattern (I_0; continuous black line) is fitted well with the refined simulated pattern of the crystallographic model of FCC FeNi (I_c; small red dots), because the residue of fitting ($I_0 - I_c$) is negligible. In addition, the characteristic Fe reflections are disappeared. These evidences prove that FCC γ-(Fe, Ni) phase (called taenite) has been completely formed. The formation of FCC γ-(Fe, Ni) phase (i.e., taenite) was also confirmed by Guittoum et al. [7] after 24 h of milling time.

The diffraction lines broadening, which is clearly observed from this figure, indicates a decrease in the crystallite size and the introduction of lattice strain. This broadening is due to the second-order internal stress which acts as a macroscopic level of the crystallites and produces a broadening of diffraction lines [7]. The Rietveld

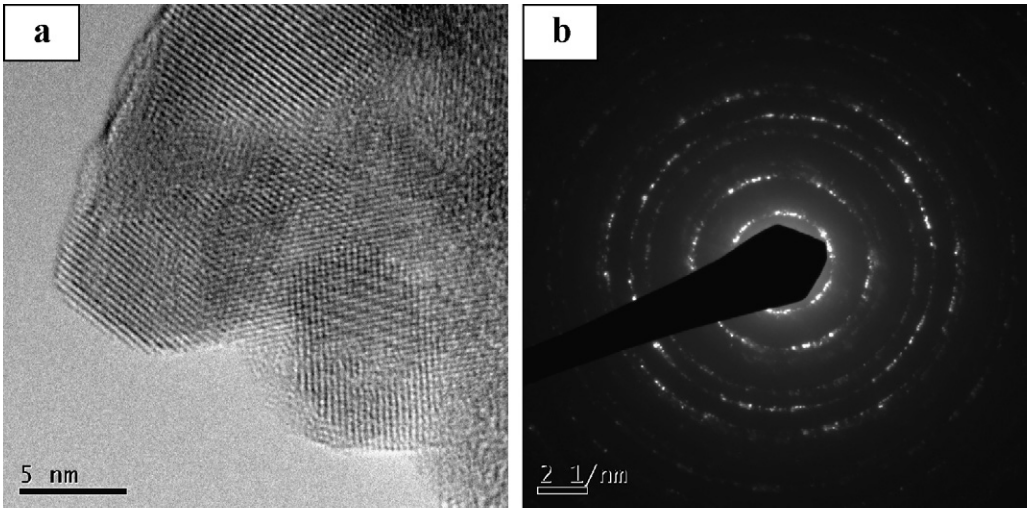

Fig. 2. (a) HRTEM image and (b) SAED pattern of a Fe–45%Ni alloy powder particle obtained after 24 h milling time.

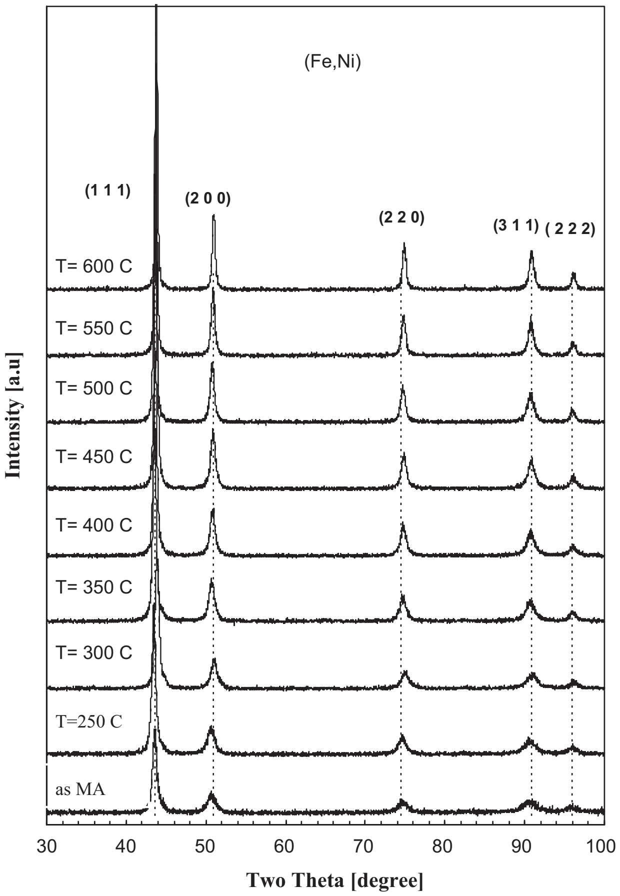

Fig. 3. X-ray diffraction patterns of mechanically alloyed Fe–45 wt.% nanostructured powders as a function of annealing temperature.

analysis of the diffraction pattern reveals that the average crystallite size and the lattice strain values of γ-(Fe, Ni) phase are 16.2 ± 0.6 nm and 0.258 ± 0.015%, respectively. It is interesting to note that Guittoum et al. [7] obtained a crystallite size and lattice strain of 25 nm and 0.25% after 24 h of milling using a high-energy planetary ball mill. Also, Lima et al. [11] obtained a crystallite size of 15 nm for nanostructured $Fe_{50}Ni_{50}$ alloy prepared by chemical reduction. It would be worth mentioning that for each material, there is a minimum grain size that is obtainable by milling, and this value is related to the intrinsic properties of the material, such as crystal structure [12,13]. In the previous study, it has shown that the minimum accessible grain size of γ-(Fe, Ni) phase obtained by milling is about 15 nm [8].

The nanocrystalline structure of the as-synthesized powder was also confirmed by high resolution electron microscope (HRTEM) micrographs. Fig. 2(a) and (b) shows the HRTEM bright field image and the corresponding selected area electron diffraction (SAED) of the as-synthesized powder, respectively. The corresponding diffraction pattern and the lattice fringes indicate an almost completely random orientation of the resultant nanocrystalline structure. The average grain size estimated from the HRTEM images is about 12 nm, which is relatively consistent with the value estimated by the analysis of the X-ray diffraction data.

Fig. 3 shows the X-ray diffraction patterns of the mechanically alloyed Fe–45 wt.% powders obtained after annealing at the various temperatures. It can be seen from this figure that FCC γ-(Fe, Ni) phase (i.e., taenite) is stable over the annealing temperature. It is also evident that the X-ray diffraction patterns of the heat treated powders are not changed significantly compared to the as-milled powder, except a progressive narrowing and slightly angular shift of the diffraction peaks and an increase in their intensity with increasing the annealing temperature. The reduction of the peak broadening is due to the increase of crystallite size and the decrease of lattice strain during the heat treatment process. The slightly angular shift is attributed to the first-order internal stress relaxation induced by the heat treatment. The first order angular stress acts as a macroscopic level by modifying the lattice parameter and consequently produces an angular shift of diffraction lines [7].

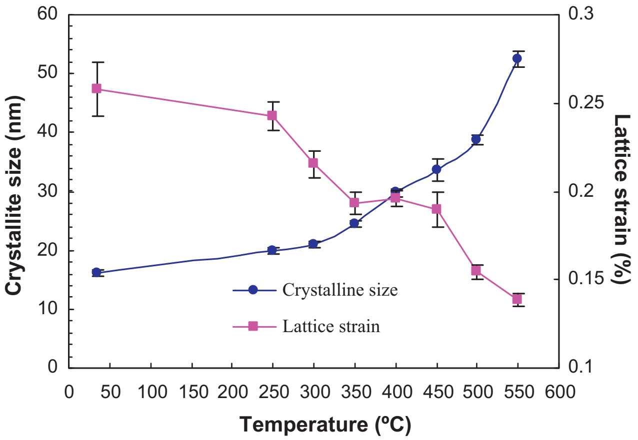

Fig. 4. Variation of lattice strain and crystallite size of γ-(Fe, Ni) phase with increasing annealing temperature.

The variation of the lattice strain (e) and crystallite size (D) of γ-(Fe, Ni) phase estimated from the Rietveld refinement of the X-ray diffraction data is shown in Fig. 4. The value of the crystallite size gradually increases from 16.2 ± 0.6 nm to 52.4 ± 1.4 nm with increasing the annealing temperature from the room temperature to 550 °C. On the contrary, the lattice strain value is found to fall moderately from 0.258 ± 0.015% to 0.138 ± 0.003%, when the annealing temperature increases from the room temperature to 550 °C. The similar trend is also reported by other authors for mechanically alloyed powders during heat treatment [14]. The lattice strain relaxation can be attributed to dislocation recovery based on dislocation annihilation and rearrangement processes. These processes are achieved by glide, climb and cross-slip of dislocations [15]. As a result, the dislocation density decreases when the lattice strain decreases at the elevated temperatures. On the other hand, grain growth occurred by the grain boundary migration during the heat treatment process. As grains increase in size, the total boundary area decreases, yielding an attendant reduction in the total energy, which is the driving force of grain growth [16].

3.2. Magnetic properties

The magnetic hysteresis loop measurements of the as-synthesized powder and an example of the annealed Fe–45 wt.% powder (heat treated at 450 °C) are shown in Fig. 5. Saturation magnetization and coercivity can be obtained from these curves. These magnetic properties, especially the intrinsic coercivity, are structure sensitive and dependent on heat treatment.

Fig. 6 shows the dependence of the saturation magnetization as a function of the annealing temperature. Referring to this figure, the saturation magnetization increases roughly with increasing the annealing temperature; probably due to the elimination of lattice strain at the high temperatures (Fig. 4). The result is also consistent with previous reports [17,18].

The coercivity variations with the heat treatment temperatures are shown in Fig. 7. In order to simplify discussion, the

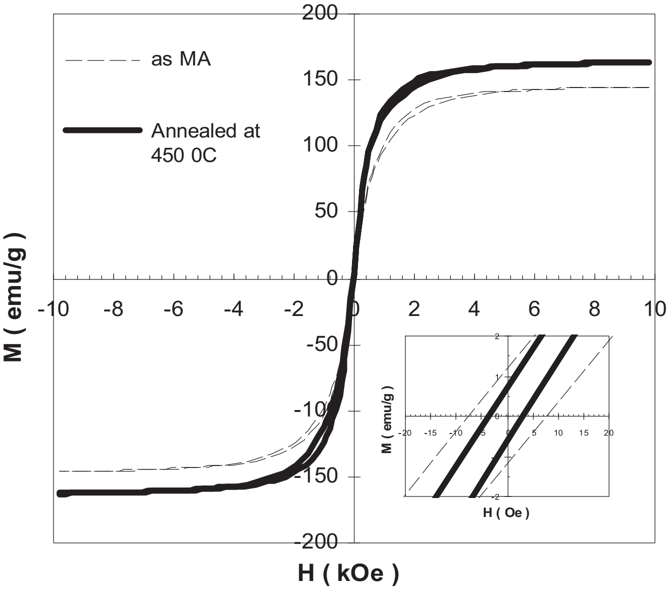

Fig. 5. Hysteresis curves of the as-synthesized powders with and without a subsequent heat treatment.

figure is divided to two stages. At the first stage, the coercivity initially decreases significantly from 8.4 Oe to 4 Oe when the annealing temperature increases from the room temperature to 350 °C, and then it remains approximately constant at about 4 Oe for the higher annealing temperature up to 450 °C. Although the nanocrystalline structure of the synthesized powders at this stage ($16.2\,\text{nm} \leq D \leq 33.7\,\text{nm}$) is ascertained by the Rietveld analysis of the X-ray diffraction data, their coercivity does not follow the Herzer's random anisotropy model ($H_c \infty D^6$). A possible reason for this unexpected behavior arises from the high level of residual stress induced by the ball milling process. Since the Herzer's random anisotropy model does not include the effect of residual stress, the model cannot be applied to the as-ball milled powders.

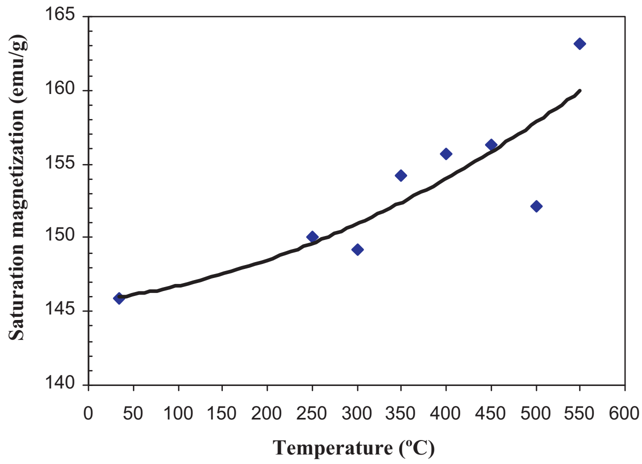

Fig. 6. Saturation magnetization as a function of annealing temperature.

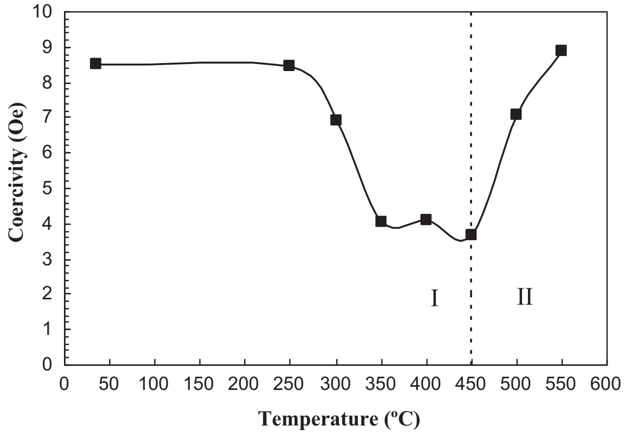

Fig. 7. Coercivity as a function of annealing temperature.

Shen et al. [1] modified this model to include the effect of residual stress, which is prevalent and unavoidable during ball milling. They has assumed that dislocations are the main contributors to the residual stress; therefore, their model predicts that the coercivity in mechanically alloyed nanocrystalline materials ($D < L_{\text{exch}}$) depends on both dislocation density (residual stress) and crystallite size. Their model can be summarized and expressed as:

$$\begin{array}{ll} \text{case 1}: & |\lambda_s| \to 0, \quad \rho \to 0, \quad H_c \propto D^6 \\ \text{case 2}: & |\lambda_s| \to 0, \ \rho \gg 0, \ H_c \propto D^6 \\ \text{case 3}: & |\lambda_s| \gg 0, \quad \rho \to 0, \quad H_c \propto D^6 \\ \text{case 4}: & |\lambda_s| \gg 0, \quad \rho \gg 0, \quad H_c \propto \sqrt{\rho} \end{array}$$

where λ_s is the saturation magnetostriction and ρ is the average dislocation density [1].

The random anisotropy model modified by Shen et al. [1] provides a satisfactory explanation for the decrease of coercivity at the first stage. The observed variation of the coercivity suggests that in this annealing range, the decrease of H_c is dominated by the removal of residual stress. In the second heat treatment range (stage 2), the coercivity increases sharply from 3.7 Oe to 8.9 Oe with increasing the annealing temperature from 450 °C to 550 °C. The variation of the coercivity in this stage can be attributed to the increase of crystallite size, which is explained by the Herzer's random anisotropy model.

4. Conclusion

The structure and magnetic properties of mechanically alloyed Fe–45%Ni nanostructured powders have been carefully studied as a function of annealing temperature. The important observations can be summarized as follows:

(i) FCC γ-(Fe, Ni) phase (taenite) with the average crystallite size of $16.2 \pm 0.6\,\text{nm}$ and the lattice strain of $0.258 \pm 0.015\%$ has been completely formed within 24 h of ball milling.
(ii) Increasing the annealing temperature led to an increase of the crystallite size (because of the grain growth process) and a decrease of the lattice strain (due to the recovery process) at the elevated temperatures.
(iii) The saturation magnetization was found to increase with the annealing temperature as a result of internal strain relaxation at the elevated temperatures.
(iv) The coercivity decreased with increasing the temperature at the low annealing temperatures ($T \leq 450\,°\text{C}$) due to the removal of residual stress being the main contributor to the coercivity. Consequently, the variation of the coercivity was consistent with the random anisotropy model modified by Shen. On the contrary, at the higher annealing temperatures ($450\,°\text{C} \leq T \leq 550\,°\text{C}$) the coercivity increased due to the dominating effect of grain growth on H_c; therefore, the variation of the coercivity followed from the Herzer's random anisotropy model in this annealing range.

Acknowledgment

The authors would like to thank the Nanyang Technological University (NTU) for providing support to this research.

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