JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 4, April 2008, p. 783 - 785

Magnetic properties of polycrystalline and nanocrystalline Zr-Co-Fe alloys

E. DOROLTI*, E. BURZO
Faculty of Physics, Babes-Bolyai University 400084 Cluj-Napoca, Romania

The magnetic properties of $ZrCo_{5.1-x}Fe_x$ polycrystalline and nanocrystalline alloys are analysed. The saturation magnetizations increase linearly with iron content in both systems, as well as Curie temperatures. The increase in the exchange interactions as result of substitutions induces additional cobalt moments. The anisotropy fields decrease when the iron content increases. This behaviour was correlated with a planar anisotropy of iron sublattice in the present system.

(Received February 25, 2008; accepted April 2, 2008)

Keywords: Nanocrystalline materials, Magnetic properties

1. Introduction

The Co-rich part of Co-Zr phase diagram evidences the presence of two ferromagnetic compounds Zr_6Co_{23} and Zr_2Co_{17} [1].The actual stoichiometry of the last phase is close to $ZrCo_{5.1}$ [2, 3]. An orthorhombic-type structure was initially proposed for $ZrCo_{5.1}$ phase [2, 4]. A latter detailed analysis of the structure, of various cast and rapidly solidified $ZrCo_{5.1}$ samples, including a single crystal, revealed the existence of two types of crystal structures [5]. One structure is rhombohedral with a_{rh}= 4.76 Å and c_{rh}=24.2Å. The other structure can be described by an orthorhombic cell with $a_{orth} \approx a_{rh}$, $b_{orth} \approx 2a_{rh}\sqrt{3}$ and $c_{orth}=c_{rh}$. It was argued that these two structures correspond to high and low-temperature phases. When cooling the solidified alloy, grains of the low-temperature orthorhombic phase were formed inside grains of the high-temperature rhombohedral phase.

The presence of $ZrCo_{5.1-x}Fe_x$ solid solution in the composition range $x \leq 0.9$ was shown. [2] Magnetic measurements indicated that the saturation magnetization and Curie temperatures increase as cobalt is partially substituted by iron.

In this paper we report comparatively the magnetic properties of nanocrystalline $ZrCo_{5.1-x}Fe_x$ and the corresponding polycrystalline alloys. It was shown a slight increase of the magnetization in nanocrystalline systems, as compared to polycrystalline one.

2. Experimental

The polycrystalline $ZrCo_{5.1-x}Fe_x$ samples with $x \leq 0.9$ were prepared by melting the constituents in an induction furnace in a purified argon atmosphere. The alloys were thermally treated at 900 °C for one week. The structure of these compounds is orthorhombic. The alloys are very hard and the preparation of powdered samples by crushing ingots results in a perturbation of the crystalline lattice.

The nanocrystalline $ZrCo_{5.1-x}Fe_x$ samples were prepared by the technique of high energy ball milling and subsequent annealing. All powder handling was performed in a glove box under high-purity Ar atmosphere with an O_2 and H_2O rate around 1 pm with vial sealed in glove box. After milling the powders 5h, in a high-energy Fritsch P7 planetary ball mill, these were treated at different temperatures between 700 °C and 1000 °C. At 700 °C, the phases are not formed while at 1000 °C, precipitation of cobalt was observed. For the same thermal treatment temperature, 900°C, the mean grain dimension increase when increasing iron content (Fig. 1).

Magnetic measurements were performed in the temperature-range 4.2-900 °C and fields up to 70 kOe. The Curie temperatures were determined from thermal variation of magnetization in field of 100 Oe. The anisotropy field was also determined in polycrystalline samples.

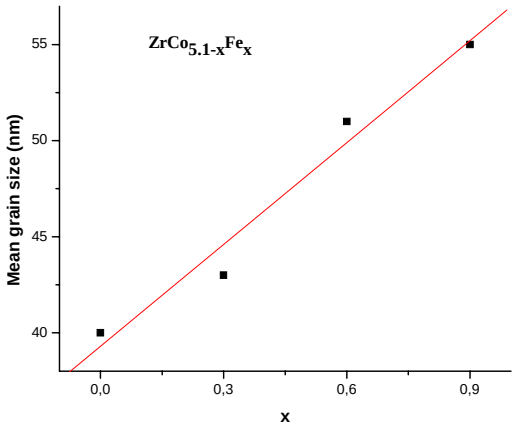

Fig. 1. Composition dependence of the mean grain dimensions.

3. Results and discussion

The magnetization isotherms, at 4.2 K, for polycrystalline samples are plotted in Fig. 2. In Fig. 3 are

given the composition dependences of the saturation magnetization, at 4.2K, for both polycrystalline and nanocrystalline samples. The magnetizations increase linearly with the iron content in both systems. The saturation magnetizations are by ≈ 0.3 μ_B higher in nanocrystalline systems. In polycrystalline samples the saturation magnetizations are obtained only in a field higher than ≈ 40 kOe. When increasing iron content, the field necessary for saturation magnetization decrease, suggesting a gradual diminution of the magnetic anisotropy. The magnetization of nanocrystalline samples saturate in lower field, thus suggesting a smaller anisotropy. The Curie temperatures increase linearly as function of iron content.

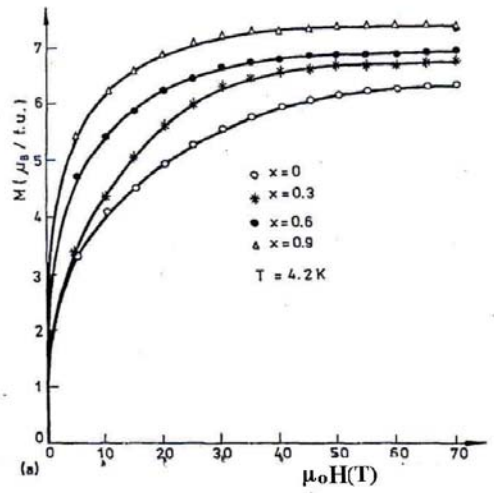

Fig. 2. Magnetization isotherms, at 4.2 K, in polycrystalline system.

The mean iron moments in rare-earth compounds are weakly dependent on composition.

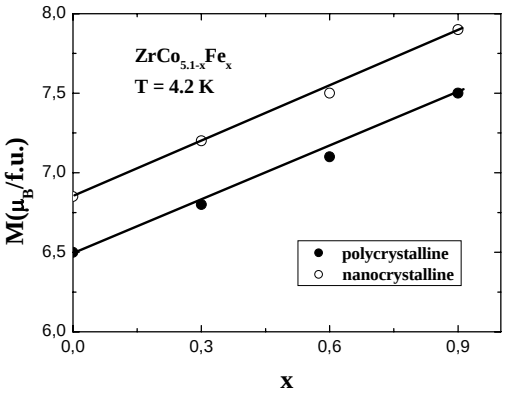

Fig. 3. Composition dependences of saturation magnetizations, at 4.2 K, for polycrystalline and nanocrystalline samples.

Taking into account the above remark, we assume that the iron moment in $ZrCo_{5.1-x}Fe_x$ system is 1.90 μ_B, as determined in $ThFe_5$ [6]. In the above supposition the cobalt moment will increase when increasing iron content from 1.24 μ_B (x = 0) up to 1.36 μ_B (x = 0.9). This behaviour can be attributed to the increase of the exchange interactions. Previously we showed [7], that the induced cobalt moment, ΔM_{Co}, is linearly dependent on the exchange field, ΔH_{exch}, $\Delta M_{Co} = V_{Co}\Delta H_{exch}$ with $V_{Co} = (3\times10^6)^{-1}$ μ_B/Oe. By using the molecular field approximation, we computed the mean values of the exchange interactions coefficients and the exchange fields acting on cobalt atoms. In the composition range $0 \le x \le 0.9$, the exchange fields increase by 1.16×10^6 Oe. This corresponds to an induced moment of 0.387 μ_B/f.u., 0.09 μ_B/Co atom, respectively for composition x = 0.9. Thus, the computed moment of 1.35 μ_B/Co atom, agrees well with the experimentally determined value of 1.36 μ_B/Co atom, for x = 0.9.

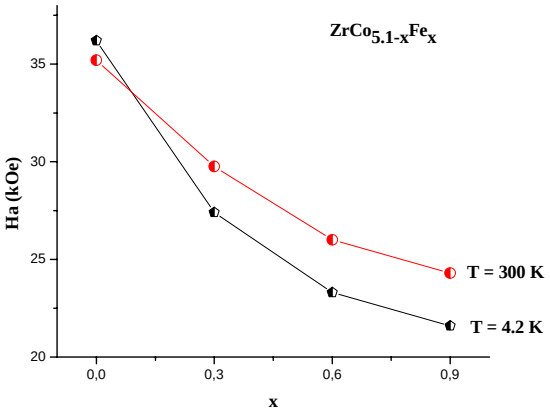

Fig. 4. Anisotropy fields at 4.2 K and 300 K as function of composition.

The anisotropy fields H_A, at 4.2 K and 300 K, are plotted in Fig. 4. The anisotropy field of $ZrCo_{5.1}$ decreases as function of temperature [2]. This dependence is close to that evidenced in hard magnetic materials [8]. When replacing cobalt by iron, the anisotropy fields decrease at both temperatures. The values obtained at 300 K for compounds having $x \ge 0.3$ are higher that at 4.2 K. This behaviour can be analyzed supposing that iron, in the above system has a planar anisotropy. The contribution of iron to the anisotropy field decreases more rapidly than that of cobalt sublattice. The temperature dependence of the anisotropy fields for $ZrCo_{5.1}$ doped with iron resemble to that shown in $R_2Fe_{14}B$ (R = Y, Gd) compounds, where iron in different lattice site have anisotropies of opposite sign and different temperature dependence [8].

5. Conclusions

The $ZrCo_{5.1-x}Fe_x$ system forms solid solutions up to x = 0.9. The mean dimension of nanoparticles prepared by high energy ball milling and thermal treatment increases as iron content is higher. The saturation magnetizations at 4.2 K both in polycrystalline and nanocrystalline systems

increase linearly with iron content. As result of the increase of exchange interactions when substituting cobalt by iron, an increase of the cobalt moments is shown. The estimated variations of cobalt moments agree with experimental values. The anisotropy fields decrease and their temperature dependences are modified as result of iron doping. This behaviour can be correlated with a planar anisotropy of iron sublattice.

References

[1] M. H. Petchin, D. E. Williams, W. E. Larsen, Trans. ASM **57**, 464 (1964).
[2] E. Burzo, R. Grössinger, P. Hundegger, H. R. Kirchmayr, R. Krewenka, O. Mayerrhofer, R. Lemaire, J. Appl. Phys. **70**, 6550 (1991).
[3] A. M. Gabay, Y. Zhang, G. C. Hadjipanays, J. Magn. Magn. Mater **236**, 37 (2001).
[4] S. F. Cheng, W. E. Wallace, B. G. Demczyk, Proc. 6th Int. Symp. Magnetic Anisotropy and Coercivity in Rare-Earth Transition Metal Alloys, Pittsburg, 1990 p. 477.
[5] G. V. Ivanova, N. N. Schegoleva, A. M. Gabay, J. Alloys Comp. **432**, 135 (2007).
[6] J. P. de Jong, Phys. Stat. Solidi **A29**, 595 (1975).
[7] E. Burzo, Solid State Commun. **25** 525 (1978); J Less Commun Met. **77**, 251 (1981).
[8] E. Burzo, Rep. Propr. Phys. **61**, 1099 (1998).

*Corresponding author: edorolti@phys.ubbcluj.ro