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A Constitutional Diagram of the System $VC_{0.88}$—$HfC_{0.98}$—(MoC)

By

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With 5 Figures

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The system $VC_{0.88}$—$HfC_{0.98}$—"MoC" was investigated by means of melting point, differential-thermoanalytical, X-ray diffraction and metallographic techniques on hot pressed and heat treated as well as melted alloy specimens and a constitutional diagram from 1500 °C through the melting range established.

The small miscibility gap within the HfC—"MoC" system (T_c = 1630 °C) interacts at lower temperatures with the solvus in a monotectoid-like reaction at ≈ 1575 °C. Additions of VC to the HfC—"MoC" solid solution gradually increase its critical temperature.

Solid state phase behaviour and melting behaviour was established within the isopleths $VC_{0.88}$—"MoC" as well as within $(V_{0.5}Hf_{0.5})C$—"MoC" and $(V_{0.75}Hf_{0.25})C$—$(Hf_{0.75}Mo_{0.25})C$.

Phase equilibria within $VC_{0.88}$—HfC—"MoC" are characterized by an extreme large miscibility gap at 1500 °C connecting the VC—HfC and HfC—MoC systems.

Originating at the VC—HfC binary an eutectic trough proceeds into the VC—HfC—MoC ternary with rising temperatures, connecting the maximum critical point of the disappearing miscibility gap [$(V_{0.31}Hf_{0.49}Mo_{0.20})C$] by a limiting tie line (2750 ± 20 °C). Isothermal sections have been calculated assuming regular solutions.

I. Introduction and Summary of Previous Work

In a series of investigations of carbide systems such as: HfC—TiC(VC)—WC(MoC) recently constitutional diagrams of the TiC—HfC—WC[1]—as well as of the VC—HfC—WC[2]—system have been presented. In both systems especially the phase behaviour of the ternary miscibility gap was studied with respect to spinodal decomposition.

The present investigation of the system VC—HfC—"MoC" should establish the phase behaviour in terms of a complete constitutional diagram.

The phase relationship within the isopleths $VC_{0.88}$—HfC as well as HfC—"MoC" have been very well established and have been recently[1,2] presented.

No complete phase diagram for the $VC_{0.88}$—"MoC"-isopleth has been reported in literature, but earlier investigations of the ternary system V—Mo—C by *Rudy*[3] revealed some data on the phase relationship within the join $VC_{0.88}$—"MoC".

No data on the system $VC_{0.88}$—HfC—"MoC" were available in literature.

II. Experimental

Raw Materials

Carbide powders VC, HfC and Mo_2C were used in preparing the experimental alloy specimens.

Vanadium monocarbide powder was purchased from Wah Chang Corporation, Albany, with an average particle size of 10 μ. The total amount of carbon was 17.23 wt% C. Major impurities (in ppm) were N: 40; O: 1200; iron metals: 1200. The measured lattice parameter was 4.167 Å.

Hafnium monocarbide powder was prepared in our laboratory by reduction of HfO_2 with lampblack carbon in a carbon furnace at ≈ 2000 °C. The total carbon content of the product was 49.5 at% C (0.2 wt% free C). Major impurities included 0.05 wt% N and O. The measured lattice parameter was 4.640 Å.

Molybdenum carbide powder was purchased from Wah Chang Gleen Cove with an average particle size of 4 μ (iron metal impurities 0.01 wt%). The total carbon content was 5.99 wt% (0.1 of which was free carbon). The lattice parameters were $a = 3.008$ Å and $c = 4.732$ Å.

Carbon was used as lampblack carbon (Wah Chang Company, major impurities in ppm: $S < 400$, $Si < 238$, iron metals < 320) and in proper amounts was added to the carbide powder mixtures in order to account for a molybdenum monocarbide "MoC".

Sample Preparation

A detailed description of the sample preparation, melting point determination, differentio-thermoanalytical, X-ray and metallographic techniques was recently presented[1] and applies as well to the present investigation.

III. Graphical Representation

Because of the substoichiometric carbon rich boundary of the monocarbide solutions, the system VC—HfC—"MoC" actually represents the section $VC_{0.88}$—$HfC_{0.98}$—"MoC" of the quaternary system V—Hf—Mo—C (see also carbon content of the powder materials used). In all cases if not specially denoted the symbols VC—HfC are used for the carbon saturated carbides $VC_{0.88}$ and $HfC_{0.98}$; the symbol "MoC" is used for a hypothetical compound at 50 at% carbon.

It should be emphasized that according to the melting behaviour within the binary systems V—C, Hf—C, Mo—C at $VC_{0.88}$, $HfC_{0.98}$, and "MoC" the system $VC_{0.88}$—$HfC_{0.98}$—"MoC" does not represent a pseudoternary system. In spite of this fact for a graphical representation the system was considered like a pseudoternary system: concentrational section $VC_{0.88}$—$HfC_{0.98}$—"MoC" as a basis and T (temperature) as vertical axis. But in this type of graphical representation interpretation of phase and melting behaviour is unlike in a true pseudoternary system: i.e. the liquidus surface in the "MoC" rich corner does not represent the primary crystallization of "MoC" but of carbon (see Fig. 2*f*, 3*a*). Similarly the $L + \delta + C$ and $L + \delta_1 + \delta_2$ phase fields do not degenerate when reaching the boundary isopleths VC—HfC, VC—"MoC" and HfC—"MoC" (see also Ref. [1, 2] and Fig. 1 *b*).

To prevent misunderstanding among the often confusingly used symbols for the molybdenum carbides, we have listed* the carbide phases, their crystallographic notation and lattice parameters as well as the symbol used throughout this work. For a more detailed information reference is made to a systematic work on the notation of transition metal carbides by *Parthé*[4].

IV. Results and Discussion

The Isopleth $VC_{0.88}$—"MoC"

According to the decomposition of δ-MoC_{1-x}: $\delta \rightleftarrows \eta + C$ at 1960 °C[5] the solid solution (B 1) within $VC_{0.88}$—"MoC" is complete above 1960 °C. Lattice parameters and solid solubility are presented in Fig. 1*a*. The lattice parameter curve at 1500 °C actually represents the location of the vertex of the three phase equilibrium $\delta + \eta + C$ at the monocarbide solution: $(V, Mo)C_{1-x}$ within V—Mo—C. At higher temperatures the carbon rich phase boundary of the VC—"MoC" solution shifts to slightly higher carbon concentrations as can be seen from the higher lattice parameters in arc melted samples (Fig. 1*a*, second curve).

Investigation of the melting behaviour along the join $VC_{0.88}$—"MoC" showed extremely flat melting temperatures and phase fields (Fig. 1*b*).

Phase Equilibria in the Range From 1500 to 2000 °C

According to earlier investigations of the Mo—C binary system[5] η-MoC_{1-x} decomposes at temperatures below 1655 °C: $\gamma \rightleftarrows \eta + C$. However X-ray investigation of samples in the very "MoC"-rich corner showed stabilization of η-MoC_{1-x} by small additions of VC and HfC (5–10 mole%) to lower temperatures $\leqslant$ 1500 °C. The stabilizing effect of HfC on η-MoC_{1-x} was also reported by *Eremenko*[6] (5 mole% HfC, $T \leqslant 1400$ °C).

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* Table 1, Mh. Chem. **108**, 1330.

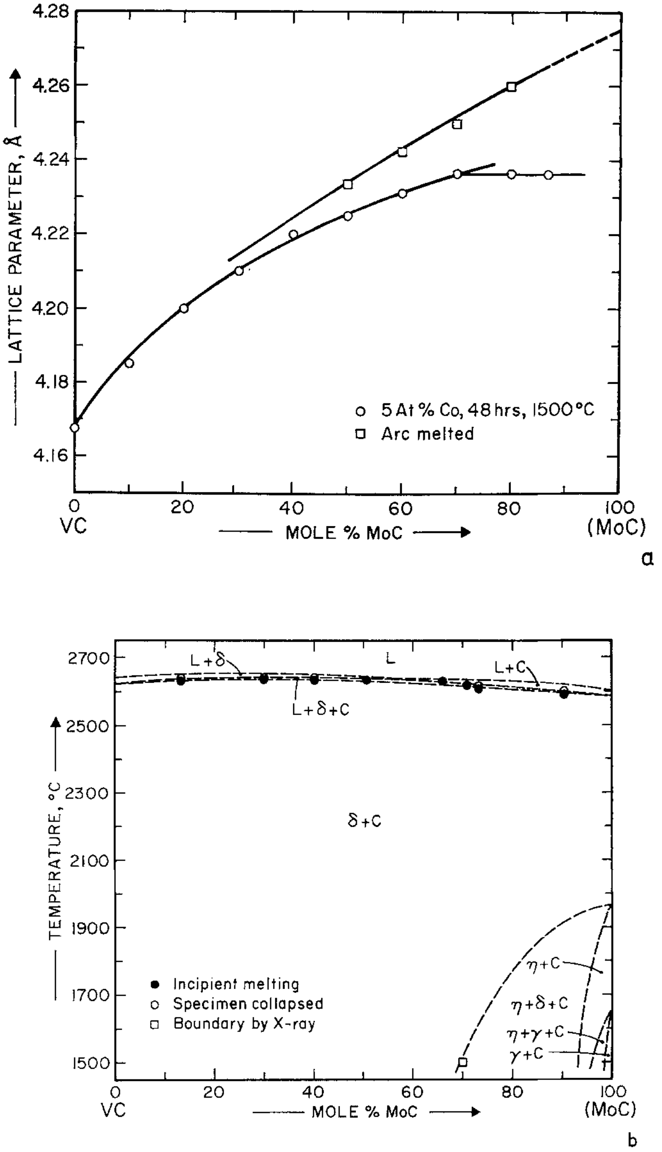

Fig. 1. *a* Location of the vertex of the three phase equilibrium (V, Mo)C + MoC (η) + C at the cubic monocarbide phase (δ) by lattice parameter measurements. *b* Experimental melting temperatures and phase distribution along the join VC$_{0.88}$—"MoC"

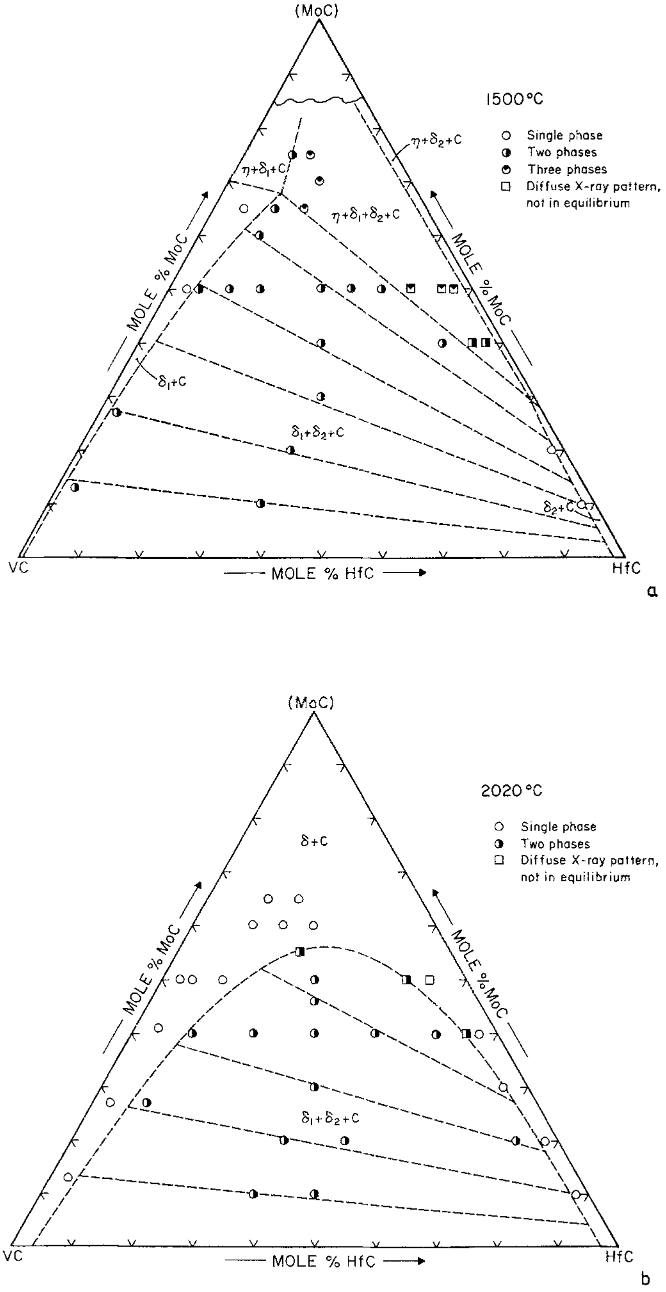

Fig. 2. Location and qualitative (X-ray) phase evaluation of alloy samples equilibrated at 1500 °C (*a*), 2020 °C (*b*); isoparametric lines

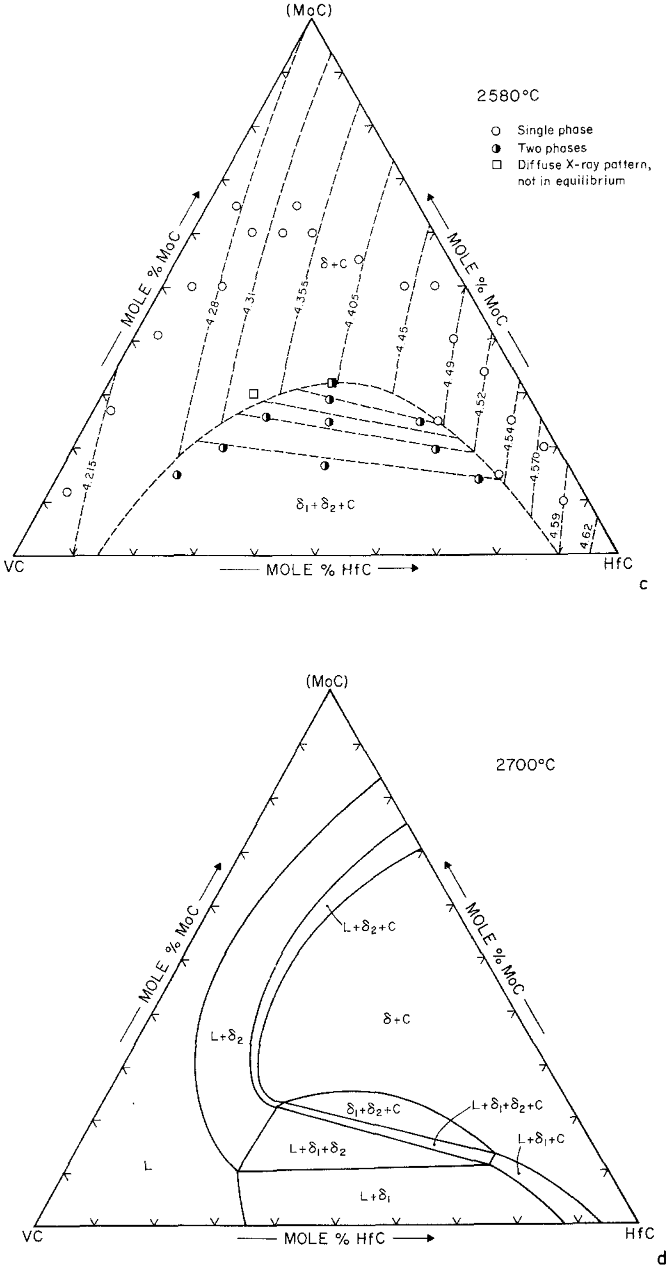

Fig. 2. Isothermal sections at 2580 °C (*c*) and 2700 °C (*d*)

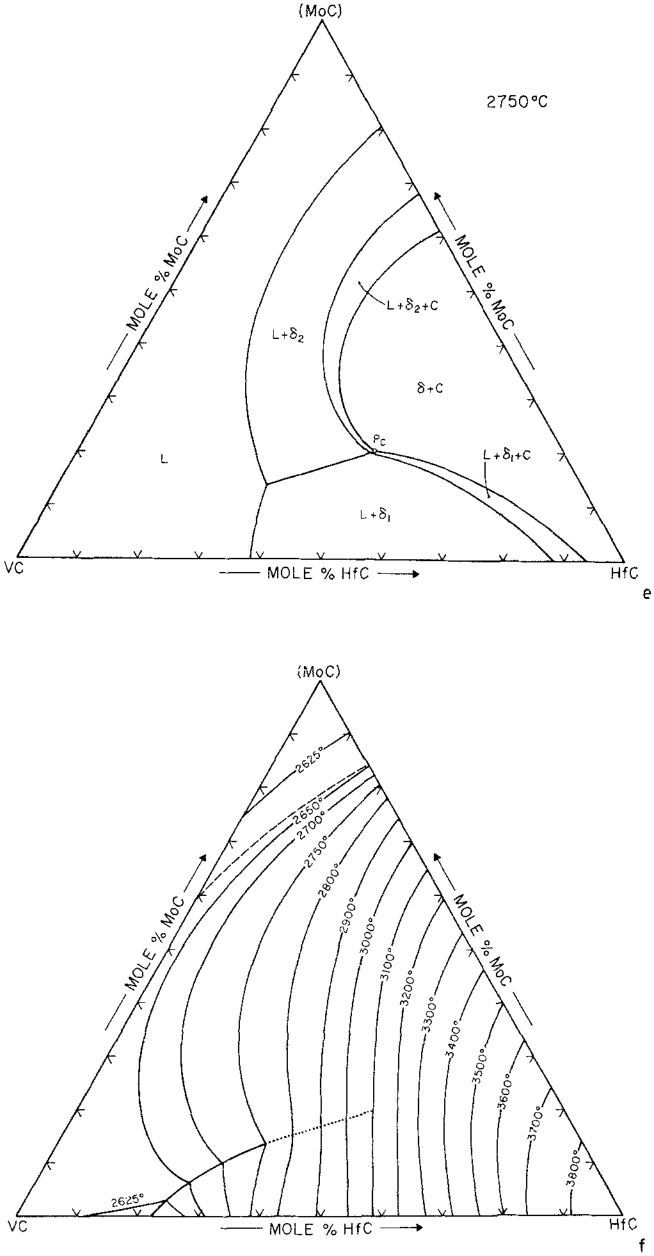

Fig. 2. *e* Isothermal section at 2750 °C. *f* Liquidus projection in the $VC_{0.88}$—$HfC_{0.98}$—(MoC) system

Phase Equilibria at 1500 °C (Fig. 2*a*) are characterized by an extremely large miscibility gap connecting the binary gaps within $VC_{0.88}$—HfC and HfC—"MoC". At 1500 °C the miscibility gap intersects the solvus surface (boundaries between the $\delta + C$ and $\eta + C$ phase fields).

The amount of carbon involved in the phase equilibria (Fig. 2*a*) is small near the $VC_{0.88}$—HfC region but becomes larger towards the "MoC"-corner (as the carbon-rich boundary of η-"MoC" is at ≈ 39 at% C); because of the weak scattering power of carbon, free carbon was not shown by the X-rays and therefore carbon was neglected in the phase determination (single phase, two phase, etc.) in all solid state isothermal sections. Phase equilibria in the very "MoC"-rich corner were not studied in detail.

Above 1630 °C (critical point of the HfC—"MoC" solid solution) the ternary miscibility gap retreats from the join HfC—"MoC": Additions of VC raise the critical temperature T_c.

At temperatures higher than 1960 °C (Decomp. of η MoC_{1-x}) phase equilibria are simply represented by a miscibility gap extending from VC—HfC into a complete solid solution (δ) (V, Hf, Mo)C + C.

An isothermal section of $VC_{0.88}$—HfC—"MoC" at 2020 °C is shown in Fig. 2*b*. The critical point at 2020 °C, determined from the experimental slope of the tie lines is at $(V_{0.1}Hf_{0.4}Mo_{0.5})C$.

Phase Equilibria at High Temperatures

Higher temperature sections at 2580, 2700, and 2750 °C have been investigated to study the phase behaviour arising from the interaction of the miscibility gap with the eutectic valley originating in the VC—HfC system [$T_E = 2580$ °C, $(V_{0.78}Hf_{0.22})C$]. Heat treatment was mostly carried out in the melting point furnace and samples whenever necessary quenched in tin. Samples near the solidus surface have been treated in the *DTA*-apparatus because of its highly stable temperature control. Sample location, X-ray evaluation, isoparametric lines as well as the resulting phase behaviour in an isothermal section at 2580 °C is shown in Fig. 2*c*. The isothermal sections at higher temperatures involving liquid as a phase were investigated in combination with the melting point determination of solidus and liquidus surfaces (Figs. 2*d*, 2*e*). Phase equilibria are very similar to the $VC_{0.88}$—HfC—WC system[2]. At 2750 °C a limiting tie line (degeneration of $L + \delta_1 + \delta_2$, $L + \delta_1 + \delta_2 + C$ phase fields) connects the "eutectic" melting trough, arising from the VC—HfC system and the maximum type critical solution point $(V_{0.31}Hf_{0.49}Mo_{0.2})C$ of the disappearing miscibility gap (mixed nodal junction III + IV)[7].

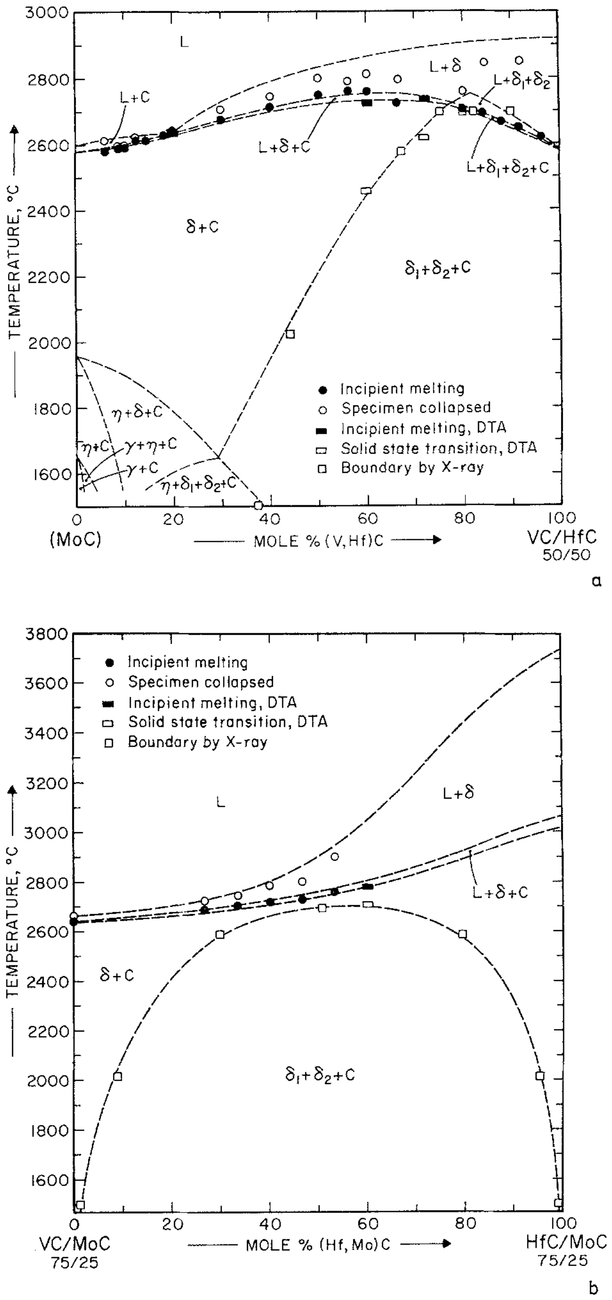

Fig. 3. Experimental melting temperatures and phase distribution: *a* along the join (MoC)—$(V_{0.5}Hf_{0.5})C$; *b* along the join $(V_{0.75}Hf_{0.25})C$—$(Hf_{0.75}Mo_{0.25})$ C

The Isopleths:

“MoC”—$(V_{0.5}Hf_{0.5})C$ *and* $(V_{0.75}Mo_{0.25})C$—$(Hf_{0.75}Mo_{0.25})C$

Fig. 3*a* shows the resulting phase—as well as melting—behaviour in the isopleth “MoC”—$(V_{0.5}Hf_{0.5})C$. The sharp maximum 2750 °C of the $L + \delta_1 + \delta_2$ field represents the intersection of the isopleth with the limiting tie line, connecting the critical solution point (i.e. the max. critical point) of the disappearing miscibility gap (see also Fig. 2*e*).

Fig. 3*b* represents melting temperatures and phase distribution along the join $(V_{0.75}Mo_{0.25})C$—$(Hf_{0.75}Mo_{0.25})C$.

Approximately 50 alloy specimens have been investigated to determine the liquidus as well as solidus surface within the system $VC_{0.88}$—$HfC_{0.98}$—“MoC” (Fig. 2*f*).

The liquidus projection is characterized by

a) a very flat liquidus surface along the join VC—MoC with gradually increasing temperatures towards the high melting HfC-corner;

b) a melting trough arising from the VC—HfC binary terminated by a limiting tie line connecting the critical solution point of the miscibility gap (dotted line in Fig. 2*f*);

c) a very flat melting trough in the “MoC”-corner: Originating at the metal—carbon binaries Hf—C and V—C, the monocarbide—carbon eutectic proceeds as a bivariant reaction into the ternaries V—Mo—C and Hf—Mo—C. Both eutectic valleys intersect the isopleths $VC_{0.88}$—“MoC” as well as HfC—“MoC”, thus creating a melting trough within $VC_{0.88}$—HfC—“MoC”. The dashed line (Fig. 2*f*) represents the bottom line of this melting trough separating the $L + C$ and $L + \delta$ field of primary crystallization.

Assembly of the Phase Diagram

All experimental data have been combined to construct a constitutional diagram of the system $VC_{0.88}$—$HfC_{0.99}$—“MoC”. A number of isothermal sections as well as isopleths have been prepared for a detailed description (Figs. 2*a* through 3*b*).

V. Thermodynamic Calculations

Recently a thermodynamic calculation of the system VC—HfC—WC was published[2]. Assuming regular solutions (following *Meijering*’s[8] formalism) very good accordance between calculated and experimentally observed isothermal sections was obtained.

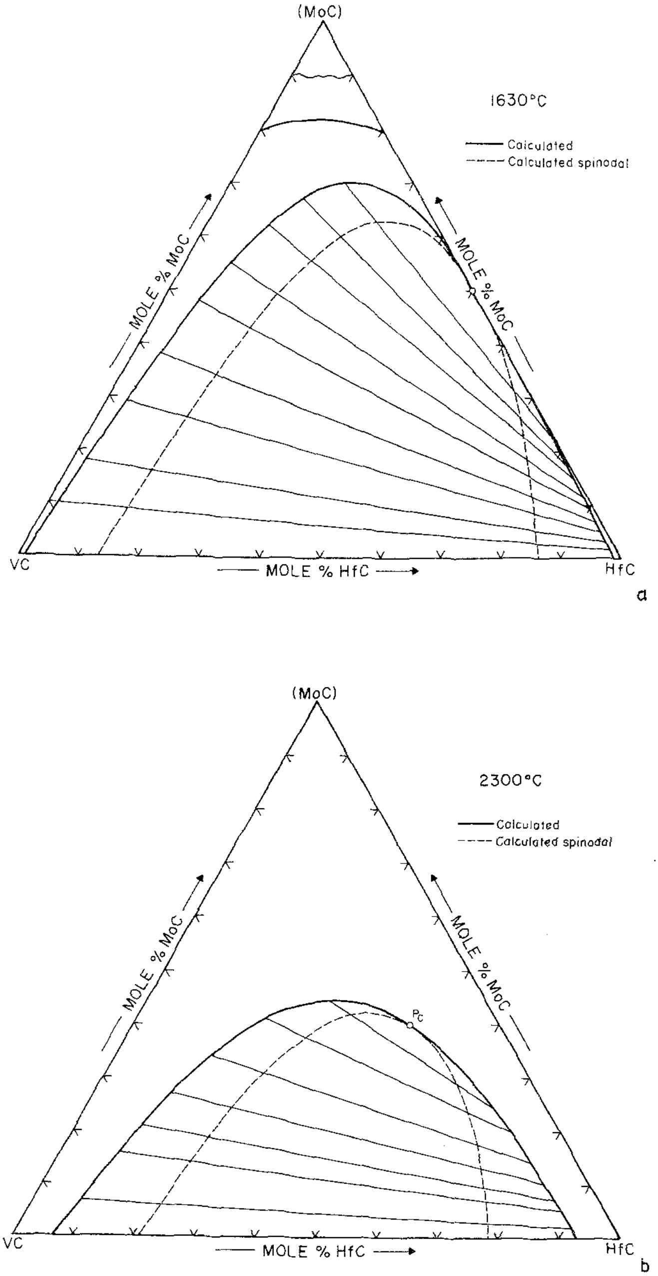

Fig. 4. Calculated isothermal sections of the system VC—HfC—(MoC): *a* at 1630 °C; *b* at 2300 °C, regular solution

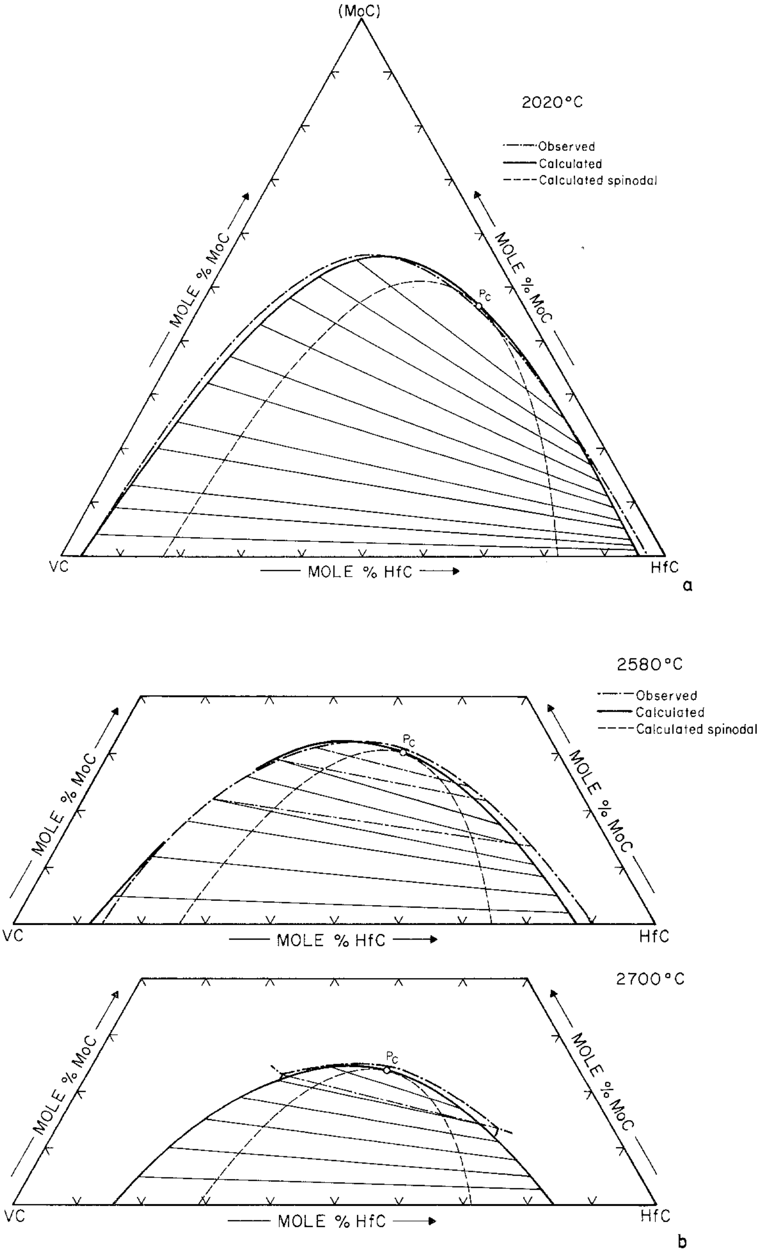

Fig. 5. Comparison between observed and calculated ternary miscibility gap of the VC—HfC—(MoC) system (regular solution): *a* at 2020 °C; *b* at 2700 °C

Therefore an extension of these calculations to the system VC—HfC—"MoC" seemed to be very promising.

For the calculations a computer program was used (Fortran II) which calculates the ternary spinodal, binodal and solvus curve, the critical point and tie lines across the miscibility gap. The possibility of a ternary isolated critical point as well as of a ternary saddle point is examined. The calculations were carried out by use of the Newton-Raphson iteration method. A detailed description of the program will be published[9].

Table 1 (interaction parameters ε of a one parameter regular solution approach, as well as transformation energies $\Delta F_{\text{cub} \rightarrow \eta}$) represents the values used in the calculation of the system VC—HfC—"MoC".

Table 1

ε (cal/mole)	$\Delta F_{\text{cub} \rightarrow \eta}$ (cal/mole)
VC—MoC = 1000	VC = 1800
HfC—MoC = 7560	HfC = 2300
	(MoC) = $0.98\,T - 2180$

Calculating isothermal sections within VC—HfC—WC, the interaction parameter ε (VC—HfC) proved to be temperature dependant and its values have been presented earlier[2].

Comparison between experimental and calculated isothermal sections of VC—HfC—"MoC" revealed very satisfactory results (Figs. 5*a*, *b*). Intermediate sections have been calculated at 1630 and 2300 °C (Fig. 4*a*, *b*).

Considering the good agreement between observed and calculated sections the very simple regular solution approach proves to be very useful in precalculating ternary sections of new systems as long as the "binary" interaction parameters are known with certain accuracy, which in turn can in most cases be easily obtained from the phase behaviour of ternary M—M'—X systems or the phase behaviour of the regarded "binaries". On the other hand calculation of "pseudo-ternary" sections which are experimentally well established can be used for optimization of the regular solution parameters, which in other combinations might be used for precalculation of a desired set of isothermal sections.

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