SHORT PAPER

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The role of the site sizes in hydridation of Laves phases (C14)[†]

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New materials, especially AB_2 substituted compounds are able to form reversible hydrides and are good candidates to substitute the cadmium in rechargeable nickel–cadmium batteries. These systems have been the subject of several theoretical and experimental studies, particularly concerning the reaction between hydrogen and the Laves phases(C14) containing zirconium. We have shown previously that the A_2B_2 site size is the basic criterion which allows manipulation of the characteristic properties (kinetic and thermodynamic) of intermetallic compound hydrides $Zr(M_xCr_{1-x})_2$ with M=Fe, Ni. In order to generalise the validity of our criterion, we have extended our study to other Laves phases (C14) in the literature. The results are found to be in good agreement.

Keywords: reversible hydrides, Laves phases, site sizes

Laves phases (C14) are defined as AB_2 type compounds adopting a compact hexagonal structure of the $MgZn_2$ type. In these structures, although the ratio of atomic radii r_A/r_B of 1.225 is expected, in reality the ratio varies between 1.08 and 1.68[1] for known phases. The sites encountered in these systems are tetrahedral distributed in three different environments: two A_2B_2 types, four AB_3 types and one B_4 type. The hydride of these Laves phases preserves the structure of the initial intermetallic compounds.[2,3] In a compact hexagonal structure,[2] hydrogen possesses an atomic radius r_H=0.37 Å, thus requiring the receiving site radius to be larger than this value.

The interstice size is related to the stability of the hydride.[4,5] Westlake[5] showed that in stable hydrides, the hydrogen is situated in the sites having a radius higher than 0.4 Å.

In intermetallic compounds,[5] the absorption of hydrogen by sites having a sufficient size leads to an increase of the lattice volume by about 20% and consequently, to an increase of the size of the other sites.

Generally, since they have a larger size site and their environment is more favorable for hydrogen absorption, A_2B_2 sites are first occupied.[6,7] Once the A_2B_2 sites occupation is complete, a part of the AB_3 sites is occupied. On the other hand B_4 sites are never occupied.[8] Indeed if all sites having a radius superior to 0.4 Å were occupied, one would measure a hydrogen storage capacity far greater than the one which is usually determined. Switendik[9] determined that the distance between hydrogen atoms d_{H-H} is higher than 2.1 Å in the known metallic hydrides, and that all sites sharing a face can not be occupied simultaneously. Consequently, no more than six sites can be occupied in the same lattice.

The occupied interstitial sites in Laves phases (C14) structure have been determined by neutron diffraction on $ZrMn_2D_3$,[10] $Zr\ (Fe_xCr_{1-x})_2D_x$ [11] and $CeMn_{1.5}Al_{0.5}D_x$.[12] The results obtained show that the deuterium is first located in A_2B_2 sites, and when the concentration becomes greater than 2D/formula, the AB_3 site sizes become superior to 0.4 Å, which makes them also accessible to deuterium.

In a previous investigation,[13] we have shown that the A_2B_2 site size is the basic criterion which allows one to manipulate the characteristic properties (kinetic and thermodynamic) of intermetallic compound hydrides $Zr(M_xCr_{1-x})_2$ with M = Fe, Ni. In order to generalise the validity of our criterion, we have extended our study to other Laves phases (C14) reported in the literature. The results are found to be in good agreement.

Experimental

The samples were prepared and characterised by the “Laboratoire de chimie metallurgique des terres rares, Meudon-Bellevues (France)”. The kinetic and thermodynamic measurements have been carried out by micro-thermo-gravimetry with a sensitivity equal to 2 µg. This device allows, on one side operation in a wide pressure (l0^{-8} – 60 bars) and temperature (20 – 600 °C) range and on the other hand, small sample quantities (10 to 50 mg). Such small quantities avoids thermal dispersion problems and facilitates hydrogen diffusion through the sample particles. We used “U” hydrogen produced by “Air Liquide”. In order to eliminate traces of oxygen and water, an oxisorb fifter was placed between the hydrogen bottle and the regulator manometer.

Results and discussion

We have mentioned above that the mean site sizes, particularly of A_2B_2 type, are the determining factor of the hydriding characteristics of this alloy family. It has been shown[13] that it is possible to establish a linear law connecting the kinetic and thermodynamic parameters to the average size of A_2B_2 sites for the studied compounds.

To test the validity of this criterion, we have represented the average values of A_2B_2 site radii of some Laves phases (C14) found in literature, versus their corresponding enthalpies and activation energies, in order to compare the position of the these points with the linear law. Figures 1, 2 and 3 show that the data found in literature are very close to the straight line drawn for ΔH_{abs}, ΔH_{des} and E_a as a function of the average A_2B_2 site sizes in the case of $Zr(M_xCr_{1-x})_2$ compounds. Thus these results confirm the validity of the criterion connecting the site sizes to the kinetic and thermodynamic properties of these hydrides.

In summary, one can say that the A_2B_2 site sizes is the basic parameter that allows to determine the hydriding characteristics of the Laves phases (C14).

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

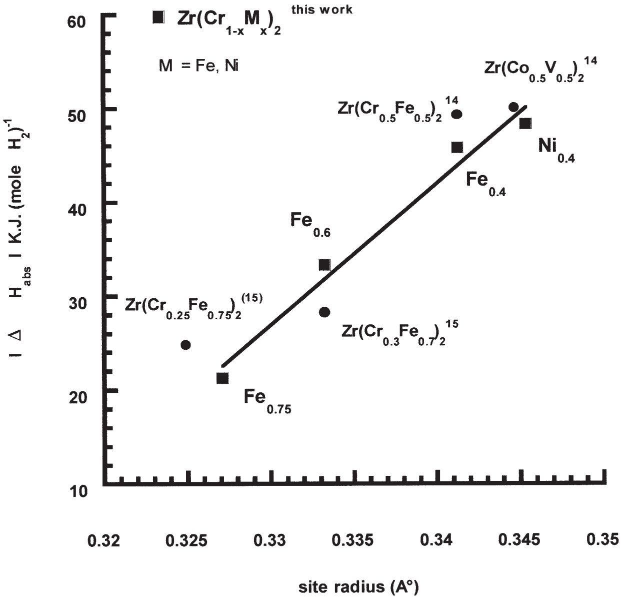

Fig.1 Diagram of ΔH_{abs} (desorption enthalpy) versus A_2B_2 site radius.

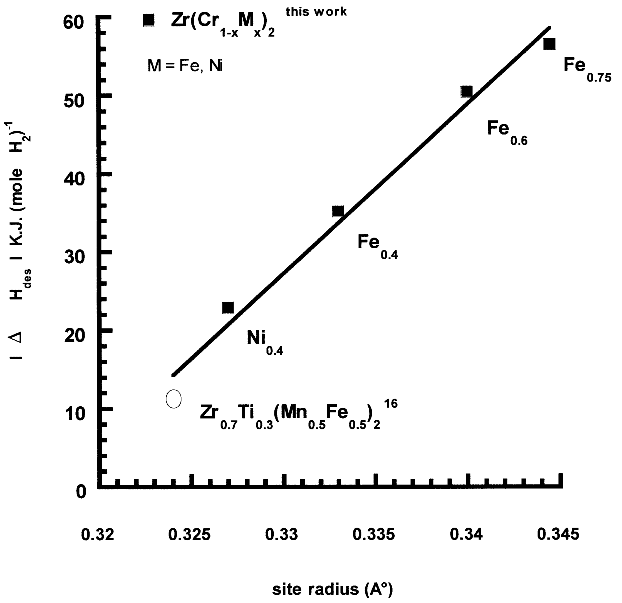

Fig.2 Diagram of ΔH_{des} (absorption enthalpy) versus A_2B_2 site radius.

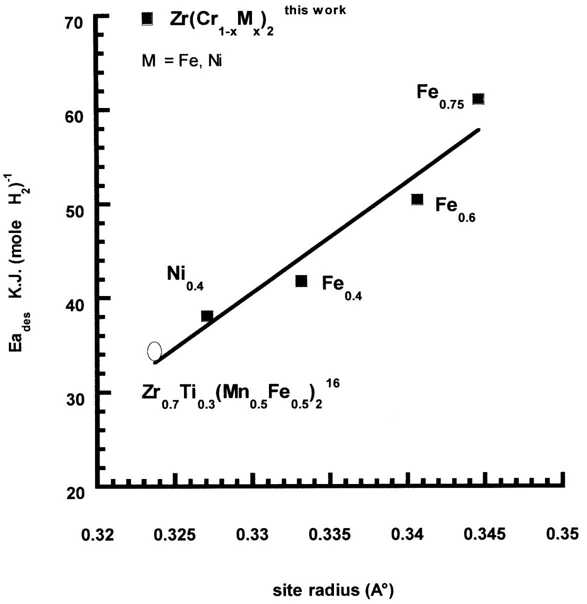

Fig.3 Diagram of Ea_{des} (activation energy) versus A_2B_2 site radius.

Conclusion

The crystallographic, thermodynamic and kinetic characteristic studies of Laves phases (C14), indicate that the site size particularly in A_2B_2 sites) is the determining factor to describe their hydriding behavior.

Thus, by application of this model, all parameters of these hydrided compounds vary linearly with the A_2B_2 site sizes. Moreover, the extension of this model to the other compounds found in the literature showed a satisfactory agreement. It is therefore possible, by the application of this criterion to determine the hydriding enthalpy and the hydriding activation energy of some Laves phases (C14) when the size of their A_2B_2 sites are known.

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