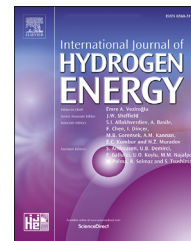


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Peculiarities of hydrogen interaction with alloys of ZrFe₂–ZrMo₂ system

S. Mitrokhin^{*}, V. Verbetsky

Chemistry Department Lomonosov Moscow State University, 119991, Moscow, Russia

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ABSTRACT

The quasi-binary ZrFe₂–ZrMo₂ system is an example of a fairly complex metal system with the structure of the Laves phases. Both ZrFe₂ and ZrMo₂ intermetallic compounds crystallize in the cubic type λ_2 -MgCu₂, for intermediate compositions ZrFe_{2-x}Mo_x an extended region with a hexagonal type of structure λ_1 -MgZn₂ is detected, and also two-phase regions ($\lambda_1 + \lambda_2$). The formation of hydrides in this system under conditions of various pressures and temperatures was investigated in a number of works. In this paper, an attempt was made to summarize all previously obtained results.

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Introduction

The alloys of the Zr–Mo–Fe system find practical application due to their high strength, heat resistance and the presence of ferromagnetic properties. From a fundamental point of view, the Zr–Mo–Fe system is interesting in the existence of a binary compounds with the structure of the Laves phases for all three components - ZrMo₂, ZrFe₂ and MoFe₂ [1]. At 900 °C, the first two have a λ_2 -cubic lattice, and the last - λ_1 -hexagonal. This becomes possible due to the atomic radii ratio of these three metals, ($r_{Zr} = 1.585$, $r_{Mo} = 1.4$, $r_{Fe} = 1.26$). It is known that one of the factors influencing the formation of the Laves phases is the ratio of the radii of metals A and B - $r_A/r_B = 1.04$ – 1.68 [2]. Molybdenum satisfies this condition - $r_{Zr}/r_{Mo} = 1.13$, $r_{Mo}/r_{Fe} = 1.11$ and can occupy both A and B atoms positions in the structures of the Laves phases with zirconium

and iron. The presence of three binary Laves phases in the system leads to the appearance of rather significant regions of solid solutions based on λ_1 and λ_2 phases. So in the quasi-binary system ZrFe₂–ZrMo₂, binary intermetallics crystallize in a cubic λ_2 lattice, for intermediate compositions ZrFe_{2-x}Mo_x a lengthy region with a hexagonal λ_1 -type structure is found, and also two-phase regions ($\lambda_1 + \lambda_2$).

The introduction of hydrogen into the lattice of intermetallic compounds leads to a significant change in their physicochemical properties. The study of the causes of these changes expands the understanding of the nature of the chemical bond. The interaction with hydrogen and the structure of the resulting hydrides based on binary and pseudobinary compounds of the quasi-binary system ZrFe₂–ZrMo₂ under conditions of different pressures and temperatures were carried out in a number of works [3–10]. At the same time, only one specific composition

^{*} Corresponding author.

E-mail address: mitrokhin@hydride.chem.msu.ru (S. Mitrokhin).

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was studied in each work. Therefore, in this paper an attempt was made to generalize all the previously obtained results.

Results and discussion

We briefly recall the main results of the above works. Table 1 shows the experimental conditions and the structural data of the obtained hydrides.

The largest number of works is devoted to the interaction with hydrogen of the $ZrMo_2$ compound. In Ref. [3], at pressures up to 1 atm, in the classical Sieverts glass installation, only a hydrogen solution in $ZrMo_2$ was obtained. Increasing the pressure to 60 atm in a metallic Sieverts-type apparatus at room temperature allowed to obtain a more hydrogen-saturated hydride phase of the $ZrMo_2H_{1.4}$ composition [4]. However, in this case, the type of isotherm testified only to the presence of a hydrogen solution without the characteristic plateau of the formation of β -hydride. With a decrease in the experimental temperature to 173 K authors of [5] assumed the formation of β -, γ - and δ -hydrides of the compositions $ZrMo_2H_{1.3}$, $ZrMo_2H_{2.3}$ and $ZrMo_2H_{2.8}$. They were characterized by a λ_2 -type enlarged lattice compared to the initial intermetallic lattice. An increase in the experimental pressure to 1500 atm [6] using modified Sieverts-type equipment with working pressure up to 3000 atm made it possible to obtain the most hydrogen-saturated hydride with the composition $ZrMo_2H_{4.0}$. According to neutron diffraction data [6], the introduction of hydrogen has led to the transformation of the cubic lattice into the tetragonal one and to the appearance of additional reflections of the tetragonal $I4_1/aO_2$ superstructure. Hydrogen atoms initially occupy positions 96 *g*, which, at its maximum content, are transformed to positions 16*f* with [Zr_2Mo_2] faceting.

Fig. 1 shows the isotherms of hydrogen desorption in the $ZrMo_2$ - H_2 system, obtained in Refs. [3,5,6]. Their joint consideration allows us to draw some conclusions and get an idea of the actual number of hydride phases in the system and their thermodynamic stability.

When comparing the isotherm at 195 K [5] with the isotherms at 273 K [3,6] and 284 K [5], it becomes obvious that in the system under consideration two hydride phases are formed – the β -phase of the dihydride and the γ -phase of the tetrahydride. The temperature near 273 K is critical for the $\beta \leftrightarrow \alpha$ transition is absent on the isotherms at 284 and 273 K [3].

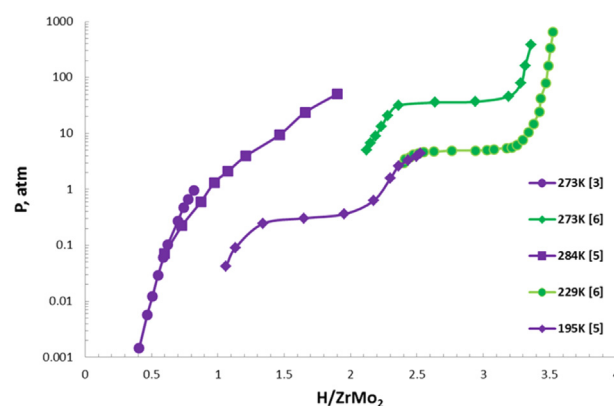


Fig. 1 – Isotherms of hydrogen desorption in the $ZrMo_2$ – H_2 system.

Therefore, the assumption of the authors [5] of the existence of a monohydride phase with a very low dissociation pressure, which is not determined at room temperature due to their instrumental limitations, is erroneous.

Thus, in the case of a $ZrMo_2$, we encounter the phenomenon of the formation of γ -hydride phase, which is rather rare for the Laves phase hydrides. For each case revealed their own peculiarities. For example, in the $TiCr_2$ - H_2 system [10], during the formation of a higher hydride, the lattice changes from the initial λ_2 to the fluorite structure. As noted above, in the case of $ZrMo_2$ - H_2 , the formation of a higher hydride is accompanied by a decrease in lattice symmetry from cubic to tetragonal.

In the $ZrFe_2$ - H_2 system, the hydride phase is formed only at very high experimental pressures [8,9]. X-ray and neutron diffraction analysis of the obtained hydrides showed that the structure of the initial metal matrix does not change upon the formation of hydrides, and hydrogen/deuterium is located in 96 *g* positions with [Zr_2Fe_2] faceting [9].

The only studied composition having a λ_1 structure, $ZrMoFe$, formed the β -hydride phase of composition $ZrMoFeH_{2.5}$ at pressures up to 60 atm and room temperature [4]. According to the data of the neutron diffraction experiment [11], deuterium is located in 6(*h*)₁ and 24(*l*) positions, which have a [$Zr_2(Mo + Fe)_2$] faceting.

The initial composition of $ZrMo_{0.2}Fe_{1.8}$ was a two-phase ($\lambda_1 + \lambda_2$) alloy, the content of the cubic phase in which, according to Rietveld refinement, was 6 wt% [7]. The hydrogen

Table 1 – Experimental conditions and the structural characteristics of the obtained hydrides.

Alloy composition	H/AB ₂	T (K)	P (atm)	a, Å	c, Å	SG	Ref.
$ZrMo_2 \lambda_2$	0.14	273–1173	$1.10^{-7} - 1$	7.651		227	3
$ZrMo_2 \lambda_2$	1.4	303	60	7.698		227	4
$ZrMo_2 \lambda_2$	2.8	173–294	0.1–100	8.05 (1)		227	5
$ZrMo_2 \lambda_2$	4.0	229–313	1–1500	5.496 (2)	7.986 (1)	88	6
$ZrMoFe \lambda_1$	2.5	303–353	0.1–100	5.385 (3)	8.814 (5)	194	4
$ZrMo_{0.2}Fe_{1.8} \lambda_1 + \lambda_2$	3.0	233–353	1–1500	5.388 (1)	8.805 (1)	194	7
$ZrFe_2 \lambda_2$	3.5	253–313	1–2000	7.595 (3)		227	8
$ZrFe_2 \lambda_2$	2.7	373	11000	7.562 (1)		227	9

content in $\text{ZrMo}_{0.2}\text{Fe}_{1.8}$ is almost the same as ZrFe_2 . However, the hydride of composition $\text{ZrMo}_{0.2}\text{Fe}_{1.8}\text{H}_{3.0}$ is formed already at a pressure of up to 100 atm, i.e. similar to the case of ZrMoFe . X-ray results detect only the extended λ_1 structure.

Consideration of the combination of the hydrogen adsorption properties of all the above compositions allows us to draw some conclusions. As follows from the type of hydrogen desorption isotherms in $\text{ZrFe}_{2-x}\text{Mo}_x - \text{H}_2$ systems, an increase in the molybdenum content leads to the expected decrease in the dissociation pressure of the β -hydride phases (Fig. 2) in the temperature range close to room temperature. This influence of molybdenum substitution was also noted in Ref. [12].

However, in the case of ZrMo_2 , the equilibrium pressure increases again, and at 284 K there is no ($\alpha + \beta$)-phase transition at the desorption isotherm. This indicates that the critical temperature for the existence of a two-phase region is exceeded. A similar dependence on the concentration of molybdenum is observed for the values of the enthalpy of hydrogen desorption (Fig. 3).

In this case, only differences in the structure of the starting compounds can be an explanation for this type of dependence. It was established that hydrogen atoms are located in crystal lattices of both the cubic and hexagonal Laves phases in positions with the same facet $[\text{Zr}_2\text{M}_2]$ ($\text{M} = \text{Mo}_x\text{Fe}_{1-x}$). Therefore, the only explanation can only be a change in the ratio of the number of atoms of molybdenum and iron in the faceting of the positions occupied by hydrogen. The Vegard rule relates linearly the concentration of the components of a binary solid solution with the volume of the unit cell. For hydrogenation-dehydrogenation reactions for various alloys belonging to the same solid solution, the change in the volume of the unit cell is proportional to the change in pressure of absorption-desorption, and, based on the van't Hoff equation, the change in enthalpy of the reaction [13]. If all studied ternary compounds had the same structure as binary ones, namely λ_2 , then the change in enthalpy would have a monotonic character from 21.3 for ZrFe_2 to 22 kJ/mol H_2 for ZrMo_2 .

An increase in the molybdenum content in the studied compositions leads to a significant increase in the length of the α -solution. If for $x = 0$ and $x = 0.2$ its length does not exceed 0.2 H/AB₂, then for ZrMoFe it is H/AB₂ = 0.6. This also

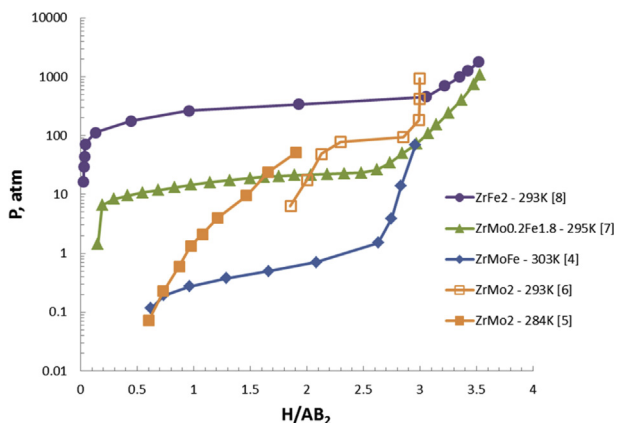


Fig. 2 – Desorption isotherms in $\text{ZrMo}_{2-x}\text{Fe}_x - \text{H}_2$ systems at ambient temperatures.

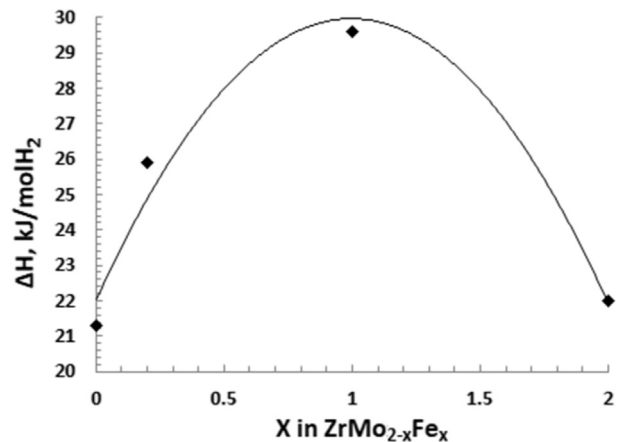


Fig. 3 – Dependence of the hydrogen desorption reaction enthalpy in $\text{ZrMo}_{2-x}\text{Fe}_x - \text{H}_2$ systems.

indicates that an increase in the molybdenum content leads to a significant decrease in the critical temperature of the ($\alpha + \beta$)-phase transition, which is observed in the $\text{ZrMo}_2 - \text{H}_2$ system already at room temperature.

Conclusion

Critical analysis of experimental data for hydrogen interaction with alloys of $\text{ZrMo}_{2-x}\text{Fe}_x - \text{H}_2$ systems showed that the main impact on the behaviour of alloys interaction with hydrogen comes from the structural characteristics of alloys. Due to the transition between λ_2 and λ_1 structures hydrogen sorption properties change is more pronounced because of the presence of 4d-metal molybdenum which dramatically decreases the critical temperature of ($\alpha + \beta$)-phase transition and enhances the α -phase region. In case of $\text{ZrMo}_2 - \text{H}_2$ system this influence led to an erroneous suggestion by authors [5] of existence of 3 hydride phases. In this work, we showed that only two hydride phases are present in the $\text{ZrMo}_2 - \text{H}_2$ system.

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