

Reference

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Absorption-desorption characteristics of hydrogen for $MmCo_5$

RNi_5 and RCo_5 (R = rare earth metal) absorb and desorb hydrogen reversibly by a pressure operation [1, 2], and are important as hydrogen storage materials. $MmNi_5$, using Mischmetall as R , also readily absorbs and desorbs large amounts of hydrogen, and forms the hydride $MmNi_5H_7$ under 10^6 Pa at room temperature [3]. In this work, the characteristics of $MmCo_5$ -H system were studied.

The composition of Mm used was (in wt %): La 32.9, Ce 47.1, Nd 13.9, Pr 4.3, and the other rare earth elements 1.0; the Co was of purity 99.99 wt %. The compounds were prepared by argon-flame melting of the elements in a water-cooled copper crucible and then homogenizing the ingots at 1100°C for 10 h *in vacuo*. After cooling to room temperature, the ingots were crushed to powder of $10\mu\text{m}$ average particle diameter. The powders were into a stainless steel specimen holder, and successively heated at 100°C under 0.13 Pa to remove surface contaminants which hinder the absorption of hydrogen before measuring.

The absorption-desorption characteristics were determined by pressure-composition isotherm measurements. The hydrogen desorption rate from the hydride was obtained by measuring the amount of hydrogen flowing into a measuring cylinder from the specimen holder, and the absorption rate was measured by pressure variation in a measuring system. The reaction between the hydrogen and the compound was examined by high pressure DTA under a hydrogen atmosphere.

The pressure-composition isotherms of $MmCo_5$ -H system are shown in Fig. 1. The curves do not show the obvious plateau at room temperature, and the absorption and desorption isotherms show hysteresis, which gradually increases with increasing temperature. The dissolved amount of hydrogen in $MmCo_5$ at 25°C and 5×10^4 Pa,

determined, from the measurement of the pressure-composition isotherm, was about $MmCo_5H_{0.25}$, and the hydride $MmCo_5H_{2.5}$ was formed at 25°C , 10^6 Pa.

The relationship between the temperature and pressure at the composition $MmCo_5H_{1.25}$ in the absorption and desorption isotherms are shown in Fig. 2. The enthalpy changes for the absorption and desorption of hydrogen calculated from the slopes are -0.34 and 0.25 eV, respectively.

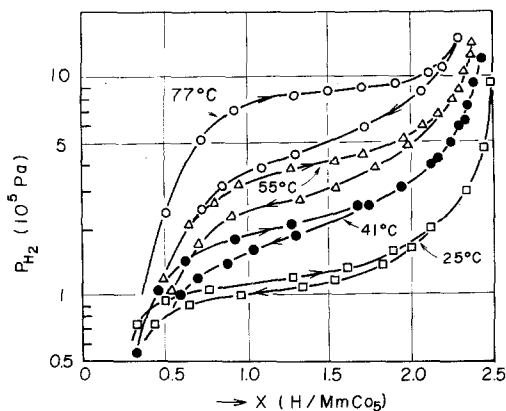


Figure 1 Pressure-composition isotherms for $MmCo_5$ -H system.

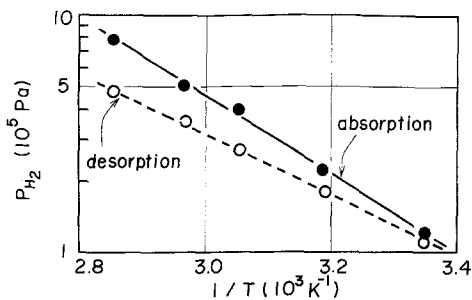


Figure 2 Relationships between the absorption and desorption pressures of hydrogen for $MmCo_5H_{1.25}$ and the reciprocal temperature.

Fig. 3 shows the high pressure DTA curve of $\text{MmCo}_5\text{-H}$ system when the $\text{MmCo}_5\text{H}_{2.5}$ was heated at 10^6 Pa of hydrogen, the curve had three endothermic peaks. It is assumed that these peaks correspond to the dissociations of three hydrides respectively, whose composition and crystal structures are each slightly different.

The composition of hydride at 25°C under 10^6 Pa, the desorption pressure of hydride

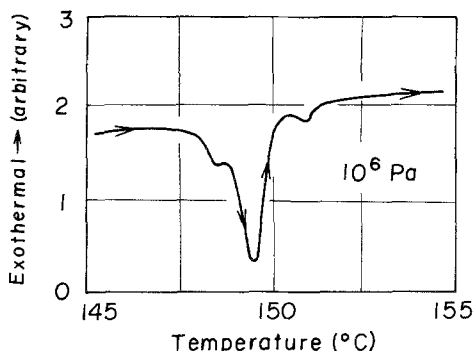


Figure 3 High pressure DTA curve for dissociation of hydride in $\text{MmCo}_5\text{-H}$ system.

$\text{MmCo}_5\text{H}_{1.25}$ at 25°C , and the enthalpy change for the dissociation of hydride, calculated using the values for $\text{CeCo}_5\text{-H}$, $\text{LaCo}_5\text{-H}$, $\text{PrCo}_5\text{-H}$ and $\text{NdCo}_5\text{-H}$ systems measured by Kuijpers [1], are $\text{MmCo}_5\text{H}_{2.5}$, 1.2×10^5 Pa, and 0.42 eV, respectively. The composition of the hydride at 25°C under 10^6 Pa, and the desorption pressure (1.1×10^5 Pa) of $\text{MmCo}_5\text{H}_{1.25}$ at 25°C in this work were in good agreement with the calculated values, but the enthalpy change for the dissociation of hydride was smaller than the calculated one. This difference may be due to the effects of element alloying.

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Factors affecting the stress dependence of creep of polycrystalline ceramics

Under high temperature creep conditions, the variation of the secondary or steady-state creep rate, $\dot{\epsilon}_s$, with stress, σ , at a constant temperature, T , can be expressed in the form

$$\dot{\epsilon}_s|_T \propto \sigma^n$$

With many polycrystalline ceramics, the stress exponent n is found to decrease from values of 3 or more, at high stresses, to values approaching unity at low stress levels. With this type of material, deformation at high stresses is considered to occur by the generation and movement of dislocations whilst, in the low-stress range, creep is usually attributed to stress-directed vacancy diffusion. It has been suggested that polycrystalline ceramics showing this type of behaviour can be classified into two groups, depending on the n value generally reported for creep in the high-stress range [1]. One group exhibits a stress exponent of approximately 5 (e.g. NaCl, LiF, CaO,

UO_2) whilst the other group displays an n value close to 3 (e.g. MgO, BeO, Al_2O_3). This difference in stress exponent is not simply a consequence of differences in the nature of the atomic bonds (2) since, for example, CaO and MgO both have a rock salt structure and similar bond-type, but display different n values at high stress levels (Fig. 1). Alternatively, the results presented in Fig. 1 are compatible with a classification [1] which links the n value to the ratio of the radii of the anion r_a and the cation r_c , with $n \approx 5$ for materials with $r_a/r_c < 2$, and $n \approx 3$ for ceramics with $r_a/r_c > 2$. However, evidence is available which indicates that a specific n value of 3 or 5 should not be assigned to each ceramic material. In particular, for polycrystalline MgO samples of similar purity, porosity and grain size, the n value has been shown to vary in the range ~ 2 to ~ 7 depending on the fabrication procedures used to prepare the testpieces [5]. The present work aims to rationalize the conflicting observations on stress exponents in terms of the slip behaviour of ceramic materials, a view consistent with the known