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P. Dalmas de Réotier, D. Fruchart, P. Wolfers, P. Vulliet+, A. Yaouanc+, R. Fruchart++ and P. L'Héritier++

Laboratoire de Cristallographie du C.N.R.S., associé à l'U.S.M.G., 166 X, 38042 Grenoble Cedex, France
+Département de Recherche Fondamentale, M.D.I.H., C.E.N.-G., 85 X, 38041 Grenoble Cedex, France
++U.A. N° 1109 du C.N.R.S., Institut National Polytechnique de Grenoble, 38402 Saint-Martin-d'Hères, France

Résumé - Les implications de l'hydruration des borures ternaires de type $TR_2Fe_{14}B$, sur leurs propriétés structurales, magnétiques et leur cohésion sont discutées. On donne quelques exemples en particulier avec TR = Y, Ce, Dy.

Abstract : Implications of the hydridation of the ternary borides $RE_2Fe_{14}B$ on the physical, crystal structure and mechanical cohesion are discussed. Some examples are given, more particularly with RE = Y, Ce, Dy.

I - INTRODUCTION

Since the recent discovery of borides $RE_2Fe_{14}B$ having high-performant permanent magnet properties, a considerable work have been done, dealing both with fundamental properties and applications. This development is favoured by large possibilities of substitution of the elements. More recently the hydridation properties of the series have been evidenced and the consequent changes in the magnetic and mechanical properties of the compounds have been preliminary analysed /1,2/.

II - HYDRIDATION PROCESS OF THE SAMPLES

A sample of a crushed ingot (dimensions of the grains ≈ 1-5 mm) is introduced in an evacuated autoclave and then outgassed to ≈ 10^{-6} Torr (of air), before high purity hydrogen (5N) is admitted at a final pressure of about 7.10^6 Pa.

In most cases the reaction is complete in few minutes, but sometimes it is necessary to initiate the hydridation by heating the sample at about 100-150°C. Furthermore, this activation process has been successfully applied even under reduced pressure of hydrogen (≈ 10^3 Pa). The final materials are stable hydrides at room temperature. The desorption process has been analysed when heating the autoclave and recording the pressure : generally it takes place between 150 and 160°C, but a second and minor gas desorption has been sometimes observed around 270°C (depending on the initial charge, and (or) the RE metal).

The first cycle "hydridation/deshydridation" initiates a disproportionation phenomena of some α-iron particles. Roughly speaking the quantity of iron detected using a very sensible thermomagnetic torque varies from ≈ 0-5 % to ≈ 0-10 % before and after the hydridation. The origin of this iron is not exactly established, since the disproportionation process mostly characterizes the first activation. It might be attributed to the effect of hydrogen on the minor phases existing in the matrix /3,4/. When heating the sample at higher temperature (∿ 600°C) an irreversible disproportionation is observed, with the formation of stable RE-hydrides and quantities of iron particles. The $RE_2Fe_{14}BH_x$ ($0 < x < 5.2$) compounds we obtain in "normal" conditions are well crystallized materials, and in contrast to many RE-3d hydrides, their diffraction lines (X-rays and neutron) remain constant in width, comparison with the uncharged compounds. This means that the dimensions of the particles are up to 2-3.10^2 nm.

Electron micrographs reveal that the handground samples (few minutes) with RE = Y and Ce are formed of relatively homogeneous particles (rather spherical and comparable with each other). The dimensions are about 1 to 10 µm before and 0.5 to 2.5 µm after hydridation. The electron diffraction patterns exhibit well defined spots, characteristic of well crystallized materials.

III - IMPLICATIONS OF HYDRIDATION ON THE CRYSTAL AND MAGNETIC PROPERTIES

The $RE_2Fe_{14}B$ compounds have a tetragonal crystallographic structure related to the σ-phase and to the Ca Cu_5 types /5,6,7/. The hydrides retain the same structure, and the lattice parameters a and c increase with the hydrogen content /1/. For example, for the Dy compound they can be expressed by linear laws of the hydrogen content x, a = 0.8757(3) + 0.0022(1).x nm, c = 1.2004(4) + 0.0029(1).x nm. Generally, the increase in volume to the hydrogen content is $\Delta V_H \approx 1.5\ 10^{-3}$ $(nm)^3$. It remains weaker for these phases than for most of the RE-3d alloys forming stable hydrides /8/. But in the case of $Ce_2Fe_{14}B$, the volume expansion is magnified by a valence change of Ce : $\Delta V_H \approx 2.7\ 10^{-3}$ $(nm)^3$. Considering the active part of the structure, in terms of sites chemically attractive for hydrogen, one has to exclude the neighborhood of the B atoms and the inner sites of the σ-slabs. So, the volume expansion normalized to the remaining $CaCu_5$ -type of environment is $\approx 3/2$. $\Delta V = 2.6\ 10^{-3}$ $(nm)^3$ that is close to the value usually found /8/.

The scheme of hydrogen filling sites was first proposed using the Westlake's criteria applied to the RE_3Fe and RE_2Fe_2 tetrahedra /8/. A maximum ratio H/M = 5.5 was predicted, instead of 5.2 as the maximum observed in our experimental conditions of preparation. Then, the model was confirmed both by neutron diffraction on $Y_2Fe_{14}BD_x(H_x)$ and Mössbauer spectroscopy (^{57}Fe, ^{161}Dy) experiments /9,10/. Two types of sites are to be distinguished and their own attractivity discriminates the physical parameters, as by example the transfered hyperfine parameters onto the two RE nuclei /10/. For example, in $Dy_2Fe_{14}BH_x$, the hydridation causes a change in the slope of the ordering temperature curve versus the H-content, for $x \approx 2$-2.5 (figure 1). In all the cases, the ordering temperature increases upon hydridation. The relative increase is generally close to 10 % excepted with RE = Ce where an increase of ≈ 25 % was observed (table I).

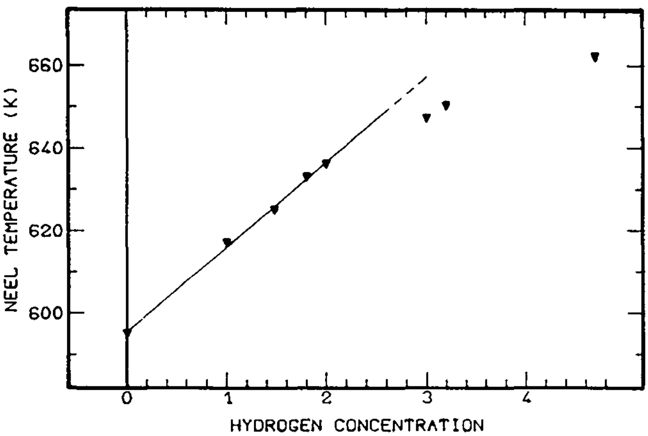

Fig. 1 - Variation of the ordering temperature in $Dy_2Fe_{14}BH_x$ versus x the hydrogen concentration.

RE	T_c(K)	x	T_c(K)	$\Delta T_c/T_c$(%)
Ce	435	2.5	543	24.8
Nd	589	4.5	676	14.8
Dy	605	3.5	650	7.4
Er	560	3.3	627	12
Y	590	3.1	639	8.9

Table I - Curie temperature, T_c, of some of the compounds. The increase of T_c in the hydride compared to the virgin compound is given in %.

A systematic change in magnetization is also observed in the series : the gain on hydriding the material is $\Delta M/M \sim$ 10-15 % at 300 K under 150 kOe. Under H = 25 kOe, we notice $\Delta M/M$ = 16 %, 30 % and 50 % for the systems $Y_2Fe_{14}BH_{0-3.6}$, $Ce_2Fe_{14}BH_{0-4.5}$, $Dy_2Fe_{14}BH_{0-4.7}$ respectively. This means that the hydrogen insertion creates conditions of an important softening of the magnetic materials. A remarkable loss of coercivity is generally observed on hydriding. Using fine crushed powder samples as starting materials (in order to compare effects on the most similar state of samples) we notice a weakening of coercivity up to 75 % in $(Nd_{0.1}Y_{0.9})_2Fe_{14}BH_{3.34}$ comparison with the uncharged material.

IV - DISCUSSION

Several minor phases (RE-rich, Fe-rich, B-rich) have been proposed to play an important role in the mechanism of the high coercivity of the new magnets $RE_2Fe_{14}B$ /4/. The external form of the sample (ingot, grains, fine powder) is expected to be relevant for this property.

The hydrogen decrepitation of materials generally causes a dramatic reduction in the coercivity. This process for reducing the particle size turns to be more efficient (in time, in cost, in dimension of the grains) than mechanical milling. Furthermore, hydrogen fills selected tetrahedral sites of the structure and modifies intrinsic fundamental properties as :

- local magnetization : electron transfer (onto 3d-metal), change in the electronic state (RE-metal)...
- anisotropy and exchange interactions : crystal field effect (RE), exchange force modifications (3d-3d with the distance changes, 3d-Re with conduction electron density...).

In this respect, the process of chemical insertion and mechanical decrepitation on hydriding the new magnet materials should have important implications.

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