JOURNAL OF MATERIALS SCIENCE 20 (1985) 817–820

The hydrogenation behaviour of the phases Sm_2Co_{17} and Pr_2Co_{17}

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The compounds Sm_2Co_{17} and Pr_2Co_{17} have been charged with hydrogen and the hydrogen compositions determined between pressures of approximately 2.5×10^{-2} and 13 atm at temperatures of 150 and 200° C. Very low rates of hydrogen absorption were observed below 150° C so that solubility measurements have not been obtained below this temperature. The X-ray diffraction studies show that the structure of the metal lattice is unchanged by the hydrogenation process, i.e. the rhombohedral, Th_2Zn_{17} structure type with space group $R\bar{3}_m$ is maintained. As a result of the expansion the alloys become cracked and friable on hydrogenation.

1. Introduction

Many of the members of the family of AB_5 compounds (where A is a rare earth element and B is nickel or cobalt) form hydrides. The equilibrium pressure of hydrogen at room temperature varies from 0.04 atm for $LaCo_5$ to more than 60 atm for $CeNi_5$ and $SmNi_5$ [1]; by making mixed compounds, any equilibrium pressure between 0.04 and 100 atm can be obtained.

The A_2B_{17} compounds are structurally very similar to the AB_5s, having either the hexagonal Th_2Ni_{17} type structure (space group $P6_3/mmc$) or the rhombohedral Th_2Zn_{17} type structure (space group $R\bar{3}_m$) [2].

Buschow and co-workers [3, 4] have produced the hydrides $Th_2Ni_{17}H_{2.0}$ and $Th_2Fe_{17}H_{1.3}$ but found that Th_2Co_{17} and Y_2Fe_{17} absorbed only very small amounts of hydrogen (< 0.05 at % H per formula unit). In their paper on the kinetics of hydriding $SmCo_5$, Raichlen and Doremus [5] found that a cobalt-rich alloy containing a mixture of the $SmCo_5$ and Sm_2Co_{17} phases would not absorb hydrogen at 100 atm pressure and room temperature. They postulated that the lack of hydride formation might be caused by mechanical strain placed on the $SmCo_5$ by the "non hydriding Sm_2Co_{17}". Clinton *et al.* [6] found that in the series of Pr–Co compounds, Pr_2Co_{17} behaves exceptionally, as it remains inert from room temperature to 200° C under 100 atm of hydrogen, and over a 20 h exposure period.

2. Experimental details

The Sm_2Co_{17} and Pr_2Co_{17} used in this work was kindly supplied by Rare Earth Products Ltd. Solid samples were examined metallographically and found to be single phase.

The hydrogen solubility data were obtained using an adapted Sartorius micro balance which allowed pressures of up to 13 atm to be employed. Pressures above 1 atm were measured using a Budenberg gauge, low pressures (< 0.13 atm) were measured using a Furness micromanometer, and intermediate pressures (0.13 to 1 atm) were measured using a Galenkamp gauge.

The powders for X-ray analysis were annealed for 2 h at 1223 K and then exposed to Cr$K\alpha$ radiation in a Philips Debye–Scherrer camera (11.483 cm diameter). The lattice spacings were derived from the diffraction patterns using the Nelson–Riley extrapolation function and an iterative method to obtain refined values of the axial ratio, c/a and of the a spacing. The relative intensities of the X-ray lines were measured using a double-beam Joyce microdensitometer. A trace of the lines on the Debye–Scherrer films was recorded and the area of a particular diffraction peak measured using a planimeter. The reproducibility

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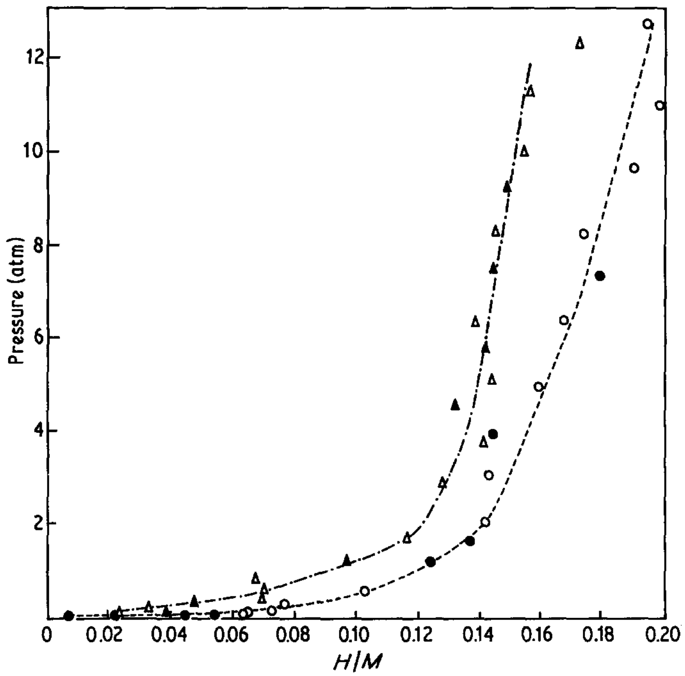

Figure 1 P–C–T data for Sm_2Co_{17}. 150° C Isotherm; ○ adsorption, ● desorption. 200° C Isotherm; △ adsorption, ▲ desorption. ⊢⊣ Typical error in *H/M*.

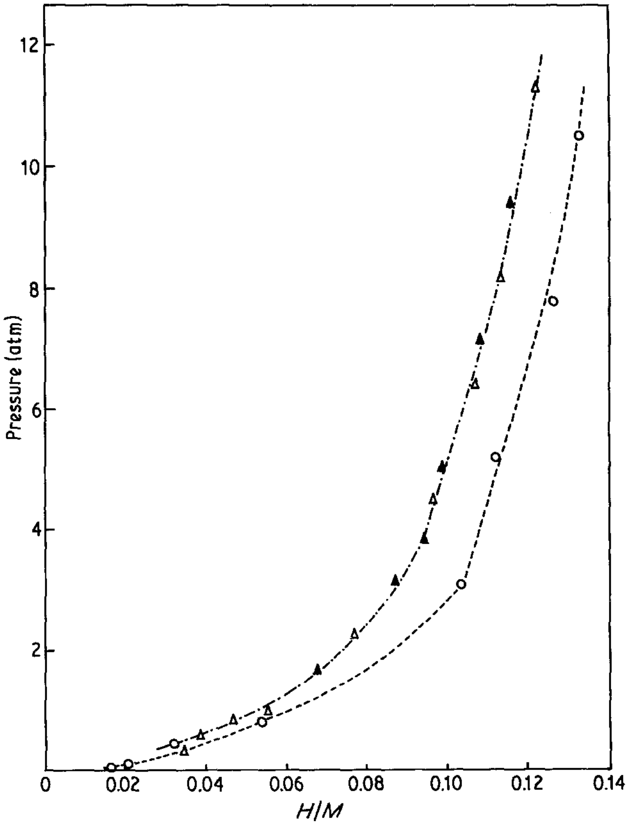

Figure 2 P–C–T data for Pr_2Co_{17}. 150° C Isotherm; ○ adsorption. 200° C Isotherm; △ adsorption, ▲ desorption. ⊢⊣ Typical error in *H/M*.

of each measurement varied from approximately ± 5% for strong lines to approximately ± 10% for weak lines.

3. Experimental results and discussion

3.1. P–C–T data

The P–C–T data were obtained using the microbalance described above. The samples consisted of approximately 0.2 g of freshly crushed powder contained in a small silica bucket. The bucket was suspended from one arm of the balance and this system allowed the weight change with hydrogen content to be measured directly. Initially the samples were activated by heating to approximately 300° C under 12 atm of hydrogen, then outgassed and the hydrogen absorption and desorption then measured at temperatures of 150 and 200° C. These isotherms for the Sm_2Co_{17}–H_2 and Pr_2Co_{17}–H_2 systems are shown in Figs. 1 and 2, respectively, and there was no significant differences between the absorption and desorption isotherms. The shapes of the isotherms for the two systems are very similar though Sm_2Co_{17} seems to absorb significantly more hydrogen than does Pr_2Co_{17} under these conditions of temperature and pressure. At 150° C, approximately 12 h were required for the samples to reach equilibrium, though at most pressures a period of 24 h was allowed between measurements. Hydrogen absorption at 120° C was extremely slow and below this temperature no weight change at all was observed over a period of 48 h.

An attempt was made to increase the hydrogen content of the samples by hydrogenation in a high pressure system at 150° C and 60 atm and an approximate value of *H*/*M* of 0.3 was obtained.

The hydrogen solubility data for both compounds indicate the absence of any phase immiscibility in these systems under the present conditions and both systems exhibit Sieverts-type behaviour

TABLE I Powder diffraction data for Sm_2Co_{17} and $Sm_2Co_{17}H_x$ (where $x \sim 5$)

Line	*d* spacing of Sm_2Co_{17} (nm)	*d* spacing of $Sm_2Co_{17}H_5$ (nm)	
2 0 1	0.3456	not measured	measured
2 0 2	0.3110	not measured	
1 1 3	0.2900	0.2929	
1 0 4	0.2792	0.2809	
1 2 1	0.2662	0.2692	
1 2 2	0.2491	0.2514	
3 0 0	0.2411	0.2444	
2 0 4	0.2325	0.2341	
1 0 5			
2 2 0	0.2094	0.2119	
3 0 3	0.2072	0.2096	
1 2 4	0.2033	0.2053	
0 0 6		0.2034	
2 0 5			
2 2 3	0.1861	0.1879	
1 1 6	0.1824	0.1835	
1 2 5			
4 0 1	0.1799	not measured	
4 0 2	0.1743	not measured	
1 4 3	0.1479	0.1493	
1 2 7	0.1470	0.1478	
2 3 4		0.1471	
2 2 6	not measured	0.1463	
4 0 5			
3 3 0	0.1398	0.1415	
2 3 5	0.1376	0.1390	
2 4 2	0.1341	not measured	
3 3 3	0.1323	0.1328	
1 3 7	0.1312	0.1323	
5 0 4			
1 1 9	0.1291	0.1295	
4 0 7	0.1252	0.1266	
2 4 4			
6 0 0	0.1212	0.1277	

at the low hydrogen concentrations. These observations indicate that the hydrogen solubility behaviours shown in Figs. 1 and 2 are characteristic of α-phase solubility regions and any hydride phases will occur at pressures in excess of the maximum pressure employed in these studies.

Similar hydrogenation experiments have been carried out on some bulk magnetic alloys with the commercial 2/17-type compositions [7, 8] and these have been effectively decrepitated by the hydrogenation process. Promising magnets have been prepared from this material and this work will be the subject of a further publication [8].

3.2. X-ray results

Sm_2Co_{17} and Pr_2Co_{17} have the rhombohedral, Th_2Zn_{17}-type structure. The structure was indexed as hexagonal though the systematic extinctions of reflections other than $h-k+l=3n$ or $-h+k+l=3n$, indicate rhombohedral symmetry.

Lattice parameter measurements were made on Sm_2Co_{17} and Sm_2Co_{17} charged with hydrogen to a composition of approximately $Sm_2Co_{17}H_5$ and the d spacings listed in Table I. From this data the following lattice parameters were obtained:

	Sm_2Co_{17}	$Sm_2Co_{17}H_x$ (where $x \sim 5$)
a (nm)	0.8400	0.8503
c (nm)	1.2197	1.2207
c/a	1.452	1.436

This corresponds to an expansion of the a parameter of 1.2% and of the c parameter of 0.08% on hydrogenation.

4. Conclusions

We have shown that the alloys Sm_2Co_{17} and Pr_2Co_{17} do absorb significant quantities of hydrogen though the rate of absorption below 150° C is extremely slow. As far as we were able to determine there is no plateau pressure for either of the alloys at the temperatures and pressure studied and the hydrogen solubility data indicates α-phase solubility regions for both systems. Lattice parameter measurements for Sm_2Co_{17} indicate a greater expansion in the a direction than in the c direction on absorption of hydrogen.

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Received 22 March
and accepted 12 April 1984