



HYDROGEN ABSORPTION CHARACTERISTICS IN Mm BASED C 15 TYPE AB₂ ALLOYS

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ABSTRACT

The pressure-composition (P-C) isotherms of Ho_{0.9}Mm_{0.1}Co₂-H and Ho_{0.7}Mm_{0.3}Co₂-H systems have been obtained in the temperature and pressure ranges 323-473 K and 0.001-1 bar respectively, by pressure reduction method. The P-C isotherms show the two plateau regions in the temperature and pressure ranges studied. The effect of substitution of Mm at Ho site in HoCo₂ on the unit cell volume and on the plateau pressure has been investigated. The dependence of the thermodynamic factors, the relative partial molar enthalpy (ΔH_H) and entropy (ΔS_H) of dissolved hydrogen on the hydrogen concentration has been discussed.

Keywords: P-C isotherms, cubic Laves phase, Enthalpy, Entropy.

1. INTRODUCTION

Hydrogen is known to react with a large number of metals, alloys, and intermetallic compounds at moderate hydrogen gas pressure. The behaviour of hydrogen in Laves phase compounds is currently a very active subject of research,^{1, 2} due to hydrogen's high solubility and high diffusivity in these compounds, characteristics that make these systems excellent candidates for use in metal hydride batteries and hydrogen storage applications. In practice, in order to meet the requirements of the applications (high equilibrium pressure and hydrogen solubility and multiple rechargeability), multicomponent alloys of the form (A_aA_b...A_n)(B_aB_b...B_n)₂^{3, 4} are used. A large number of AB₂ compounds, where A is a transition or rare-earth element and B = Mn, Fe, Co, or Ni, crystallize in one of the closely related Laves phases, either the cubic C-15 or the hexagonal C-14 and C-36 phases,^{5, 6} and can accommodate a wide mixer of metals on either the A or B site. RCo₂ (R = rare earth) has the cubic C-15 (MgCu₂) structure; the R atoms form a diamond-type lattice and Co atoms form a corner linked tetrahedral array. The interstitial sites occupied by hydrogen in AB₂ Laves phases are tetrahedral sites formed by two A atoms and two B atoms (2A2B site) or by one A atom and three B atoms (1A3B site) or four B atoms (4B site). There are 17 tetrahedral interstitial sites per formula unit; 12 2A2B sites, four 1A3B sites, and one 4B site. This structure has 17 tetrahedral interstitial sites per formula unit; their coordination environment and number are R₂Co₂ (12), RCo₃ (4), and Co₄ (1).⁷ Absorbed hydrogen may occupy one or more of these three types of tetrahedral interstices. However, because of electrostatic effects, most of the sites remain unoccupied on hydriding, resulting in a maximum sorption of about 6 H atoms per AB₂ formula unit.⁸

The ability of a metal to absorb hydrogen is largely governed by the heat of solution ΔH , which represents the heat involved during the absorption of hydrogen. For very stable metal-hydrogen systems such as Y-H and La-H, ΔH is typically \approx - 100 kJ/mol H. Entropy effects play a secondary role because the entropy of hydrogen solution in a metal, ΔS arises almost totally from the entropy loss of gaseous hydrogen during hydrogen uptake by the metal.⁹ In this paper,

we report the hydrogen storage properties of $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2$ (Mm = Mischmetal) systems in the temperature and pressure ranges 323-473 K and 0.001-1 bar respectively. The effect of substitution of Mm at Ho site in HoCo_2 on their hydrogen storage properties has been studied and is discussed.

2. EXPERIMENTAL

$\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2$ alloys have been prepared by arc melting in a water-cooled copper electrode under an atmosphere of purified argon gas and were homogenized under vacuum at 1100 K for 8 days to obtain single-phase compounds. The powder X-ray diffraction patterns of these alloys have taken at room temperature using Cu-K_α radiation. The P-C absorption isotherms were obtained using a conventional gasometric technique. Samples were powdered to fine particles and then introduced into a reactor cell connected to the hydriding system. Before introducing hydrogen gas (99.999 % pure), the whole system was pumped out with a diffusion pump and the system pressure was measured using a pressure transducer. The hydrogen storage capacity has been calculated from the pressure drop during the hydrogen adsorption at constant temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the room temperature Cu-K_α powder X-ray diffraction patterns of $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2$, which crystallize in cubic C-15 Laves phase structure and the corresponding diffraction peaks are indexed. The lattice parameters and unit cell volumes of these alloys were evaluated using least square refinement technique and are listed in Table 1. The X-ray diffraction patterns show that the lattice parameters increase with increase in Mm concentration.

The P-C isotherms of $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2\text{-H}$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2\text{-H}$ systems are shown in Figs. 2 and 3 respectively. These isotherms indicate that there are two plateau regions in the temperature and pressure ranges studied, similar to the multiplateau behaviour observed in the $\text{ErFe}_2\text{-H}$ system at 293 K.¹⁰ The hydrogen storage capacity increases with increase of hydrogen equilibrium pressure. The plateau pressure has been obtained by taking pressure at the mid point of the first plateau region.¹¹

The P-C isotherms shows that at any particular temperature, the plateau pressure decreases with increase in unit cell volume, which could be due to the larger size of the interstitial sites. Such behaviour of the decrease in the plateau pressure due to the expansion of the host lattice by substitutional elements has been reported in the literature.¹² Maximum hydrogen storage capacity of around 3.5 hydrogen atoms per formula unit is obtained at 323 K and 1 bar.

The thermodynamic factors, relative partial molar enthalpy ΔH_H and relative partial molar entropy ΔS_H , of the dissolved hydrogen in these alloys have been determined with the help of the van't Hoff equation¹³

$$\ln P_{\text{eq}} = 2 \left[\frac{\Delta H_H}{RT} - \frac{\Delta S_H}{R} \right]$$

where R is the ideal gas constant. ΔH_H and ΔS_H of dissolved hydrogen for a particular hydrogen concentration ($r = n_H/n_{\text{f.u.}}$) value have been obtained by a least square technique from the slope and intercept of $\ln P_{\text{eq}}$ and $1/T$ plot, respectively. Fig. 4 shows the van't Hoff plots for $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2\text{-H}$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2\text{-H}$ systems at $r (n_H/n_{\text{f.u.}}) = 1$.

The values of ΔH_H and ΔS_H for $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2\text{-H}$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2\text{-H}$ are -7.1 kJ/mol H, -11.8 J/K/mol H and -13.3 kJ/mol H, -23.9 J/K/mol H, respectively. Comparison of ΔH_H value of $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2\text{-H}$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2\text{-H}$ system indicates that $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2$ forms stable hydride compared to $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2$.

4. CONCLUSION

$\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2$ crystallize in cubic C-15 Laves phase structure. P-C isotherms of $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2\text{-H}$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2\text{-H}$ systems show the existence of two plateau regions and at any particular temperature, the plateau pressure of $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2\text{-H}$ is lower than that of $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2\text{-H}$, which could be due to the increase of unit cell volume. The maximum hydrogen storage capacity is around 3.5 hydrogen atoms per formula unit at 323 K and 1 bar. The ΔH_H values show that $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2\text{-H}$ system is more stable than the $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2\text{-H}$ system.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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TABLES

Table 1: Lattice parameters (a), unit cell volumes (V) of $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2$ and $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2$

Alloy	a (\AA)	V (\AA^3)
$\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2$	7.185	370.92
$\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2$	7.200	373.25

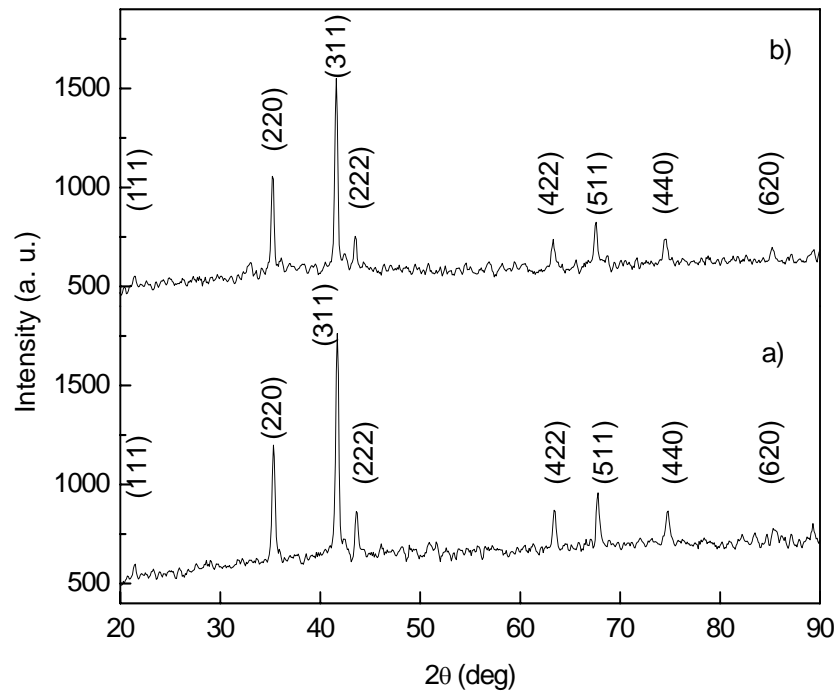


Fig. 1: The room temperature powder X-ray diffraction patterns of a) $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2$ and b) $\text{Ho}_{0.7}\text{Mm}_{0.3}\text{Co}_2$

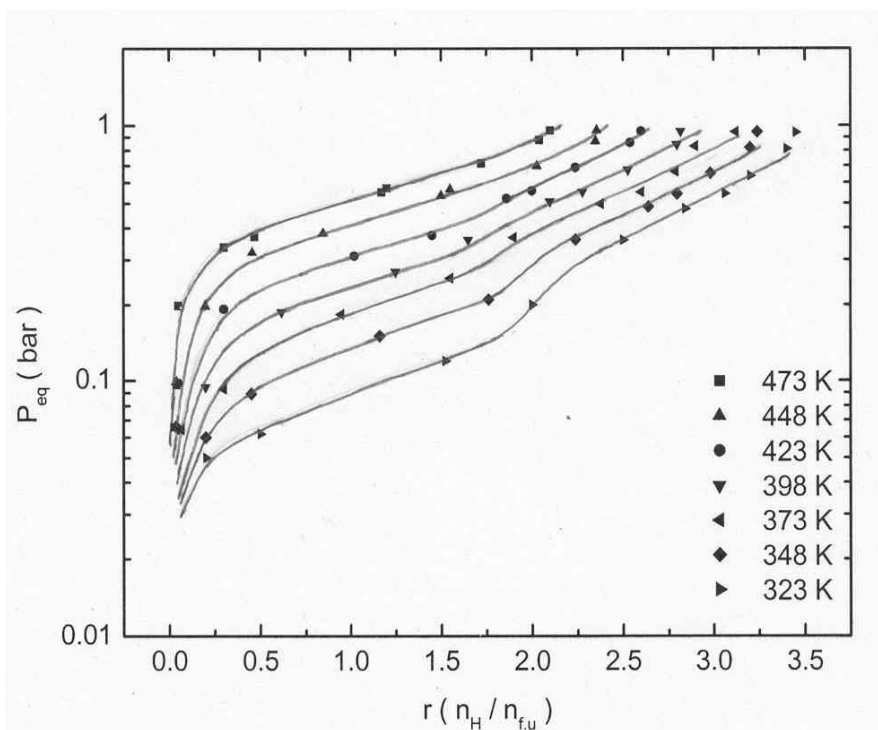


Fig. 2: P-C isotherms of $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2\text{-H}$ system in the temperature range 373 - 473 K

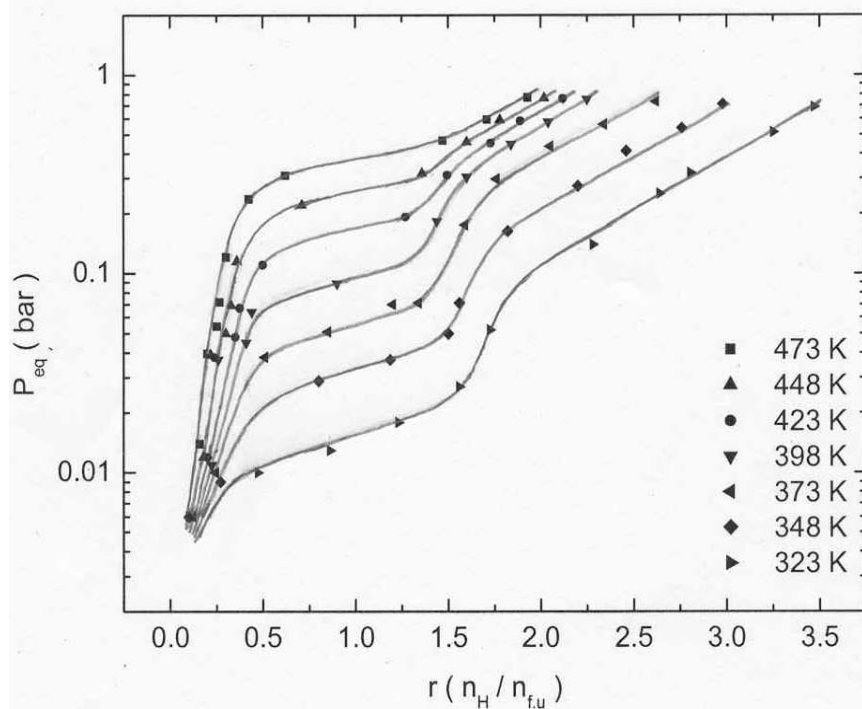


Fig. 3: P-C isotherms of $\text{Ho}_{0.9}\text{Mm}_{0.1}\text{Co}_2\text{-H}$ system in the temperature range 323 - 473 K

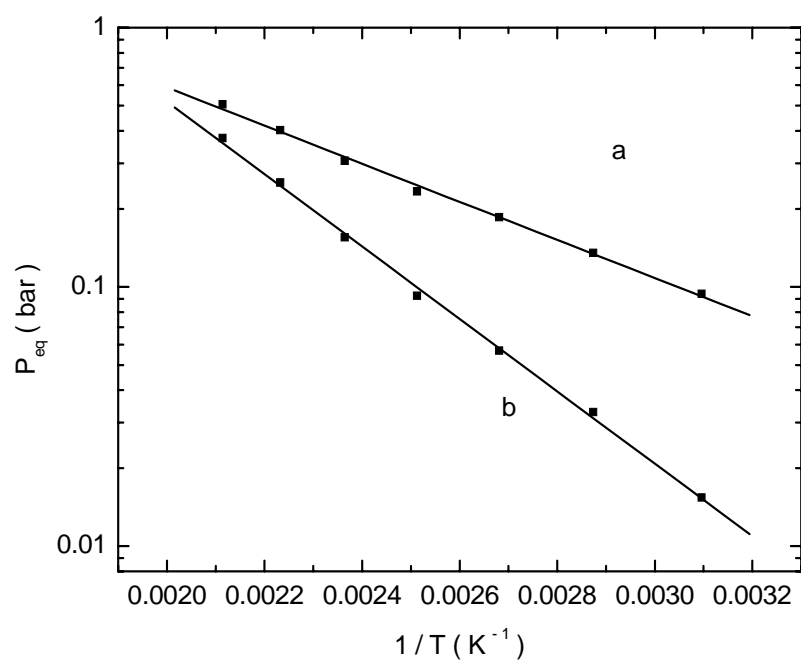


Fig. 4: The van't Hoff plots for a) $Ho_{0.9}Mm_{0.1}Co_2-H$ and b) $Ho_{0.7}Mm_{0.3}Co_2-H$ systems