Short Communication

New κ-Phases in the Systems Hf−W−{S,As,Se} and Hf−Re−{Si,P,S,Ge,As,Se,Fe,Co,Ni}

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The hexagonal κ-phase has been found to occur in a great number of ternary systems as reported by Rogl and Nowotny [1] and references given therein. In a recent communication,[2] κ-phases were reported in the ternary systems Hf−Mo−{Si,P,S,Ge,As,Se} and Hf−W−P. Studies have now been extended to further combinations and the present communication reports the results from an investigation of the following ternary systems: Hf−Mo−{C,N,Al,Sb}, Hf−W−{S,As,Se}, Hf−Re−{Si,P,S,Ge,As,Se,Fe,Co,Ni} and Sc−Mo−Ni.

Most of the starting materials for the syntheses of the different alloys have been described elsewhere.[2] Additional starting materials are listed in Table 1. Ternary alloys containing Si,Ge,Al,Sb,Fe,Co or Ni were prepared directly by arcmelting mixtures of the constituent elements. Due to the high volatility of the other nonmetals, samples of Hf_3P, Hf_2S, Hf_3As 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 arcmelted. All the arcmelted alloys were subsequently annealed at 1400 °C, except Hf−Re−{Fe,Co,Ni} which were annealed at 1300 °C, and Sc−Mo−Ni which was annealed at 1030 °C. For further experimental details see Ref. 2. The cell dimensions of the new κ-phases are presented in Table 2. Attempts to prepare κ-phases in the other of the above-mentioned ternary systems were unsuccessful.

The unit cell volumes of the new κ-phases show some interesting trends. In the two series of compounds κ-Hf−Re−{Si,P,S} and κ-Hf−Re−{Ge,As,Se}, the unit cell volumes decrease in the order Si→P→S and Ge→As→Se, respectively. This would be in accordance with the normal atomic sizes of these nonmetals, provided that the structures are completely ordered and do not contain vacancies. In contrast, the unit cell volumes increase in the corresponding series of κ-phases containing molybdenum instead of rhenium.[2] Recent results indicate that this effect might be connected with an increasing degree of Hf/Mo substitution on the molybdenum positions.[3] The difference in cell volume trends between the rhenium- and the molybdenum-containing κ-phases may accordingly be due to a much more restricted Hf/Re substitution on the rhenium sites. This hypothesis agrees very well with the substitutional solid solubility behaviour of hafnium in elemental molybdenum and rhenium. In molybdenum, the hafnium solubility extends to over 30 at%[4] while, in rhenium, the maximum solid solubility is at least ten times smaller.[5]

Table 1. Starting materials for the syntheses.

Substance	Supplier	Purity
Re	Hereaus, Hanau, Germany	>99.8 %
MoC	Highways International, Baarn, The Netherlands	>99 %
$Mo_2N + MoN$		>99.5 %
Si		>99.999 %
Al	Gränges SM, Finspång, Sweden	>99.999 %
Sb	Johnson & Matthey, London	<1 ppm metallic impurities
Fe		<15 „
Co		<20 „
Ni		<20 „

Table 2. Cell dimensions and cell volumes for the new κ-phases. Standard deviations are given in parentheses. The approximate composition is Hf_9M_4X where $M = W$ or Re and $X = Si,P,S,Ge,As,Se,Fe,Co$ or Ni.

Phase	a (Å)	c (Å)	V (Å^3)
κ-Hf − W − S	8.6682(5)	8.5627(5)	557.18(5)
κ-Hf − W − As	8.6741(5)	8.6967(9)	566.67(7)
κ-Hf − W − Se	8.7073(6)	8.6674(5)	569.10(5)
κ-Hf − Re − Si	8.5643(6)	8.6377(10)	548.68(7)
κ-Hf − Re − P	8.5666(5)	8.6221(8)	547.97(6)
κ-Hf − Re − S	8.5907(5)	8.5008(9)	543.32(7)
κ-Hf − Re − Ge	8.5771(5)	8.6642(5)	552.00(5)
κ-Hf − Re − As	8.5968(4)	8.6075(10)	550.91(7)
κ-Hf − Re − Se	8.6050(10)	8.5614(12)	549.00(10)
κ-Hf − Re − Fe	8.5830(5)	8.4178(9)	537.04(7)
κ-Hf − Re − Co	8.6077(2)	8.4281(4)	540.80(3)
κ-Hf − Re − Ni	8.6261(5)	8.4367(5)	543.66(5)

For the three phases κ-Hf − Re − {Fe,Co,Ni}, the unit cell volumes increase in the order Fe→Co→Ni, and this is true also of the κ-Hf − Mo − {Fe,Co,Ni} series. An opposite trend would normally be expected considering the decrease in atomic size of passing from Fe to Co to Ni. A single crystal structure refinement of κ-Hf − Mo − Ni revealed no significant deviations from the ideal crystallographic formula Hf_9Mo_4Ni, except for a minor amount of dissolved oxygen.[6] It would thus appear that atomic substitutions or vacancies must occur to a much greater extent in the cobalt- and iron-containing phases.

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4. Garg, S. P. and Ackermann, R. J. *Metall. Trans. A 8* (1977) 239.
5. Ageev, N. V., Ed., *Phase Diagrams of Metallic Systems*, Acad. Sci., Moscow 1969, p. 31.
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