Crystal structure of κ-Hf$_9$Mo$_4$SiD$_{16.8}$ deuteride

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The κ-Hf$_9$Mo$_4$SiD$_{16.8}$ deuteride was prepared by deuteration of the intermetallic alloy at room temperature and 0.1 MPa D$_2$ pressure. Synchrotron X-ray and neutron powder diffraction studies revealed that the initial crystal structure is preserved upon deuterium absorption (sp.gr. _P6$_3$/mmc_, _a_ = 8.9553(1), _c_ = 9.0947(2) Å, Δ_a/a_ = 4.0%; Δ_c/c_ = 5.5%; Δ_V/V_ = 14.1%; Δ_V/at.D_ = 2.33 Å^3). The deuterium atoms occupy four interstitial positions: two tetrahedral Hf$_2$Mo$_2$ and Hf$_3$Si sites and two triangular Hf$_3$ sites.

Hafnium alloys / Hydrides / Crystal structure / X-ray and neutron diffraction analysis

Introduction

Intermetallic κ-phases with Hf$_9$Mo$_4$B structure type [1] were found in a number of ternary Hf-Mo-X systems (X = Si, P, S, Ge, As, Se) [2]. Phase analytical and crystallographic results indicate that Hf→Mo substitution in the *6h* and *2a* sites is the cause of variations in the composition and lattice parameters [3,4]. In our previous work we have synthesised the Zr$_9$V$_4$SH$_{~23}$ hydride and analysed the possible structure of its hydrogen sublattice. A neutron powder diffraction study of the Zr$_9$V$_4$SD$_{~23}$ deuteride was carried out to localize the deuterium atoms [5]. A number of κ-phases, Zr$_9$Mo$_4$NiO$_x$ (x = 0÷3) and Hf$_9$Mo$_4$Ge, as well as their hydrides, have been synthesized and characterised [6]. A comparison of the hydrogenation capacities of Zr$_9$Mo$_4$NiO$_x$ compounds with the Zr$_9$V$_4$SD$_{~23}$ structural data allowed us to suggest that the presence of oxygen atoms in octahedral interstices blocks filling of Zr$_3$ triangular faces by hydrogen atoms, thus decreasing the maximum hydrogen storage capacity by 25%. In this work we present results on the preparation and crystal structure of the deuteride of the κ-Hf$_9$Mo$_4$Si phase.

Experimental details

A Hf$_9$Mo$_4$Si alloy was prepared by arc melting of the constituent elements followed by high temperature annealing in an evacuated quartz ampoule (1170°C, 5 h). The deuteride of this alloy was synthesised by gas-solid reaction at room temperature and 0.1 MPa D$_2$ pressure. The deuterium content was measured by a standard volumetric technique. The parent and deuterated alloys were examined by X-ray powder diffraction (DRON-3.0, Cu-Kα radiation and Bruker D8, Cu-Kα$_1$ radiation). The crystal structure of the deuteride was determined by a joint Rietveld refinement of synchrotron X-ray (SNBL, ESRF, France, λ = 0.3748 Å) and neutron powder diffraction data (Paul Scherrer Institute, Switzerland, HRPT instrument, λ = 1.494 Å) using GSAS software [7].

Results and discussion

The κ-Hf$_9$Mo$_4$Si phase with Hf$_9$Mo$_4$B structure type was found as the main constituent phase in the parent alloy. The presence of Hf$_2$Si (sp.gr. *I4/mcm*, *a* = 6.5268(8), *c* = 5.212(1) Å), HfMo$_2$ (sp.gr. *Fd-3m*, *a* = 7.5696(6) Å), and β-Hf$_{0.7}$Mo$_{0.3}$ (sp.gr. *Im-3m*, *a* = 3.4167(3) Å) as additional phases is in agreement with the phase diagram of the Hf-Mo-Si system. The content of the κ-Hf$_9$Mo$_4$Si phase in the parent alloy was ~ 60 wt.% according to the Rietveld refinement of the powder X-ray diffraction (XRD) data. XRD profiles of the parent alloy are presented in Fig. 1 and the corresponding crystal structure data for the main κ-Hf$_9$Mo$_4$Si phase are described in Table 1.

The hydrogen (deuterium) absorption capacity of the alloy obtained by volumetric measurements was 1.12 D/M (M=Hf, Mo and Si). The analysis of the powder diffraction data showed that all the constituent phases formed corresponding deuterides. A multiphase Rietveld refinement on synchrotron and neutron diffraction data (Fig. 2) showed the following phase composition of the deuterated alloy: Hf$_9$Mo$_4$SiD$_{16.8}$ (57.1(1) wt.%);

Table 1 Crystallographic parameters of κ-Hf₉Mo₄Si.
Sp.gr. $P6_3/mmc$, $a = 8.6116(6)$, $c = 8.6188(8)$ Å, $V = 553.53(8)$ Å³.

Atom	Site	x/a	y/b	z/c
Hf1	6h	0.5386(6)	0.0772(12)	1/4
Hf2	12k	0.1994(4)	0.3988(8)	0.0522(6)
Mo1	2a	0	0	0
Mo2	6h	0.8914(8)	0.7828(16)	1/4
Si	2c	1/3	2/3	1/4

Note: atomic displacement parameters U_{iso} for all atoms were set to 0.005 Å².

Table 2 Crystallographic parameters of the Hf₉Mo₄SiD₁₆.₈ deuteride (filled Hf₉Mo₄B type).
Sp.gr. $P6_3/mmc$, $a = 8.9553(1)$, $c = 9.0947(2)$ Å, $V = 631.66(4)$ Å³.

Atom	Site	Surrounding	x/a	y/b	z/c	$U_{iso} \times 100$ (Å²)	Occupation
Hf1	6h	–	0.5401(1)	0.0802(2)	1/4	0.73(2)	1.0(–)
Hf2	12k	–	0.20185(8)	0.4037(2)	0.0526(1)	= U_{iso}(Hf1)	1.0(–)
Mo1	2a	–	0	0	0	1.10(6)	1.0(–)
Mo2	6h	–	0.8958(2)	0.7916(3)	1/4	= U_{iso}(Mo1)	1.0(–)
Si	2c	–	1/3	2/3	1/4	1.7(3)	1.0(–)
D1	24l₁	T: Hf1Hf2₂Mo2	0.3383(4)	0.0419(3)	0.1251(3)	1.61(5)	0.816(6)
D3	2d	Δ: Hf1₃	1/3	2/3	3/4	= U_{iso}(D1)	0.999(17)
D4	12k₄	T: Hf1Hf2₂Si	0.428(1)	0.572(1)	0.148(2)	= U_{iso}(D1)	0.219(5)
D5	12k₅	Δ: Hf1Hf2₂	0.5862(2)	0.1724(5)	0.0470(5)	= U_{iso}(D1)	0.781(5)

Note: T: tetrahedral, Δ: triangular interstices.

Table 3 Crystallographic parameters of Hf₂SiD (filled CuAl₂ type).
Sp.gr. $I4/mcm$, $a = 6.5126(2)$, $c = 5.4124(3)$ Å, $V = 229.56(2)$ Å³.

Atom	Site	Surrounding	x/a	y/b	z/c	$U_{iso} \times 100$ (Å²)	Occupation
Hf	8h	–	0.1649(2)	0.6649(2)	0	0.20(3)	1.0(–)
Si	4a	–	0	0	1/4	0.7(2)	1.0(–)
D	4b	T: Hf₄	0	1/2	1/4	2.8(2)	1.02(2)

Table 4 Crystallographic parameters of HfMo₂D₁.₃ (cubic Laves phase deuteride).
Sp.gr. Fd-$3m$ [setting 2], $a = 7.6799(2)$ Å, $V = 452.97(2)$ Å³.

Atom	Site	Surrounding	x/a	y/b	z/c	$U_{iso} \times 100$ (Å²)	Occupation
Hf	8b	–	3/8	3/8	3/8	1.52(6)	1.0(-)
Mo	16c	–	0	0	0	1.24(6)	1.0(-)
D	96g	T: Hf₂Mo₂	0.203(2)	0.547(2)	0.370(2)	2.5(5)	0.109(6)

Table 5 Crystallographic parameters of Hf₀.₇Mo₀.₃D₁.₇ (ε-ZrH₂ type).
Sp.gr. $I4/mmm$, $a = 3.3046(4)$, $c = 4.4940(9)$ Å, $V = 49.07(1)$ Å³.

Atom	Site	Surrounding	x/a	y/b	z/c	$U_{iso} \times 100$ (Å²)	Occupation
M	2a	–	0	0	0	1.06(7)	0.73 Hf + 0.27 Mo
D	4d	T: M₄	0	1/2	1/4	2.0(–)	0.86(2)

Hf₂SiD (13.0(1) wt.%), HfMo₂D₁.₃ (14.7(1) wt.%) and Hf₀.₇Mo₀.₃D₁.₇ (15.2(1) wt.%). The total hydrogenation capacity, calculated from these data, is 1.02 D/M, which is close to the result of the volumetric measurements. The obtained crystal structure data are summarized in Tables 2-5. The crystal structure of the κ-Hf₉Mo₄SiD₁₆.₈ deuteride is shown in Fig. 3.

Similarly to other studied κ-phase hydrides [5,6], Hf₉Mo₄SiD₁₆.₈ preserves the initial symmetry of the metal matrix. The relative changes in the unit cell parameters during its formation ($\Delta a/a = 4.0\%$; $\Delta c/c = 5.5\%$; $\Delta V/V = 14.1\%$; ΔV/at.D = 2.33 Å³) are comparable to those of Zr₉Mo₄NiOₓHy and Hf₉Mo₄GeH₁₆.₀ [6], which may indicate similarities of the hydrogen sublattice of these hydrides. An analysis of the types of interstitial site available for hydrogen insertion and the possible models for the hydrogen sublattice of κ-phase hydrides was performed in [5]. The refinement on neutron diffraction data allowed us to locate four crystallographic sites occupied by D
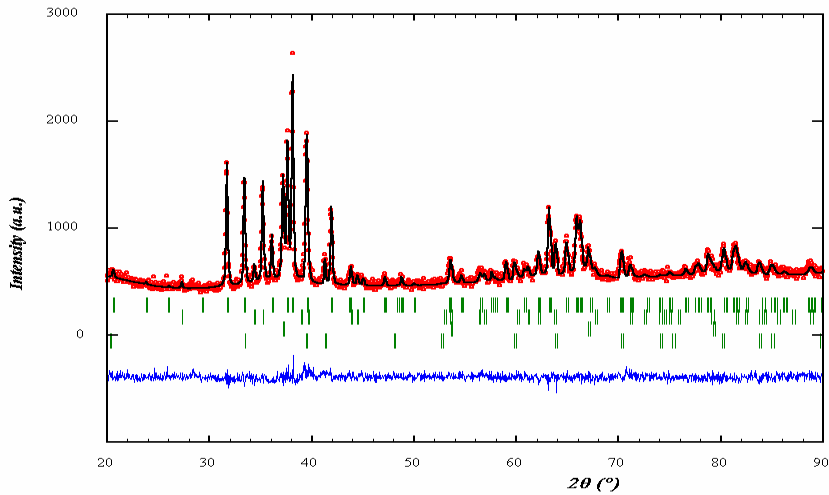
Fig. 1 Observed (+), calculated (line) and difference (bottom line) X-ray powder diffraction patterns of the parent alloy. Vertical bars indicate Bragg positions of the constituent phases (from top to bottom): Hf_9Mo_4Si, Hf_2Si, $Hf_{0.7}Mo_{0.3}$ and $HfMo_2$. *R*-factors of the refinement: R_{wp}=4.73%, R_p=3.74%, χ^2=1.35.
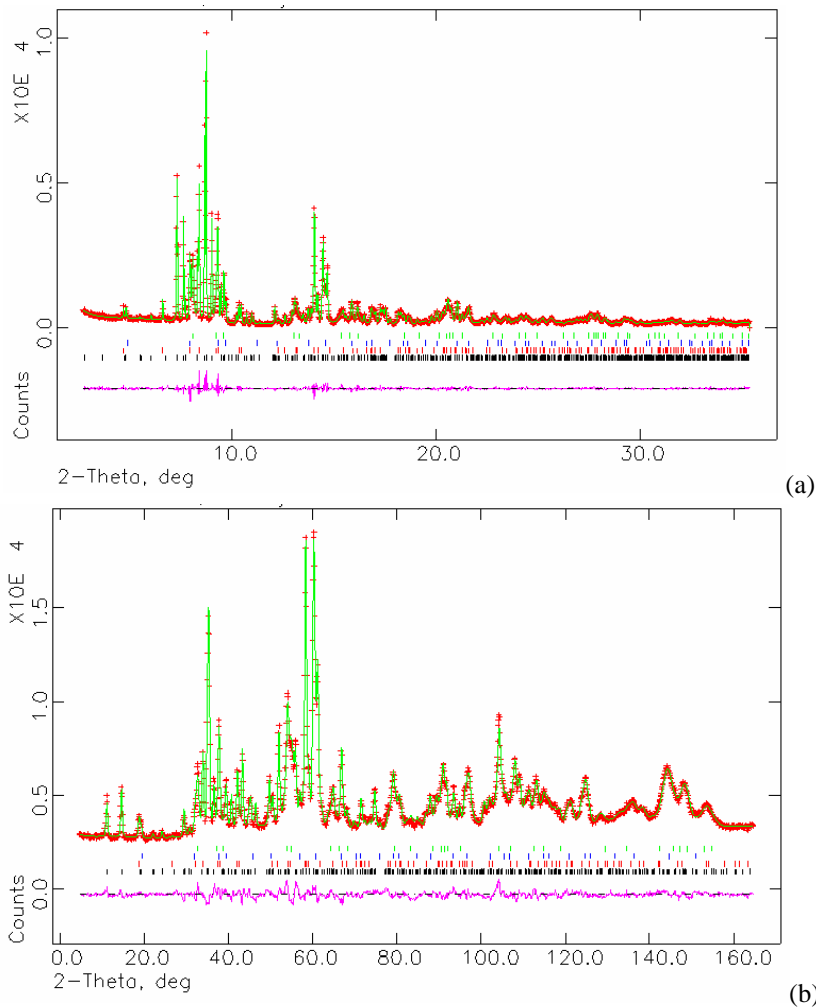

Fig. 2 Observed (+), calculated (line) and difference (bottom line) SRXRD (a) and PND (b) patterns of the deuterated alloy. Vertical bars indicate Bragg positions of the constituent phases (from bottom to top): $Hf_9Mo_4SiD_{16.8}$; Hf_2SiD; $HfMo_2D_{1.5}$ and $Hf_{0.7}Mo_{0.3}D_{1.7}$. *R*-factors: PND: R_{wp}=3.53%, R_p=2.72%; SXRD: R_{wp}=7.37%, R_p=5.90%; combined: R_{wp}=5.94%, R_p=3.99%; χ^2=2.95.
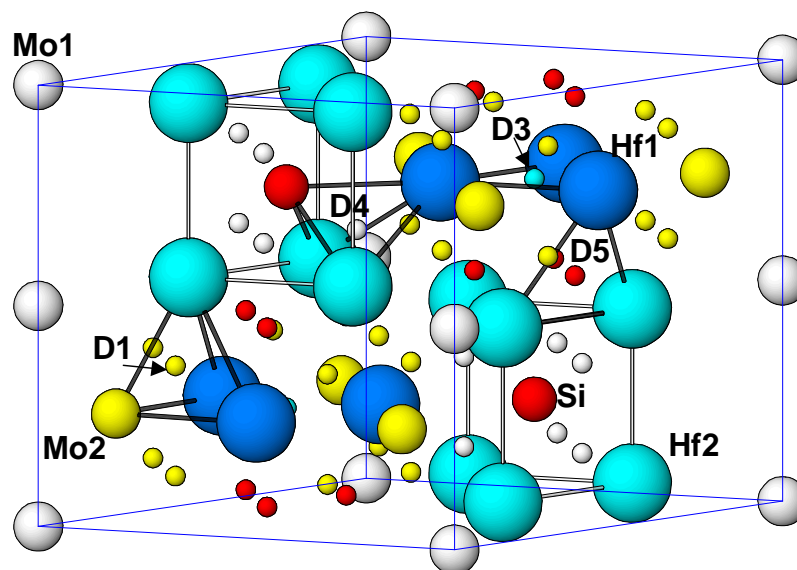
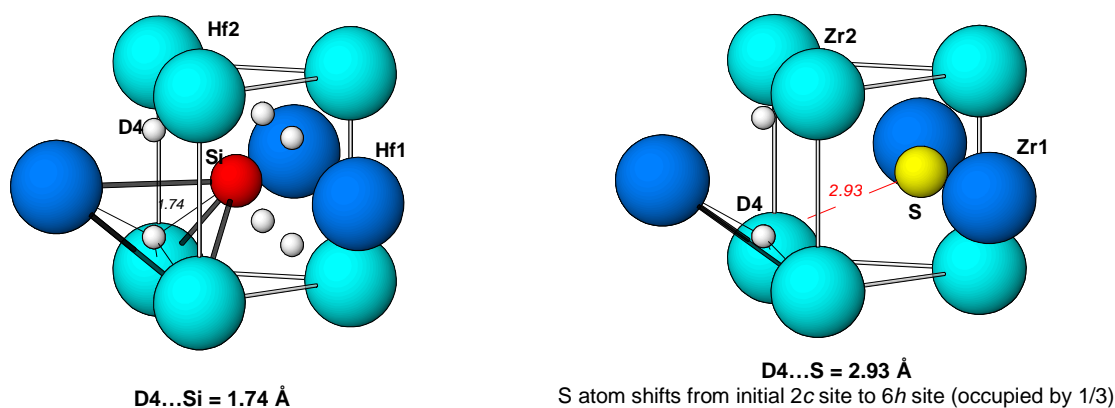**Fig. 3** Crystal structure of κ-Hf$_9$Mo$_4$SiD$_{16.8}$.

D4…Si = 1.74 Å

D4…S = 2.93 Å
S atom shifts from initial 2*c* site to 6*h* site (occupied by 1/3)

Fig 4 Comparison of structure fragments of Hf$_9$Mo$_4$SiD$_{16.8}$ (left) and Zr$_9$V$_4$SD$_{~23}$ (right).

atoms (see Table 2, the D sites are labelled according to [5]). Contrary to the Zr$_9$V$_4$SD$_{~23}$ structure, the D2 site (HfMo$_3$ interstice, which corresponds to ZrV$_3$ in Zr$_9$V$_4$SD$_{~23}$) is vacant, which can be explained by the smaller hydrogen affinity of Mo compared to V. Another difference between the structures of Hf$_9$Mo$_4$SiD$_{16.8}$ and Zr$_9$V$_4$SD$_{~23}$ [5] is that the atoms of the *p*-element (Si) in Hf$_9$Mo$_4$SiD$_{16.8}$ remain in the initial position, whereas the sulphur atoms are shifted from the 3-fold axis (2*c* position) by 1.1 Å into a 6*h* position, filled by 1/3. (see Fig. 4). Such a displacement is attributed to a repulsive deuterium–sulphur interaction (all observed deuterium–sulphur distances are longer than 2.9 Å), and allows the filling of Hf$_3$ faces (D4) by deuterium. The D4 atom in the structure of Hf$_9$Mo$_4$SiD$_{16.8}$ is shifted from the triangular Hf$_3$ face towards a Si atom and occupies the centre of a Hf$_3$Si tetrahedron. Thus, we observe direct contact between the *p*-element and deuterium (d_{D4-D5} = 1.74(2) Å).

The D4 site is occupied by 22 % only due to self-blocking (d_{D4-D4} = 1.85(3) Å) and filling of the neighbouring D5 position (d_{D4-D5} = 1.79(2) Å). The sum of the occupancy factors of the D4 and D5 sites cannot exceed unity. The D1 and D3 sites do not have any D sites in their nearest surrounding and can be filled up completely. However, a full occupancy of only the D3 site is observed, giving a refined deuterium content of 16.8(1) D/f.u. The maximum possible capacity of the deuteride, taking into account blocking between the D4 and D5 sites, is 19 D/f.u. The distances between D atoms and the metal/silicon atoms in their surrounding are presented in Table 6. They are in agreement with the sum of the radii of these atoms. The separation between the nearest deuterium atoms in the Hf$_9$Mo$_4$SiD$_{16.8}$ structure exceeds 2 Å.

Conclusions

The Hf$_9$Mo$_4$SiD$_{16.8}$ deuteride has been synthesized. The crystal structure of this deuteride has been studied by synchrotron X-ray and neutron powder diffraction.

Table 6 Selected interatomic distances in the structure of Hf$_9$Mo$_4$SiD$_{16.8}$.

Atoms	d, Å	Atoms	d, Å
Hf1…4 D1	2.013(3)	Hf2…2 D1	2.042(3)
Hf1…D3	1.963(2)	Hf2…2 D5	1.998(2)
Hf1…2 D5	1.980(4)	Hf2…2 D4	2.019(8)
Hf1…2 D4	1.97(2)	Mo2…4 D1	1.898(3)
Hf2…2 D1	2.007(3)	Si…6 D4	1.74(2)

The Hf$_2$SiD, HfMo$_2$D$_{1.3}$ and Hf$_{0.7}$Mo$_{0.3}$D$_{1.7}$ deuterides were found as additional phases. It has been shown that κ-Hf$_9$Mo$_4$SiD$_{16.8}$ belongs to the filled Hf$_9$Mo$_4$B-type structure (sp.gr. *P6$_3$/mmc,* a = 8.9553(1) Å, c = 9.0947(2) Å, $\Delta a/a$ = 4.0%; $\Delta c/c$ = 5.5%; $\Delta V/V$ = 14.1%; ΔV/at.D = 2.33 Å^3). The deuterium atoms occupy four crystallographic positions: two types of tetrahedral interstice, Hf1Hf2$_2$Mo2 and Hf1Hf2$_2$Si; and two types of triangular face, Hf1$_3$ and Hf1Hf2$_2$.

Acknowledgements

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