PHASE SEPARATION IN HYDRIDES OF Zr_2Ni

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Room temperature X-ray and Mössbauer measurements show three single phase fields for hydrogen concentrations up to $Zr_2NiH_{5.1}$. Narrow two phase regions exist around $Zr_2NiH_{4.1}$ and between $Zr_2NiH_{4.9}$ and $Zr_2NiH_{5.1}$. Hydrogen effusion curves at constant pressure indicate two different desorption stages with activation energies of 50 kJ $(mol\ H_2)^{-1}$ and 110 $kJ(mol\ H_2)^{-1}$ which are in general agreement with theoretical values.

1. Introduction

The ability of Zr-based intermetallic compounds such as Zr_3Fe [1] and Zr_2Ni [2] to absorb large amounts of hydrogen is reflected by the strong interest shown in their structural [3] and dynamic [4–6] properties in recent years. Hydrides of Zr_2Ni have attracted particular interest with, for example, the activation energies for hydrogen diffusion being determined by nuclear magnetic resonance [4,6] and perturbed angular correlation [5] measurements and structural and hydrogen site aspects being studied by neutron diffraction [3].

Following on from an investigation of the effect of hydrogen charging on the Mössbauer spectrum of Zr_2Ni doped with ^{57}Fe [2], here we report details of the structural and spectral changes occurring in a wide range of hydrogen concentrations up to $Zr_2NiH_{5.1}$. The earlier work established that the ^{57}Fe probe atoms are located at the Ni sites in the lattice [2]. The X-ray and Mössbauer measurements reveal individual hydride phases. These results are supported by temperature resolved hydrogen effusion measurements on a sample of $Zr_2NiH_{4.7}$.

2. Experimental

The preparation of the Zr_2Ni ingots and the hydrogen charging procedure at ambient temperature and pressure not exceeding atmospheric pressure have been described in earlier publications [2,4]. The hydrogen concentrations of the samples were determined by the hot extraction method using a gas chromatograph. All Mössbauer spectra were recorded in transmission geometry with ^{57}Co in Rh sources. The isomer shift values are given with respect to the centre of an α-Fe spectrum at room temperature.

3. Results and discussion

3.1. X-RAY AND MÖSSBAUER

The X-ray diffraction measurements showed that hydrides of Zr_2Ni retain the tetragonal $CuAl_2$ structure up to hydrogen concentrations of $Zr_2NiH_{4.9}$. For $Zr_2NiH_{5.1}$ the diffraction pattern is more complex indicating lower symmetry or larger volume of the unit cell. Similar changes were found in the room temperature neutron diffraction data of the deuteride $Zr_2NiH_{4.8}$ [3]. They have been interpreted in terms of an orthorhombic deuterium superstructure with the unit cell dimensions approximately doubled in the a and c directions while b remains constant. However, the number of peaks in the X-ray pattern of $Zr_2NiH_{5.1}$ exceeds that expected for an orthorhombic distortion of the metal sublattice. We find better agreement with a monoclinic distortion of the basal plane of the formerly tetragonal unit cell. Figure 1 shows the lattice parameters a and c for the hydrides studied. A monotonic increase in lattice constants, consistent with the lattice expansion expected on hydrogen uptake, is observed up to Zr_2NiH_4. At the concentration $Zr_2NiH_{4.1}$ a narrow two phase region is encountered where discrete jumps in the a and c values can be observed while the lattice symmetry
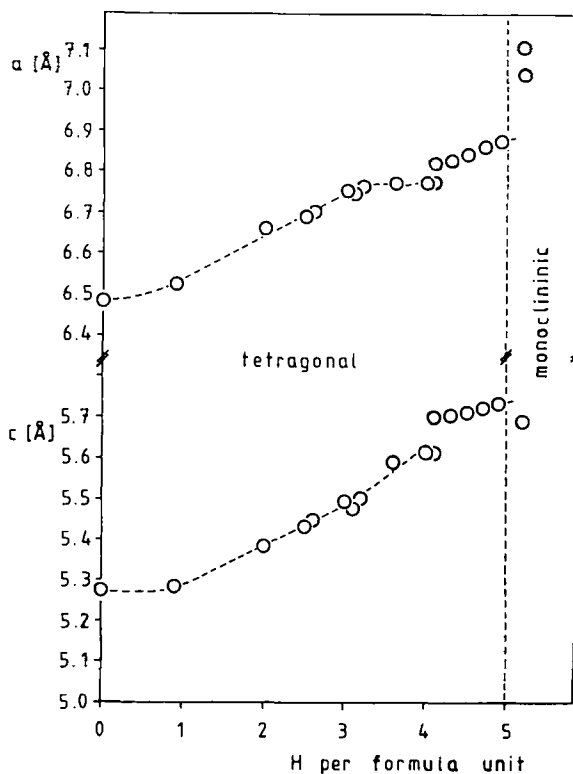

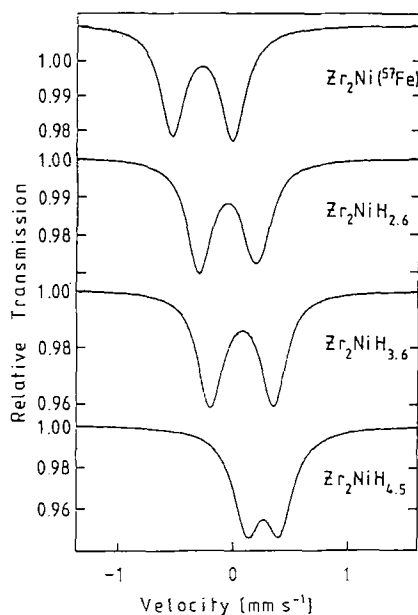Fig. 1. The lattice parameters a and c of Zr_2Ni hydrides as a function of hydrogen concentration.

Fig. 2. The room temperature Mössbauer spectra of Zr_2Ni, $Zr_2Ni\,H_{2.6}$, $Zr_6NiH_{3.6}$ and $Zr_2NiH_{4.5}$.

itself remains unchanged. It is not until the composition $Zr_2NiH_{5.1}$ is reached that the monoclinic distortion of the metal sublattice is observed.

Figure 2 shows the room temperature Mössbauer spectra for several samples. All spectra of single phase samples are well described by one quadrupole doublet of isomer shift (IS) and quadrupole splitting (QS) values presented in figs. 3 (a) and (b). As discussed previously [2] the monotonic increase in IS with hydrogen concentration to Zr_2NiH_4 reflects volume expansion as well as charge transfer effects. The distinct jump in both IS and QS values at $Zr_2NiH_{4.1}$ is further evidence of the coexistence of two phases around this hydrogen concentration. The phase equilibrium of this sample becomes clearer on varying the temperature. Figure 4 shows the Mössbauer spectra of $Zr_2NiH_{4.1}$ over the temperature range 77–430 K. Only one phase is observed at high temperatures as indicated by the single quadrupole doublet used to fit the 430 K spectrum (fig. 4 (a)). The lower temperature spectra however can only be described using two doublets (figs. 4(b), (c) and (d)). The individual QS values of the subspectra remain approximately constant with only their fractional areas changing.

In considering the variation of the QS value with hydrogen concentration (fig 3(b)), this behaviour reflects the changes in the immediate environment of the probe [57]Fe atom as the hydrogen atoms occupy the various interstitial sites available in the $CuAl_2$ lattice. As already noted the [57]Fe atoms occupy Ni sites in the lattice [2]. Following the hydrogen site occupation model considered for the related Hf_2Ni hydrides [7] and neutron diffraction on Zr_2Ni deuterides [3], hydrogen concentrations up to Zr_2NiH_2 can be explained by assuming only 16 1
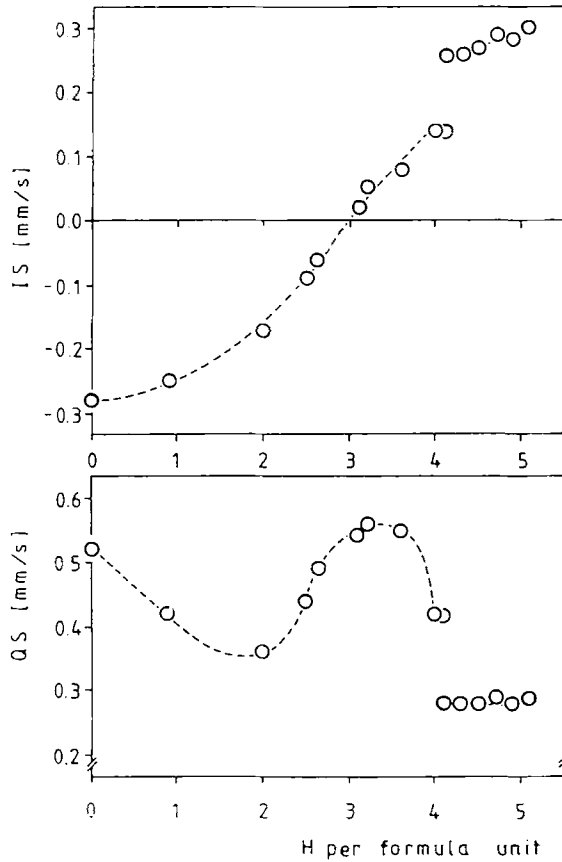
Fig. 3. (a) Variation of the isomer shift (IS) and (b) the quadrupole splitting (QS) with hydrogen content for the room temperature spectra of Zr_2Ni hydrides.

type interstitial site occupation. Then 32 m sites become large enough to accomodate hydrogen atoms and their exclusive occupation (keeping mutual hydrogen distances larger than 2.1 Å [8]) would account for the composition Zr_2NiH_4. Above this concentration the simultaneous occupation of predominantly 32 m and 4 b (or 8 g with coordinate $z = 0.25$ [3]) sites is consistent with both the preservation of the tetragonal $CuAl_2$ structure and the increase of the lattice constant ratio c/a which is caused by the mutual repulsion of hydrogen atoms. At concentrations above Zr_2NiH_5 the strong hydrogen-hydrogen interaction causes the monoclinic distortion of the lattice.

The concentrations obtained by considering the exclusive occupation of individual sublattices coincide approximately with the hydrogen concentrations at which significant changes in the lattice constants and hyperfine parameters of the Mössbauer spectra are observed. Although a mixed occupation of various sites by deuterium was observed at room temperature the predominant fractions followed the trend outlined above [3]. The apparent insensitivity of the [57]Fe Mössbauer
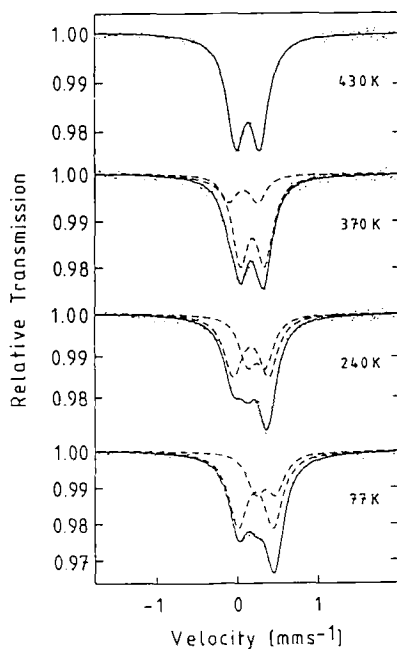
Fig. 4. The Mössbauer spectra of $Zr_2NiH_{4.1}$ at (a) 430 K, (b) 370 K, (c) 240 K and (d) 77 K.

spectra for crystallographic changes at high hydrogen concentrations may be linked with the lesser hydrogen affinity of iron as compared to nickel and will be subject of further investigation [9].

3.2. HYDROGEN EFFUSION

Confirmation of the presence of distinct hydrogen environments with different binding energies was obtained on evolution of the hydrogen from the $Zr_2NiH_{4.7}$ sample. The effusion rate at constant base pressure ($3 * 10^{-2}$ Pa H_2) as a function of temperature for this hydride shows two maxima at 550 K and 750 K (fig. 5(a)). Integration of this curve leads to the isobaric gas effusion curve shown in fig. 5(b) with curves for hydrogen partial pressures of $7 * 10^{-3}$ and $2 * 10^{-1}$ Pa being obtained in a similar way. The curves show that $Zr_2NiH_{4.7}$ remains stable to 450 K before losing approximately one hydrogen atom per formula unit with increasing temperature. This desorption probably corresponds to the surplus of hydrogen when changing the preferred sites of residence from mixed tetrahedra (three Zr and one Ni (32 m)) to pure tetrahedra (four Zr (16 l)). The isothermal time dependence of hydrogen effusion is well described by a monomolecular reaction. The rate constants show Arrhenius type behaviour leading to activation energies of 50 kJ(mol H_2)$^{-1}$ for the lower temperature weakly bound state and 110 kJ(mol H_2)$^{-1}$ for the higher temperature state where the hydrogen is more strongly
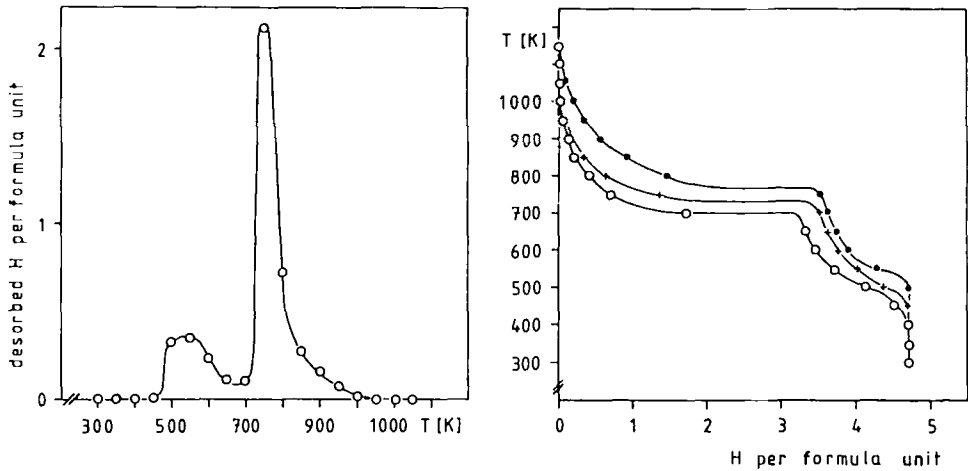
Fig. 5. (a) The hydrogen effusion from $Zr_2NiH4.7$ as a function of temperature ($3*10^{-2}$ Pa H_2), (b) the integrated effusion curves obtained from $Zr_2NiH_{4.7}$ at partial hydrogen pressures of $7*10^{-3}$ Pa (○), $3*10^{-2}$ Pa (+) and $2*10^{-1}$ Pa (●).

bound in the lattice. These values compare well with theoretical values of heats of formation [10,11].

4. Conclusions

The $CuAl_2$ structure of Zr_2Ni is retained with expanded lattice on charging with hydrogen to $Zr_2NiH_{4.9}$. Above this concentration a monoclinic structure of the metal sublattice is observed by X-ray diffraction. Evidence for a narrow two phase region around $Zr_2NiH_{4.1}$ at room temperature has been obtained from X-ray and Mössbauer measurements. Variable temperature Mössbauer spectra (77–430 K) confirmed the presence of the two phases at low temperatures. Two desorption stages were found in the hydrogen effusion curves from a $Zr_2NiH_{4.7}$ sample and the activation energies compare well with theoretical predictions.

References

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