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Hydrogen absorption characteristics of oxygen-stabilized rare-earth iron intermetallic compounds

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Résumé. — Le comportement thermique des systèmes hydrogène-composés stabilisés par l'oxygène, $R_3Fe_8O_x$ ($R = Y, Dy, Ho$) a été étudié par gravimétrie et analyse thermique. Les résultats sont comparés à ceux obtenus sur les composés binaires RFe_2 et RFe_3 .

Abstract. — The thermal behavior of oxygen-stabilized $R_3Fe_8O_x$ -hydrogen ($R = Y, Dy, Ho$) systems was studied by means TGA-DTA techniques. The results were compared to those obtained on binary RFe_2 and RFe_3 compounds.

1. Introduction. — Even though considerable efforts have been devoted in the course of the last decade to the study of the hydrogenation characteristics of a variety of intermetallic compounds, our understanding of the basic factors which determine hydrogen absorption is still rudimentary. In particular, the relative importance of electronic factors as compared to structural (i.e. size) factors has not yet been clarified. In order to gain more insight into these aspects we have recently investigated the effect of oxygen on Ti_2Ni -type, oxygen-stabilized compounds [1]. Oxygen is an electron acceptor in these compounds, its presence affects the electron concentration. Moreover, oxygen occupies interstitial sites which otherwise would be available to hydrogen atoms.

Oxygen-stabilized compounds of formula $R_3Fe_8O_x$ ($x \leq 0.5$) have recently been reported in R (rare-earth)-Fe systems [2]. The objective of the present study was to investigate the hydrogen absorption characteristics of this family of compounds. We also expected to further our understanding of the mechanism of hydrogen absorption in R-Fe compounds by studying the effect of oxygen in a structure completely unrelated to the $CaCu_5$ -type structure from which all the other RFe_n structures are derived.

2. Experimental. — The binary R-Fe intermetallic compounds were prepared by arc-melting followed by a homogeneity anneal. The oxygen-stabilized compounds were prepared using powder technological methods previously detailed [2]. The hydrogen absorp-

tion characteristics were studied in a Mettler thermobalance which allowed the simultaneous recording of DTA and TGA curves. After an initial in situ degassing at 800 C and 10^{-5} torr, high purity hydrogen was introduced into the system at room temperature. In all instances the hydrogen uptake took place immediately without any measurable incubation period. The $Y_3Fe_8O_x$ sample displayed high sensitivity to the presence of gaseous impurities e.g. O or He. A high temperature, vacuum treatment was necessary for renewed hydrogen absorption. Several heating-cooling cycles were carried out at constant, 700 torr hydrogen pressure. The hydrogen absorption characteristics at various temperatures were deduced from the TGA curves.

3. Results and discussion. — The temperature-composition (T - C) curves for the various oxygen-stabilized $R_3Fe_8O_x$ -H systems ($R = Y, Dy, Ho$) determined at 700 torr hydrogen are shown in figure 1. After the initial hydrogen uptake — which took place upon the exposure of the samples to hydrogen — the increasing temperature caused a gradual release of hydrogen until a decomposition temperature, T_d , is reached. At T_d a phase-transition-like decomposition occurs with an endothermic peak in the DTA curve. The decomposition temperatures of the $R_3Fe_8O_x$ -hydrides increase with the increasing size of the corresponding lanthanide. The values of 120, 90 and 50 C were obtained for the Y, Dy and Ho compounds, respectively.

The decomposition of the $R_3Fe_8O_x$ -hydrides at T_d does not proceed to completion (figure 1), a certain amount of hydrogen is retained in the solid. This

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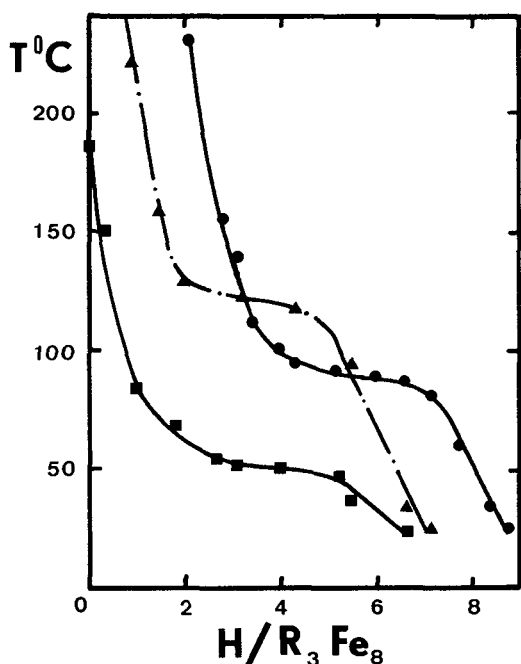


Fig. 1. — Temperature-composition curves of oxygen-stabilized $R_3Fe_8O_x$ compounds. The filled squares, circles and triangles stand for the Ho, Dy and Y compounds, respectively.

hydrogen is in solution in the $R_3Fe_8O_x$ structure and is released gradually by raising the temperature. Structural considerations suggest that the $16f(x, x, x, x = 0.28/3)$ interstitial sites in the $Im\bar{3}m$ structure of the oxygen-stabilized compound [2] should be favored for hydrogen occupancy as a result of the relatively large number (3) of nearest-neighbor R atoms which surround these sites (figure 2). This would lead to a

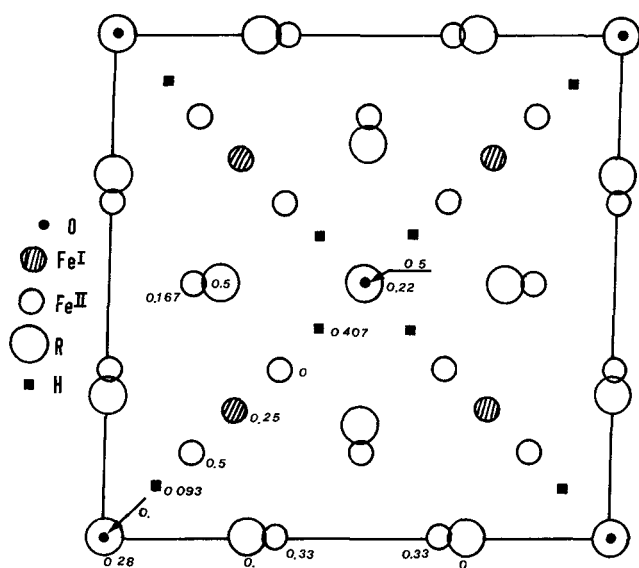


Fig. 2. — Projection on the (100) plane of the $R_3Fe_8O_x$ structure with the suggested position of the 16 H-atoms.

maximum uptake of hydrogen corresponding to the ratio $H/R_3Fe_8O_x = 4$. According to figure 1, the solubility limit of hydrogen in these compounds, i.e. the left-hand edges of the plateaus in the T - C curves indeed occur at values of $H/R_3Fe_8O_x$ between 2 and 4, lending support to the suggested hydrogen location. Neutron diffraction studies are underway to verify this model and to establish the location of the hydrogen atoms in the higher hydrides.

With increasing temperature above 400 C, the $R_3Fe_8O_x$ -H phases undergo an irreversible phase separation into the corresponding RH_3 trihydrides, R_2O_3 sesquioxides and elemental Fe. The phase separation is a result of the metastable character of the compound hydrides. The metastable character of some ternary hydrides has been discussed recently [3, 4]. It was pointed out that if the heat released during a hydrogenation reaction is sufficiently large and occurs at a high rate, the temperature may raise locally and enable the diffusion of the metal constituents and lead, hence, to phase separation. The phase separation may reach different degrees of completeness depending on the thermal properties of the system. In particular, it may lead to the crystallization of one or more phases. Thus, for example, for the Dy-compound both DyH_3 and Fe crystallized, whereas for the Y-compound only the Fe pattern was detectable, YH_3 remaining amorphous. We have also studied the thermal behavior of RFe_2 and RFe_3 intermetallics with R/Fe composition ratios close to that of the $R_3Fe_8O_x$ compounds. The results, normalized per Y atom, are shown in figure 3. The maximum hydrogen uptake at 700 torr is lower than that previously reported [5]. The results

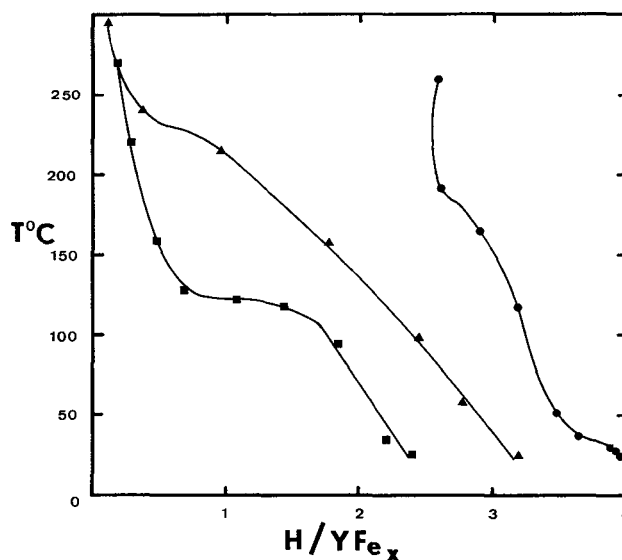


Fig. 3. — Temperature-composition curves of the three Y-compound hydrides, normalized per Y-atom. The filled squares, circles and triangles stand for the $YFe_{2.67}(Y_3Fe_8)$, YFe_2 and YFe_3 compounds, respectively.

do not indicate any regular dependence of the hydrogen uptake on the R/Fe ratio. Any regularity, if present, is masked by the combined effect of different crystal structures and electron concentrations. Thus, it was not possible to distinguish between these two

effects as was done for the oxygen stabilized Ti_2Ni -type compounds [1].

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