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THE MAGNETIC BEHAVIOR OF Cu-Ni-Co-Fe QUATERNARY ALLOYS PREPARED BY MECHANICAL ALLOYING

B.N. Mondal[ξ], A. Basumallick, P.P. Chattopadhyay
Department of Metallurgy & Materials Engineering,
Bengal Engineering and Science University, Shibpur. Howrah-711 103, India

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Abstract

The Cu-Ni-Co-Fe alloys with average grain size~10nm have been prepared by mechanical alloying. The ball milled and annealed samples were characterized by XRD, HRTEM and magnetic measurement. In the case of ball milled sample, superior magnetic properties have been achieved for sample comprising dispersed magnetic phases in Cu-rich matrix. In the case of annealed sample magnetic properties are improved due to precipitation of hard magnetic phase Co(fcc) from single phase Cu-rich solid solution.

Introduction

Mechanical alloying is a versatile technique for the synthesis of equilibrium and non-equilibrium powder material by solid state reaction at room temperature [1-2]. Microstructure evolution during mechanical alloying process is overseen by a competition between cold welding and fracturing of powder particles under the repetitive events of impact [3-4]. Earlier, a variety of nanocrystalline magnetic alloys, such as Cu-Ni-Co and Cu-Ni-Fe have been produced by mechanical alloying. Cu-Ni-Fe and Cu-Ni-Co alloys have a wide range of application such as magnetic tape, loud speaker, magnetic sensor and listening devices [5-6]. These alloys have high coercivity and remanence with ductility providing the necessary flexibility to fabricate hard magnets with complex geometrical shapes [5-8]. The magnetic properties of these alloys depend significantly on grain size, lattice strain and crystal structure of alloys [9-10].

In the present work, the nanocrystalline quaternary Cu-Ni-Co-Fe alloys were prepared by mechanical alloying. The structure and magnetic properties of ball milled and annealed Cu-Ni-Co-Fe alloys were studied depending on the content of the elements such as Cu, Ni, Co and Fe.

Experimental Procedure

Cu, Ni, Co and Fe powders with the compositions (wt %) of 35Cu-25Ni-20Co-20Fe(C_{35}NCF),50Cu-20Ni-15Co15Fe(C_{50}NCF) and 60Cu-15Ni-12.5Co-12.5Fe(C_{60}NCF) (>99.9% of purity and ~50 μm particle size) were ball milled in Fritsch P6 planetary ball mill using WC vials and balls with ball to powder weight ratio of 10:1 for 30 h at room temperature. Toluene was used as the milling medium to minimize oxidation, agglomeration and cold welding of the constituents. The ball milled powder after sealing in glass tube under vacuum were annealed in the range of 350-650 ^{o}C for 1 h followed by furnace cooling.

Structural characterization of the ball milled and annealed sample were performed by X-ray diffraction (XRD) analysis using a Philips, PW 1830 diffractometer using Cr- filtered Co-K_{α} (0.179 nm) radiation generated at 35 kV/25 mA.

Average grain size and lattice strain of the samples were determined from the broadening of the most intense peak of the chosen phases using single line profile analysis (SLPA) based on equivalent Voigt representation [11].

High resolution transmission electron microscopy (HRTEM) and corresponding selected area diffraction (SAD) analysis were carried out to study the microstructural features of the phases formed in the mechanically alloyed product using a JEM-2011 operated at an acceleration voltage of 200 kV.

The temperature dependence of magnetization of the ball milled powder samples was measured from room temperature to 650^{o}C at the heating rate of 10^{o}C using a pulsed field AC magnetization system.

Magnetic properties such as coercivity (H_c) and remanence (M_r) of ball milled and annealed samples have been determined by a hysteresis loop tracer at room temperature.

Results and Discussion

XRD Analysis of Ball Milled Samples

Figure 1 shows the XRD patterns of C_{60}NCF, C_{35}NCF and C_{50}NCF obtained after 30 h of milling. XRD pattern of C_{60}NCF sample obtained after 1h of ball milling is also appended for indicating the peak position of the constituent elements. It is evident that after 1 h of milling of the sample C_{60}NCF all the elemental constituents such as Cu, Ni, Co and Fe are present as the elemental form. A complete single phase Cu-rich solid solution has been formed after 30 h of milling of the sample C_{60}NCF. In the case of C_{35}NCF and C_{50}NCF samples, perceptible amount of magnetic constituents elements such as Ni, Fe and Co remain undissolved in the solid solution of Cu. The average grain sizes of the solid solution of Cu of the samples C_{35}NCF, C_{50}NCF and C_{60}NCF determined by SLPA method are 9.28nm, 11.7 nm and 10.5 nm, respectively.

[ξ] email : bholanath_mondal@yahoo.co.in

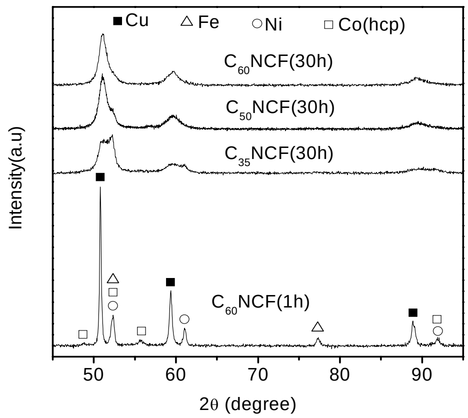
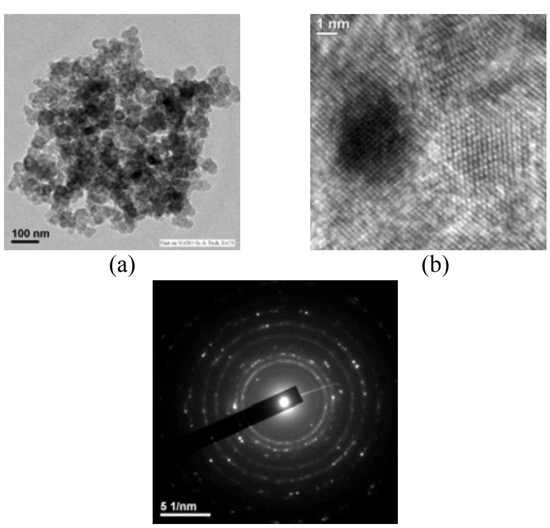


Figure 1. XRD patterns of C_{60}NCF alloys obtained after 1h and 30 h of milling and C_{35}NCF and C_{50}NCF alloys obtained after 30 h of milling

HRTEM Analysis of Ball Milled Sample

Figure 2(a) reveals the low magnification HRTEM micrograph showing the agglomerated particles of the ball milled C_{35}NCF sample. The small particle size is responsible for the high specific surface energy of Cu-Ni-Co-Fe ball milled sample resulting in agglomeration of the particles. The micrograph reveals the particles of spherical and elliptical shapes in nanometer scale having 5-25 nm in size. The lattice fringe pattern obtained from one of such a particle is shown in Fig. 2(b). The centre part of the image shows clear lattice fringe representing nanocrystalline phase. Presence of the smeared lattice fringe in some location indicates partial amorphisation of the sample. The selected area diffraction pattern exhibits diffraction rings as shown in Fig. 2(c). It is evident that the smallest diffraction ring is continuous indicating formation of nanocrystalline phase. Diffraction spots observed in the diffraction pattern are due to coarser crystalline phases.



(a) (b) (c)

Figure 2 (a) and (b) HRTEM image, and (c) corresponding SAD pattern of the mechanically alloyed C_{35}NCF alloys

XRD Analysis of As-milled and Annealed Samples

Figure 3 represents the XRD patterns of C_{35}NCF, C_{50}NCF and C_{60}NCF samples obtained after annealing at 650 ^{o}C for 1 h. It is clear that fcc Co has precipitated out from the solid solution of Cu.

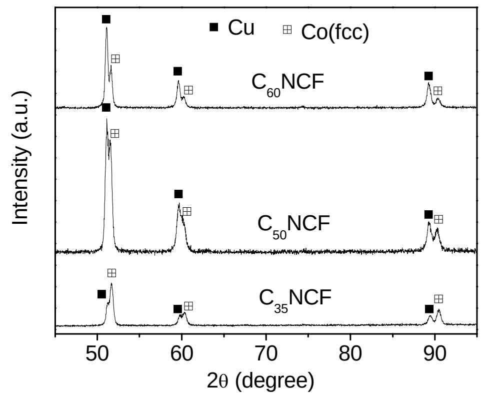


Figure 3. XRD pattern of the samples C_{35}NCF, C_{50}NCF and C_{60}NCF obtained after annealing at 650^{o}C for 1h

Figure 4 represents the variation of grain size and lattice strain of ball milled and annealed samples of C_{35}NCF, C_{50}NCF and C_{60}NCF. It is evident that grain size increases and lattice strain decreases with increasing annealing temperature for all the samples.

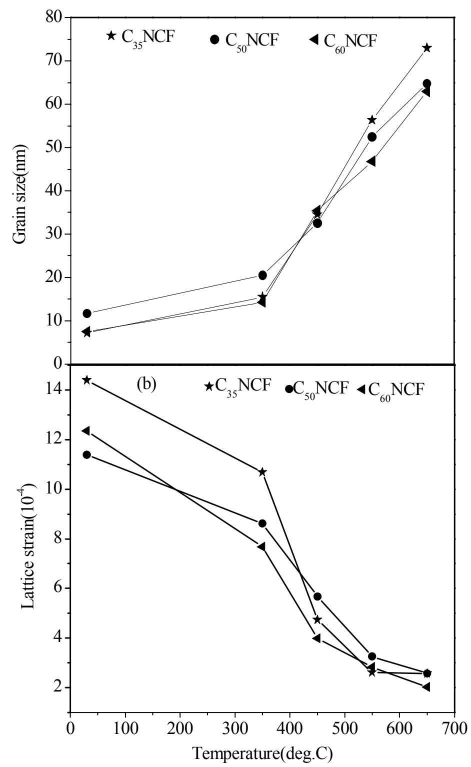


Figure 4. Variation of grain size and lattice strain of ball milled and annealed alloys C_{35}NCF, C_{50}NCF and C_{60}NCF with increase in annealing temperature

Magnetic Properties of As-milled and Annealed Samples

Figure 5 shows the variation of magnetization (M) of the as-milled samples C_{35}NCF, C_{50}NCF and C_{60}NCF with increasing temperature. Table 1 represents coercivity (H_c) and remanence (M_r) values of the as-milled and annealed samples C_{35}NCF, C_{50}NCF and C_{60}NCF. It is evident that the magnetic properties i.e. M, H_c and M_r of the as-milled samples increase with decrease in Cu-content. In the case of C_{35}NCF, it is attributed to the higher concentration of undissolved magnetic constituents present in the alloys, which are expectedly having ultrafine grain size. A small peak at 150 ^oC as seen in the M-T plot of the sample C_{35}NCF due to relaxation of lattice strain which is accumulated during mechanical alloying (Fig. 4). Magnetization decreases gradually with increase in temperature upto 325 ^oC for all the samples shown in Fig. 5 due to the formation of homogenized solid solution [12]. A plateau has been initiated to form at the temperature 325 ^oC and ends at 400, 500 and 525 ^oC for the samples C_{35}NCF, C_{50}NCF and C_{60}NCF respectively as seen in the M-T plot which may be attributed to the precipitation of hard magnetic Co (Fig. 3) in Cu matrix .

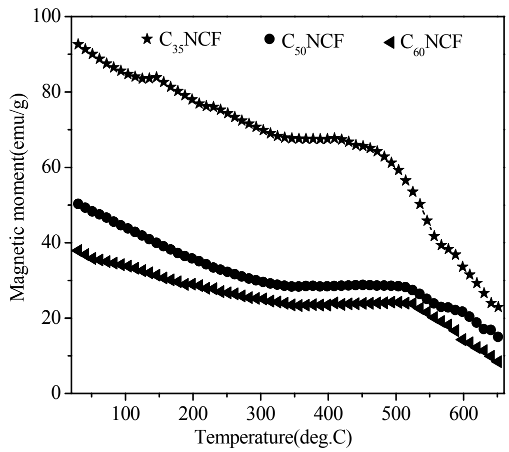


Figure 5. Variation of magnetization of the as-milled samples C_{35}NCF, C_{50}NCF and C_{60}NCF with increasing temperature

Table1 exhibits reduction of H_c and M_r in the case of C_{35}NCF sample with increase in temperature while the same for C_{50}NCF and C_{60}NCF samples, increase upto 350 ^oC and 450 ^oC, respectively. During annealing, in the case of C_{35}NCF sample, the undisolved magnetic phases continue to dissolve in Cu-rich solid solution, in order to reduce the high interfacial energy and the stored mechanical energy. On the other hand in C_{60}NCF, precipitation of magnetic phases is energetically favoured from the Cu-rich supersaturated solid solution. In the case of C_{50}NCF, the dissolution and precipitation are apparently energetically competitive. It is evident that the magnetic properties are favoured in microstructure comprising hard magnetic precipitates distributed in Cu-rich matrix. This is why better magnetic properties are achieve in C_{35}NCF sample in ball milled condition while in C_{60}NCF sample, the magnetic properties are improved after annealing. At higher temperature (> 450 ^oC) of annealing, coarsening and/or dissolution of precipitates deteriorates the magnetic properties.

Table1. Summary of the magnetic properties of ball milled and annealed samples of C_{35}NCF, C_{50}NCF and C_{60}NCF

Alloys	Isothermal annealing temperature (^oC)	Coercivity (Oe) (H_c)	Remanence (emu/g) (M_r)
C_{35}NCF	As-milled	333.33	18.18
	350	189.4	8.74
	450	151.5	6.99
	550	78.55	4.58
	650	68.18	4.22
C_{50}NCF	As-milled	212.34	4.81
	350	246.10	9.26
	450	174.24	6.58
	550	136.36	5.81
	650	87.12	4.37
C_{60}NCF	As-milled	202.56	4.81
	350	287.88	6.56
	450	295.88	6.79
	550	174.28	4.8
	650	53.03	2.21

Conclusions

A complete solid solution has been formed after ball milling for 30 h for the alloy C_{60}NCF. The grain size of the alloys increases and lattice strain decreases with increasing annealing temperature. Co has been precipitated out with fcc crystal structure from the Cu-rich solid solution after annealing. The C_{35}NCF and C_{60}NCF samples show the superior magnetic properties after ball milling and annealing, respectively due to presence of dispersed magnetic phases in Cu-rich matrix.

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