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Synthesis and characterization of nanocrystalline Co-Fe-Nb-Ta-B alloy

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ABSTRACT

In this research work, structural and magnetic evolution of $Co_{57}Fe_{13}Nb_8Ta_4B_{18}$ alloy, during mechanical alloying process, have been investigated by using, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, electron dispersive X-ray spectroscopy, differential thermal analysis and also vibrating sample magnetometer. It is observed that at 120 milling time, the crystallite size reaches to about 7.8 nm. Structural analyses show that, the solid solution of the initial powder mixture occurs at160 h milling time. The coercivity behavior demonstrates a rise, up to 70 h followed by decreasing tendency up to final stage of milling process. Thermal analysis of 160 h milling time sample reveals two endothermic peaks. The characterization of annealed milled sample for 160 h milling time at 427 °C shows crystallite size growth accompanied by increasing in saturation magnetization.

1. Introduction

Recently, a great attention has been paid to nanocrystalline materials due to their structural and functional properties. Nanocrystalline (Fe- and Co based systems) exhibit good soft magnetic properties, while Fe- and Ni based systems present high corrosion resistance [1–3]. These properties are attributed to the crystallite size refinement results in high interface density and also residing of remarkable fraction of atoms at the grain boundaries [4,5]. Nanostructure alloy can be produced by solid-state process, such as mechanical alloying technique. By this technique, nanocrystalline materials can be easily produced with relatively affordable equipment [6]. Mechanical alloying induces strain deformations, resulting in substantial amounts of defects such as dislocations, vacancies and grain boundaries. This technique involves repeated fragmentation and welding of component particles, leading to alloy formation, refinement of crystallite size and particles and also producing of metastable phases, such as nanocrystalline and amorphous phases [7]. Cobalt rich amorphous alloys display good soft magnetic properties which is attributed to the relatively less magnetostriction coefficient and averaging out of the magnetocrystalline anisotropy [8,9]. Some studies have been performed on Co-based materials, such as Co-Fe-Zr-B [10], Co-Fe-(Zr,Ti)-B [11], Co-Nb-Zr-B [12]. There are also studies on multicomponent Co-Fe-M-B (M = Nb, Zr) [13,14] and Co-Fe-Ta-B [1] produced by melt spinning and copper-mold casting techniques respectively, exhibiting high permeability and low coercivity. It has been shown that the addition of transition metals such as titanium, zirconium, niobium and tantalum resulted in the formation of amorphous phases. Wu et al. [15] reported the formation of amorphous $Co_{70-x}M_x\ Ti_{25}B_5$ (M = Fe, Nb) system with x = 5, 15, 25, 35. The results indicated that the substitution of cobalt with iron and niobium led to reduction of thermal stability of mixed powders. Taghvaei et al. [16] also showed the increasing of amorphous phase of $Co_{40}Fe_{22}Ta_8B_{30}$ alloy with milling time. However, Moreno et al. [12] produced amorphous alloyed powder $Co_{62}Nb_6Zr_2B_{30}$ by mechanical alloying with different types of boron powders. We also showed the induced crystallization in cobalt based $Co_{40}Fe_{10}\ Zr_{10}\ B_{40}$ alloy [10]. More recently, Avar [17] applied mechanical alloying to $Co_{65}Ti_{25}W_5B_5$ alloy and indicated that, W was not fully dissolved even at higher milling time. To the best our knowledge, no results have been reported about the multicomponent alloy $Co_{57}Fe_{13}Nb_8Ta_4B_{18}$ at (%) composition. In this present research, magnetic and structural properties of $Co_{57}Fe_{13}Nb_8Ta_4B_{18}$ at (%) obtained by mechanical alloying are investigated.

2. Experiment

The starting materials used in this study were obtained by Co (99%, <3 μm), Fe (98%, <10 μm), Nb (98%, <45 μm), Ta (98%, <42 μm) and B (98%, <3 μm) powders. The samples with composition $Co_{57}Fe_{13}Nb_8Ta_4B_{18}$ were prepared by using mechanical alloying at different milling times. The powders were sealed in a cylindrical stainless steel vial containing a blend of stainless steel balls. The milling process was carried out in a planetary ball (NARYA- MPM 2⁎250) mill under protective argon. The ball- to-

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powder weight ratio was 20: 1. The loaded balls were in two sizes ($\phi = 10$ mm, mass = 4.11 g and $\phi = 20$ mm, mass = 32.59 g). The powders were milled for 4, 12, 24, 48, 70, 96, 120 and 160 h. The rotation speed was 350 rpm. The milling process was performed as a sequence of 30 min of milling followed by 15 min pause. Structural parameters (crystallite size and microstrain) and phase analyses of the samples were determined by X-ray diffraction (XRD), using Philips diffractometer with Cu K_α ($\lambda = 1.54$ Å) radiation over 2θ in the range: 20–100°. The crystallite size and lattice strain were estimated by Scherrer method and Tangent formula respectively by using Xpert software. The morphology of milled samples was examined by using scanning electron microscope (SEM) and transmission electron microscope (TEM). The TEM measurements were performed by using a Philips- CM300 microscope operated at 150 kV; the as- milled powders were immersed in pure ethanol and then dispersed by using an ultrasonic vibrator for 5 min. The elemental identification was obtained by energy dispersive X-ray spectroscopy (EDX) analysis. Magnetic properties were estimated at room temperature by a vibrating sample magnetometer (VSM) (Daghigh Meghnatis Kashan Co, Kashan, Iran). The thermal behavior was measured by differential thermal analysis (DTA) and performed by NETZSCH (STA 449F3) instrument at a heating rate 10 °C/min under pure argon atmosphere.

3. Results and discussion

3.1. Structural study

The change of morphological shape of the milled powder at different milling times is depicted in Fig. 1. As seen in Fig. 1a, the unmilled powders exhibit non-uniform in shape and size. After 24 h milling time, the particles are flattened by progressive forces induced by the impacts between the balls and/or balls and vial (Fig. 1b); this causes an increase of particle sizes. Prolonging the milling time up to 96 h, the particles separated into smaller parts with more uniform size (Fig. 1c). As depicted in Fig. 1d, the particles shape becomes more regular and spherical, revealing a balance between the fracturing and welding process which is achieved after 160 h of milling.

The EDX point chemical analysis of the 160 h milled sample shown in Fig. 2 reveals both constituent and oxygen elements. The oxygen contamination is expected and can be stemmed from powder handling. The oxygen atoms can be located on the surface of the powders due to their large surface areas. The boron element is not observed due to the limitation of light element detection.

The XRD patterns of the unmilled and milled samples at different milling times are illustrated in Fig. 3. All characteristic peaks of constituent elements (FCC and HCP- Co, BCC-Fe, BCC-Nb and BCC-Ta) are observed for the starting mixed powders. (see Fig. 3a) .Both HCP and FCC- Co structure are coexistence in the premixed powder [18]. The boron element peaks are not revealed because it is amorphous in nature. With increasing the milling time, the peaks broadening increases which can be ascribed to both the reduction in grain size and increase in lattice strain. After 4 h milling time, the main diffraction peak of only HCP-Co is observed. This may be arisen from allotropic transformation of cobalt from FCC to HCP phase. The FCC cobalt phase is metastable at room temperature and this structure tends to unstable state by applying external mechanical or thermal energy [19]. Furthermore, the formation of a (Fe,Co) solid solution is started at this stage.

There is a peak shift toward lower angle, after 12 h milling time, resulting from solid solutioning process. Meanwhile, a decrease of both BCC tantalum and niobium peaks intensity are also happened in the whole process. The peak positions of niobium and tantalum elements are much close to each other and it is hard to distingush their peak positions separately. Therefore, only based on the XRD results, it would not be determined which elements (Ta and Nb) dessolve earlier into the cobalt lattice. Sharma et al. [20] reported, the addition of niobium to $Fe_{42}Ni_{28}Zr_{10}B_{20}$ powder mixture, causes to complete glass forming earlier than in the case of niobium free alloy; we have to note that the heat of mixing of niobium with zirconium is positive. (+17 kJ mol^{-1}). Moreover, tantalum is dissolved in (Fe,Co) solid solution at high milling time [16]. The dissolution of tantalum into cobalt lattice enhances the elastic energy for the solid solution phase formation which is attributed to the size mismatch effect. The lattice mismatch between iron and cobalt is lower that the lattice mismatch between cobalt and tantalum. Therefore a larger elastic energy is required to dissolve tantalum in the cobalt lattice as compared to dissolution of iron. This causes, a longer milling time is needed to dissolve tantalum than that required for dissolution of iron into cobalt lattice. Thus, we can conclude that the existence of unreacted tantalum is more likely than niobium element at the late stages of milling time.

The peak position of (Fe,Co) alloy is shifted toward right angle, from $2\theta = 44.65°$ at 12 h to $2\theta = 44.78°$ at 24 h and peak broadening also becomes wider (see Fig. 3c); this trend is also significantly occurred after 96 h milling time, where the peak is positioned at angle, 45.17 °. This peak shift to the higher value of 2θ, suggesting the lattice contraction has happened during solid solution process. The lattice contraction of alloy during the milling process has been also reported particularly for cobalt rich alloys [16,21–23]. The decrease of lattice parameter can be stemmed from the allotropic phase transformation of cobalt (FCC–HCP) and/or to the triple defect disorder [6,22]. It has to be noted that the HCP cobalt peaks vanishes after 96 h milling time, resulting in completion of the formation of BCC-(Fe,Co) solid solution. As seen in Fig. 3b, the intensity of tantalum and/ or niobium diffraction peak decreases abruptly. This can result in substitutional dissolution of tantalum and/or niobium into BCC- (Fe, Co) alloy lattice and therefore the lattice expansion occurs due to the larger atomic size of both niobium and tantalum atoms as compared to the atomic size of both iron and cobalt atoms. The dissolution of boron atom in interstitial sites can be also resulted in the lattice contraction at the aforementioned milling time [20].

With continuing milling process up to 160 h, the BCC- (Fe, Co, Ta, Nb) phase peak is observed which is much broadened. Meanwhile, the diffraction peaks of Nb and/or Ta disappear at this stage.

The alloying mechanism stems from relatively high negative heat of mixing between constituent elements [24]. In this system, the heat of mixing for each pair Co-Fe, Co-Nb, Co-Ta and Co-B is -1, -25, -24 and -24 kJmol^{-1} respectively [25].The boron atoms can be diffused into the interstitial sites lattice defects of the structure. This is due to the severe powder plastic deformation [26]. The preferential diffusion of boron into the dislocations of BCC-Fe prevents the dislocations movement [27]. This causes to produce an intense locked dislocation, leading to a sharp decrease in grain growth phenomena and thereby the grain refinement increases. [26,28]. This can provide the nanocrystalline structure [26].

The variations of crystallite size and lattice strain based on BCC-(Fe, Co) (110) phase are shown in Fig. 4a. After 12 h of milling time, a rapid decrease of crystallite size to about 23 nm is observed which is ascribed to the formation of solid solution. Between 12 and 24 h, the crystallite size increases; the temperature of the powders during the milling process can be increased due to the following reasons, 1) the kinetic energy of the grinding medium and 2) exothermic process during the milling process may occur and this can produce heat [6]. Therefore, the temperature rising of the powders can lead to the dynamical recrystallization effect, giving rise to grow the crystallites [10,29]. A sudden decrease of the crystallite size is observed between 24 and 70 h and also between 96 to120 h milling time. This can be attributed to the dissolution of