STABILITIES, STOICHIOMETRIES AND SITE OCCUPANCIES IN HYDRIDES OF INTERMETALLIC COMPOUNDS

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ABSTRACT

In the literature, one can find numerous attempts to explain the observed stabilities, stoichiometries and site occupancies in hydrides of the various families of intermetallic compounds. Some of the approaches to these problems are critically reviewed here. For some, but not all such hydrides, the stabilities have been shown by different researchers to correlate with the enthalpy for formation of the intermetallic compound, itself, or with cell size, or electronic properties, or elastic properties. It appears, therefore, that all of these effects may play a role, but none is dominant in all cases. The development of the procedure for qualitative and quantitative determinations of H-site occupancy from calculations of enthalpies for the formation of imaginary binary hydrides was reviewed. Such inspection raises the question of possible fortuitous agreement between experimental observations and predictions arising from the technique. The concepts of minimum hole size for H occupation and minimum H-H distance in stable hydrides of metals or intermetallic compounds have been discussed in terms of their importance to preferred H sites and to stoichiometry, and considerations necessary to a geometric model have been outlined. The model is used to rationalize observed H sites and stoichiometry of LaNi₅Hₓ. The review points up the need for theoretical treatment leading to fundamental understanding of such systems.

INTRODUCTION

Some intermetallic compounds absorb almost no hydrogen, even under very high H₂ pressure, while others absorb as much as, or more
than, two H atoms per metal atom under only moderate H$_2$ pressure, and still others absorb intermediate amounts of hydrogen. Numerous studies have been conducted to gain an understanding of the factors that influence the hydriding behavior of the various intermetallic compounds in terms of their stability, their stoichiometry and the preferred interstitial sites for occupation by H.

In a pioneering report, Beck$^1$ stated, "One of the purposes of this investigation was to amass a wealth of information concerning the hydriding characteristics of intermetallic compounds as a means for discovering some of the factors which govern hydride formation". From his compilations, he concluded that several of the structure types seemed to have critical lattice parameters, i.e., minimum cell sizes, for hydride formation. "An attempt was made to relate these apparent critical parameters to various factors such as electronegativity, valence, electron transfer and the mechanism and temperature of formation. However, the only variable which appeared to be of significance was the size factor itself." Because it was assumed that the relative size of any interstice within a given structure type would be proportional to the overall size of the unit cell, it was concluded that there must be a critical hole size for each structure type below which hydrogen occlusion would not occur.

In his review, Oesterreicher$^2$ concluded that the influence of size is beyond doubt, but, often, it is not possible to distinguish clearly between size and electronic effects as both vary periodically with atomic number. An early attempt to explain the stoichiometry of metal hydrides was made by Robins$^3$, who assumed that H contributes electrons to the metal (protonic theory). Energy band calculations$^4$ show, however, that the addition of hydrogen to a metal introduces new states, below the Fermi level of the metal, that can be filled with the added electrons. Switendick$^5$ has treated the case of simultaneous occupation of tetrahedral and octahedral interstices in YH$_x$ with $2 < x < 3$. Addition of H's to octahedral interstices changes the band structure importantly. Each hydrogen added lowers one band that was already partially filled. There is little difference in charge on the octahedral and tetrahedral interstices, but that charge is significantly greater than that of a comparable atomic sphere; thus, the protonic model is simply not applicable.

Maeland et al.$^6$ have demonstrated the importance of the availability of appropriate sites to H-absorption capacity by studying both amorphous and crystalline hydrides of TiCu. Amorphous TiCu absorbs H to a composition of TiCuH$_{1.35}$ at room temperature and one atmosphere H$_2$ pressure compared with a composition of TiCuH for crystalline TiCu. They suggest that, possibly, the maximum hydrogen capacity is determined by electronic structure, which probably would not be greatly different for the amorphous and crystalline structures, but the number, type and size of the available interstices