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A Low Temperature Route for the Synthesis of Rare Earth Transition Metal Borides and Their Hydrides

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Synthesis of rare earth-based alloys by the ORD technique consists in the reduction of rare earth oxides in a melt of calcium under argon, and simultaneous diffusion–reaction of the just formed rare earth metal with the other elements. This method has been applied with success to numerous ternary borides containing transition metals such as the magnetic alloys $Y_2Co_{14}B$, $LnCo_4B$, and YCo_3B_2. By using a small excess of Ca, boride particles grow in a viscous slurry media containing unreacted (melted) Ca and nanosize CaO particles. Single phase boride alloys can be obtained at 1000°C as loose micrometer-size particles of very high crystal quality as confirmed by the sharp diffraction peaks on the corresponding X-ray diagrams. Particles can be easily recovered by gentle washing in diluted weak acid solution, and dried under vacuum at room temperature. This rather low temperature technique is particularly adapted to the synthesis of incongruent melting phases, as well as for the alloys containing volatile rare earth elements (Sm, Yb, Tb, . . .). © 1997 Academic Press

1. INTRODUCTION

Many rare earth–transition metal–boron ternary phase diagrams have been thoroughly investigated with the aim to discover new alloys with potential magnetic or superconductor properties. Each diagram contains a large number of intermetallic phases of well definite composition, such as for example the tetragonal $RE_2M_{14}B$ phases, the hexagonal phases $REM_{12}B_6$ ($SrNi_{12}B_6$ type), or the series of phases of general composition $RE_{m+n}M_{5m+3n}B_{2n}$, whose hexagonal structures are closely related to that of $CaCu_5$.

The phases are generally prepared either by melting a mixture of raw components of convenient stoichiometry in a high frequency furnace or by the arc melting technique. The as grown cast ingots or buttons are most of the time not single phase, particularly in the case of incongruent intermetallic phases. Several operations of remelting of the alloy followed by several days or weeks of annealing at 900–1000°C under argon atmosphere are sometimes necessary to ensure a good homogeneous single phase composition.

The oxides-reduction-diffusion (ORD) method, operated in a melt of calcium in small excess at a temperature below 1000°C, will be demonstrated as an alternative "low temperature" route for the synthesis of many borides of the above series.

Besides, it has been extensively used for several years for the commercial production of magnetic powders $SmCo_5$ (1–3) and $Nd_2Fe_{14}B$ (4), and more recently for the synthesis of many rare earth-based powder alloys for hydrogen storage electrodes batteries (5–8) or for bonded magnets (9–17).

2. EXPERIMENTAL PROCEDURE

The process is illustrated below by the chemical reaction leading to the synthesis of a single phase ternary alloy YCo_4B made of loose micrometer-size single crystal particles:

$$0.5\ Y_2O_3 + 4\,Co\ (10\text{–}20\ \mu m) + B\,(1\text{–}3\ \mu m) + 2\,Ca\ (\text{granulés}) \xrightarrow[950^\circ C,\ 4\,h]{\text{argon}} YCo_4B\ (1\text{–}5\ \mu m) + 1.5\ CaO + 0.5\ Ca\ (\text{melt}). \quad [1]$$

One of the major advantages of the method is avoiding the handling of very reactive powders of the rare earth elements, which easily oxidize when in contact with traces of humidity or oxygen, shifting the actual composition of the aimed starting mixture and thus frequently resulting in multiphase alloys, due to the loss of rare earth metal.

In the ORD technique used here, very tiny rare earth oxide (or fluoride) powders are thoroughly grinded with transition metal and boron powders, then the mixture is roughly mixed with Ca granules and compacted into a flat pellet or a cylindrical rod; the sample is then heated at 950–1100°C for a few hours in an iron or inox boat of flat and elongated shape, under argon atmosphere.

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The reaction runs in a bath of liquid calcium (melting temperature 842°C) that acts as a solvent and ensures a very rapid diffusion of the components, so that equilibrium is reached within a few hours, depending on the size of the sample. The low temperature used (< 1000°C) prevents a rapid volatilization of the just-reduced very reactive rare earth element and ensures a very precise control of the stoichiometry. In the case of very volatile rare earth elements (Sm, Tb, Yb, …), a small excess of the rare earth oxide can be used, which can be adjusted by controlling precisely the experimental conditions in order to end up with single phase samples.

A 25 to 50% excess of Ca above what is necessary to reduce all the rare earth oxide (Eq. [1]) is added to the starting mixture, in order to preserve a sufficient amount of Ca melt until the end of the run. In turn, a too large excess of Ca within the pellet containing the components is not recommended as their difference in solubility and even more their difference in specific mass would result in a segregation through the melt and the production of inhomogeneous samples.

The highly refractory character of the reaction product CaO prevents its rapid diffusion and crystal growth in the viscous melted pellet. As a consequence, the just-formed CaO clusters or nanoparticles spread out all over the melted slurry are very efficient as inhibitors against the growth of large metal boride particles. On the contrary, borides grow as micrometer-size loose particles of roundish shape that can be easily separated from the CaO–Ca slurry through gentle washing in a moderated amount of slightly acidic aqueous solution; then they are recovered with a hand magnet and dried under vacuum at room temperature.

3. RESULTS AND DISCUSSION

Figure 1a represents microcrystals of a ternary boride just after cooling, embedded in a slurry of Ca + CaO byproducts. At 950°C, the slurry is still rather viscous and closely coats the crystals, preventing them from sintering.

Figures 1b and 1c represent $NdCo_4B$ and $PrCo_4B$ ORD crystals ($\sim$ 5–10 μm) after the slurry has been washed in diluted acid solution. Hollow prints at the surface of the roundish crystals represent the initial position of CaO agglomerates, or in some cases the position of contact with other crystals. In that case a gentle grinding during the washing operation can be necessary to recover loose particles.

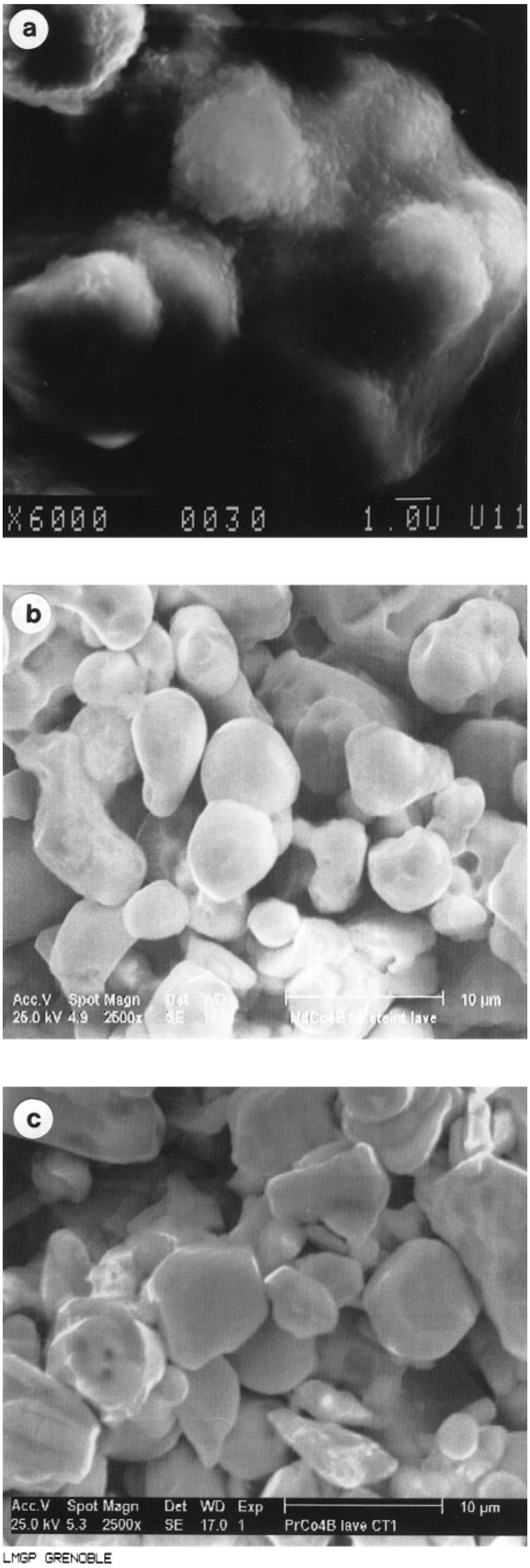

FIG. 1. Microcrystals of $PrCo_4B$ embedded in a slurry of CaO + Ca (a). Microcrystals of $NdCo_4B$ and $PrCo_4B$ after washing in diluted acidic solution (b, c).

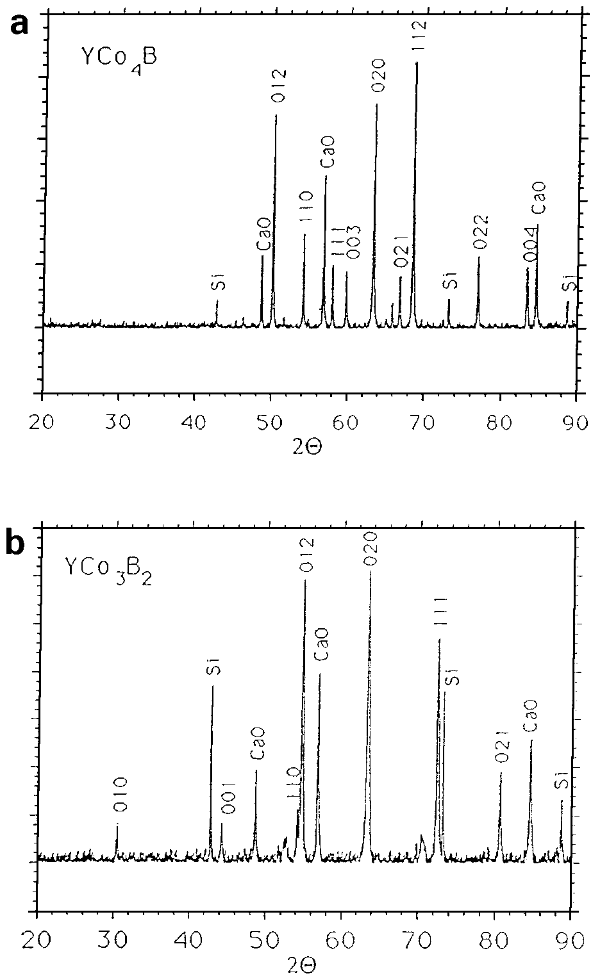

FIG. 2. X-ray patterns of as grown YCo_4B (a) and YCo_3B_2 (b) microcrystals.

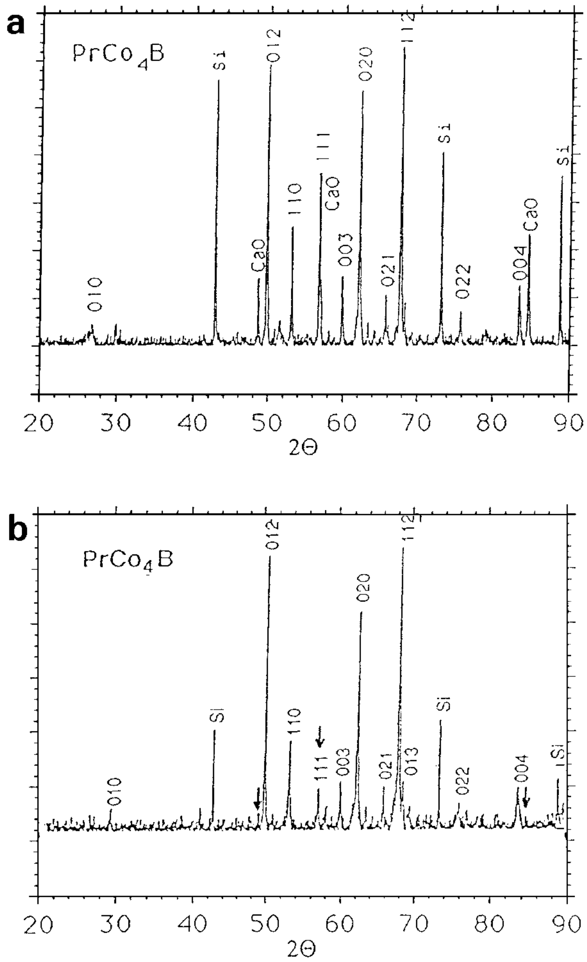

FIG. 3. X-ray patterns of $PrCo_4B$ before (a) and after (b) washing in cold water.

Despite these rather rough growth conditions, one always observes a remarkable crystal quality, with very sharp and narrow X-ray diffraction lines.

Figures 2a and 2b represent the X-ray patterns ($\lambda CrK\alpha$) of the as grown (before washing) borides YCo_4B and YCo_3B_2, respectively.

Figures 3a and 3b represent the phase $PrCo_4B$ before and after washing in cold water. One can see that the CaO lines do not show after washing. When washing is incomplete, the CaO lines are replaced by narrow and well-identified $Ca(OH)_2$ lines.

4. PROPERTIES OF RARE EARTH TRANSITION METAL BORIDES OBTAINED BY ORD

The magnetic alloy particles are easy to recover from the washing solution by using a small permanent hand magnet attached on the outside wall of the glass container. Due to the small size and loose character of the magnetic particles, which can be easily adjusted below 1 to 2 μm, powder samples showing a very high coercivity have been obtained without any grinding operation. For instance, in the case of 1/5 SmCo alloys, a coercivity as high as 25 kOe has been obtained for the as grown particles, and 17 kOe after washing the CaO.

Coercivities of 7500 Oe have been obtained for the as grown $Pr_2Co_{14}B$ particles and about 11,000 Oe for an as grown mixture ($y = 0.5$) of $Pr_2Co_{14}B$ and $PrCo_5$ particles, prepared according to the reaction (14)

$$\left(\frac{2-y}{6}\right)Pr_6O_{11} + (14-9y)Co + (1-y)B + \left[11\frac{(1+x)(2-y)}{6}\right]Ca \rightarrow y\ PrCo_5 + (1-y)\,Pr_2Co_{14}B + 11\left(\frac{2-y}{6}\right)CaO + \left[11\frac{x(2-y)}{6}\right]Ca. \qquad [2]$$

The magnetization amplitude under saturation conditions —sometimes very difficult to achieve due to the high values of anisotropy—is lower by no more than 5 to 10% than the corresponding bulk alloys, demonstrating that the passivation layer developed at the surface of the particles after washing and drying represents no more than 10% of the volume, at least for particles with an average size around 5 μm.

The simplicity of the experimental conditions of the ORD method makes it possible to prepare rapidly many samples of neighboring compositions; for instance, samples of the series $Ce(Co_{1-x}Fe_x)_4B$, with very high magnetic anisotropy properties, have been obtained as totally pure phases up to the limit composition $CeCoFe_3B$ ($x = 0.75$), while the use of the arc melting technique only allowed the synthesis of pure phases corresponding to $x = 0.05$, with unidentified second phases for $x = 0.1$ and $x = 0.2$ (18). The solid solutions of many ternary borides are currently under interest as their anisotropy properties are very sensitive to the composition. See, for example, several investigations by Burzo *et al.*:

$(Gd_xY_{1-x})Co_2B_2$ (19),

$(Gd_xY_{1-x})_2Co_7B_3$ (20),

$R_{n+1}Co_{3n+5}B_{2n}$, R = Y or Gd (21), $(Gd_xY_{1-x})Co_3B_2$ (22),

$YCo_{4-x}Fe_xB$ (23),

$(Gd_xY_{1-x})Co_4B$ (24),

$GdCo_{4-x}M_xB$, M = Fe, Ni (25).

Most of the samples have been prepared by the arc-melting technique under purified argon atmosphere, followed by annealing at 850°C for one week.

The ORD method would offer a considerable simplification of the experimental process for the synthesis of the many samples required for the investigation of these solid solutions.

But our interest recently concerning the ternary borides has been concentrated on their potentiality to store large quantities of interstitial hydrogen. This property has been investigated in detail on $LaNi_5$ by Buschow *et al.* (26), and more recently on RCo_4B (R = La, Pr, Sm) and RNi_4B (R = Ca, La, Pr) by Spada and Oesterreicher (27), and reflects the structural similarities between these hexagonal phases and the hexagonal phase $LaNi_5$, currently used as hydrogen storage electrodes in H–Ni batteries.

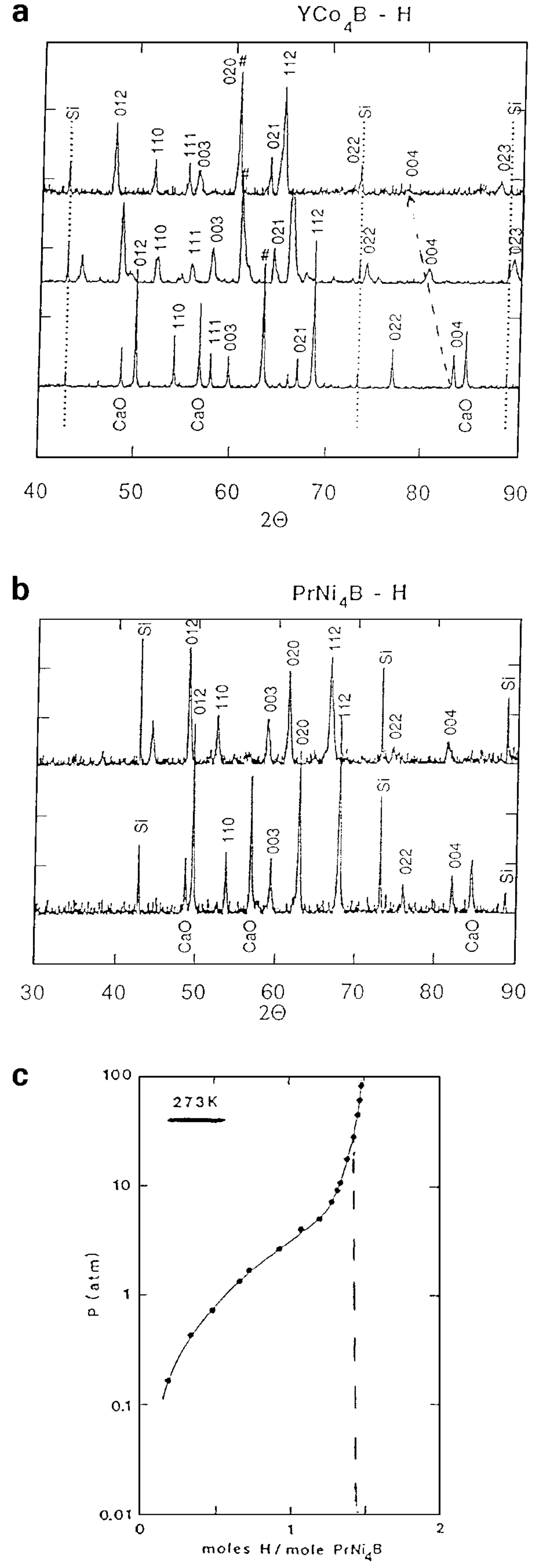

FIG. 4. X-ray patterns of as grown YCo_4B (a) and $PrNi_4B$ (b) before and after soaking in $NaBH_4$ solution. The cell increase is due to hydrogen intercalation (c). Pressure-composition diagram $PrNi_4B$–H is given as standard to estimate the H_2 pressure equivalence of the soaking solution.

TABLE 1
Rare Earth Transition Metal Boride Hydrides Obtained via the Chemical Route

Intermetallic compound	Structure	Cells of ORD alloys (Å)	Cell parameters of Hydrides (Å)	Structure	Parameters (Å)	ΔV (%)
$Nd_2Fe_{14}B$	tetr.	$a = 8.79$ $c = 12.24$	$Nd_2Fe_{14}BH_{\sim 4}$	tetr.	$a = 8.96$ $c = 12.44$	5.8
$Y_2Fe_{14}B$	tetr.	$a = 8.756$ $c = 12.01$	$Y_2Fe_{14}BH_3$		$a = 8.89$ $c = 12.16$	4.25
$Pr_2Co_{14}B$	tetr.	$a = 8.63$ $c = 11.87$	$Pr_2Co_{14}BH_{x \sim 0.4}$		$a = 8.653$ $c = 11.881$	0.6
$La_2Co_{14}B$	tetr.	$a = 8.67$ $c = 12.01$	$La_2Co_{14}BH_{x \sim 0.2}$		$a = 8.685$ $c = 12.01$	0.3
YCo_4B	hex.	$a = 5.0109$ $c = 6.8764$	$YCo_4BH_{0.9}$	hex.	$a = 5.0952$ $c = 6.8798$	2.6
			$YCo_4BH_{2.7}$		$a = 5.2081$ $c = 7.0816$	10.3
			$YCo_4BH_{3.6}$		$a = 5.2353$ $c = 7.2496$	14.1
$LaCo_4B$	hex.	$a = 5.1642$ $c = 6.8799$	$LaCo_4BH_{1.04}$	hex.	$a = 5.2604$ $c = 6.9373$	3.7
			$LaCo_4BH_{2.82}$		$a = 5.3395$ $c = 7.1510$	10.2
			$LaCo_4BH_{4.4}$		$a = 5.3856$ $c = 7.3957$	16
$CeCo_4B$	hex.	$a = 5.0097$ $c = 6.9290$	$CeCo_4BH_{0.03}$	hex.	$a = 5.0347$ $c = 6.9274$	0.1
$PrCo_4B$	hex.	$a = 5.1042$ $c = 6.8723$	$PrCo_4BH_{2.8}$	hex.	$a = 5.2992$ $c = 7.0932$	10.3
			$PrCo_4BH_{3.6}$		$a = 5.3068$ $c = 7.2776$	13.5
			$PrCo_4BH_{4.2}$		$a = 5.3264$ $c = 7.3684$	15.8
$HoCo_4B$	hex.	$a = 4.9981$ $c = 6.8727$	$HoCo_4BH_3$	hex.	$a = 5.2124$ $c = 7.1114$	11.6
$ErCo_4B$	hex.	$a = 4.9883$ $c = 6.8723$	$ErCo_4BH_{3.1}$	hex.	$a = 5.2015$ $c = 7.1348$	11.9
YNi_4B	hex.	$a = 4.9743$ $c = 6.9324$	$YNi_4BH_{1.2}$	hex.	$a = 5.0929$ $c = 6.9829$	4.8
$LaNi_4B$	hex.	$a = 5.1642$ $c = 6.8799$	$LaNi_4BH_{1.9}$	hex.	$a = 5.2722$ $c = 7.0469$	6.9
$CeNi_4B$	hex.	$a = 4.9912$ $c = 6.9703$	$CeNi_4H_{\sim 0}$	hex.	$a = 4.99$ $c = 6.97$	~ 0
$PrNi_4B$	hex.	$a = 5.0530$ $c = 6.9563$	$PrNi_4BH_{1.45}$	hex.	$a = 5.1830$ $c = 7.0293$	5.4
$CeCo_2Fe_2B$	hex.	$a = 5.0426$ $c = 6.9022$	$CeCo_2Fe_2BH_{0.3}$	hex.	$a = 5.0891$ $c = 6.9192$	1.24
			$CeCo_2Fe_2BH_{0.9}$		$a = 5.1268$ $c = 6.9726$	3.5
$CeCoFe_3B$	hex.	$a = 5.0495$ $c = 6.9567$	$CeCo_3FeBH_{0.3}$	hex.	$a = 5.1372$ $c = 7.0039$	3.3
			$CeCo_3FeBH_{2.1}$		$a = 5.2038$ $c = 7.1226$	7.8
YCo_5	hex.	$a = 4.9434$ $c = 3.9567$	$YCo_5H_{0.76}$	hex.	$a = 4.9995$ $c = 4.0086$	2.6
			$YCo_5H_{2.43}$		$a = 3.0605$ $b = 4.4482$ $c = 4.0078$	
YCo_3B_2	hex.	$a = 5.0119$ $c = 3.0251$	$YCo_3B_2H_{\sim 0}$	hex.	$a = 5.01$ $c = 3.02$	~ 0

Instead of submitting the ORD particles to increasing pressures of H_2 gas, we followed the elegant soft chemical route proposed by Murphy *et al.* in the case of tiny grinded bulk alloys of varied compositions (28).

In an adaptation of this method, a sample of a few grams of the as grown ORD rare earth transition metal boride particles still within their slurry of Ca + CaO was soaked for a few hours at room temperature in 50 to 100 CC of a saturated aqueous solution of $NaBH_4$, according, for instance, to the reaction

$$\mathrm{LnCo_4B + BH_4^- + Na^+ + 3H_2O}$$
$$\rightarrow \mathrm{LnCo_4B\,H_n + H_2BO_3^- + H} \quad \text{(excess)}.$$

The hydride alloy particles are easily recovered by washing and decantation.

Figures 4a and 4b represent the X-ray patterns of the two phases YCo_4B, $PrNi_4B$ before and after soaking of the ORD particles in the $NaBH_4$ solution. The shift of the lines is more important for the large intercalation rates (for example, YCo_4B). This shift compared to that observed in hydrides of the same alloys obtained by a solid H_2 reaction allows a close determination of the amount of interstitial hydrogen, and in addition a good estimation of the H_2 pressure equivalence obtained in the soaking solution (Fig. 4c).

Several degrees of H intercalation are obtained on some samples depending on the time of soaking and of the initial

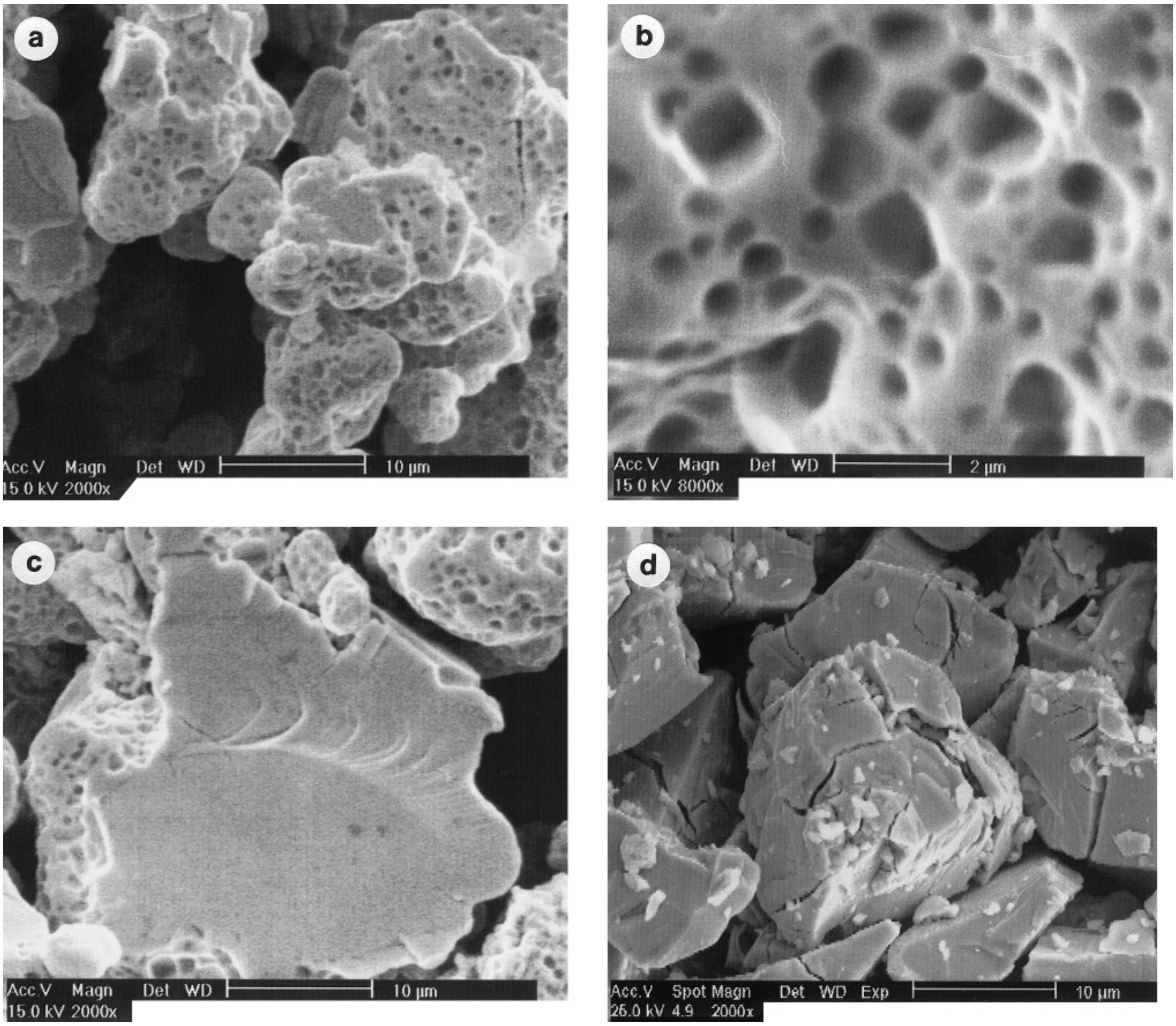

FIG. 5. ORD crystals soaked for 12 h in a concentrated $NaBH_4$ solution at room temperature (a, b, c). Particles of the same alloy—grinded from an arc-melted button—after soaking under the same conditions (d). The large volume increase due to intercalation leads in that case to many cracks at the surface of the crystal, indicating that the insertion reaction proceeds very rapidly through the surface but that the diffusion in the bulk is not so rapid.

concentration of the borohydride solution. They generally correspond to different hydride phases.

More than 4 H per formula unit are intercalated in some alloys ($PrCo_4B$, $LaCo_4B$, …), leading to a volume cell increase of more than 15% (Table 1). By comparison with the gas intercalation technique, a pressure equivalence of more than 50 atm at 60°C can be obtained within a fresh saturated solution of $NaBH_4$ (19, 20).

In addition, in opposition to the gas pressure technique, no activation period or extra heating is necessary to initiate the intercalation reaction. The very reducing $NaBH_4$ immediately cleans the surface of the particles by dissolving any passivation layer, thus improving considerably the kinetics of diffusion of H species through the surface of the alloy particles. The Ca + CaO slurry only increases the pH of the soaking solution, slowing down the hydrolysis of the BH_4^- active cations. Besides, the surface of the ORD particles often presents holes that are due to the CaO grains that dissolved in the aqueous borohydride solution (they could as well be washed in slightly acidic solution).

It is remarkable that these particles (10 μm size) are apparently not affected (Figs. 5a, 5b, 5c) by the big change of volume due to H intercalation and can be cycled several times with no apparent damage; particles of comparable size obtained by crushing and grinding bulk ingots are completely broken up with many cracks and fine fragments or flakes at the surface after one night of soaking in a $NaBH_4$ solution (Fig. 5d). It seems thus that the morphology of the ORD particles could present an interesting potential for the hydrogen storage alloy electrodes used in H–Ni batteries.

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