

Structural and magnetic properties of rare earth-transition metal compounds for hydrogen storage materials

S.S. Makridis^{a,*}, M. Konstantakou^a, Th.A. Steriotis^a, K.G. Efthimiadis^b,
E. Pavlidou^b, E.S. Kikkinides^{c,d}, A.K. Stubos^a

^a Institute of Nuclear Technology and Radiation Protection, NCSR “Demokritos”, Ag. Paraskevi, Athens GR-15310, Greece

^b Department of Physics, Aristotle University, Thessaloniki 54124, Greece

^c Department of Energy Resources Engineering and Management, University of West Macedonia, Kastorias and Fleming St. 50100, Kozani, Greece

^d Chemical Process Engineering Research Institute, Centre for Research and Technology Hellas, 6th km. Charilaou-Thermi Road, P.O. Box 361, 57001 Thermi-Thessaloniki, Greece

Received 18 June 2004; received in revised form 21 September 2004; accepted 6 October 2004

Available online 25 July 2005

Abstract

In this work we investigate the effect of hydrogen absorption/desorption at 0 and 25 °C on the structural, magnetic and microstructural characteristics of bulk samples with $\text{Sm}(\text{Co}_{0.6}\text{Fe}_{0.2}\text{Zr}_{0.16}\text{B}_{0.04})_{7.5}$ and $\text{Sm}(\text{Co}_{0.74}\text{Fe}_{0.1}\text{Cu}_{0.12}\text{Zr}_{0.04})_8$ stoichiometries. The B-doped sample absorbs 0.8 wt.% at room temperature under 15 bar of hydrogen pressure while the B-free one absorbs less than 0.01 wt.% under the same conditions. The B-free bulk sample has $H_c = 1.5$ kOe while after hydrogenation this value increases slightly. Hydrogenation of the B-free bulk sample results in stronger dipolar interactions between the hard grains, as revealed from δM plots. SEM with EDAX was used in order to examine the composition and surface morphology of bulk samples.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Rare earth-transition metals; Hydrogen storage materials; X-ray diffraction; Magnetic measurements

1. Introduction

High temperature permanent magnets based on the $\text{Sm}(\text{Co},\text{Fe},\text{Cu},\text{Zr})_z$ system after long heat treatment have outstanding magnetic properties (coercive field, magnetization) [1]. A new family of rare earth-transition metal compounds with boron has been recently discovered. The effect of boron substitution on microstructure of bulk and as spun ribbons is responsible for the excellent magnetic properties [2].

2. Experimental procedure

The bulk samples have been prepared by melting the pure metals of Sm, Fe, Co, Cu, Zr and Fe_3B under a voltaic arc.

Repeating the melting procedure five times by inverting the side of the sample each time has produced homogeneous microstructure. Annealing has not been used for higher solidification. Before and after the hydrogen absorption/desorption (AD) process, we have studied the effect of remaining hydrogen in the alloys.

Both samples were investigated by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation in a Philips equipment. Microstructure was investigated by using scanning electron microscopy (SEM), and microprobe analysis (EDAX) was used to examine the stoichiometry of the samples. For the hydrogenation of these materials outgassing has been performed at 100 °C (3 °C/min) under high vacuum (10^{-5} mbar) for 12 h (this was deemed sufficient since no mass change was observed any more). After cooling down to room temperature the sample container was immersed in a PID temperature controlled oil bath preset at 25 °C (or ice/water bath for 0 °C). For each equilibrium point, H_2 was admitted automatically

* Corresponding author. Tel.: +30 694 457 3831; fax: +30 210 650 5004.
E-mail address: sofmak@ipta.demokritos.gr (S.S. Makridis).

and the pressure was kept constant throughout equilibration by means of motor driven, PID controlled admit and exhaust valves.

3. Results and discussion

X-ray diffraction patterns of both samples have been traced by using an X-ray diffractometer with Cu K α radiation. The bulk $\text{Sm}(\text{Co}_{0.74}\text{Fe}_{0.1}\text{Cu}_{0.12}\text{Zr}_{0.04})_8$ sample has the rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type of structure (Space Group $\text{R}\bar{3}\text{m}$, $Z = 3$), while the $\text{Sm}(\text{Co}_{0.6}\text{Fe}_{0.2}\text{Zr}_{0.16}\text{B}_{0.04})_{7.5}$ bulk sample is a multiphase compound.

Results of chemical analysis (EDAX) on the bulk boron-doped sample have shown that white regions are Sm–Co phases only (Sm rich) and black regions are $\text{Sm}(\text{Co},\text{Zr},\text{Fe})$ phases (Sm poor) while general analysis reveals $\text{Sm}(\text{Co},\text{Fe},\text{Zr})_{7.3}$ analogy. Microstructure/microchemistry, as shown in Fig. 1, is responsible for the huge difference regarding the absorption/desorption behavior of the two bulks $\text{Sm}(\text{Co}_{0.74}\text{Fe}_{0.1}\text{Cu}_{0.12}\text{Zr}_{0.04})_8$ and $\text{Sm}(\text{Co}_{0.6}\text{Fe}_{0.2}\text{Zr}_{0.16}\text{B}_{0.04})_{7.5}$. B-doped (Zr-rich) sample absorbs 0.8 wt.% at room temperature while the B-free (Zr-poor) one absorbs less than 0.01 wt.% under the same conditions, as shown in Fig. 2. One reason for this significant difference on hydrogen content is that the B-free bulk sample would possibly absorb hydrogen at pressures much higher than 15 bar. The

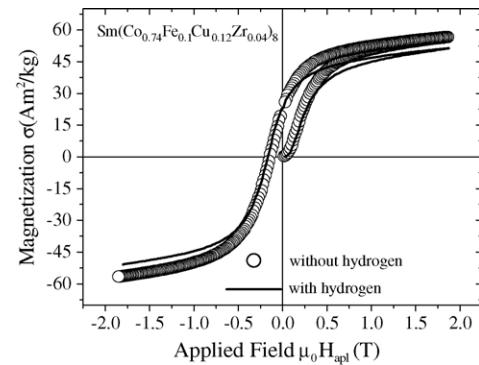


Fig. 3. Hysteresis loops of as made sample $\text{Sm}(\text{Co}_{0.74}\text{Fe}_{0.1}\text{Cu}_{0.12}\text{Zr}_{0.04})_8$ at RT.

bulk samples $\text{Sm}(\text{Co}_{0.86}\text{Fe}_{0.1}\text{B}_{0.04})_{7.5}$ and $\text{Sm}(\text{Co}_{0.86}\text{Fe}_{0.1}\text{Zr}_{0.04})_8$ do not exhibit any noticeable hydrogen absorption up to 15 bar of hydrogen. Experiments have already shown that boron is needed when copper is missing, for the development of a proper microstructure and the subsequent high hydrogen absorption in this kind of materials. Besides boron, the presence of zirconium is also required for the formation of the necessary microstructure but its precise role has not been fully understood yet.

As cast high temperature stoichiometry at 22 °C, before AD, has $\sigma_s = 56.6 \text{ A m}^2/\text{kg}$ and after AD, has $\sigma_s = 51.3 \text{ A m}^2/\text{kg}$ (σ denotes the mass magnetization). The

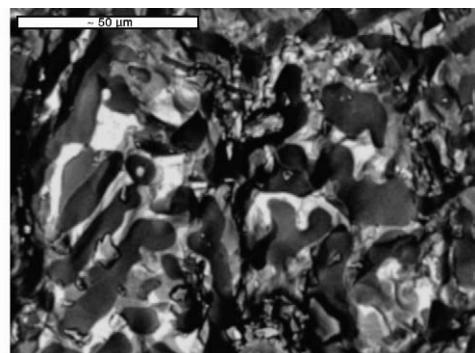
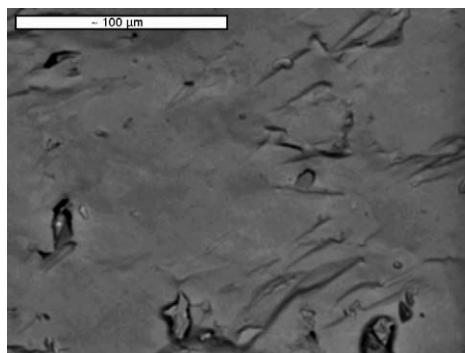


Fig. 1. $\text{Sm}(\text{Co}_{0.74}\text{Fe}_{0.1}\text{Cu}_{0.12}\text{Zr}_{0.04})_8$ (left) and $\text{Sm}(\text{Co}_{0.6}\text{Fe}_{0.2}\text{Zr}_{0.16}\text{B}_{0.04})_{7.5}$ (right) microstructures as cast bulk samples.

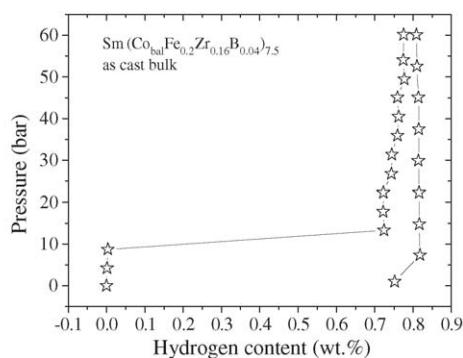
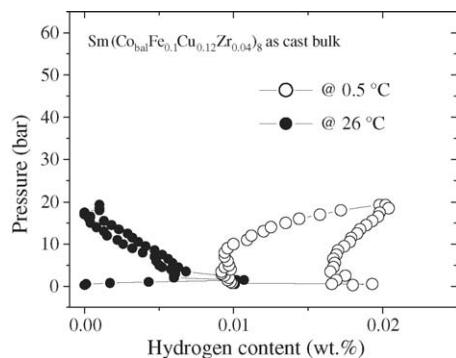


Fig. 2. P – C curves for $\text{Sm}(\text{Co}_{0.74}\text{Fe}_{0.1}\text{Cu}_{0.12}\text{Zr}_{0.04})_8$ (left at 0.5 and 26 °C) and $\text{Sm}(\text{Co}_{0.74}\text{Fe}_{0.2}\text{Zr}_{0.16}\text{B}_{0.04})_{7.5}$ (right at 26 °C).

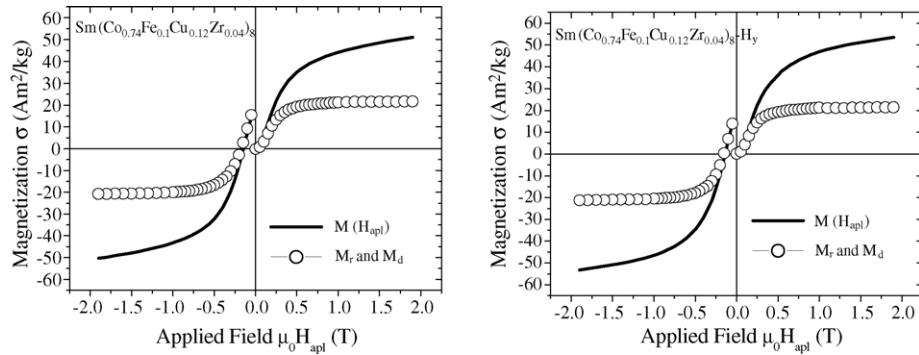


Fig. 4. $M_r(H_{\text{apl}})$, $M(H_{\text{apl}})$ of the boron free sample before and after AD at RT.

remanent magnetization is the same for both conditions (before and after hydrogenation) i.e. $\sigma_{r,\text{without H}} \equiv \sigma_{r,\text{with H}} = 30 \text{ A m}^2/\text{kg}$ while the coercive field increases after hydrogenation by 13%: $\mu_0 H_{c,\text{without H}} = 0.15 \text{ T}$ and $\mu_0 H_{c,\text{with H}} = 0.17 \text{ T}$.

Reduced remanence ($m_r = M_r/M_s = \sigma_r/\sigma_s$) increases after AD since $m_{r,\text{without H}} = 0.53$ while $m_{r,\text{with H}} = 0.58$, as shown in Fig. 3. Generally speaking, the remanence ratio of ideally isotropic permanent magnets (ensemble of randomly oriented single domain particles with easy-axis anisotropy without interaction between each other) is 0.5 according to the Stoner–Wohlfarth model [3]. The nature of magnetic interactions between the grains has been examined by means of δM plots of remanence curves for as spun and annealed ribbons. δM is defined as $\delta M = [M_d - (1 - 2M_r)]/M_r(\infty)$, where M_r and M_d are the remanent magnetizations after the removal of the applied fields of the magnetization and demagnetization procedure, respectively. According to Wohlfarth, the deviation is zero for non-interacting uniaxial single-domain particles [4]. It is commonly accepted that a negative δM value indicates dipole interactions [5] and a positive value indicates ferromagnetic exchange interactions between isolated single-domain particles. In Fig. 4 we show the values of M_r and M_s after a number of field applications in the range of -1.9 to 1.9 T. From them and after dividing by $M_{r,\max}$ we obtain the values of δM . Fig. 5 depicts the δM -plot for $\text{Sm}(\text{Co}_{0.74}\text{Fe}_{0.1}\text{Cu}_{0.12}\text{Zr}_{0.04})_8$ as cast sample.

Fig. 4 indicates that saturation is attained after ~ 1 T of external field for both samples, because after the application of that field, $M_r(H_{\text{apl}})$ does not increase any more contrary to $M(H_{\text{apl}})$. This phenomenon is explained by the shape anisotropy which is attributed to the shape of the sample that the external field passes through.

According to Fig. 5, the δM values are negative indicating the dipolar interactions between the hard 2:17 grains. The value of $-\delta M_{\max}$ is 0.27 for the H_2 free sample. This is not very high (27% recovery of remanence) but it can explain the fact that the values of reduced remanence ($m_r = 0.53$) are close to that of the non-interacting grains ($m_r = 0.5$). The highest values in the plot of Fig. 5 are observed at the coercive

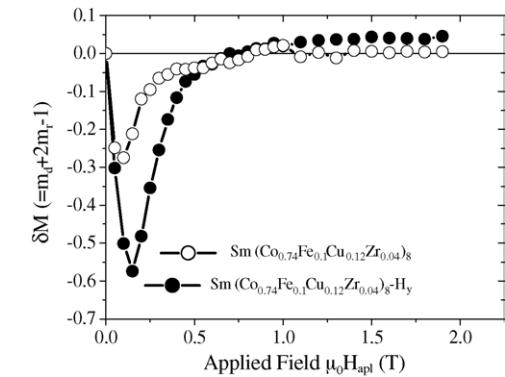


Fig. 5. σM -plot of as made boron free samples at RT.

field of each sample. Higher coercive field characterizes the sample where the interactions are stronger (higher $-\delta M_{\max}$).

4. Conclusions

In this work a new rare earth-transition metal compound has been found to absorb considerable amounts of hydrogen at relatively low pressure and room temperature. Most of the absorbed hydrogen remains in the material after desorption. Zirconium and boron effect the microstructure and subsequently the degree of reaction with hydrogen. On the hysteretic material, hydrogen absorption changes the interactions between the grains. A new generation of hydrogen absorbing materials may be developed based on the present results. Indeed, a new class of compounds $\text{Sm}(\text{Co}_{1-x-y}\text{Zr}_y\text{B}_x)_{7.5}$ are currently under study. Optimization of the above composition will probably help to understand the role of Zr (with Cu or B in the compound) concerning the storage of hydrogen.

Acknowledgement

This work has been partially supported by the European Commission through Contract “HYSTORY” N. ENK6-CT2002-00600.

References

- [1] G.C. Hadjipanayis, in: J.M.D. Coey (Ed.), *Rare Earth Iron Permanent Magnets*, Oxford University Press, 1996.
- [2] S.S. Makridis, G. Litsardakis, K.G. Efthimiadis, G. Papathanasiou, I. Panagiotopoulos, S. Höfinger, J. Fidler, G.C. Hadjipanayis, D. Niarchos, *IEEE Trans. Magn.* 39 (2003) 2869–2871.
- [3] E.C. Stoner, E.P. Wohlfarth, *Philos. Trans. Roy. Soc.* 240 (1948) 599.
- [4] E.P. Wohlfarth, *J. Appl. Phys.* 29 (1954) 595.
- [5] J. Garcia-Otero, M. Porto, J. Rivas, *J. Appl. Phys.* 87 (2000) 7376.