High pressure phase diagrams of transition metal-hydrogen systems

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Phase diagrams of a series of 3d transition metal-hydrogen systems have been studied over a wide range of hydrogen pressure (≤ 5 GPa) and temperature (≤ 1100 ^{o}C), using X-ray diffraction spectrometer MAX80. High-pressure hydrogen was generated by thermal decomposition of an internal hydrogen source ($NaBH_4$ + $Ca(OH)_2$), and was sealed in a miniature NaCl capsule together with a metal sample.

Results obtained for Mn-H and Fe-H systems are shown in Figs.1 and 2. Characteristic features can be summarized as follows: (1) The metal lattice is transformed into close-packed structures at reasonably low hydrogen pressures of a few GPa. (2) The close-packed structure appears in the order hcp→(dhcp)→fcc with increasing temperature. (3) A drastic reduction of the melting point takes place.

To the right of the Periodic Table, the fcc structure of Co is strongly stabilized with respect to the hcp structure by dissolution of H, and the structure of Ni-H alloys is always fcc but undergoes separation into two phases having different H concentrations. H concentrations of these phases are [H]/[M] ≤ 1.0. To the left of the Periodic Table, Cr shows very similar overall features, but V and Ti form more complex phase diagrams containing higher hydrides having fcc and bct structures [1].

It should be added that, in the course of these experiments, a gradual lattice contraction was often observed in the fcc phase at high temperatures; The lattice parameter decreased by a few % over several hours [2,3]. This phenomenon is interpreted as being due to the formation of superabundant metal-atom vacancies, amounting to ~ 10 at% [3,4]. Evidence of vacancy formation of comparable magnitude in bcc phases was also obtained from other experiments [2,5]. One of the important implications of superabundant vacancy formation in the present context is that the real stable structure of M-H systems is the defect structure containing a large number of vacancies, and phase diagrams reported heretofore are metasatable ones.

The experiments are still in progress, and will be published in due course.

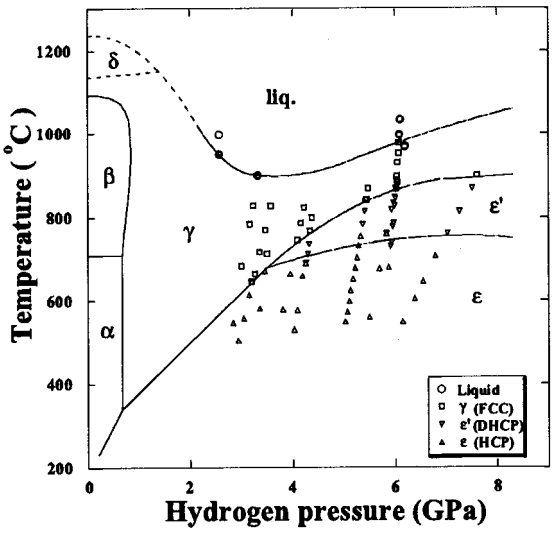

Fig.1 Phase diagram of Mn-H system as a function of hydrogen pressure and temperature. Crystal structures are: α (complex cubic), β (complex cubic), γ(fcc), δ (bcc), ε(hcp), ε ' (dhcp).

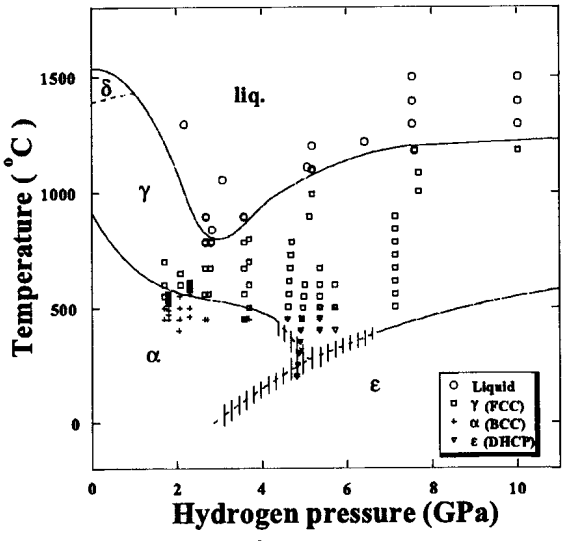

Fig.2 Phase diagram of Fe-H system as a function of hydrogen pressure and temperature. Crystal structures are: : α(bcc), γ(fcc), δ (bcc), ε (dhcp).

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References

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