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Journal of Alloys and Compounds 404–406 (2005) 118–121

Journal of ALLOYS AND COMPOUNDS

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Synthesis and crystal structure of κ-$Zr_9V_4SH_{\sim 23}$

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Received 4 August 2004; received in revised form 20 December 2004; accepted 27 December 2004

Abstract

The $Zr_9V_4SH_{\sim 23}$ hydride was synthesized by saturation from gaseous hydrogen at room temperature and 0.12 MPa hydrogen pressure. The measured hydrogen absorption capacity of the κ-Zr_9V_4S was 1.77 H/M. The refinement of the hydride structure with the use of X-ray powder diffraction data confirmed the preserved symmetry of the metallic matrix (sp.gr. $P6_3/mmc$, $a = 9.2715(2)$, $c = 9.0756(4)$Å, $\Delta a/a = 7.3\%$, $\Delta c/c = 6.1\%$, $\Delta V/V = 22.1\%$, $\Delta V/\text{at.H} = 2.62$ Å^3). The analysis of interstices in this compound revealed that without positioning hydrogen atoms in triangular Zr_3 interstices it is impossible to model the structure of k-hydride with the experimentally observed capacity. Neutron powder diffraction study of the $Zr_9V_4SD_{\sim 23}$ deuteride (sp.gr. $P6_3/mmc$, $a = 9.2779(5)$, $c = 9.0779(5)$ Å) revealed deuterium atoms filling two tetrahedral and three triangular interstices. A full occupancy of only one site (D4) was observed in our sample giving the refined deuterium content of 20.8(2) D/f.u. Filling of the D4 site causes a displacement of the sulphur atoms from the three-fold axis (splitting of 2c to 6h position).

Keywords: Hydrogen storage materials; Intermetallics; Crystal structure and symmetry; X-ray diffraction; Neutron diffraction

1. Introduction

Light interstitial non-metallic atoms, even at low concentrations, can stabilise new phases in the d-metal systems. For example, phases of $A_4B_2O_x$–$A_3B_3O_x$ and A_3BO_x stoichiometries with the O-content varying in the $x = 0, \ldots, 1$ range are formed in Ti-,Zr-,Hf-based systems and belong to the filled Ti_2Ni (η-Fe_3W_3C) and filled Re_3B-types of structure, respectively. Changing oxygen content causes variation of hydrogen absorption/desorption characteristics [1–7]. Several features of this behaviour should be mentioned: (1) the higher is the oxygen content the lower is the hydrogenation capacity ($Ti_4Fe_2O_x$, $Zr_3V_3O_x$, $Zr_4Fe_2O_x$, $Zr_3Fe(Co,Ni)O_x$) [1,2,4–6]; (2) the redistribution of oxygen atoms in the unit cell during the hydrogenation ($Zr_3V_3O_x$, Zr_3NiO_x) [5,6] and (3) decrease of ability to disproportionation with the increase of non-metallic interstitial atoms concentration [2,7].

A new object of our studies is formation and crystal structure of the hydrides of high-temperature IMC with Hf_9Mo_4B-type structure (so called κ-phases), which are formed in systems of d-metals in the presence of p-elements (B, P, S, O, etc.). The structure of its metallic matrix is related to the Mn_3Al_{10} type, p-elements atoms filling triangular-prismatic and/or octahedral interstices. The number of inserted non-metallic atoms varies in a wide range (up to $A_9B_4S_4$ stoichiometry for $Zr_9V_4S_4$, $Zr_9Nb_4S_4$, etc.) [8–10]. The occupation of both octahedral and trigonal-prismatic interstices by the p-element causes different hydrogen absorption-desorption properties and hydrogenation capacities. Hydrogenation of Ti-, Zr- or Hf-based κ-phases has not been studied before. In this work we present new experimental results on the formation of κ-$Zr_9V_4SH_{\sim 23}$ hydride and results of crystal structure determination of the corresponding deuteride by means of X-ray and neutron powder diffraction.

2. Experimental details

The alloys were prepared from pure metals and sulphur by arc melting in a purified argon atmosphere on a water-cooled copper hearth. Further homogenisation of the as cast samples was performed by an annealing at 1200 °C for

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doi:10.1016/j.jallcom.2004.12.168

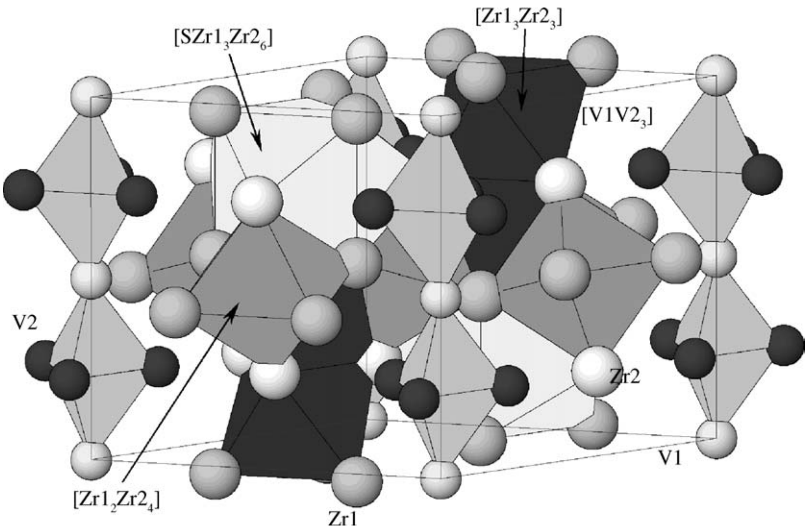

Fig. 1. Structure of Zr_9V_4S κ-phase.

~10 h with the subsequent quenching into the iced water. Hydrogen/deuterium was injected into a stainless steel reactor containing a preliminary activated sample (350–400 °C for 0.5 h in ~1 Pa vacuum). The exposure of the samples to 0.12 MPa of the hydrogen/deuterium pressure for 5–10 h was sufficient for achieving saturation of the alloys with hydrogen/deuterium. The hydrogen (deuterium) absorption capacity was measured by a standard volumetric method.

Characterization of the parent alloys and their hydrides was carried out by X-ray powder diffraction (powder diffractometers DRON-3.0 and SCINTAG XDS-2000, Cu Kαa radiation). Crystal structure study of the deuteride was performed using X-ray as well as neutron powder diffraction (Paul Scherer Institute, Switzerland, diffractometer HRPT, $\lambda = 1.494$ Å). The crystal structure was refined by the Rietveld technique using the program CSD [11] for X-ray data and the program GSAS [12] for the refinement of the structure of the deuteride. The hydrogen/deuterium absorption characteristics were determined by a standard volumetric technique. The sizes of interstices in the crystal structure of the synthesized deuteride were determined using the rigid ball model (atomic radii, $r_{Zr} = 1.602$ Å, $r_V = 1.346$ Å, were taken from [13]), graphical presentations of the structure were prepared using ATOMS-4.1 software [14].

3. Results and discussion

The parent alloy contains κ-phase with traces of α-Zr and λ_2-ZrV_2. Lattice parameters for the hexagonal κ-Zr_9V_4S

Table 1
Interstices in the structure of $Zr_9V_4SH_{\sim 23}$

Interstice	Site	x	y	y	r Å	Neighbours
Octahedral interstices						
$Zr1_3Zr2_3$	$4f_1$	1/3	2/3	0.5952	0.95	$4\times12k_1$; $4f_1$; $2\times6g$; S[b]
$Zr1_2Zr2_4$	6g	1/2	0	0	0.90*e*, 0.75*a*[a]	$4\times24l_1$; $2\times4f_1$; $2\times$S
Tetrahedral interstices						
$Zr1Zr2_2V2$	12j	0.0526	0.3241	1/4	**0.51**[c]	$2\times24l_2$; 6h; S
$Zr1_2Zr2V2$	$12k_1$	0.2083	0.4166	0.6775	0.57	$2\times24l_1$; $12k_1$; $4f_1$
$Zr1Zr2_2V2$	$24l_1$	0.3290	0.0506	0.1315	**0.52**	12j; $12k_1$; $24l_2$; 6g
$Zr2_2V2_2$	6h	0.1265	0.2530	1/4	0.50	$2\times12k_2$; 2×12j
$Zr2_2V1V2$	$24l_2$	0.1931	0.0234	0.0694	0.49	$24l_1$; $2\times24l_2$; $12k_2$
$Zr2V1V2_2$	$12k_2$	0.0809	0.1618	0.1342	**0.44**	$2\times24l_2$; 4e; 6h
$V1V2_3$	4e	0	0	0.1821	0.32	4e; $3\times12k_2$
Triangular interstices						
$Zr1_3$	2d	1/3	2/3	3/4	**0.52**	$2\times4f_1$
$Zr2_3$	$4f_2$	1/3	2/3	0.0594	0.52	$4f_1$
$Zr1Zr2_2$	$12k_3$	0.5797	0.1594	0.462	**0.47**	$4f_1$; 6g
$Zr1Zr2_2$	$12k_4$	0.5626	0.1252	0.6129	0.40	6g; S

Structure of metallic matrix of the $Zr_9V_4SH_{\sim 23}$ hydride: $P6_3/mmc$; $a = 9.2715(2)$, $c = 9.0756(4)$ Å; 6 Zr1 in 6h: 0.5445 2*x* 1/4; 12 Zr2 in 12k: 0.201 2*x* 0.0565; 2 V1 in 2*a* 0 0 0; 6 V2 in 6h 0.8784 2*x* 1/4; 2 S in 2*c* 1/3 2/3 1/4.

[a] Indices *e* and *a* mean equatorial and axial radii of octahedron.

[b] Polyhedron S denotes the trigonal prism with additional caps over lateral faces (see Fig. 3a), centred by S atom.

[c] Radii of interstices, occupied in the proposed model are shown in bold.

($a = 8.6321(5)$, $c = 8.6241(7)$ Å) fit well with the literature data [8]. The measured hydrogen (deuterium) absorption capacity of κ-Zr_9V_4S is 1.77 H/M, which is slightly higher than that of other earlier studied Zr-based IMC (Zr_2Fe–1.66, $Zr_3V_3O_{0.6}$–1.6, ZrV_2–1.63). The Rietveld refinement of hydride structure with the use of X-ray data confirmed preserved metal atoms substructure (sp.gr. $P6_3/mmc$, $a = 9.2715(2)$, $c = 9.0756(4)$ Å, $\Delta a/a = 7.3\%$, $\Delta c/c = 6.1\%$, $\Delta V/V = 22.1\%$, $\Delta V/\text{at.H} = 2.62$ Å^3). The fragment of structure of the Zr_9V_4S κ-phase with outlined frameworks of Zr and V atoms is shown in Fig. 1. The Zr-framework is made of two types of Zr_6 octahedra and S-centred trigonal prism with three additional caps. The V-framework consists of chains of V_4-tetrahedra. The rest of unit cell space is divided between different tetrahedra having both Zr- and V-atoms in their surrounding.

The analysis of types and sizes of available interstices and interconnections between them in the structure of $Zr_9V_4SH_{\sim 23}$ hydride has been performed to predict the possible models of the hydrogen sublattice and to facilitate the experimental determination of the crystal structure by neutron diffraction. The characteristics of interstices in this structure are provided in Table 1.

The unit cell of the $Zr_9V_4SH_{\sim 23}$ hydride contains 104 interstices, including 10 Zr_6 octahedra of two types, 94 tetrahedra — Zr_3V (48: 3 types), Zr_2V_2 (30: 2 types), ZrV_3 (12) and V_4 (4). Analysis of possible location of hydrogen atoms in these interstices, which accounts the size of the filled interstice (should be larger than 0.4 Å) and the distance between two neighbouring H atoms (> 2 Å) revealed that these interstices could accommodate not more than 18 at. H/f.u., which is much lower than the experimentally observed ∼ 23 at. H/f.u. Higher capacity could be possible when H atoms are situated in the Zr_3 triangles between Zr_6 octahedra rather than in the centres of these octahedra. Such filling of triangular face between empty octahedra is observed as well in the structures of $Zr_3V_3O_{0.6}D_{9.6}$ [5] and Hf_2FeD_4 [15].

The most probable model of the structure of the hydrogen sublattice with completely occupied $Zr1Zr2_2V2$ ($24l_1$), $Zr2_2V2_2$ (6h), $Zr1_3$ (2d) and $Zr1Zr2_2$ ($12k_3$) sites gives a capacity of 22 at. H/f.u. In this model almost 1/3 of H atoms fill triangles between Zr_6 octahedra. The

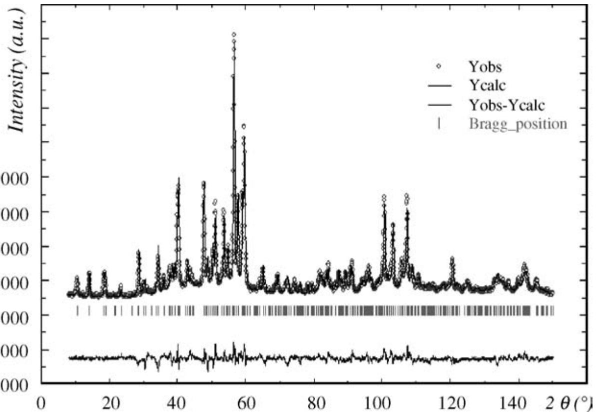

Fig. 2. Rietveld plot of neutron powder diffraction data of $Zr_9V_4SD_{\sim 23}$ deuteride.

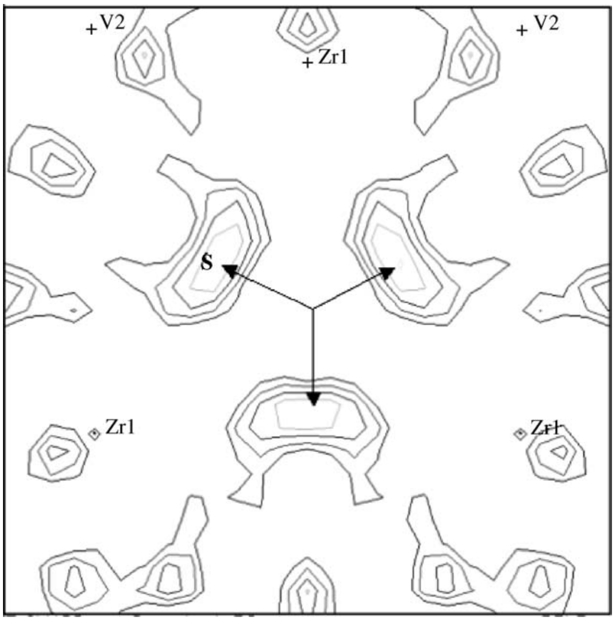

Fig. 3. Splitting of sulphur position in the structure of $Zr_9V_4SD_{\sim 23}$ revealed by the differential Fourier synthesis (neutron diffraction data).

Table 2
Crystallographic data of $Zr_9V_4SD_{\sim 23}$ ($P6_3/mmc$, $a = 9.2779(5)$, $c = 9.0779(5)$ Å, $R_{wp} = 0.046$, $\chi^2 = 6.43$)

Atom	Site	Surrounding	x/a	y/b	z/c	B(Å^2)	Occupation
Zr1	6h	–	0.5445(6)	0.0891(6)	1/4	1.18(3)	1.0
Zr2	12k	–	0.2010(4)	0.4019(4)	0.0565(3)	1.18(3)	1.0
V1	2a	–	0	0	0	1.18(3)	1.0
V2	6h	–	0.8784(9)	0.7569(9)	1/4	1.18(3)	1.0
S	6h	–	0.264(3)	0.5286(33)	1/4	1.18(3)	1/3
D1	$24l_1$	O: $Zr1Zr2_2V2$	0.3361(4)	0.0464(3)	0.1268(3)	1.64(3)	0.840(6)
D2	$12k_2$	O: $Zr2V1V2_2$	0.0797(6)	0.1595(6)	0.1339(7)	1.64(3)	0.638(4)
D3	2d	Δ:$Zr1_3$	1/3	2/3	3/4	1.64(3)	0.852(6)
D4	$12k_4$	Δ:$Zr1Zr2_2$	0.435(1)	0.870(1)	0.366(1)	1.64(3)	0.334(0)
D5	$12k_3$	Δ:$Zr1Zr2_2$	0.5890(8)	0.178(1)	0.4555(7)	1.64(3)	0.668(5)

Notes: T: tetrahedral, Δ: triangular interstices.

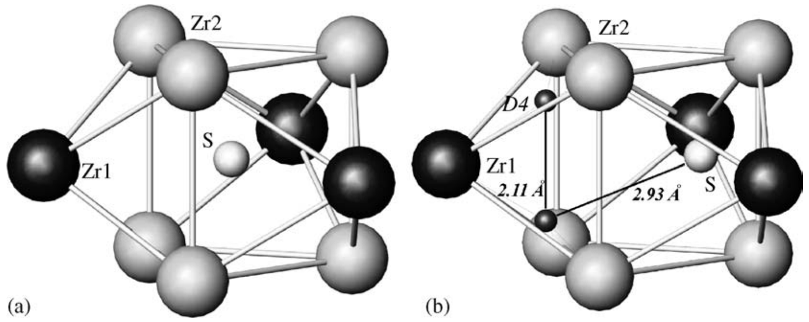

Fig. 4. Cluster of Zr atoms around S atom in structures of Zr_9V_4S (a) and $Zr_9V_4SD_{\sim 23}$ (b). In parent compound S atom occupies the centre of trigonal prism (1/3 2/3 1/2). In hydride S atom shifts from the three-fold axis, allowing positioning D4 atoms in $Zr1_2Zr2$ triangles (both S and D4 in this case are occupied by one third).

proposed model meets the criterion of interstices size ($r_{\text{int}} = 0.44, \ldots, 0.52$ Å), which values are close to those of other Zr-based hydrides. All distances between two neighbouring H-atoms are longer than 2 Å.

Neutron powder diffraction study of $Zr_9V_4SD_{\sim 23}$ deuteride (single phase sample) was carried out to localize the deuterium atoms. Experimental, theoretical and differential neutron diffraction profiles are shown in Fig. 2. The crystallographic parameters are given in Table 2. Locating 14 deuterium atoms (7 D/f.u.) by neutron diffraction in Zr_3 triangular faces has confirmed the theoretical prediction. This feature makes the structure similar to those of related deuterides $Hf_2FeD_{4.5}$ [15], $Zr_3V_3O_xD_{9.6}$ [5] and $Zr_3NiO_xD_y$ [6]. The deuterium sites can be theoretically fully occupied, which would give 25 D/f.u. However, a full occupancy of only one site (D4) was observed in our sample giving the refined deuterium content of 20.8(2) D/f.u.

The refinement using the neutron powder diffraction data showed the absence of the sulphur atom in the initial 2*c* positions. The differential Fourier synthesis (Fig. 3) demonstrated that these atoms are shifted from the 3-fold axes by 1.1 Å into 6g position, filled by 1/3. Such displacement of sulphur atoms, probably due to a repulsive deuterium–sulphur interaction (all observed deuterium–sulphur distances are longer than 2.9 Å), allows the filling of D4 triangular sites by deuterium (Fig. 4). The difference between some predicted deuterium sites and the experimental result (D2 atoms fill 12k instead of 6h sites) as well as a slightly lower deuterium content (20.8 D/f.u.) in the refined composition compared to the predicted and volumetric method result need an additional analysis.

4. Conclusions

The $Zr_9V_4SH_{\sim 23}$ hydride was synthesized for the first time by saturation from gaseous hydrogen at ambient temperature and pressure. The analysis of interstices in this compound revealed that without positioning hydrogen atoms in triangular Zr_3 interstices it is impossible to model the structure of *k*-hydride with a capacity, close to the experimentally observed value. Neutron powder diffraction study of the $Zr_9V_4SD_{\sim 23}$ deuteride revealed deuterium atoms filling two tetrahedral and three triangular interstices. The deuterium sites can be theoretically fully occupied, which would give 25 D/f.u. However, a full occupancy of only one site (D4) was observed in our sample giving the refined deuterium content of 20.8(2) D/f.u. Filling of the D4 and D5 triangular sites causes a displacement of the sulphur atoms from the three-fold axis (splitting of 2c to 6h position).

Acknowledgements

This work was carried out in the frame of INTAS 99-01884 project. The help of P. Fischer (PSI) with the neutron powder diffraction experiment is highly appreciated.

References

[1] K. Hiebl, E. Tuscher, H. Bittner, Monatsh. Chem. 110 (1979) 9.
[2] M.H. Mintz, Z. Hadari, M.P. Dariel, J. Less-Common Met. 74 (1980) 287.
[3] B. Rupp, J. Less-Common Met. 104 (1984) 51.
[4] I.Yu. Zavaliy, J. Alloys Compd. 291 (1999) 102–109.
[5] I.Yu. Zavaliy, W.B. Yelon, P.Yu. Zavalij, I.V. Saldan, V.K. Pecharsky, J. Alloys Compd. 309 (2000) 75–82.
[6] I.Yu. Zavaliy, R. Černý, I.V. Koval'chuck, I.V. Saldan, J. Alloys Compd. 360 (2003) 173–182.
[7] I.Yu. Zavaliy, O. Gutfleisch, V. Yartys, I.R. Harris, Proceedings of the VIIth International Conference Hydrogen Materials Science and Chemistry of Metal Hydrides, Alushta, Ukraine, 16–22 September (1996) 336–339.
[8] G.A. Marking, V.G. Young, H.F. Franzen, J. Alloys Compd. 241 (1996) 98–111.
[9] A. Harsta, S. Randqvist, J. Solid State Chem. 70 (1987) 210–218.
[10] R. Mackay, H.F. Franzen, Z. Anorg. Allg. Chem. 616 (1992) 154–156.
[11] L.G. Akselrud, Yu.N. Grin, P.Yu. Zavalii, V.K. Pecharsky, B. Baumgartner, E. Wolfel, Mater. Sci. Forum (1993) P. 133–136, 335–340.
[12] C.A. Larsen, R.B. Von Dreele, GSAS: General Structure Analisys System, LANL, Los Alamos, New Mexico, USA, 1990.
[13] W.B. Pierson, The Crystal Chemistry and Physics of Metals and Alloys, Interscience, New York, 1972.
[14] Dowty, E., (1993): ATOMS. Version 4.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
[15] C. Stioui, D. Fruchart, A. Rouaut, R. Fruchart, E. Roudaut, J. Rebiere. Mater. Res. Bull. 16 (1982) 869.