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Crystal Structure Refinement of κ-Hf_9Mo_4Ni

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The crystal structure of κ-Hf_9Mo_4Ni has been refined using X-ray single-crystal diffractometry. κ-Hf_9Mo_4Ni crystallizes in the space group $P6_3/mmc$ (No. 194) with the cell dimensions: a= 8.6550(3) Å, c=8.4626(6) Å. κ-Hf_9Mo_4Ni has the same structure as κ-Hf_9Mo_4B and belongs to the same structure-type as κ-(W–Co–C). The structure has been refined on F^2 to an $R(F^2)$-value of 0.1724 without excluding any reflexions.

A hexagonal phase of composition $\sim Co_3W_{10}C_4$ was first reported by Rautala and Norton [1] and denoted κ. The crystal structure was determined by Schönberg [2] by X-ray powder diffraction methods. Since then several κ-phases have been found in different ternary systems. The first single crystal investigation of a κ-phase was performed on κ-Hf_9Mo_4B.[3]

Rogl *et al.*[3] reported compounds crystallizing with this structure type in the systems Zr–Mo–{Fe,Co,Ni} and Hf–Mo(W)–{Fe,Co,Ni}. They made the interesting observation that the unit cell volume for these κ-phases increases in the order Fe→Co→Ni, whereas a decrease would be expected on the basis of the atomic radii of these metals. The present X-ray single crystal investigation of κ-Hf_9Mo_4Ni was performed in order to investigate this anomaly.

EXPERIMENTAL

Preparation. The starting materials for the synthesis of the κ-(Hf–Mo–Ni) alloys were: Turnings of hafnium from Materials Research S. A., London, containing 3 % zirconium; molybdenum powder from Koch Light Laboratories, Colnbrock, England, claimed purity 99.99 %; turnings of nickel from Johnson & Matthey, London, England, less than 20 ppm metallic impurities. Two identical alloys of composition Hf_9Mo_4Ni were prepared in the following way: A pellet of molybdenum powder and a pellet of hafnium and nickel turnings were arc-melted on a water-cooled Cu-hearth in a purified Ar atmosphere. These were then melted together and remelted after inverting them to insure homogeneity. The weight loss was less than 1 %. One of the two pellets was used for determination of the melting point in a high-frequency induction furnace using a cold crucible technique in a purified Ar atmosphere. The melting point was found to be ~1450 °C. The other pellet was heat-treated at 1370 °C for three hours using the same furnace and the same experimental conditions. The alloy was crushed and a small fragment was found to be a single crystal when examined in a Weissenberg camera.

X-Ray diffraction measurements and data reduction. X-ray powder photographs were taken using a Guinier-Hägg-type focusing camera with $CrK\alpha_1$ radiation (λ=2.289753 Å) and Si (a= 5.431065 Å)[4] as internal standard. The unit cell dimensions were refined using the local program CELNE.[5] A Nonius CAD 4-F diffractometer controlled by a PDP 8/A computer was used to record the intensity data. Graphite-monochromatized $MoK\alpha$ radiation (λ=0.71069 Å) and the $\omega/2\theta$-scan technique were employed. During the data collection four reflexions were used as monitors and checked after every 20th reflexion scanned. The differences in intensity of these reflexions were within the limits of the random statistical fluctuations. F^2_o and $\sigma_c(F^2_o)$ values were obtained from the integrated peak intensities by applying corrections for background, Lorentz and polarization effects (assuming the monochromator to be ideally imperfect), and for absorption. The crystal was of irregular shape and was approximated with eight boundary planes to a polyhedron with dimensions of the order of 0.04×0.03×0.02 mm. Corrections for absorption were applied, using the Gaussian grid method and a calculated linear absorption factor of 899 cm^{-1}. The transmission factors were found to vary from 0.10 to

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0.34. In total 2425 reflexions up to 94.4° in 2θ were recorded. (These included 24 symmetry related reflexions of the form $\{21\bar{3}2\}$, which were used to check the absorption correction.) The symmetry related reflexions were weighted together, giving a total of 988 independent reflexions.

Calculations. All calculations were performed with NORD 100 and IBM 1800 computers using a system of programs described by Lundgren.[6]

Structure analysis and results. The diffraction symmetry and the systematic absences of reflexions confirmed the space group to be $P6_3/mmc$ (No. 194) as in the case of κ-(Hf–Mo–B).[3] The structure was refined using a full-matrix least-squares program using the atomic coordinates of κ-(Hf–Mo–B) as initial values for the positional parameters, with nickel replacing boron. The atomic scattering factors for neutral atoms were used and corrected for anomalous dispersion [7] (real as well as imaginary parts). The quantity minimized was $\Sigma w(|F_o^n| - k^n|F_c^n|)^2$ with $n=1$ or 2 and the weight w given by

$$w^{-1} = \sigma_c^2(F_o^n) + (p|F_o^n|)^2$$

where σ_c is the standard deviation of F_o^n based on counting statistics and p an empirical parameter, chosen to obtain a satisfactory weight analysis (p was 0.12 in the final refinement). The agreement indices are defined as

$$R(F^n) = \Sigma(|F_o^n| - |F_c^n|)/\Sigma|F_o^n|$$

$$R_w(F^n) = [\Sigma w(|F_o^n| - |F_c^n|)^2/\Sigma|F_o^n|^2]^{1/2}$$

with $n=1$ or 2, and where F_o has been multiplied by $1/k^n$. Extinction effects were hardly discernible and no correction for them was applied.

The first refinement was based on the 544 strongest reflexions $[>3\sigma_c(F_o)]$ and an $R(F)$ value of 0.060 was obtained. In subsequent refinements all reflexions were included to avoid bias of the input data by the exclusion of "unobserved" reflexions.[8,9] Since the crystal was rather small, the measured intensities were weak and some 40 % of the reflexions had an intensity less than $2\sigma_c(F_o^2)$. This made the agreement factors for a refinement omitting observations with $F_o^2 < 2\sigma_c(F_o^2)$ much lower than those from the refinement using the complete material (Table 1). The standard deviations obtained on using the complete intensity material were about 6 % smaller than those based on the restricted material. Introduction of anisotropic temperature factors led to a somewhat improved agreement (see Table 1), and a Hamilton R-factor significance test [10] favoured the anisotropic model at the 99.5 % confidence level. The intensity data could suffer from systematic errors, however, considering the very strong absorption and the experimental difficulties in making a proper geometrical description of the irregular shape of the crystal fragment. As a further check, a ΔR normal probability plot [11] was therefore made after the anisotropic refinement. The points were all very close to a straight line with a slope of 1.01 and an intercept at 0.07. Only one value fell outside the range $\pm 4\sigma$. This result indicates that the Hamilton test is not invalidated by the influence of systematic errors.

At this stage of refinement, a Fourier difference synthesis was calculated. Although the difference synthesis indicated no major deviations from the assumed structure model, some minor modifications appeared possible, and three alternatives were tested. First, the position 6*g* was assumed to be partially occupied by oxygen atoms. Refinement of the occupancy parameter gave a value of 28(7) %. Secondly, the possibility of Hf/Mo substitution on the 2*a* position was examined. The occupation parameters refined for hafnium and molybdenum, respectively, were 5.2 (1.6) % and 94.8(1.6) %. Finally, the occupancy of nickel in the 2*c* site was refined. This yielded an occupation of 91.6(3.3) % for this site. R-values corresponding to these three refinements are given in Table 1.

No further improvements were attempted, and the results from the final refinement, including oxygen at 6*g* but no Hf/Mo substitution at 2*a* and no Ni vacancy at 2*c*, are presented in Table 2, and corresponding interatomic distances in Table 3. The total number of parameters varied were 21 (one scale factor, 4 positional parameters, one occupancy parameter and one isotropic temperature factor for oxygen, and 14 anisotropic thermal vibration parameters for the remaining atoms).

Table 1. R-Factors from isotropic and anisotropic refinements on F^2 of κ-Hf_9Mo_4Ni.

No. of refl.	No. of param.	$R(F^2)$	$R_w(F^2)$	$R(F)$
Isotropic refinement				
579($>2\sigma$)	10	0.1209	0.1511	0.0625
988	10	0.1760	0.1897	0.1407
Anisotropic refinement				
988	19	0.1735	0.1863	0.1400
988[a]	18	0.1712	0.1853	0.1397
988[b]	20	0.1740	0.1857	0.1405
988[c]	21	0.1724	0.1832	0.1395

[a] A mixture of molybdenum and hafnium in the position 2*a*. [b] Ni vacancies in the position 2*c*. [c] Oxygen present in the position 6*g*.

Table 2. Structure data for κ-Hf_9Mo_4Ni. Standard deviations are given in parentheses. Space group $P6_3/mmc$ (No. 194), $Z=2$. Cell dimensions: $a=8.6550(3)$ Å, $c=8.4626(6)$ Å. The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{23}klb^*c^*)]$.

Atom	Position	Positional parameters $U_{ij}\times10^5$(Å^2) $x(y=2x)$	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B(Å^2)
Hf(1)	12k	0.20122(5)	0.05670(8)	758(30)	739(29)	731(25)	384(29)	−123(41)	−62(21)	0.57(1)
Hf(2)	6h	0.54240(8)	1/4	602(39)	675(41)	802(34)	327(41)	0	9	0.54(1)
Mo(1)	6h	0.88900(16)	1/4	532(69)	476(72)	589(60)	210(72)	0	0	0.44(2)
Mo(2)	2a	0	0	425(79)	425(79)	750(126)	213(40)	0	0	0.42(4)
Ni	2c	1/3	1/4	834(147)	834(147)	902(219)	417(74)	0	0	0.68(8)
O[a]	6g	1/2	0	–	–	–	–	–	–	0.2(8)

[a] Occupancy 28(7) %.

A list of observed and calculated structure factors has been deposited at the Institute of Chemistry, Uppsala, and can be obtained on request.

DISCUSSION

The structure is depicted in Fig. 1. In an investigation by Rogl and Nowotny,[12] they detected κ-phases in the ternary systems Zr(Hf)−{Mo, W,R}−O with oxygen occupying the position 6g. It is very difficult to obtain alloys of κ-(Hf−Mo−Ni) free from oxygen due to the strong affinity of hafnium for this element, and the possibility that oxygen is present was therefore tested. The refinements indicate the 6g position to be partly occupied by oxygen (see Table 1). For a comparison the interatomic distances in HfO_2 were calculated by using positional parameters from those reported for ZrO_2[13] and lattice parameters from a study by Adam and Rogers.[14] The Hf−O distances thus obtained were found to be between 2.02−2.24 Å, which are shorter than those for κ-(Hf−Mo−Ni) (see Table 3).

Table 3. Interatomic distances (Å) for κ-Hf_9Mo_4Ni. Distances short than 4.00 Å are listed. The estimated standard deviations are less than 0.002 Å for all distances.

Hf(1)−2O	2.334	Mo(1)−2Mo(2)	2.692
−Ni	2.569	−2Mo(1)	2.882
−Mo(1)	2.927	−2Hf(2)	2.893
−Mo(2)	3.054	−2Hf(1)	2.927
−2Mo(1)	3.086	−4Hf(1)	3.086
−2Hf(1)	3.166	−4O	3.674
−2Hf(2)	3.196		
−2Hf(2)	3.231	Mo(2)−6Mo(1)	2.692
−Hf(1)	3.272	−6Hf(1)	3.054
−2Hf(1)	3.430		
		Ni −6Hf(1)	2.569
Hf(2)−2O	2.209	−3Hf(2)	3.134
−2Mo(1)	2.893	−6O	3.274
−Ni	3.134		
−4Hf(1)	3.196	O −2Hf(2)	2.209
−2Hf(2)	3.227	−4Hf(1)	2.334
−4Hf(1)	3.231	−2Ni	3.274
		−4Mo(1)	3.674

Regarding the position 2a, no significant Hf/Mo substitution was found. Such substitution would, furthermore, lead to an extremely short Hf−Mo distance (see Table 3). Ni/Mo substitution would be possible, and in κ-(W−Fe−C) substitution of iron in this site was proved by both diffraction data and Mössbauer data.[15] In the final difference synthesis, the scattering power associated with this position was observed to be higher rather than lower than with the site fully occupied by molybdenum, however.

The distance between the site 2c and the neighbouring Hf(1) atoms is very small (Table 3). In investigations by Bsenko[16−18] of the intermediate phases in the system Hf−Ni, no Hf−Ni distance shorter than 2.592 Å was found. Among the κ-carbides[15,19] this position is not fully occupied, but in the present study neither the refinements nor the final difference synthesis indicated any Ni vacancies.

A comparison with the interatomic distances in κ-Hf_9Mo_4B shows the Hf(1)−Ni distance (2.569 Å) in κ-Hf_9Mo_4Ni to be actually shorter than the corresponding Hf−B distance (2.588 Å). The other interatomic distances in κ-Hf_9Mo_4Ni are, however, somewhat longer and the volume 548.99 Å^3 is significantly larger than the volume 539.5 Å^3 for κ-Hf_9Mo_4B.

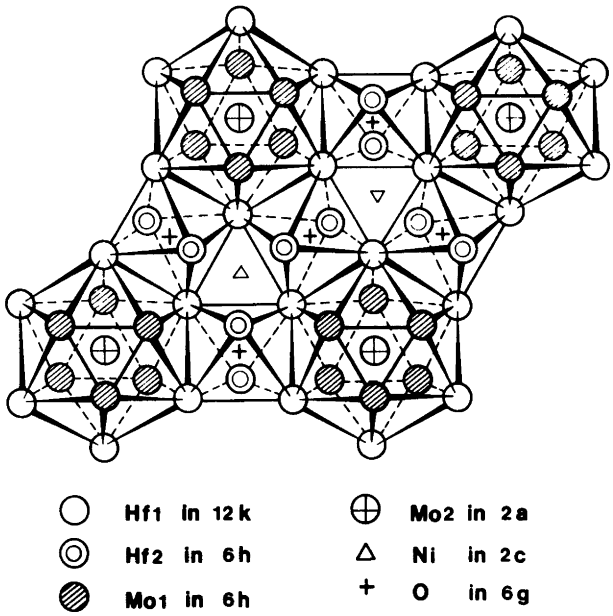

Fig. 1. The structure of κ-(Hf–Mo–Ni) projected along the hexagonal axis.

The present refinement does not provide any definite conclusions regarding the cell volume anomaly among the κ-phases. It seems unlikely that variations of the impurity oxygen content would be responsible for the large volume differences observed. Within the limits of error, there are no substitutions or other defects in κ-(Hf–Mo–Ni). It would, therefore, appear probable that such defects must be present in the iron- and cobalt-containing κ-phases. In order to investigate this possibility, a crystallographic study of κ-(Hf–Mo–Fe) has been started. Unfortunately, attempts to prepare single-crystals have so far been unsuccessful, but the X-ray diffraction powder profile refinement method might be sufficiently accurate to provide the necessary information.

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