On the Homogeneity Range of the κ Phases in the Hf–Mo–{Si, P, S, Ge, As, Se} Systems

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A survey of the various two- and three-phase equilibria involving the κ phases in the subsolidus regions of the ternary Hf–Mo–{Si, P, S, Ge, As, Se} systems has been made. The κ phases have homogeneity ranges, accompanied by variations in the unit-cell volumes. The hexagonal κ-phase structure is composed of a transition metal sublattice with triangular prismatic and octahedral interstices. The nonmetal atoms may occupy one or both types of interstices. Phase-analytical and crystallographic results suggest a variable degree of hafnium substitution on the molybdenum sites in the metal sublattice as the major cause of the variations in composition observed. The κ phase in the Hf–Mo–S system exhibits a particularly large extension of the homogeneity range. This fact might be interpreted in terms of an enhanced thermodynamic stability of this phase, connected with the filling of both octahedral and triangular prismatic sites by sulfur in the structure, in contrast to the empty octahedral sites in the remaining κ phases. © 1985 Academic Press, Inc.

Introduction

In previous exploratory studies new κ phases were discovered in the ternary systems Hf–Mo–{Si, P, S, Ge, As, Se}, Hf–W–{P, S, As, Se}, and Hf–Re–{Si, P, S, Ge, As, Se} (*1, 2*). The unit-cell volumes of these phases displayed certain trends, which seemed to be connected with the nonmetal atomic species involved but could not be immediately explained in terms of atomic size differences between the nonmetal atoms. A closer investigation of the κ phase in the Hf–Mo–P system has shown that this compound has an extended range of homogeneity, which is most probably due to a variable Hf/Mo substitution in the metal atom sublattice (*3*). An analogous situation might prevail also in other κ phases.

The present study was undertaken in order to examine the unit-cell volume variations for the κ phases in the ternary systems Hf–Mo–{Si, P, S, Ge, As, Se} and to obtain some information on the various phase equilibria involving the κ phases.

Experimental Details

Preparation

The starting materials (purity about 99.9%) for the syntheses have been described elsewhere (*1*). Ternary alloys containing silicon or germanium were prepared directly by arcmelting mixtures of the constituent elements under purified argon. Due to the high volatility of the other nonmetals, samples of MoP, Mo_5As_4, MoS_2, Hf_2S, and

Hf_2Se were initially prepared in evacuated and sealed silica tubes. These compounds were then mixed with appropriate amounts of the transition metal components and arc-melted. The alloy buttons were inverted and remelted to promote homogenization. During the arcmelting of the alloys in the Hf–Mo–S and Hf–Mo–Se systems appreciable weight losses occurred. This was probably due to losses of the nonmetal components. In further experiments it was found that the weight losses were considerably reduced if MoS_2 instead of Hf_2S was used as starting material for the syntheses of the Hf–Mo–S alloys, and this procedure was therefore employed in the preparation of alloys for chemical analysis.

All the arcmelted alloys were subsequently annealed at 1850 K under argon of high purity using a cold-crucible levitation technique (4) in a high-frequency induction furnace for periods initially between 6 and 24 hr. The annealing process was interrupted by switching off the power in the furnace. Depending on the size and shape of the alloys the cooling rate varied somewhat from one experiment to another. The results of the phase analyses must therefore be regarded with some caution, since the equilibrium state of some of the alloys might change quite rapidly with temperature.

The temperature was measured by optical pyrometry on the upper part of the alloys, but the temperature might be somewhat higher in the lower part (5). This effect is likely to be enhanced with larger sample size, but the error is estimated to be less than 50 K. Most of the alloys examined weighed about 0.5 g, while those used for chemical analysis weighed about 2 g.

X-Ray Diffraction

Phase analysis and determination of unit-cell dimensions were made by X-ray powder diffraction using a Guinier–Hägg-type focusing camera with $CrK\alpha_1$ radiation and

TABLE I

THE RESULT OF THE CHEMICAL ANALYSES OF THE Hf–Mo–S ALLOYS

Sample	wt% Hf	wt% Mo	wt% S	Composition of the κ phase
5	84.2(2)	14.07(2)	1.88(2)	$Hf_{9.92}Mo_{3.08}S_{1.23}$
6	80.7(2)	18.08(2)	1.56(2)	$Hf_{9.25}Mo_{3.75}S_{1.18}$
7	80.4(2)	17.81(2)	1.99(2)	$Hf_{9.21}Mo_{3.79}S_{1.26}$

Note. The sample numbers correspond to those of Table IV. The compositions of the κ phase have been calculated neglecting the presence of a second phase except in sample No. 6.

Si ($a = 5.431065$ Å) (6) as an internal standard. Unit-cell dimensions were refined using the local program CELNE (7).

Chemical Analysis

Sulfur. The samples were dissolved in a mixture of bromine, nitric acid, and hydrofluoric acid. The hydrofluoric acid was evaporated with perchloric acid and the sulfate was separated according to Nydahl (8). The sulfate was eluated with ammonia, reduced to hydrogen sulfide, and determined as methylene blue according to Gustafsson (9, 10).

Molybdenum and hafnium. The methods of analysis have been described (3), but the present analyses were facilitated by the absence of phosphorus. The result for Hf includes Zr and the calculations were based on the assumption of 3 wt% Zr in the hafnium as analyzed in the hafnium initially used for the syntheses.

The results of the analyses are summarized in Table I.

Results

Hf–Mo–Si System

The nominal compositions of selected alloys, the phases present, and the unit cells of the κ phase and the β-Hf(Mo) solid solution are presented in Table II. The rate of formation of the κ phase and the approach

TABLE II

THE NOMINAL COMPOSITIONS OF THE Hf–Mo–{Si, Ge, As, Se} ALLOYS, THE PHASES DETECTED BY MEANS OF X-RAY POWDER DIFFRACTION, AND THE UNIT-CELL DIMENSIONS OF THE κ PHASES AND THE β-Hf(Mo) SOLID SOLUTION

| Composition | Phase detected | κ | | | β-Hf(Mo) |
		a (Å)	c (Å)	V (Å^3)	a (Å)
$Hf_{10.0}Mo_{3.0}Si_{1.0}$	κ, β-Hf(Mo), Hf_2Si	8.6269(3)	8.5809(4)	553.07(5)	3.432(1)
$Hf_{8.5}Mo_{4.5}Si_{1.1}$	κ, β-Hf(Mo), Hf_2Si, $HfMo_2$	8.6194(4)	8.5923(10)	552.83(8)	3.402(1)
$Hf_{8.0}Mo_{5.0}Si_{0.4}$	κ, β-Hf(Mo), Hf_2Si, $HfMo_2$	8.6227(5)	8.5779(22)	552.33(15)	3.401(1)
$Hf_{9.7}Mo_{3.3}Ge_{0.9}$	κ, β-Hf(Mo), Hf_3Ge	8.6460(3)	8.6701(5)	561.28(5)	3.424(1)
$Hf_{8.9}Mo_{4.1}Ge_{1.6}$	κ, Hf_3Ge, $HfMo_2$	8.6409(5)	8.6827(8)	561.44(8)	
$Hf_{8.0}Mo_{5.0}Ge_{0.5}$	κ, $HfMo_2$, β-Hf(Mo), Hf_3Ge	8.6422(3)	8.6782(12)	561.32(9)	3.395(1)
$Hf_{10.1}Mo_{2.9}As_{1.3}$	κ, β-Hf(Mo), Hf_3As	8.6643(5)	8.6774(7)	564.15(8)	3.418(1)
$Hf_{8.5}Mo_{4.5}As_{1.6}$	κ, Hf_3As, $HfMo_2$	8.6551(6)	8.6672(10)	562.28(10)	
$Hf_{7.5}Mo_{5.5}As_{0.5}$	κ, $HfMo_2$, β-Hf(Mo)	8.6563(5)	8.6702(11)	562.63(9)	3.387(1)
$Hf_{11.0}Mo_{2.0}Se_{2.2}$	κ, Hf_2Se, α-Hf	8.7014(4)	8.6063(9)	564.32(8)	
$Hf_{10.5}Mo_{2.5}Se_{0.9}$	κ, α-Hf, β-Hf(Mo)	8.7059(4)	8.6292(8)	566.40(8)	3.471(1)
$Hf_{9.2}Mo_{3.8}Se_{2.3}$	κ, $HfMo_2$, Hf_2Se	8.6953(4)	8.6141(6)	564.03(6)	
$Hf_{7.5}Mo_{5.5}Se_{0.5}$	κ, $HfMo_2$, β-Hf(Mo)	8.6977(3)	8.6162(5)	564.49(5)	3.389(1)

toward equilibrium is very slow in this system. In spite of very prolonged annealing times, alloys in certain composition ranges invariably consisted of four phases, and no definite conclusions regarding the phase equilibria can therefore be drawn. However, the observed variations in unit-cell volume of the κ phase between different alloys are small, indicating a rather restricted range of homogeneity.

Hf–Mo–Ge System

The rate at which equilibrium is approached is also very slow in this system, and alloys in one composition region consisted of four phases despite very long annealing times (see Table II). The variations in unit-cell volume of the κ phase between different alloys are here very small, indicating that the range of homogeneity is quite limited.

In contrast to the present findings, it was reported earlier (1) that the κ phase was formed readily in the Hf–Mo–Ge system. This discrepancy might possibly be due to accidental contamination by oxygen during the synthesis in the earlier study. In order to test this hypothesis, an alloy with the nominal composition $Hf_9Mo_4GeO_{0.5}$ was prepared. In this alloy the κ phase was formed on annealing for only 6 hr. A single-crystal structure analysis (11) indicates that the promotive effect of oxygen is connected with the formation of a quaternary κ-(Hf–Mo–Ge–O) phase.

Hf–Mo–P System

This system was selected for a closer study of the phase equilibria involving the κ phase. Six alloys were initially prepared using annealing times of 6 hr. From the data obtained a preliminary isothermal section was constructed. In order to check the observed three-phase equilibria, three additional alloys were prepared. The annealings were interrupted after 6 hr and the unit-cell dimensions were determined. The alloys were subsequently annealed for another 6 hr and the unit-cell dimensions were again determined. The initially observed three-phase equilibria were verified and the results are presented in Table III. The ob-

TABLE III

THE NOMINAL COMPOSITIONS OF THE Hf–Mo–P ALLOYS, THE PHASES DETECTED BY MEANS OF X-RAY
POWDER DIFFRACTION AND THE UNIT-CELL DIMENSIONS OF THE κ PHASE
AND THE β-Hf(Mo) SOLID SOLUTION

			κ			β-Hf(Mo)
Sample	Composition	Phase detected	a (Å)	c (Å)	V (Å^3)	a (Å)
I	$Hf_{9.69}Mo_{3.31}P_{0.90}$	κ, Hf_3P, β-Hf(Mo)	8.6286(10)	8.6183(11)	555.69(15)	3.436(1)
II	$Hf_{9.33}Mo_{3.67}P_{1.35}$	κ, Hf_3P	8.6181(4)	8.6057(6)	553.53(6)	
III	$Hf_{8.90}Mo_{4.10}P_{1.60}$	κ, Hf_3P, $HfMo_2$	8.6131(6)	8.5986(9)	552.43(10)	
IV	$Hf_{8.70}Mo_{4.30}P_{0.93}$	κ, $HfMo_2$	8.6160(3)	8.6030(5)	553.09(5)	
V	$Hf_{7.49}Mo_{5.51}P_{0.49}$	κ, $HfMo_2$, β-Hf(Mo)	8.6213(6)	8.6072(12)	554.04(11)	3.388(1)
VI	$Hf_{8.91}Mo_{4.09}P_{0.66}$	κ, β-Hf(Mo)	8.6221(4)	8.6063(5)	554.08(6)	3.401(1)
VII a	$Hf_{10.0}Mo_{3.0}P_{1.1}$	κ, Hf_3P, β-Hf(Mo)	8.6274(6)	8.6187(7)	555.57(10)	3.431(1)
b			8.6312(8)	8.6195(10)	556.10(12)	3.437(4)
VIII a	$Hf_{8.5}Mo_{4.5}P_{1.5}$	κ, Hf_3P, $HfMo_2$	8.6151(5)	8.5996(11)	552.75(9)	
b			8.6137(7)	8.6025(13)	552.76(12)	
IX a	$Hf_{8.0}Mo_{5.0}P_{0.6}$	κ, $HfMo_2$, β-Hf(Mo)	8.6213(4)	8.6091(7)	554.16(7)	3.387(1)
b			8.6217(4)	8.6049(7)	553.94(7)	3.397(1)

served differences in unit-cell dimensions between alloys within the same three-phase area are quite small and can probably be attributed to minor uncontrollable variations in the rapid cooling process of the alloys.

As seen from Table III, κ-(Hf–Mo–P) enters into equilibria involving $HfMo_2$, β-Hf(Mo), and Hf_3P. The unit-cell volume of the κ phase varies between 552.43 Å^3 (three-phase equilibrium κ + Hf_3P + $HfMo_2$) and 556.10 Å^3 (three-phase equilib-

rium κ + Hf_3P + β-Hf(Mo)). The homogeneity range is most probably associated with a variable degree of Hf/Mo substitution, as indicated by the results of the previous single-crystal structure refinement (3). Vacancy formation, for instance on the phosphorus position, cannot be entirely excluded, but the structure refinement does not support this possibility. The isothermal section at 1850 K of the hafnium-rich corner of the Hf–Mo–P system is presented in Fig. 1; the estimated homogeneity range of
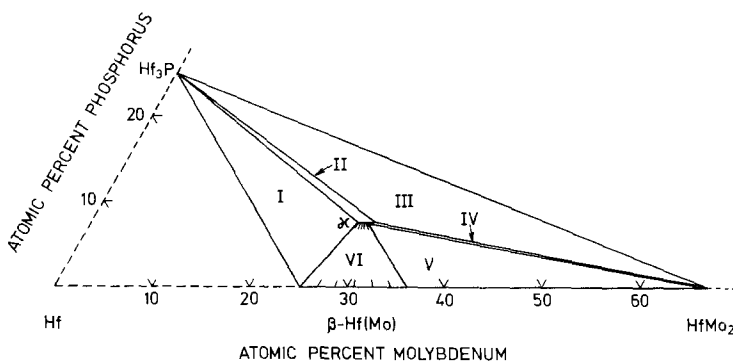

FIG. 1. Isothermal section at 1850 K for the hafnium-rich corner of the Hf–Mo–P system. The Roman numerals I–VI correspond to the two- and three-phase areas in which samples I–VI (Table III) were found to be situated.

TABLE IV

The Nominal Compositions of the Hf–Mo–S Alloys, the Phases Detected by Means of X-Ray Powder Diffraction, and the Unit-Cell Dimensions of the κ Phase and the β-Hf(Mo) Solid Solution

| Sample | Composition | Annealing temperature (K) | Phase detected | κ | | | β-Hf(Mo) |
				a (Å)	c (Å)	V (Å^3)	a (Å)
1a	$Hf_{11.6}Mo_{1.4}S_{2.7}$	1850	κ + Hf_2S + α-Hf	8.7447(5)	8.5831(7)	568.41(8)	
b	$Hf_{11.6}Mo_{1.4}S_{2.7}$	1700	κ + Hf_2S + α-Hf	8.7284(7)	8.5713(10)	565.52(12)	
c	$Hf_{11.0}Mo_{2.0}S_{2.0}$	1920	κ + Hf_2S + β-Hf(Mo)	8.7610(5)	8.6003(7)	571.68(8)	3.493(3)
2a	$Hf_{10.5}Mo_{2.5}S_{1.0}$	1850	κ + β-Hf(Mo)+ α-Hf	8.7406(4)	8.5834(6)	567.90(7)	3.488(1)
3a	$Hf_{8.0}Mo_{5.0}S_{2.3}$	1850	κ + Hf_2S + $HfMo_2$	8.6912(3)	8.5335(4)	558.24(4)	
b	$Hf_{8.0}Mo_{5.0}S_{2.2}$	1560	κ + Hf_2S + $HfMo_2$	8.6794(4)	8.5207(6)	555.31(6)	
c	$Hf_{8.0}Mo_{5.0}S_{2.0}$	1920	κ + Hf_2S + $HfMo_2$	8.7386(6)	8.5782(14)	567.29(12)	
4a	$Hf_{7.5}Mo_{5.5}S_{0.7}$	1850	κ + $HfMo_2$ + β-Hf(Mo)	8.6656(3)	8.5160(5)	553.82(5)	3.389(1)
5	$Hf_{9.90}Mo_{3.10}S_{1.25}$	1850	κ + β-Hf(Mo)	8.7469(4)	8.5932(5)	569.37(7)	3.486(1)
6	$Hf_{9.18}Mo_{3.82}S_{1.00}$	1850	κ + β-Hf(Mo)	8.6952(3)	8.5512(5)	559.91(5)	3.404(1)
7	$Hf_{9.18}Mo_{3.82}S_{1.30}$	1850	κ + $HfMo_2$	8.7018(3)	8.5502(4)	560.70(5)	

the κ phase has been indicated as well as the variable degree of molybdenum substitution in β-Hf(Mo). The various two- and three-phase areas are labeled with Roman numerals corresponding to the alloys listed in Table III.

Hf–Mo–As System

The alloys prepared in this system were annealed for 6 hr and the results are presented in Table II. This system exhibits a close resemblance to the Hf–Mo–P system, but the variations in the unit-cell volume of the κ phase between different three-phase areas are somewhat smaller. The κ-(Hf–Mo–As) phase enters into equilibria involving $HfMo_2$, β-Hf(Mo), and Hf_3As.

Hf–Mo–S System

Initially four alloys were prepared using annealing times of 6 hr, and the results are presented in Table IV (alloy Nos. 1a–4a). The κ-(Hf–Mo–S) phase enters into equilibria involving $HfMo_2$, β-Hf(Mo), Hf_2S, and hexagonal α-Hf. A comparison with the ternary systems discussed above reveals two main differences. First, the κ phase en-

ters into equilibria involving four other phases, and second, the variations in unit-cell volume between different three-phase areas are much larger than in the other systems. In order to investigate the extent of the homogeneity range more closely, three alloys were selected for chemical analysis (Table IV, sample Nos. 5–7). In addition to the κ phase, these alloys contained minor amounts of a second phase as revealed by heavily overexposed X-ray powder photographs. In alloy No. 6 the diffraction lines of the second phase (β-Hf(Mo)) were very much stronger than in the other two alloys, and an attempt to estimate the β-Hf(Mo) content of this alloy was made as follows. Starting from the original sample, two additional samples were prepared by adding 6.5 and 13 wt% β-Hf(Mo), respectively. Powder-diffraction films were recorded for the three samples, and the intensities of the β-Hf(Mo) reflections relative to the κ-phase reflections were determined. Assuming a linear relationship between the β-Hf(Mo) content and relative diffraction line intensities, the β-Hf(Mo) content was estimated to be 15 wt%. This value is, however, some-
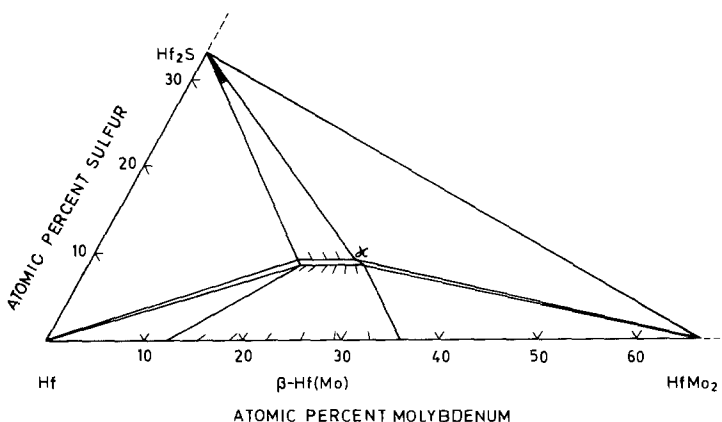
FIG. 2. A tentative isothermal section at 1850 K for the hafnium-rich corner of the Hf–Mo–S system.

what uncertain due to the broad and diffuse diffraction lines of the β-Hf(Mo) phase.

As mentioned in the experimental section the alloys prepared for the chemical analysis (Table IV, sample Nos. 5–7) were larger than the other alloys, which might influence the effective annealing temperature. The unit-cell volumes of these alloys, notably sample Nos. 5 and 7, are larger than would be expected from the volumes of sample Nos. 1a–4a. This might be explained if the width of the homogeneity range of the κ phase changes with temperature. In order to test this hypothesis some additional alloys were prepared using different annealing temperatures. The results indicate that the κ-phase volume increases with increasing annealing temperature (Table IV, samples 1b,c and 3b,c), which suggests that the effective annealing temperature was higher than 1850 K for alloy Nos. 5–7. It is also noteworthy that one of the three-phase equilibria shifts from κ + Hf$_2$S + α-Hf to κ + Hf$_2$S + β-Hf(Mo).

A tentative isothermal section at 1850 K of the hafnium-rich corner of the Hf–Mo–S system, subject to the experimental limitations mentioned above, is presented in Fig. 2. The homogeneity range of the κ phase has been indicated as well as the variable

degree of molybdenum substitution in β-Hf(Mo).

Hf–Mo–Se System

The alloys prepared in this system were annealed for 6 hr, and the results are presented in Table II. The Hf–Mo–Se system is similar to the Hf–Mo–S system, but the variations in unit-cell volume of the κ phase between different three-phase areas are much smaller. The κ-(Hf–Mo–Se) phase enters into equilibria involving HfMo$_2$, β-Hf(Mo), Hf$_2$Se, and α-Hf.

The β-Hf (Mo) Phase

In all of the above ternary systems the κ phase was found to enter into equilibria involving the β-Hf(Mo) solid solution. The body-centered cubic β-Hf phase dissolves molybdenum to a considerable degree (12), and the relationship between unit-cell dimensions and molybdenum content is presented graphically in Fig. 3 of Ref. (12). Using this graph and the unit-cell dimensions as determined in the present study, the extent of molybdenum substitution in the β-Hf phase can be estimated. This method was employed for estimating the limits of the homogeneity range of the β-

Hf(Mo) phase in the isothermal sections presented above.

According to the Hf–Mo phase diagram presented by Taylor *et al.* (*12*) the maximum solid solubility of molybdenum in β-Hf is 34 at.% at 1850 K. This result was checked by preparing an alloy with the nominal composition $Hf_{60}Mo_{40}$, using the same experimental conditions as before with an annealing time of 6 hr. In addition to the β-Hf(Mo) phase, X-ray powder photographs showed the presence of $HfMo_2$. The unit-cell dimension of β-Hf(Mo) was found to be $a = 3.392(1)$ Å, corresponding to a molybdenum content of 35 at.% using the above-mentioned graph. The result is thus in good agreement with that of Taylor *et al.* (*12*).

The unit-cell dimensions of the β-Hf(Mo) phase at the molybdenum-rich side of the κ phase in the ternary systems Hf–Mo–{P, As, S, Se} are nearly constant, varying only between 3.387 and 3.389 Å (see Tables II–IV). This corresponds to a molybdenum content of ~36 at.%, in reasonable agreement with the value obtained in the binary system Hf–Mo. In contrast, the corresponding unit-cell dimensions of β-Hf(Mo) in the ternary systems Hf–Mo–{Si, Ge} are significantly larger (see Table II). As mentioned before, these alloys were not in an equilibrium condition.

Discussion

The present study has shown that all κ phases examined have finite homogeneity ranges, the extent of which is in some cases quite considerable. In the following, an attempt is made to derive quantitative estimates of the compositional variations, and to relate them to the crystallographic properties of the κ-phase structure.

The structure of the κ phase is depicted in Fig. 3, and belongs to the space group $P6_3/mmc$. It invariably contains two transition metal components (M and M') distrib-
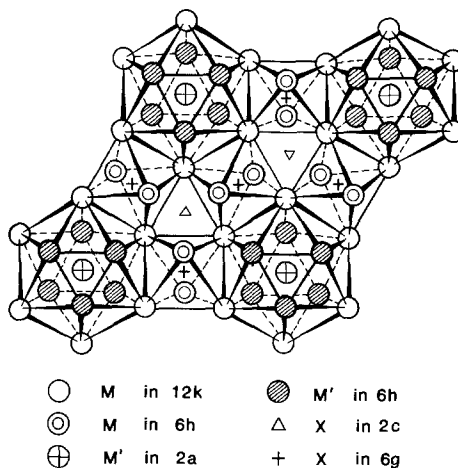

$\bigcirc$	M	in 12k		$\oslash$	M'	in 6h
$\circledcirc$	M	in 6h		$\triangle$	X	in 2c
$\oplus$	M'	in 2a		+	X	in 6g

FIG. 3. The structure of the κ phase projected along the hexagonal axis.

uted on the 12k position, two 6h positions, and the 2a position, and a third component (X) which might be either a 3d transition element or a nonmetal distributed on one or both of the positions 6g and 2c. Only κ phases containing a nonmetal will be considered in the following discussion.

In the ideal κ-phase structure, one of the transition metal components should occupy the 12k and one of the 6h positions and the other transition metal component should occupy the 2a and the second 6h position. Together, these atoms constitute a sublattice containing two types of interstices: the octahedral 6g site and the trigonal prismatic 2c site. Variations of the composition of the κ phases can occur in the following ways: (1) substitution of M atoms on the M' sites or vice versa; (2) vacancy formation on the M or M' sites; (3) various modes of filling of the 2c and 6g sites.

(1) Metal–Metal Substitution

A single-crystal structure refinement of the κ phase in the Hf–Mo–P system revealed the occurrence of hafnium substitution on the molybdenum sites (*3*). Similar substitutions have also been found to occur

in the κ-(Fe–W–C) phase (13) and recently also in the κ phases in the systems Hf–Mo–Se and Hf–Mo–Ge (11). A variable degree of Hf/Mo substitution might actually be the major mechanism responsible for the observed variations in unit-cell volumes among the κ phases examined in the present study.

(2) Metal Vacancies

This type of vacancy has not been observed in any of the κ phases examined so far by X-ray single-crystal structure analysis.

(3) Filling of the Holes

According to the result of the structure refinement of κ-(Hf–Mo–P) the trigonal prismatic 2c site is fully occupied by the nonmetal atom, whereas the octahedral 6g site is empty (3). The same is true for the κ-(Hf–Mo–Se) phase (11) and also for the κ-(Hf–Mo–B) phase (14). None of these investigations indicated any vacancies on the 2c site. As mentioned in the previous section the formation of the κ phase in the Hf–Mo–Ge system is promoted by the presence of oxygen and in the resulting quaternary κ-(Hf–Mo–Ge–O) phase the germanium atoms fill the 2c position only to 88%, whereas the oxygen atoms fill the 6g position to 49% (11). In the κ-carbides both positions are simultaneously occupied by carbon (13, 15), but the 2c position is occupied only to a fractional degree. Finally, in the κ-oxides the oxygen atoms exclusively occupy the 6g position (16). Observed variations in unit-cell volumes indicated a small range of homogeneity, which was proposed to be due to a variable degree of vacancies on the 6g site.

As mentioned above the nonmetal atoms P, Se, and Ge exclusively enter the trigonal prismatic 2c site and the nonmetals Si, S, and As are also expected to do so. The nonmetal having the smallest radius, sulfur,

might possibly also occupy the rather small octahedral 6g site, at least to some extent. In this context it might be mentioned that the unit-cell volume of α-Hf in the three-phase area κ + Hf$_2$S + α-Hf was found to be 45.53(1) Å^3. This is significantly larger than the value 44.86(3) Å^3 obtained for the hafnium used for the syntheses. According to Taylor et al. (12) α-Hf dissolves only minor amounts of molybdenum with no appreciable changes in lattice parameters. The observed increase in unit-cell volume might thus indicate that α-Hf dissolves sulfur. The sulfur atoms most probably occupy the octahedral interstices in the HCP lattice, thereby causing the expansion. The Hf–S distance in α-Hf (2.25 Å) has about the same magnitude as the Hf–S (octahedron) distances in κ-(Hf–Mo–S) (2.24–2.36 Å).

From the chemical analysis data of the Hf–Mo–S alloys it is possible to estimate the composition of the κ phase. The chemical formulae given in Table I were calculated neglecting the presence of the second phase in sample Nos. 5 and 7 (Tables I and IV), and by subtraction of 15 wt% β-Hf(Mo) (the molybdenum content was estimated to be 32 at.% from the unit-cell dimension) from sample No. 6 as obtained earlier. The formulae have been normalized to contain 13 metal atoms according to the crystallographic formula of the κ phase, and can be expressed as Hf$_{9+x}$Mo$_{4-x}$S$_y$.

Two of the alloys (Nos. 5 and 6) are situated in the two-phase area κ + β-Hf(Mo) having quite different degrees of Hf/Mo substitution ($x = 0.92$ and $x = 0.25$), while the sulfur content differs only slightly. As seen from Table IV the decrease in hafnium substitution is accompanied by a large decrease in unit-cell volume. The observed variations in unit-cell volume are thus connected to a variable degree of hafnium substitution on the molybdenum sites, and Hf/Mo substitution is accordingly confirmed to be an important cause of the extended

homogeneity range of the κ-(Hf–Mo–S) phase.

Another contributing factor to the variation in unit-cell volume of κ-(Hf–Mo–S) might be a variable sulfur content. This is actually a thermodynamic necessity for the construction of a reasonable isothermal section, since the unit-cell volume of the κ phase in the three-phase area κ + HfMo$_2$ + Hf$_2$S (558.24 Å^3) is larger than in the three-phase area κ + HfMo$_2$ + β-Hf(Mo) (553.82 Å^3) (see Fig. 2). The result from the chemical analysis of alloy Nos. 6 and 7 (Table I) also indicates a variable sulfur content, since they are situated in different two-phase areas and have nearly the same hafnium and molybdenum content but have a slightly different sulfur content. The increase in sulfur content of the κ phase between alloy Nos. 6 and 7 enlarges the unit-cell volume by only 0.81 Å^3 and is thus likely to play a minor role in determining the unit-cell volume. it should be observed that the sulfur content of the κ phase exceeds $y = 1$ in the formula Hf$_{9+x}$Mo$_{4-x}$S$_y$ (Table I). If only the trigonal prismatic $2c$ site were occupied the y value would be ≤ 1 and it must therefore be concluded that sulfur atoms also enter the octahedral $6g$ site. This is supported by the indications of some sulfur occupation in the octahedral sites of α-Hf, since the octahedron in the κ phase has about equal size. Assuming the $2c$ site to be fully occupied by sulfur, the degree of sulfur occupancy on the $6g$ site can be estimated to vary between 6 and 9%.

Evidently there are two factors responsible for the unit-cell volume variation of the κ-(Hf–Mo–S) phase. These are a variable degree of hafnium substitution on the molybdenum sites and a variable degree of sulfur occupation of the $6g$ site. The extension of the homogeneity range depending on the latter factor is, however, rather small and in the κ phases of the other ternary systems examined, the $6g$ site is most likely empty. The major mechanism responsible for the

TABLE V

THE MAXIMUM AND MINIMUM UNIT-CELL VOLUMES OF THE κ PHASES IN THE TERNARY SYSTEMS Hf–Mo–{Si, P, S, Ge, As, Se}, AND THE DIFFERENCES $\Delta = V_{max} - V_{min}$

System	V_{max} (Å^3)	V_{min} (Å^3)	Δ (Å^3)
Hf–Mo–Si	553.07	552.33	0.74
Hf–Mo–P	556.10	552.43	3.67
Hf–Mo–S	567.90	553.82	14.08
Hf–Mo–Ge	561.44	561.28	0.16
Hf–Mo–As	564.15	562.28	1.87
Hf–Mo–Se	566.40	564.03	2.37

observed homogeneity range is thus a variable degree of Hf/Mo substitution. As seen from Table V, the variations in unit-cell volume between different three-phase areas, and hence the width of the homogeneity ranges, increase on passing from Si to P to S. A similar trend is found for the κ phases containing Ge, As, and Se, and it may also be noted that these variations decrease on passing from $3p$ to $4p$ elements, e.g., from P to As. The extremely large variation in unit-cell volume of the κ-(Hf–Mo–S) phase is most probably due to the filling of both the $2c$ and the $6g$ sites. This might enhance the thermodynamical stability of the κ phase and, as discussed below, increase the width of the homogeneity range. This hypothesis is further supported by the results in the Hf–Mo–Ge system, where the introduction of oxygen on the $6g$ site seems to promote the formation of the κ phase.

A common feature of the investigated ternary systems is the occurrence of the two three-phase areas κ + β-Hf(Mo) + HfMo$_2$ and κ + HfMo$_2$ + Hf$_m$X, where Hf$_m$X denotes Hf$_2$Si, Hf$_3$Ge, Hf$_3$P, Hf$_3$As, Hf$_2$S, and Hf$_2$Se, respectively. For the more hafnium-rich alloys two alternatives exist. First, an isothermal section might contain one additional three-phase area κ + β-Hf(Mo) + Hf$_m$X, and second it might
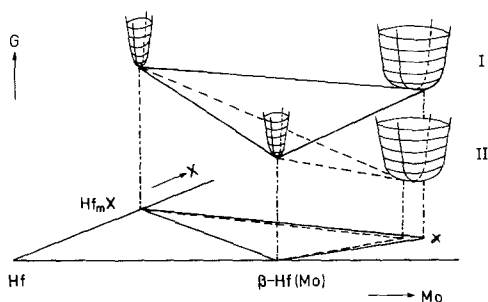
FIG. 4. Schematic free-energy surfaces of the phases κ, β-Hf(Mo), and Hf_mX, and their relationship to the isothermal section of a Hf-Mo-X system. In case II the relative stability of the κ phase has been increased, thus shifting the hafnium-rich composition of the κ phase toward a larger hafnium content.

contain two additional three-phase areas, κ + β-Hf(Mo) + α-Hf and κ + α-Hf + Hf_mX. The isothermal section of the Hf-Mo-P system (Fig. 1) is an example of the first type and further representatives are the ternary systems Hf-Mo-{Si, Ge, As}. Also, Zr-Mo-B system (14) belongs to this category since the κ phase enters into equilibria involving $ZrMo_2$, ZrB_2, and the β-Zr(Mo) solid solution. The second type is illustrated by the Hf-Mo-S system (Fig. 2) and further representatives are the Hf-Mo-Se system and the Hf-Mo-B system (17).

The variations in the width of the homogeneity ranges might be interpreted thermodynamically as follows. Consider the three-phase area κ + β-Hf(Mo) + Hf_mX, where Hf_mX denotes Hf_2Si, Hf_3Ge, Hf_3P, and Hf_3As, respectively, in a free-energy diagram. If the stability of the κ phase relative to that of the other two phases is increased, i.e., the free-energy surface is lowered, this would imply an increase in the width of the homogeneity range, since the tangent point on the free-energy surface of the κ phase is shifted toward a larger hafnium content (see Fig. 4). While the width of the homogeneity ranges of the κ phases increases in the order Ge → Si → As → P, this suggests the relative stability of the κ phases to increase

in the same order. A lower relative stability of the κ phases in the Hf-Mo-{Si, Ge} systems would also be a plausible explanation of the observed problems in reaching equilibrium conditions in these systems.

The occurrence of α-Hf in equilibrium with the κ phase can also be interpreted in a similar way. Assuming the free-energy surface of α-Hf to lie well above the phases κ, β-Hf(Mo), and Hf_mX, α-Hf would not enter into any equilibria involving the κ phase. If the free-energy surface of the κ phase is sufficiently lowered, α-Hf will become thermodynamically stable and enter into equilibria involving the κ phase. Such equilibria are observed in the Hf-Mo-S and Hf-Mo-Se systems, suggesting that the κ phases in these systems are very stable relative to the neighboring phases. The shift of one of the three-phase equilibria in the Hf-Mo-S system from κ + Hf_2S + α-Hf to κ + Hf_2S + β-Hf(Mo) by increasing the annealing temperature might analogously be interpreted as being due to a simultaneous increase in the relative stability of the β-Hf(Mo) phase.

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