Hyperfine interactions in mechanosynthesized and thermally treated Co-Fe-Ni alloys

T Pikula1, D Oleszak2 and E Jartych1

1Department of Experimental Physics, Institute of Physics, Technical University of Lublin, Nadbystrzycka str. 38, PL-20-618 Lublin, Poland

2Faculty of Materials Science and Engineering, Warsaw University of Technology, Wołoska str. 141, PL-02-507 Warsaw, Poland

E-mail: t.pikula@pollub.pl

Abstract. A series of Co-rich Co$_x$Fe$_y$Ni$_z$ alloys was successfully produced using the mechanical alloying method. To check the stability of their structure thermal treatment was applied subsequently. Mössbauer spectroscopy and X-ray diffraction were used to investigate some structural and micro-magnetic properties of mechanosynthesized as well as thermally treated alloys. X-ray diffraction measurements proved that during mechanical alloying solid solutions with b.c.c. or f.c.c. lattices were formed, while thermal processing in some cases provided to decomposition into the mixture of b.c.c. and f.c.c. phases. Mössbauer spectra were fitted using hyperfine magnetic field distribution method. The average value of hyperfine magnetic field induction ranged from 31.5 to 35.5 T. In the case of some thermally treated samples, shapes of distributions reflect two-phase character of the alloys. For this reason curves of distribution were numerically fitted using two Gaussian functions, which were attributed to the suitable phases. The area of individual components was calculated.

1. Introduction

Co-Fe - based alloys have been extensively studied due to their soft magnetic properties. Beside permalloy they may form competitive material for production of write-read heads in hard-disk drives [1-3]. While the structure and macroscopic magnetic properties of these alloys have been studied quite widely, the literature reports focused on hyperfine interactions are scant.

Mechanical alloying (MA) represents a simple way of fabricating a variety of materials e.g., crystalline, nanocrystalline, amorphous materials. MA is a fundamentally different approach to alloy-manufacture because it relies on deformation processes to mix materials [4]. Here alloying is a result of repeated cold welding and crushing of particles. However, different alloy systems react to milling in different ways depending on the mutual solubility and reactivity of the components, their mechanical properties and the type of used milling equipment [4].

This work follows our systematic investigations [5-6] of the mechanically synthesized Co$_x$Fe$_y$Ni$_z$ alloys in the context of their structure and hyperfine interactions. Products of milling reach saturation magnetization of the order of 2T and coercive field about 15-67Oe [6], therefore MA may represent potential technology of production of soft magnetic powders. After milling the obtained structures of alloys are often in the non-equilibrium state. Heat treatment may cause structural changes, i.e. an increase in the grain size accompanied by a decrease in the level of internal strains, the change of the
crystalline lattice type or alloy decomposition into a mixture of two phases [6]. The aim of this work was: (1) to group and compare hyperfine magnetic field (HMF) distributions of the alloys after MA processes as well as after thermal processing and (2) to estimate the contributions of the suitable solid solutions in the decomposed alloys on the basis of the HMF distributions.

2. Experiment

Co, Fe and Ni powders were subjected to the MA process to obtain a series of Co\textsubscript{x}Fe\textsubscript{y}Ni\textsubscript{z} alloys. The compositions of alloys were chosen on the basis of the phase diagram reported for bulk, melted Co-Fe-Ni alloys in [2]. We concentrated on Co-rich compositions mainly, because of their location in a transitional area of the phase diagram. Milling was performed in a Fritsch P5 planetary ball mill. All MA processes were conducted up to 100h under an argon atmosphere.

X-ray diffraction (XRD) measurements were carried out using a Philips PW1830 diffractometer working in a continuous scanning mode with CuK\textsubscript{α} or CoK\textsubscript{α} radiation. The lattice constants were determined from the shift of the diffraction lines. The Williamson–Hall approach was used for determination of the average grain sizes, D, and the mean level of internal strains, ε [7].

Mössbauer measurements were performed at room temperature in standard transmission geometry using a source of \textsuperscript{57}Co in a rhodium or chromium matrix.

Thermal treatment of the mechanosynthesized Co\textsubscript{x}Fe\textsubscript{y}Ni\textsubscript{z} alloys was performed in two ways: (1) heating from the room temperature up to 993 K in a calorimeter under an argon atmosphere with the rate of 20 K per min and (2) isothermal annealing in a furnace at 1173 K for 1 h in vacuum.

3. Results and discussion

Detailed analysis of XRD patterns allowed stating that during milling process of Co\textsubscript{65}Fe\textsubscript{23}Ni\textsubscript{12}, Co\textsubscript{52}Fe\textsubscript{26}Ni\textsubscript{22} and Co\textsubscript{40}Fe\textsubscript{35}Ni\textsubscript{25} alloys the disordered solid solutions with f.c.c. lattice were formed, while for remnant samples solid solutions with b.c.c. crystalline lattice were obtained. In comparison with results for bulk, melted alloys reported in [3] after the MA processes two-phase samples were not formed. The final products of MA were alloys in powder state with D about tens of nanometers and ε of the order of 0.6 - 1.3 %. The lattice constants for b.c.c. alloys were from 0.2839 to 0.2865 nm and for f.c.c. alloys 0.3575 to 0.3581 nm.

The products of milling were often in non-equilibrium state. It may be stated that Co\textsubscript{40}Fe\textsubscript{60}, Co\textsubscript{52}Fe\textsubscript{28}Ni\textsubscript{15} and Co\textsubscript{45}Fe\textsubscript{35}Ni\textsubscript{15} which lie relatively far from the phase boundary region predicted in [2] were the most stable. The other alloys were decomposed into the mixture of b.c.c. and f.c.c. phases during heating. After annealing in most of alloys the f.c.c. phase was dominating. Only Co\textsubscript{40}Fe\textsubscript{25}Ni\textsubscript{15}, Co\textsubscript{30}Fe\textsubscript{40}Ni\textsubscript{10} and Co\textsubscript{30}Fe\textsubscript{40}Ni\textsubscript{10} became two-phase samples, while in the case of Co\textsubscript{20}Fe\textsubscript{60}Ni\textsubscript{15}, Co\textsubscript{20}Fe\textsubscript{55}Ni\textsubscript{25} and Co\textsubscript{15}Fe\textsubscript{65}Ni\textsubscript{20} the type of crystalline lattice was changed from b.c.c. to f.c.c. In this context e/a ratio (number of valence electrons per atom) seems to be an important parameter. Alloys with the same e/a value present a lot of similarities in the case of structural properties.

Mössbauer studies allowed determining the hyperfine interactions in the mechano-synthesized and thermally treated alloys. The spectra after MA as well as after thermal treatment were six-line patterns. Fig. 1, as an example, presents spectra for the final products of alloying with f.c.c. and b.c.c. lattice.
Mössbauer measurements were performed after 5, 20, 50, 100 hours of milling, which also allowed monitoring the alloy formation process. For the longer milled samples, the spectral lines were slightly broadened up to $0.15 - 0.17 \text{ mms}^{-1}$. This broadening was the result of decreasing of the grain sizes as well as the alloy formation, i.e. different atomic configurations in the nearest neighbourhood of $^{57}\text{Fe}$ atoms appear. Taking this fact into consideration the HMF distribution seems to be the best numerical fitting of the spectra.

From the HMF distribution, the average ($<B_{hf}>$) and the most probable ($B_{max}$) values of magnetic field induction were determined and in the case of some $\text{Co}_x\text{Fe}_y\text{Ni}_z$ alloys they are listed in Table 1. Generally, for mechanosynthesized alloys values of $<B_{hf}>$ ranged from about 31.5 to 35.5 T, and they depended on two main factors: (1) the number of valence electrons per atom, $e/a$, and (2) concentration of iron in the alloy. In Fig. 2 the HMF distribution curves are arranged in the direction of increasing $e/a$ value from the top. It may be stated that with an increase of $e/a$ the value of $<B_{hf}>$ decreases. For alloys with the same $e/a$ ratio with the increasing of iron concentration in the sample, the value of $<B_{hf}>$ increases.

![Figure 2. HMF distributions for final products of milling; $P(B_{hf})$ – probability in arbitrary units.](image)

![Figure 3. HMF distributions fitting for (a) heated alloys, (b) annealed alloys.](image)

As mentioned, in some cases thermal treatment caused the formation of the mixture of b.c.c. and f.c.c. solid solutions. It is also reflected in HMF distributions. It may be noted that the shape of distributions obtained for mechanosynthesized samples is quite regular and similar to simple Gaussian function (Fig. 2), while for the thermally treated two-phase alloys, curve of distribution seems to be a combination of two components (Fig. 3a,b). However, in not all cases it is clearly visible probably because of a low amount of the second phase.

In order to estimate the contributions of the suitable phases in the decomposed alloys the experimental HMF distributions were numerically fitted using two Gaussian functions, which were attributed to the individual phases (Fig. 3a,b). Some starting parameters, i.e. center position of Gaussian curve were restricted to avoid the ambiguity of such procedure. The area of individual Gaussian components (in %) was calculated and attributed to the content of f.c.c. and b.c.c. phases in
the alloy. Moreover, the average value of HMF, \( <B> \), for each component was calculated. Both values mentioned above are listed in Table 1. Generally, it may be noted that values of \( <B> \) for components with b.c.c. lattice are larger than those with f.c.c. structure by about 1-2 T.

The isomer shift (IS) values for studied samples were ranged from 0.01 to 0.04 mm/s\(^{-1}\) and they were slightly different for fcc and bcc components in two-phase alloys. Unfortunately, these differences did not exceed the measuring errors and it was impossible to notice any trends. Furthermore, larger influence on the IS values in this case may have number of Co and Ni atoms in the nearest neighborhood of \(^{57}\)Fe atoms than the type of crystalline lattice.

Table 1. Hyperfine magnetic fields and contributions of phases for mechanosynthesized Co\(_x\)Fe\(_y\)Ni\(_z\) alloys before and after heat treatment; A – area of the component.

| Alloy       | State          | \( e/a \) | \( <B_{hf}> \) [T] | \( B_{\max} \) [T] | \( f.c.c. \) | \( <B> \) [T] | \( b.c.c. \) A | \( <B> \) [T] |
|-------------|----------------|-----------|-------------------|-------------------|--------------|----------------|-------------|-------------|
| Co\(_{50}\)Fe\(_{40}\)Ni\(_{10}\) | after MA       | 26.7      | 32.03             | 33.41             | -            | -              | 100 %       | -           |
|             | heated up      |           | 33.12             | 34.03             | 30 %         | 32.5           | 70 %        | 33.8        |
|             | annealed       |           | 33.06             | 33.38             | 20 %         | 32.1           | 80 %        | 33.5        |
| Co\(_{60}\)Fe\(_{35}\)Ni\(_{15}\) | after MA       | 26.7      | 33.50             | 33.24             | -            | -              | 100 %       | -           |
|             | heated up      |           | 33.30             | 33.72             | 48 %         | 32.8           | 52 %        | 33.8        |
|             | annealed       |           | 33.25             | 33.24             | 24 %         | 32.4           | 76 %        | 33.6        |
| Co\(_{40}\)Fe\(_{40}\)Ni\(_{20}\) | after MA       | 26.8      | 33.09             | 33.48             | -            | -              | 100 %       | -           |
|             | heated up      |           | 32.87             | 33.79             | 32 %         | 31.5           | 68 %        | 33.5        |
|             | annealed       |           | 32.80             | 32.76             | 100 %        | -              | -           | -           |
| Co\(_{50}\)Fe\(_{35}\)Ni\(_{15}\) | after MA       | 26.8      | 33.02             | 33.07             | -            | -              | 100 %       | -           |
|             | heated up      |           | 33.02             | 33.83             | 50 %         | 32.4           | 50 %        | 33.9        |
|             | annealed       |           | 32.93             | 33.07             | 100 %        | -              | -           | -           |

4. Conclusions

This work was extension of our previous studies concerned on ternary Co\(_x\)Fe\(_y\)Ni\(_z\) alloys obtained during mechanical synthesis and thermally treated subsequently. Performed investigations allowed to state that structure of mechanosynthesized alloys was often different comparing with the structure of the same alloys obtained by melting. The main difference was that after milling processes the two-phase samples were not formed. Furthermore, the structure of such alloys was unstable and thermal treatment often provided to decomposition into two-phases.

Final products of MA processes were characterized by the relatively broad but smooth and regular HMF distributions similar to Gaussian functions. In the case of the thermally treated two-phase alloys, curve of distribution seems to be a combination of two Gaussian components. Moreover, it was possible to estimate contribution of the suitable phase in the alloy using HMF distribution fitting but only as a complementary method. It turned out that the value of \( e/a \) ratio plays important role in the context of similarities in structure properties of the alloys as well as in the case of the values of average hyperfine magnetic field induction.

References

[1] Osaka T 2000 Electrochim. Acta 45 3311
[2] Jen S U, Chiang H P, Chung C M, Kao M N 2001 J. Magn. Magn. Mater. 236 312
[3] Khomenko E V, Shalyguina E E, Chechenin N G 2007 J. Magn. Magn. Mater 316 451
[4] Harris J R 2002 PhD thesis submitted to The University of Nottingham
[5] Pikula T, Oleszak D, Pękała M, Mazurek M, Żurawicz J K, Jartych E 2008 Acta Phys. Pol. A 114 1545
[6] Pikula T, Oleszak D, Pękała M, Jartych E 2008 J. Magn. Magn. Mater 320 413
[7] Williamson G K, Hall W H, 1953 Acta Metallurg. 1 22