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Structure and magnetic properties of mechanically synthesized nanocrystalline $Co_{52}Fe_{26}Ni_{22}$ alloy

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Mechanical alloying method was used to prepare nanocrystalline $Co_{52}Fe_{26}Ni_{22}$ alloy. X-ray diffraction was applied for determination of the structure of the alloy. During milling Co-based solid solution with f.c.c. lattice was formed. After 80 h of synthesis the lattice parameter was equal to 0.3575 nm while the average grain sizes and the mean level of internal strains were about 24 nm and 0.72%, respectively. Mössbauer spectroscopy was adopted to characterize the local atomic order of the $Co_{52}Fe_{26}Ni_{22}$ alloy. In the nearest neighbourhood of ^{57}Fe isotopes there are at least six Co atoms, three Ni atoms and three Fe atoms giving the hyperfine magnetic field equal to 32.45(1) T. Magnetization measurements allowed to determine the effective magnetic moment of the $Co_{52}Fe_{26}Ni_{22}$ alloy to be equal to 1.63 μ_B per formula unit. Curie temperature of the obtained alloy is equal to 1000 K.

1. Introduction

Powdered ferromagnetic solids with small grain sizes have magnetic properties different than bulk materials. For example, coercivity H_c increases when the dimension of grains decreases to about 20–30 nanometers [1–4]. However, continued decreasing of grain sizes causes the change in magnetic properties from hard to soft, what is explained by random anisotropy model [5].

Ternary alloys Co-Fe-Ni exhibit promising soft magnetic properties. Recently, thin films of Co-Fe-Ni alloys with extremely high saturation magnetization B_s of 2.0–2.1 T and low coercivity around 1 Oe have been obtained by electrodeposition [6, 7]. Radio frequency magnetron-sputtering method was also used to obtain materials with equivalent soft magnetic properties, however for another alloys composition as compared to the electrodeposited films [8].

The aim of this work was to apply mechanical alloying method for obtaining ternary $Co_{52}Fe_{26}Ni_{22}$ alloy. Properties of mechanically synthesized Co-Fe-Ni alloys are not well known and they are supposed to exhibit good soft magnetic properties. The structure and some magnetic properties of the $Co_{52}Fe_{26}Ni_{22}$ alloy were determined using X-ray diffraction (XRD), Mössbauer spectroscopy (MS) and magnetization measurements.

2. Experimental details

Mechanical alloying process was performed starting from the powders of Co, Fe and Ni with a purity of 99.8 and 99.9%, respectively. The initial dimensions of particles were 10 μm for Co, 6–9 μm for Fe and 3–7 μm for Ni. A Fritsch P5 planetary ball mill with stainless-steel vial and balls was used to synthesize alloy with composition of $Co_{52}Fe_{26}Ni_{22}$.

XRD measurements were carried out using a Philips PW 1830 diffractometer working in a continuous scanning mode with Co K_α radiation. The Williamson-Hall

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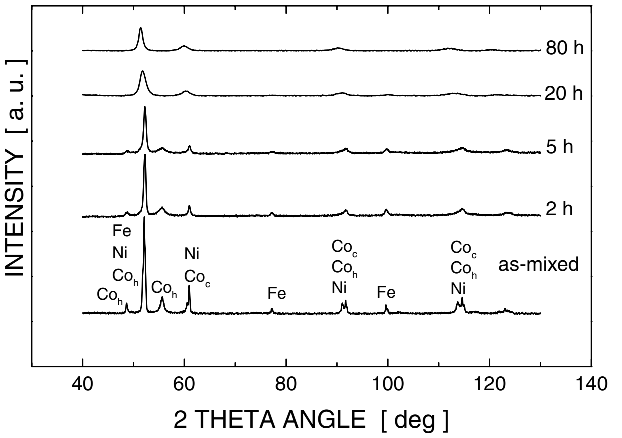

Figure 1 XRD patterns of the $Co_{52}Fe_{26}Ni_{22}$ alloy mechanosynthesized in high-energy Fritsch mill for various milling times; Co_h—hexagonal cobalt, Co_c—cubic cobalt.

approach was used for determination of the average grain sizes and the mean level of internal strains [9].

MS studies were performed at room temperature in standard transmission geometry using a source of ^{57}Co in a rhodium matrix.

Temperature dependencies of magnetization were measured on a Faraday balance in magnetic fields up to 1.5 T with the relative accuracy better than 1%. The temperature was stabilised within ±0.5 K and the heating rate was up to 4 K/min.

3. Results and discussion

XRD patterns obtained for samples milled up to 80 h are presented in Fig. 1. In the pattern for pristine powder all the expected lines of Co, Fe and Ni are observed. For samples milled longer than 20 h the Bragg peaks of Fe and of hexagonal fraction of Co disappear. In the pattern of the sample milled for 80 h the angular position of the diffraction lines approximate the equilibrium positions of cubic fraction of Co as well as Ni. However, because the Co content in the mixture is significantly larger than Ni content, it may be stated that during mechanical alloying process Co-based solid solution with f.c.c. (face centred cubic) lattice was formed. This result agrees well with the phase-diagram for the bulk Co-rich Co-Fe-Ni alloys obtained by melting [10].

Detailed analysis proved that after 80 h of synthesis the lattice parameter of the alloy was equal to 0.3575(1) nm. It is another evidence that the solid solution is based on the cobalt because the lattice parameter of cubic Co is equal to 0.3552 nm while for Ni–0.3524 nm. During mechanical alloying process the iron and nickel atoms dissolve in Co matrix causing the increase of the cobalt lattice dimension. The mean level of internal strains is relatively high and it is equal to 0.72%. The average grain sizes D were about 24 nm. On the basis of the coherent polycrystal model [11] and assuming that the average grain boundary thickness is 1 nm (as suggested by Refs. [12, 13]) the volume fraction of the grains f_g was determined using the formula:

$$f_g = \frac{(D-d)^3}{D^3}, \tag{1}$$

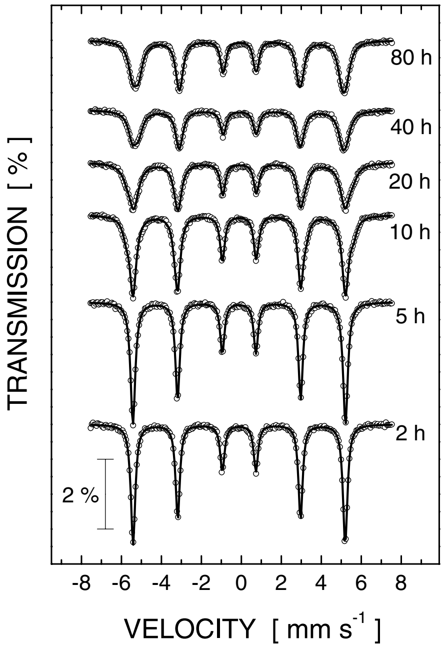

Figure 2 Room-temperature Mössbauer spectra of the mechanosynthesized $Co_{52}Fe_{26}Ni_{22}$ alloy for various milling periods.

where d is the effective grain boundary thickness. The volume fraction of the grain boundaries C_{gb} given by

$$C_{gb} = 1 - f_g \tag{2}$$

is equal to 12% for the mechanically synthesized $Co_{52}Fe_{26}Ni_{22}$ alloy.

Mössbauer spectroscopy allows not only monitoring the process of the alloy formation but also determining its magnetic state and local configuration of atoms in the so-called NN shell (Nearest Neighbourhood) of ^{57}Fe isotopes. For all milling times the mixtures are ferromagnetic as proved by the six-line patterns (Fig. 2). The first two spectra are characteristic for α-iron, the value of the hyperfine magnetic field B_{hf} is equal to 33.03(1) T and the half widths at half maximum of spectral lines is about 0.12 mm s^{-1}. As milling time increases the lines are broadened up to 0.19 mm s^{-1}. The spectrum of the sample milled for 10 h was fitted by two components: $B^1_{hf} = 35.42(4)$ T and $B^2_{hf} = 33.06(1)$ T. The first one may be caused by two Ni atoms that are located in the NN shell of ^{57}Fe isotope because it is known that one nickel atom increases hyperfine magnetic field by about 0.9 T [14]. The second component is still connected with α-iron. Similarly, the spectrum of the sample milled for 20 h was fitted by two components: $B^1_{hf} = 35.10(9)$ T and $B^2_{hf} = 32.87(3)$ T. In this case, the first component is connected with nickel while the second one may originate from Co atoms. Spectra of the samples milled for 40 and 80 h reveal the average hyperfine magnetic field $B_{hf} = 32.45(1)$ T, which is attributed to mechanically synthesized $Co_{52}Fe_{26}Ni_{22}$ alloy.

It is difficult to determine the local atomic order in the obtained $Co_{52}Fe_{26}Ni_{22}$ alloy. As the chemical composition suggests the number of Co atoms is twice and more larger than Fe and Ni atoms. So, in the NN shell of ^{57}Fe isotope at least six atoms from twelve neighbours

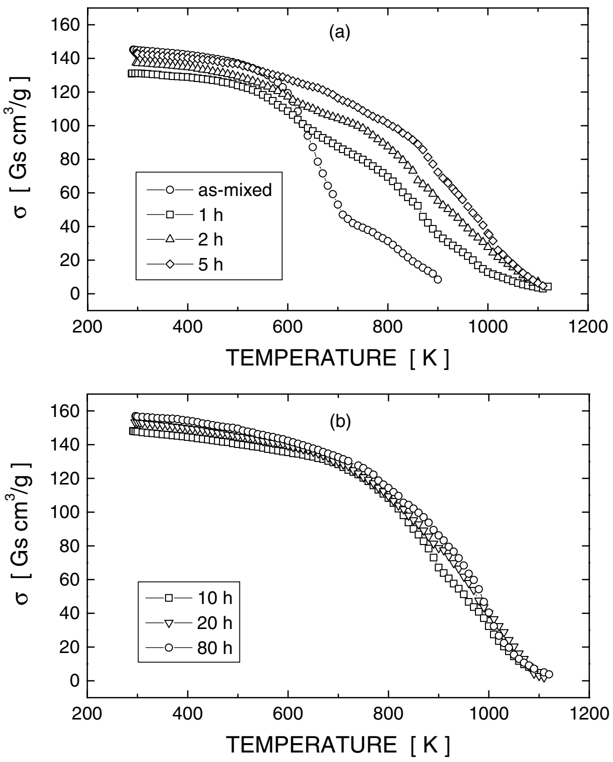

Figure 3 Temperature dependencies of magnetization of $Co_{52}Fe_{26}Ni_{22}$ alloy: (a) as-mixed and milled for 1, 2 and 5 h; (b) milled for 10, 20 and 80 h.

are Co atoms. On the other hand, it is known that the dependence of the hyperfine magnetic field on the Co concentration in Co-Ni alloys is linear [15, 16]. For $Co_{50}Ni_{50}$ alloy doped with small amount of ^{57}Fe isotopes $B_{hf} = 29.5$ T [16]. The most probable configuration of atoms is following: six Co atoms and six Ni atoms in NN shell. In the $Co_{52}Fe_{26}Ni_{22}$ alloy we may assume six Co atoms, three Ni atoms and three Fe atoms in the NN shell of ^{57}Fe. From this simple image it may be estimated that one Fe atom substituting for Ni atom in the NN shell causes an increase in the hyperfine magnetic field of about 0.98 T.

Magnetization is a smoothly decreasing function of temperature (Fig. 3), as in strong ferromagnetic materials. The most abrupt changes in magnetization occur during first 20 h of milling. The alloys milled for 1 and 2 h exhibit the relative drop in magnetization around 550 to 600 K, which reveals a presence of unreacted nickel with the Curie temperature of 630 K (Fig. 3a). This result agrees with Mössbauer investigations because during the first 2 h of milling spectra are characteristic for α-iron. No traces of unreacted nickel are seen in the magnetization curve after 5 h of milling suggesting that alloy becomes a single phase. However, in Mössbauer spectrum after 5 h of milling there are still no traces of nickel reaction with iron. This reaction starts after 10 h of milling as proved by the component of the Mössbauer spectrum with high hyperfine magnetic field $B_{hf} = 35.42(4)$ T.

At room temperature the effective magnetic moment per formula unit raises monotonically from $\mu_{eff} = 1.36\ \mu_B$ to $\mu_{eff} = 1.63\ \mu_B$ when a mean grain size diminishes down to 24 nm during milling time scanning from 1 to 80 h. The last value is very close to $\mu_{eff} = 1.6\ \mu_B$ obtained simply using the formula:

$$\mu_{eff} = a\mu_{Co} + b\mu_{Fe} + c\mu_{Ni}, \tag{3}$$

where a, b, c are the chemical fractions of Co, Fe and Ni in the alloy and $\mu_{Co} = 1.72\ \mu_B$, $\mu_{Fe} = 2.22\mu_B$, and $\mu_{Ni} = 0.606\mu_B$ are magnetic moments of Co, Fe, and Ni atoms, respectively. The value of μ_{eff} obtained for mechanosynthesized $Co_{52}Fe_{26}Ni_{22}$ alloy lies between the values of the magnetic moments for bulk $Fe_{50}Co_{50}$ alloy which has $\mu_{eff} = 2.41\mu_B$ and $Co_{50}Ni_{50}$ alloy with $\mu_{eff} = 1.19\mu_B$ [17].

Values of the Curie temperature T_C shift up from 660 K for pristine alloy to 970 K after 20 h of milling. After 80 h of milling the Curie temperature attains 1000 K, being close to the Curie temperature of pure iron equal to 1043 K. Such value of T_C for the alloys containing 52% of cobalt is considerably lower than $T_C = 1393$ K of pure cobalt. It is also lower than T_C for bulk Co-Fe alloys ($T_C = 1213$ K for $Co_{52}Fe_{48}$) and Co-Ni alloys ($T_C = 1123$ K for $Co_{50}Ni_{50}$) [18]. The reduced Curie temperature of the milled alloys may be partially caused by the lattice strains achieving 0.72% for 80 h of milling as revealed by X-ray diffraction. Value of T_C may be additionally reduced by 12% of atoms located in strongly disordered grain boundaries.

4. Conclusions

As proved by XRD, MS and magnetization studies during mechanical alloying process the $Co_{52}Fe_{26}Ni_{22}$ alloy starts to form after 10 h of milling. Mössbauer spectra revealed that location of Ni and Co atoms in the NN shell of ^{57}Fe is a dynamic process. In the resulting mixture the average hyperfine field is equal to 32.45(1) T. The most probable configuration of atoms in the NN shell of ^{57}Fe isotope is: Six Co atoms, three Ni atoms and three Fe atoms. This configuration arising from the chemical concentration of $Co_{52}Fe_{26}Ni_{22}$ alloy is confirmed by the value of the effective magnetic moment $\mu_{eff} = 1.63\ \mu_B$.

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References

1. F. E. LUBORSKY, *J. Appl. Phys.* **32** (1961) 171 S.
2. G. HERZER, *IEEE Trans. Magn.* **26** (1990) 1397.
3. *Idem.*, *J. Magn. Magn. Mater.* **112** (1992) 258.
4. J. F. LÖFFLER, J. P. MEIER, B. DOUDIN, J. P. ANSERMET and W. WAGNER, *Phys. Rev.* B **57** (1998) 2915.
5. R. ALBEN, J. J. BECKER and M. C. CHI, *J. Appl. Phys.* **49** (1978) 1653.
6. T. OSAKA, *Electrochim. Acta* **45** (2000) 3311.
7. X. LIU, G. ZANGARI and L. SHEN, *J. Appl. Phys.* **87** (2000) 5410.
8. Y. M. KIM, D. CHOI, S. R. KIM, K. H. KIM, J. KIM, S. H. HAN and H. J. KIM, *J. Magn. Magn. Mater.* **226–230** (2001) 1507.

9. G. K. WILLIAMSON and W. H. HALL, *Acta Metallurg.* **1** (1953) 22.
10. S. U. JEN, H. P. CHIANG, C. M. CHUNG and M. N. KAO, *J. Magn. Magn. Mater.* **236** (2001) 312.
11. H. W. SONG, S. R. GUO and Z. Q. HU, *Nanostruct. Mater.* **11** (1999) 203.
12. J. E. CARSLEY, J. NING, W. W. MILLIGAN, S. A. HACKNEY and E. C. AIFANTIS, *ibid.* **5** (1995) 441.
13. G. PALUMBO, S. J. THORPE and K. T. AUST, *Scripta Metall. Mater.* **24** (1990) 2347.
14. I. M. KOVENSCKY and V. V. POVETKIN, *Hyperfine Interations* **52** (1989) 367.
15. S. V. KAPELNICKI, V. S. POKATILOV and V. V. GOLIKOVA, *Sov. Phys.-Solid State* **31** (1989) 261.
16. E. JARTYCH, J. OLCHOWIK, J. K. ŻURAWICZ and M. BUDZYŃSKI, *J. Phys.: Condens. Matt.* **5** (1993) 921.
17. P. SÖDERLIND, O. ERIKSSON, B. JOHANSSON, R. C. ALBERS and A. M. BORING, *Phys. Rev.* B **45** (1992) 12911.
18. T. B. MASSALSKI, “Binary Alloy Phase Diagrams” (ASM, Metals Park, Ohio, USA, 1990) p. 1187.

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