



On the isomorphous phase transformation in the solid f.c.c. solutions Co–H at high pressures

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Abstract

Samples of Co containing 0.2 at.% Fe and consisting of a mixture of approximately equal amounts of the h.c.p. (stable) and f.c.c. (metastable) phases were loaded with hydrogen by a 24 h exposure to a hydrogen atmosphere at 325°C and pressures up to 9 GPa. X-ray diffraction at ambient pressure and 100 K has revealed a steep increase in the lattice parameter of the f.c.c. phase in the samples hydrogenated at 4–6 GPa, corresponding to an increase in the hydrogen content from few atomic per cent to an H/Co atomic ratio of approximately 0.95. This behaviour is interpreted as a supercritical anomaly of an isomorphous phase transformation in the f.c.c. solid solutions. The topology of the T - P phase diagram of the Co–H system is discussed in view of these observations.

Keywords: Cobalt hydride; High pressure

1. Introduction

At atmospheric pressure, the low temperature h.c.p. (ϵ) modification of cobalt transforms into the high temperature f.c.c. (γ) modification at $T_\gamma \approx 450^\circ\text{C}$. The application of pressure results in a monotonic increase of T_γ with an initial slope $dT_\gamma/dP \approx 40^\circ\text{C GPa}^{-1}$ [1,2].

Experiments at pressures up to 2.5 GPa have shown [2] that for cobalt in an atmosphere of molecular hydrogen the dependence of T_γ on pressure remains nearly the same as in an inert medium up to about 2 GPa; at higher pressures, T_γ begins to rise faster in hydrogen than in an inert medium. At 250°C and 350°C, the solubility of hydrogen in ϵ -Co has been found to increase monotonically with pressure up to a hydrogen-to-metal atomic ratio of $n \approx 0.6$ at 7 GPa [3,4]. A further increase of the hydrogen pressure causes an $\epsilon \rightarrow \gamma$ phase transformation, which is accompanied by an abrupt increase in the hydrogen content to $n \approx 1$ [3,4].

The dissolution of hydrogen in cobalt thus stabilizes the ϵ phase at pressures below 2.5 GPa and the γ phase at pressures above 7 GPa. In order to explain

these observations, it was suggested [3,4] that an isomorphous phase transformation occurs in the metastable γ solutions somewhere between 2.5 and 7 GPa in the region of the T - P_{H_2} diagram where the ϵ solutions are the thermodynamically stable phase.

In the present work we have observed this transformation experimentally by using samples of cobalt doped with 0.2 at.% Fe which, in the initial state before hydrogenation, already contained both the ϵ and γ phases.

2. Sample preparation and experimental details

An ingot of a $\text{Co}_{99.8}\text{Fe}_{0.2}$ alloy was melted from cobalt of 99.98 wt.% purity and isotopically enriched ^{57}Fe in a levitation induction furnace in an argon atmosphere and then homogenized in a vacuum of 10^{-4} Pa at 1000°C for 24 h. Isotopically enriched ^{57}Fe was used because Mössbauer studies of the hydrides were to be performed; these will be reported elsewhere. Samples of 0.2 mm thickness were cut from the ingot with an abrasive wire saw, cold rolled to 0.02 mm and annealed in vacuum for stress relief at 1000°C for

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10 min and cooled within the furnace at approximately $-5^{\circ}\text{C min}^{-1}$.

The samples were hydrogenated by a 24 h exposure to a hydrogen atmosphere at 325°C and pressures up to 9 GPa with subsequent cooling to 120 K. The method of hydrogenation is described elsewhere [4]. The pressure was determined with an accuracy of about 5%, the temperature to within $\pm 7^{\circ}\text{C}$.

At ambient pressure, the hydrides thus obtained did not lose the hydrogen at temperatures below 200 K. To avoid hydrogen losses, the samples were handled at temperatures not higher than 100 K. When not in use, they were stored in liquid nitrogen.

The X-ray studies of the samples were performed at 100 K by a photographic technique with a DRON-2.0 diffractometer using Fe $K\alpha$ radiation. The hydrogen content of the samples was determined with an accuracy of 1% from the amount of hydrogen liberated during their decomposition at temperatures up to 200°C .

3. Results and discussion

The X-ray examination showed that the initial $\text{Co}_{99.8}\text{Fe}_{0.2}$ samples consisted of a mixture of approximately equal amounts of the h.c.p. ϵ phase with the lattice parameters $a_0 = 2.507 \text{ \AA}$ and $c_0 = 4.067 \text{ \AA}$, and the f.c.c. γ phase with $a_0 = 3.540 \text{ \AA}$. The presence of the metastable γ phase is attributed to the decrease in the temperature of the $\epsilon \rightarrow \gamma$ phase transformation in cobalt due to alloying with iron [5]. Indeed, the γ phase was also observed in some of the ^{57}Fe -doped cobalt foils used in our earlier Mössbauer studies of cobalt hydrides [6,7]. In those specimens, however, the f.c.c. phase had already completely disappeared after exposure of the samples to hydrogen pressures of 2–3 GPa, which resulted in hydrogen concentrations in the f.c.c. phase of few atomic percent only.

In the present work, according to the X-ray data, the fraction of the γ phase in the initial $\text{Co}_{99.8}\text{Fe}_{0.2}$ alloy samples was higher than in the samples studied previously [6,7] and, more importantly, this fraction was still largely unchanged after hydrogenation at 325°C and pressures as high as 5–6 GPa. Therefore, we were able to study the interstitial solutions of hydrogen which form on the basis of the γ phase in the T - P_{H_2} region where these γ solutions are not thermodynamically stable and should transform to the ϵ solutions if equilibrium were attained.

In order to be sure that the difference in the thermal stability of the γ phase in the samples studied now and in those used in the previous work [6,7] was not caused by a contamination of the samples with impurities other than iron, the rolled and annealed foils were examined by an electron microprobe. No traces

of any other metals but Co and Fe were detected, and the iron was found to be uniformly distributed in the cobalt matrix.

Fig. 1 shows the results of the X-ray examination of the $\text{Co}_{99.8}\text{Fe}_{0.2}$ samples after their exposure to high hydrogen pressures. The volume per metal atom V_a in transition metal hydrides is known to increase approximately linearly with increasing hydrogen-to-metal ratio. The value of $\partial V_a / \partial n$ is close to 2 \AA^3 for all these hydrides [4,8–10]. As can be seen from Fig. 1(b), the ΔV_a values for the γ solutions are small at pressures below 4–4.5 GPa, increase steeply between 4.5 and 5.5 GPa, and continue to increase, but much more slowly, at higher pressures. One can thus conclude that the hydrogen solubility in γ -Co rises rapidly within a relatively narrow pressure interval between 4.5 and 5.5 GPa. The occurrence of a sample with an intermediate value of the volume expansion of the γ phase ($\Delta V_a = 0.67 \text{ \AA}^3$ per Co atom at $P_{\text{H}_2} = 5.2 \text{ GPa}$) suggests that in this interval one observes a supercritical anomaly rather than a first order isomorphous phase transformation from the γ_1 to the γ_2 phase.

A decrease in the rate of hydrogen diffusion in the supercritical region [11] may explain the noticeable scatter in the experimental data on the lattice parameters (Fig. 1) and on the mean hydrogen content (Fig. 2) of the corresponding samples, because these might still not have reached equilibrium after the 24 h exposure to hydrogen pressures in the vicinity of the supercritical anomaly. The dashed curve in Fig. 2 shows the change of the mean hydrogen content of $\text{Co}_{99.8}\text{Fe}_{0.2}$ -H samples expected on the basis of the X-ray data and

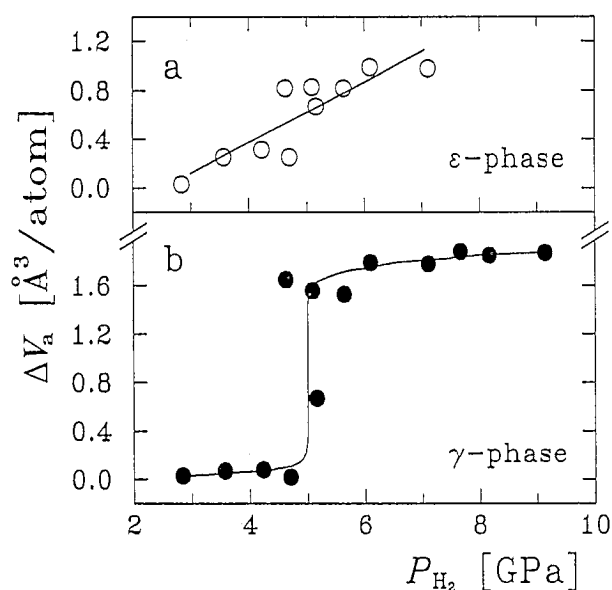


Fig. 1. Increase in the volume per metal atom ΔV_a at ambient pressure and 100 K for the h.c.p. (ϵ) and f.c.c. (γ) modifications of a $\text{Co}_{99.8}\text{Fe}_{0.2}$ alloy loaded with hydrogen at 325°C and the hydrogen pressures given on the abscissa.

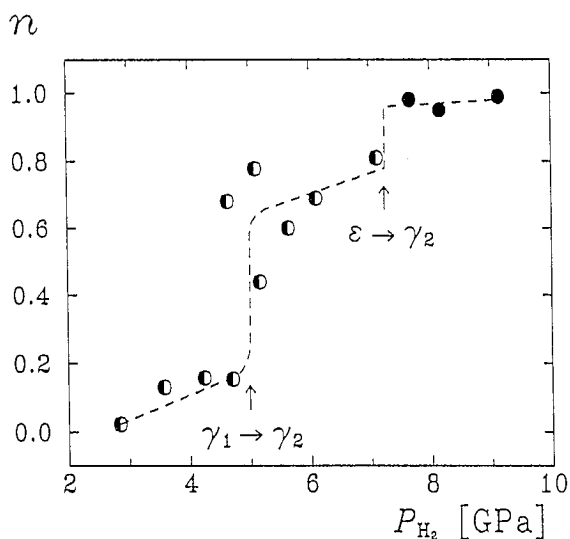


Fig. 2. Hydrogen-to-metal atomic ratio n for the $\text{Co}_{99.8}\text{Fe}_{0.2}\text{-H}$ samples produced by a 24 h exposure at 325°C to the hydrogen pressures indicated on the abscissa. Filled circles stand for single phase γ solid solutions, half-filled circles for two phase $\varepsilon + \gamma$ mixtures. The dashed curve represents the $n(P_{\text{H}_2})$ dependence expected under the conditions described in the text.

the plausible assumptions that (i) the dependences of ΔV_a on (P_{H_2}) for the ε and γ solutions are as shown by solid lines in Fig. 1; (ii) the hydrogen concentrations in these solutions are given by $n^\varepsilon = \Delta V_a^\varepsilon / 1.8$ and $n^\gamma = \Delta V_a^\gamma / 1.9$ as follows from the X-ray data for the pure Co-H solutions [4]; (iii) the $\varepsilon \rightarrow \gamma$ transition occurs at 7.2 GPa, also as for the pure Co-H solutions [3,4], and (iv) the samples synthesized at $P_{\text{H}_2} < 7.2$ GPa contain equal amounts of the ε and γ phases. The latter is at least in qualitative agreement with the X-ray patterns obtained for the respective samples. As can be seen from Fig. 2, the experimentally determined hydrogen contents roughly follow the prediction of the dashed curve, albeit with a considerable scatter, as was already discussed above. The fair agreement between the data points and the dashed curve in Fig. 2 shows that the assumptions made above are reasonably well fulfilled.

The observed supercritical anomaly of a $\gamma_1 \rightleftharpoons \gamma_2$ transformation in the $\text{Co}_{99.8}\text{Fe}_{0.2}\text{-H}$ system is quite pronounced and one does not expect that it would disappear if the 0.2 at.% Fe were removed from the samples. Hence, such an anomaly should also be observed to exist in the γ solutions of hydrogen in pure cobalt, if these were sufficiently stable. It is, however, questionable to what extent the position of this anomaly in the $T\text{-}P_{\text{H}_2}$ diagram would shift on removal of the iron. In fact, the alloying of cobalt with 0.2 at.% Fe strongly hinders the $\gamma \rightarrow \varepsilon$ transition both in the starting metal and in the hydrogen solutions on its basis, and it is this effect that permitted the present investigation. Therefore, one could not exclude that this alloying also essentially affects other transitions in

the Co-H system. In the following we will give some arguments why the position of the $\gamma_1 \rightleftharpoons \gamma_2$ supercritical anomaly in the phase diagram of the iron-free Co-H system should not differ much from that observed in the $\text{Co}_{99.8}\text{Fe}_{0.2}\text{-H}$ system.

First of all, the behaviour of the ε phase in the $\text{Co}_{99.8}\text{Fe}_{0.2}\text{-H}$ samples under high hydrogen pressures is practically the same as that of the ε phase in the pure Co-H system. In particular, the pressure dependence of the hydrogen solubility in $\varepsilon\text{-Co}_{99.8}\text{Fe}_{0.2}$ at 325°C derived as above from the linear approximation of the $\Delta V_a(P_{\text{H}_2})$ dependence (solid line in Fig. 1(a)), is practically the same as in pure $\varepsilon\text{-Co}$ [3]. Moreover, the pressures of the $\varepsilon \rightarrow \gamma$ phase transformation at 325°C also coincide in the $\text{Co}_{99.8}\text{Fe}_{0.2}\text{-H}$ and Co-H systems within the limits of experimental error. At temperatures between 250 and 350°C , the $\varepsilon \rightarrow \gamma$ transformation in the Co-H system occurs at 7.0–7.5 GPa [3,4]. In the $\text{Co}_{99.8}\text{Fe}_{0.2}\text{-H}$ system at 325°C , the ε phase transforms to the γ phase in the same pressure interval, as is shown by the disappearance of its lines in the X-ray photographs (Fig. 1(a)) and by an increase in the average hydrogen content of the samples from $n \approx 0.8$ to $n \approx 0.95\text{--}0.98$ (Fig. 2).

One more indication that alloying of Co with 0.2 at.% Fe does not essentially affect the $\gamma_1 \rightleftharpoons \gamma_2$ phase transformation in the Co-H system, comes from the results of earlier studies of Ni and f.c.c. Ni-Co alloys with 5, 10 and 60 at.% Co at high hydrogen pressures [4,12]. In the Ni-H system, the hydrides have the same f.c.c.-type metal lattice as hydrogen-free nickel, and the line of the $\gamma_1 \rightleftharpoons \gamma_2$ phase transformation in the $T\text{-}P_{\text{H}_2}$ diagram terminates at a critical point near 390°C and 1.8 GPa [4]. The alloying of Ni with Co shifts the line of the $\gamma_1 \rightleftharpoons \gamma_2$ transformation to higher pressures and decreases the critical temperature below 325°C for the alloy with 60 at.% Co [4,12]. The points in Fig. 3 represent isothermal sections of the $T\text{-}P_{\text{H}_2}$ diagrams of the Ni-Co-H and $\text{Co}_{99.8}\text{Fe}_{0.2}\text{-H}$ systems at 325°C . As is seen from Fig. 3, the pressure of the $\gamma_1 \rightleftharpoons \gamma_2$ supercritical anomaly observed in the $\text{Co}_{99.8}\text{Fe}_{0.2}\text{-H}$ system agrees well with the value expected in the Co-H system if the pressure at which the $\gamma_1 \rightleftharpoons \gamma_2$ transformation and the corresponding supercritical anomalies occur in the Ni-Co-H solutions depends linearly on the cobalt content of the starting Ni-Co alloys.

An extrapolation from Ni-Co alloys to pure cobalt also suggests that the line of the $\gamma_1 \rightleftharpoons \gamma_2$ phase transformation in the Co-H system terminates in a critical point below 325°C (again as in the $\text{Co}_{99.8}\text{Fe}_{0.2}\text{-H}$ system) and that the supercritical anomalies at higher temperatures lie on a curve that does not differ much from a vertical line at $P_{\text{H}_2} = 5$ GPa. The hatched area in Fig. 4 schematically shows the region in the $T\text{-}P_{\text{H}_2}$ phase diagram where the hydrogen concentration in

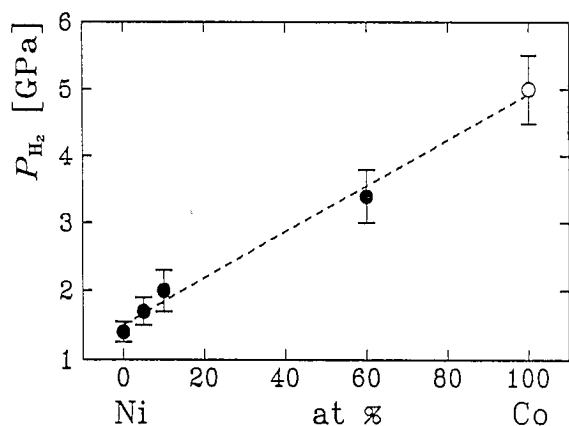


Fig. 3. Hydrogen pressures of the $\gamma_1 \rightleftharpoons \gamma_2$ phase transformation at 325°C in the systems Ni-H [4], Ni₉₅Co₅-H and Ni₉₀Co₁₀-H [12], and of the corresponding supercritical anomaly in the systems Ni₄₀Co₆₀-H [4] and Co_{99.8}Fe_{0.2}-H (present work) as a function of the Co concentration in the starting alloys.

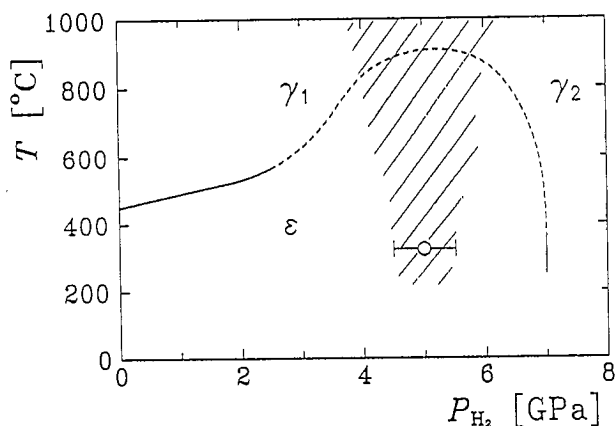


Fig. 4. Tentative T - P_{H_2} phase diagram of the Co-H system. The solid lines represent the two portions of the $\epsilon \rightarrow \gamma$ boundary measured experimentally [4]. The dashed line schematically shows the behaviour of this boundary in the unexplored region. The open circle marks the position of the $\gamma_1 \rightleftharpoons \gamma_2$ supercritical anomaly in the Co_{99.8}Fe_{0.2}-H system determined in the present work. The hatched area schematically depicts the expected region of supercritical anomalies in the γ solutions of hydrogen in Co.

the γ solutions of hydrogen in cobalt is expected to change most steeply with pressure.

The difference in the hydrogen solubilities in ϵ -Co and γ -Co allows one to speculate about the shape of the stable T - P_{H_2} phase diagram of the Co-H system [4]. Owing to the large specific volume of molecular hydrogen, the formation of the Co-H solid solutions is accompanied by a decrease in the specific volume v of the system Co + H₂. The specific volumes of the ϵ and γ solid Co-H solutions are close to one another at any attainable hydrogen concentration [4]. Hence, owing to the $\int v dP$ term in the Gibbs free energy, the thermodynamic equilibria will be shifted with increasing pressure towards the formation of the solution in

which the hydrogen solubility is higher at given T and P_{H_2} .

As follows from the X-ray data in Fig. 1 and the discussion above, the hydrogen solubility at 325°C is highest in ϵ -Co at $P_{H_2} < 4$ GPa and in γ -Co at $P_{H_2} > 6$ GPa. Since the supercritical anomaly of the $\gamma_1 \rightleftharpoons \gamma_2$ transformation at 325°C is large, a substantial increase in the hydrogen solubility can also be expected to occur in a relatively narrow pressure interval at much higher temperatures (hatched region in Fig. 4). Thus, at $P_{H_2} \ll 4$ GPa the hydrogen solubility in ϵ -Co will be higher than in γ -Co up to high temperatures. The temperature interval where the ϵ phase is stable should therefore increase with pressure. This corresponds to an increase in the temperature T_γ of the $\epsilon \rightarrow \gamma$ transition in the Co-H system relative to its value in an inert medium at the same pressure. At pressures above that of the supercritical anomaly, the γ phase will contain more hydrogen and hence be favoured. This should result in an increase of the temperature interval of thermodynamic stability of the γ phase and thus in a decrease of the temperature T_γ at which it forms. Near the pressure of the anomaly, i.e. somewhere between 4 and 6 GPa, the temperature of the $\epsilon \rightarrow \gamma$ transition should therefore reach a maximum and then decrease to 350–250°C at 7–7.5 GPa, where the transition is in fact observed.

The described possible behaviour of the dependence of T_γ on P_{H_2} in the unexplored region of the stable phase diagram is shown in Fig. 4 as a dashed curve smoothly connecting the experimentally determined portions of this dependence, which are depicted by solid lines. One should note, however, that this curve reflects the topology of the Co-H phase diagram only qualitatively, while the real values of T_γ at pressures between 2.5 and 7 GPa may be quite different from those shown in Fig. 4.

4. Conclusions

An extrapolation from the behaviour of the Co_{99.8}Fe_{0.2}-H and of the Ni-Co-H systems shows that an isomorphous phase transformation should occur at high hydrogen pressures in metastable solid solutions of hydrogen in the f.c.c. (γ) modification of cobalt. The critical temperature of the transformation is below 325°C. The curve of the supercritical anomalies of this transformation in the T - P_{H_2} diagram of the Co-H system is expected to be close to a vertical line at $P_{H_2} = 5$ GPa.

These findings allow a prediction (Fig. 4) of the qualitative behaviour of the phase equilibrium between the ϵ (h.c.p.) and γ phases in the Co-H system. The curve suggested in Fig. 4 incorporates two sec-

tions previously [4] observed experimentally at pressures below 2.5 GPa and near 7 GPa. The hatched area outlines the expected region of supercritical anomalies in the γ solutions of hydrogen in cobalt in the thermodynamically stable state above the line of the $\varepsilon \rightleftharpoons \gamma$ transformation and in the metastable state below this line.

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