Monatshefte für Chemie 108, 1189—1211 (1977)

Monatshefte für Chemie

A Constitutional Diagram of the System TiC—HfC—WC

By

Peter Rogl*, **Subhash K. Naik**, and **Erwin Rudy**

Materials Science Department, Oregon Graduate Center for Study and Research, Beaverton, Oregon, U.S.A.

With 7 Figures

(Received January 12, 1977)

The system TiC—HfC—WC 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 complete constitutional diagram from 1500 °C through the melting range established. According to the peritectic melting of hexagonal WC both isopleths, TiC—WC as well as HfC—WC show a class II reaction at 2760 °C in Ti—W—C and at 2730 °C in Hf—W—C.

The phase behaviour within the TiC—HfC—WC system is characterized by the presence of a (binary) miscibility gap within TiC—HfC [$T_c = 1780$ °C, $(TiC)_{0.55}(HfC)_{0.45}$] which extends into the ternary forming a closed ternary miscibility gap at higher temperatures with an isolated ternary critical point: $T_c = 1800$ °C, $(TiC)_{0.55}(HfC)_{0.45}(WC)_{0.05}$. Interaction of the solvus (boundary of the cubic-B 1 monocarbide solid solution) and the ternary miscibility gap was established at 1540 °C and $(TiC)_{0.27}(HfC)_{0.41}(WC)_{0.32}$: Alloys of this composition enter a decomposition reaction on cooling into two isotypic cubic B 1 phases and hexagonal WC.

Isothermal sections were calculated assuming regular solutions.

I. Introduction and Summary of Previous Work

Monocarbides of the refractory transition metals in combination with iron metal binders form the basis of modern cutting tool materials[1].

---

* Present address: Institute of Physical Chemistry, University of Vienna, Währinger Straße 42, A-1090 Wien, Austria.

A systematic investigation of the phase relationships in binary as well as ternary (metal—metal—carbon) systems was carried out by *Rudy*[2]. Careful investigations have shown that certain solid state reactions in carbide solutions can be used with advantage to obtain ultrafine dispersions of carbides in refractory metal binders[3]. Furthermore it was shown by *Rudy*[4] that phase stability induced critical solution phenomena offer many interesting possibilities for microstructure and property control of alloys. For further application of the principle of spinodal decomposition to the development of high quality cutting tool materials, a basic investigation of the phase and solution behaviour among systems such as $\{WC(MoC_{1-x})\}$—$\{TiC(VC)\}$—HfC seemed to be very promising as well as necessary as literature data on this subject are relatively scarce.

Among the boundary systems of TiC—HfC—WC the phase relationship within the isopleth TiC—WC has been very well established in terms of a complete constitutional diagram of the Ti—W—C ternary by *Rudy*[5]. According to this investigation[5] three characteristic elements influence the phase behaviour within the isopleth TiC—WC (see Fig. 6*c*):

a) A congruent maximum melting point of the cubic monocarbide solution $(Ti, W)C_{1-x}$ at 3130 °C and $(Ti_{0.56}W_{0.44})C_{0.78}$.

b) A pseudobinary eutectic: monocarbide B 1 + C at 3030 °C and Ti(21)W(23)C(56).

c) A class II reaction $L + C = B\,1 + WC_{\text{hex.}}$ at 2760 °C.

No complete isopleth: HfC—WC has been reported in literature.

The pseudobinary system TiC—HfC has been the subject of numerous investigations. *Nowotny*[6] found a homogeneous series of solid solutions at temperatures higher than 2000 °C whereas a thermodynamic evaluation of an isothermal section VC—TiC—HfC at 2050 °C by *Rudy*[7] revealed strong indication of a miscibility gap at temperatures lower than 1750 °C. *Brukl*[8] investigated isothermal sections within the system Ti—Hf—C at 1500, 1700, and 1900 °C and found evidence of a miscibility gap in alloy samples along the carbon rich boundary of the monocarbide solution (Ti, Hf)C but the miscibility gap was found to be closed at the low carbon boundary (1500 °C). No data on the melting behaviour were given.

A more recent study of the TiC—HfC system by *Kieffer*[9] established the miscibility gap at the carbon rich boundary: $T_c = 1830$ °C, $(TiC)_{0.55}(HfC)_{0.45}$. The miscibility gap is asymmetrically transferred to the lower melting carbide (Fig. 1*b*).

The solid state phase behaviour within TiC—HfC—WC was investigated by *Kieffer*[10] in four isothermal sections (1600, 1800, 2000, and 2200 °C); an isolated ternary miscibility gap was found (2000 °C).

II. Experimental

Raw Materials

Monocarbide powders TiC, HfC, WC were used in preparing the experimental alloy specimens.

Titanium monocarbide powder (325 mesh) was purchased from H. C. Starck, Berlin (Goslar). The total carbon content was 49.2 at% C (0.2 wt% free C, $TiC_{0.97}$). Major impurities included 0.065 wt% N and 0.1 wt% O. The measured lattice parameter was $a = 4.328$ Å.

Tungsten monocarbide powder (Teledyne Wah Chang-Huntsville, Huntsville, Alabama) with average particle size 2 μ contained a total amount of 50.0 at% C (0.02 wt% free C, WC). Iron metal impurities were less than 0.02 wt%. The measured lattice parameters were $a = 2.905$ and $c = 2.837$ 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 was 49.5 at% C (0.2 wt% free C, $HfC_{0.98}$).

Major impurities included 0.05 wt% N and O. The measured lattice parameter was 4.640 Å.

Sample Preparation

The majority of experimental alloys were prepared by short duration (≈ 2 min.) hot pressing of the powder mixtures in graphite dies. A sectional view of the equipment was shown earlier[5]. After hotpressing, the surface zones were removed by grinding and the samples were then homogenized in a tungsten mesh furnace of the R. Brew Company. To all alloy samples initially 1 at% Cobalt was added as a diffusion aid. To enhance the equilibrium reaction the samples were crushed to 60 μm after hotpressing and heat treated with additional 1–3 at% Co.

Some alloys at 1500 °C were heat treated in an auxiliary metal bath (Cobalt). The auxiliary metal bath technique was described in detail by *Jangg*[11] and proved to be very suitable for the production of solid solutions of carbides at the high carbon boundary. The resulting solutions were reported to be very low in oxygen and nitrogen and well crystallized.

In our laboratory cylindrical containers of low ash CS-grade graphite were filled with a cobalt : carbide mixture (approximate ratio 3 : 1). Heat treatments were performed at 1500 °C for 12 hrs. under argon, but helium was used for a rapid quench. After heat treatment the reguli were removed from the graphite containers, crushed and the cobalt metal was quickly dissolved in a HCl (1 : 1) solution while heating at ≈ 65 °C. The obtained carbide powders were washed in acetone and mounted for X-ray investigation. Both the hotpressed and subsequently powdered (300 mesh) samples were used as well as powder mixtures of the starting materials. The auxiliary metal bath technique revealed very satisfactory results in establishing the binary as well as the ternary miscibility gap at 1500 °C. Determination of the miscibility gap boundary at higher temperatures (1600, 1700, 1730, 1750, 1780, and 1800 °C) was carried out by X-ray evaluation of samples which had been treated in two ways at each temperature:

a) Samples heat treated previously at high temperatures (single phase) with subsequent heat treatments at lower temperatures.

b) Samples previously heat treated at lower temperatures and following heat treatment at higher temperatures.

In some cases (2000 °C) alloy samples were prepared as "cold pressed" carefully blended powder mixtures of the starting materials with subsequent heat treatment (5 at% Co, no compacting agents).

Equilibration treatments at 1500 °C were carried out under vacuum (10^{-5} Torr, 120 hrs.) and those at higher temperatures (1750 °C, 48 hrs., 2000 °C, 8 hrs.) under high purity argon. Heat treatments in excess of 2200 °C were carried out in our *Pirani* melting point furnace. Where required specimens were equilibrated and then quenched in tin. A piece of each alloy was arc melted under high purity helium for metallographic studies.

Melting Point Determinations

The melting temperatures of about 70 alloys were measured by the *Pirani* method. Design details of the apparatus as well as temperature calibration and correction procedures were described earlier by *Rudy*[12]. The samples were first degased at lower temperatures in vacuum and then preequilibrated at subsolidus temperatures under helium. All measurements were carried out under a helium pressure af 1.5 atm.

Differential Thermal Analysis

Using annealed graphite as reference standard the thermal behaviour of about 15 alloys was studied in the *DTA* apparatus described earlier[5]. All the *DTA* experiments were carried out under 1.2 atm argon. For high temperature investigations ($\geqslant$ 2800 °C) high purity CS-graphite holders were used.

Metallographic and X-Ray Analysis

For microscopic studies the specimens were mounted in a mixture of diallyl phtalate and lucite copper powder and were preground on silicon carbide papers and diamond wheels. The samples were then polished on nylon cloth using a slurry of Linde B alumina (0.3 μ) and 5% chromic acid solution.

Samples in or near the TiC—HfC pseudobinary were electroetched in 5% sulfuric acid solution, tungsten rich alloys in 20% *Murakami*'s solution.

Powder diffraction patterns were prepared from all experimental alloys and the X-ray films were evaluated with respect to number, structure and lattice parameters of the observed phases. The disappearing phase and lattice parameter technique was used to determine boundaries and tie lines of the phase equilibria.

III. Graphical Representation

Because of the substoichiometric carbon-rich boundary of the B1 monocarbides the system TiC—HfC—WC actually represents the concentrational section $TiC_{0.97}$—$HfC_{0.98}$—WC of the quaternary system Ti—Hf—W—C. Furthermore in all cases if not especially denoted the symbols TiC and HfC are used for the carbon-saturated carbides $TiC_{0.97}$ and $HfC_{0.98}$ (see section: raw materials).

Due to peritectic melting of WC as well as due to the phase relationship within the Ti—C and Hf—C binaries at ≈ 50 at% C, the system TiC—HfC—WC does not represent a pseudoternary system. In spite of this fact a graphical representation was tried analogous to pseudoternary systems (concentrational section $TiC_{0.97}$—$HfC_{0.98}$—WC as basis and temperature as vertical axis). But it shall be noted that in this representation i.e. the liquidus surface near the WC-rich corner does not represent the field of primary crystallization of WC (as would be the case in a pseudoternary system) but of carbon. Similarly $L + \delta + C$ fields do not degenerate when reaching the boundary isopleths TiC—HfC, TiC—WC and HfC—WC (see also Fig. 6*d*).

IV. Results and Discussion

The Isopleth TiC—HfC

a) Solid State Phase Behaviour

Lattice parameters and phase evaluation of samples along the join TiC—HfC showed a complete solid solution at high temperatures ($\geqslant$ 2000 °C) with small positive deviation of *Vegard*'s law (Fig. 1*a*). The parameter values are in excellent agreement to the values reported by *Nowotny*[6].

Heat treatment at 1500 °C (high vacuum) revealed even after 400 hrs. nonequilibrium conditions. Subsequent crushing and addition of cobalt to a total amount of 5 at% Co (64 hrs., high vacuum) resulted in much sharper X-ray patterns but did not provide complete equilibrium.

The most satisfying results at 1500 °C were obtained from samples treated by the auxiliary metal bath technique. The miscibility gap reported by *Kieffer*[9] at 1500 °C is relatively close to the miscibility gap boundary obtained from our samples. Reconsideration of the X-ray data reported by *Brukl*[8] showed that his very narrow miscibility gap obviously is due to nonequilibrium conditions.

For the higher temperatures careful lattice parameter evaluation allowed satisfactory good determination of the miscibility gap boundary as well as of the critical point (Fig. 1*a*). Fig. 1*b* shows the comparision of the miscibility gap determined in this investigation [T_c = 1780 °C, $(Ti_{0.55}Hf_{0.45})C$] to those reported by *Kieffer*[9] and *Brukl*[8].

Due to the very sluggish decomposition on the one hand, and the small energy changes involved in the decomposition when entering the miscibility gap from higher temperatures on the other hand, a differentiothermoanalytical investigation of a sample at the critical point did not result in a significant reaction peak (cooling 1 °C/sec, *DTA* apparatus).

b) High Temperature Range

Melting within the pseudobinary TiC—HfC (Fig. 1*c*) occurs in the immediate vicinity of the cubic monocarbide solution δ-$(Ti, Hf)C_{1-x}$, whose boundary is located at slightly substoichiometric compositions

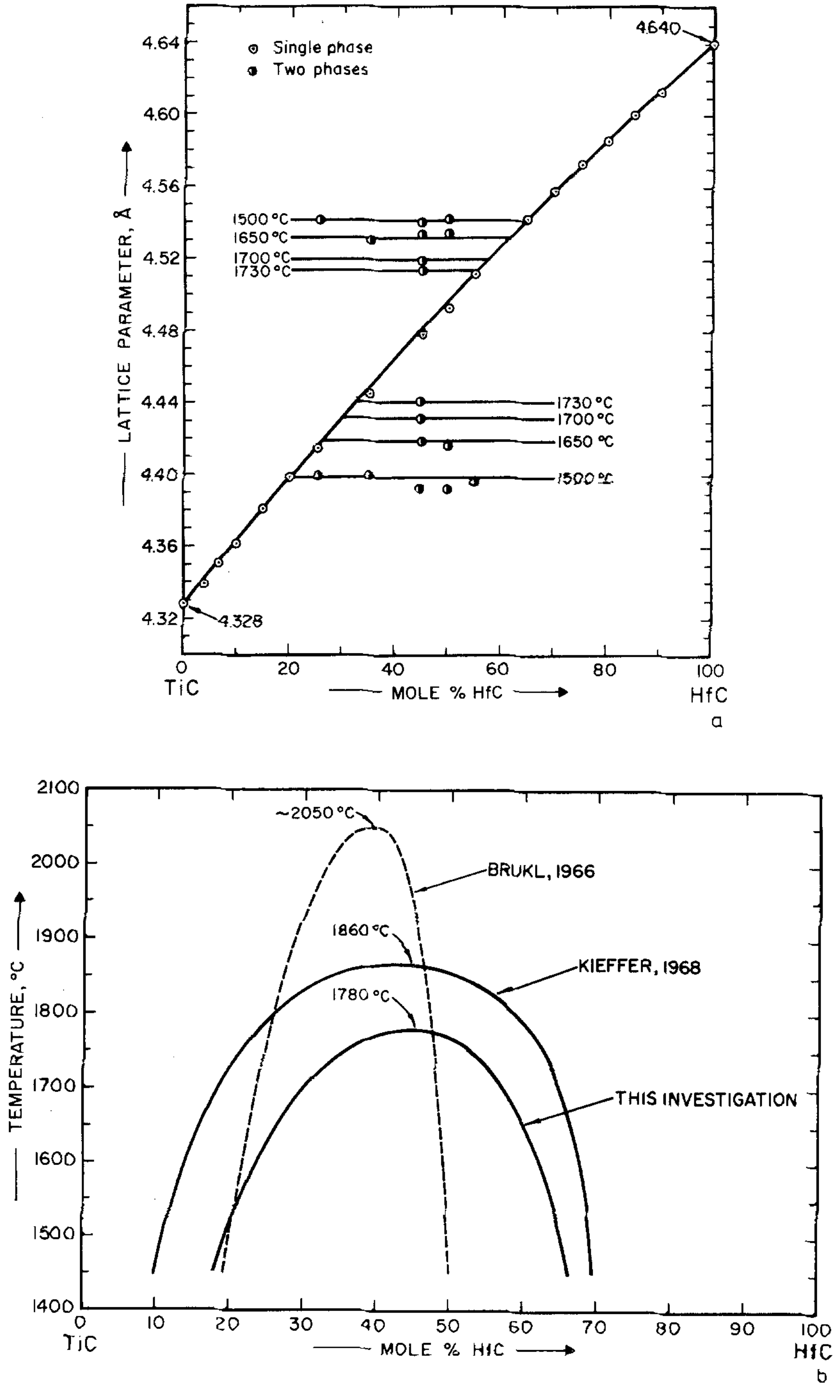

Fig. 1. *a* Lattice parameters of (Ti, Hf)C alloys at different temperatures. *b* Miscibility gap in the system TiC—HfC according to earlier work[8, 9] and this investigation

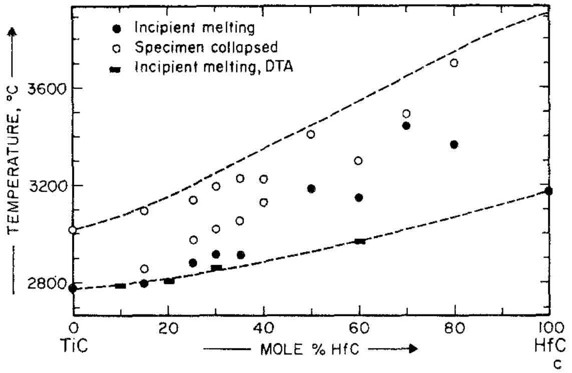

Fig. 1. c Melting temperatures of the monocarbide solution (Ti, Hf)C at approximately at 50 at% carbon

and according to this extremely small quantities of liquid are formed during the melting process. Thus for data of incipient melting, *DTA*-experiments were employed as the differential thermoanalytical method has proved to be very sensitive in recording extremely small quantities of liquid involved in a melting process. Because of the immediate vicinity of the cubic monocarbide solution a very narrow $L + \delta + C$ field with a very narrow range is accomodated between the $L + \delta$ and $\delta + C$ fields. The amount of carbon involved in $L + \delta + C$ as well as in the $\delta + C$ field is very small according to the slightly substoichiometric composition of the δ-monocarbide solution $(Ti, Hf)C_{1-x}$ $(x = 0.01–0.02)$.

The Isopleth HfC—WC

a) Solid State Phase Behaviour

Lattice parameter evaluation on samples within the isopleth HfC—WC (Fig. 2*a*) showed increasing temperature dependency of the location of the vertex of the $\varepsilon + \delta + C$ phase field. Extrapolation of the initial slope of the lattice parameter curve of tin quenched samples shows a theoretical value of ≈ 4.32 Å for a hypothethical stoichiometric cubic tungsten carbide (Fig. 2*b*). This value is in good agreement to earlier extrapolations[5] (4.315–4.32 Å). At higher WC concentrations the lattice parameter curve moves towards the value of 4.22 Å of the substoichiometric cubic tungsten carbide $W_{0.62}C_{0.38}$, as the vertex of the three phase equilibrium $\varepsilon + \delta + C$ (within the ternary Hf—W—C) approaches the W—C binary. Before this three-phase field reaches the W—C binary it takes part in the class II reaction at 2730 °C as shown in Fig. 2*c*.

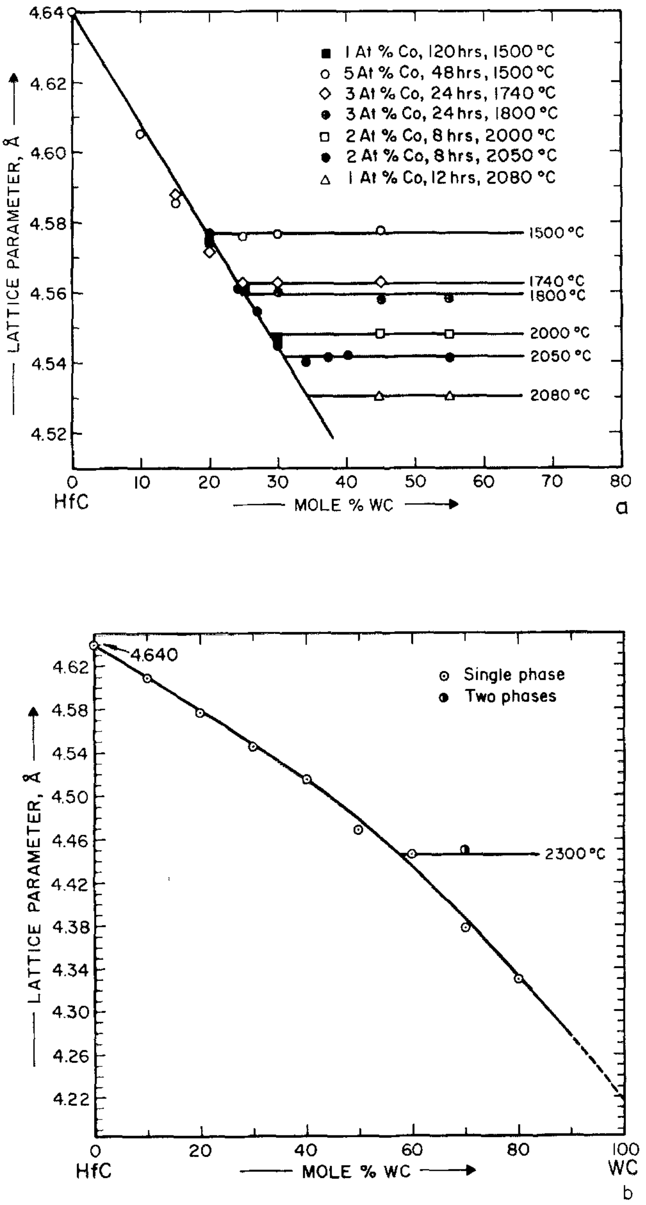

Fig. 2. *a* Location of the vertex of the three phase equilibrium (Hf, W)C + $WC_{hex.}$ + C at the cubic monocarbide phase by lattice parameter measurements on samples equilibrated at different temperatures. *b* Lattice parameters of the carbon saturated cubic monocarbide phase. Tungsten-rich samples quenched in tin

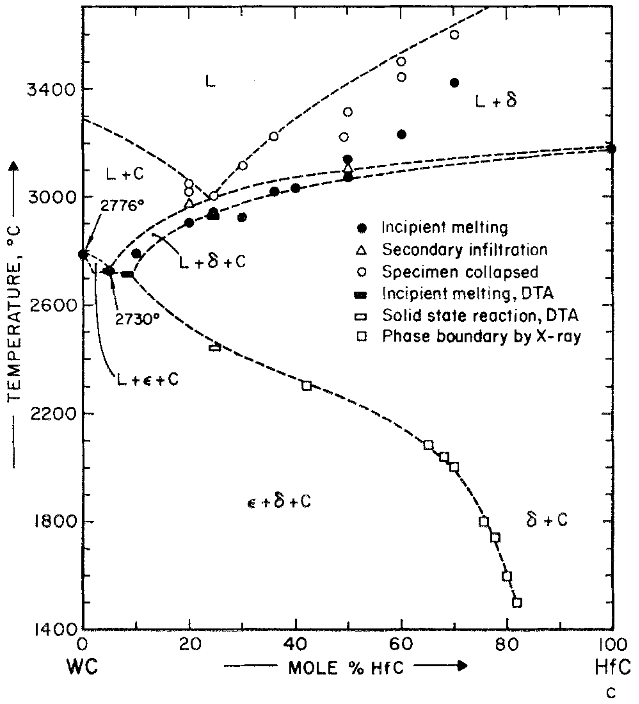

Fig. 2. c Experimental melting temperatures and phase distribution along the join HfC—WC

b) High Temperature Phase Equilibria

The melting behaviour within the HfC—WC isopleth (Fig. 2*c*) is similar to TiC—WC: peritectic melting of hexagonal WC[2] results in a class II reaction at 2730 °C, but the $(Hf, W)C_{1-x}$ solid solution does not exhibit a maximum congruent melting point. For an easier interpretation of Fig. 2*c* it might be stated, that i.e. the boundary between the $\varepsilon + \delta + C$ and the $\delta + C$ phase fields (in Fig. 2*c*) is represented by the trace of the intersection of the isopleth HfC—WC (of the Hf—W—C ternary) and the surface of the threedimensionally shaped body $\delta + \varepsilon + C$ in this concentrational section.

Phase Equilibria in the Range From 1500 to 2000 °C

As can be noted from Fig. 3*a* (isothermal section at 1500 °C) the binary miscibility gap opens up in entering the ternary diagram thus indicating a closed loop outside the triangle. With higher WC contents the miscibility gap becomes narrower but before it closes it is cut by

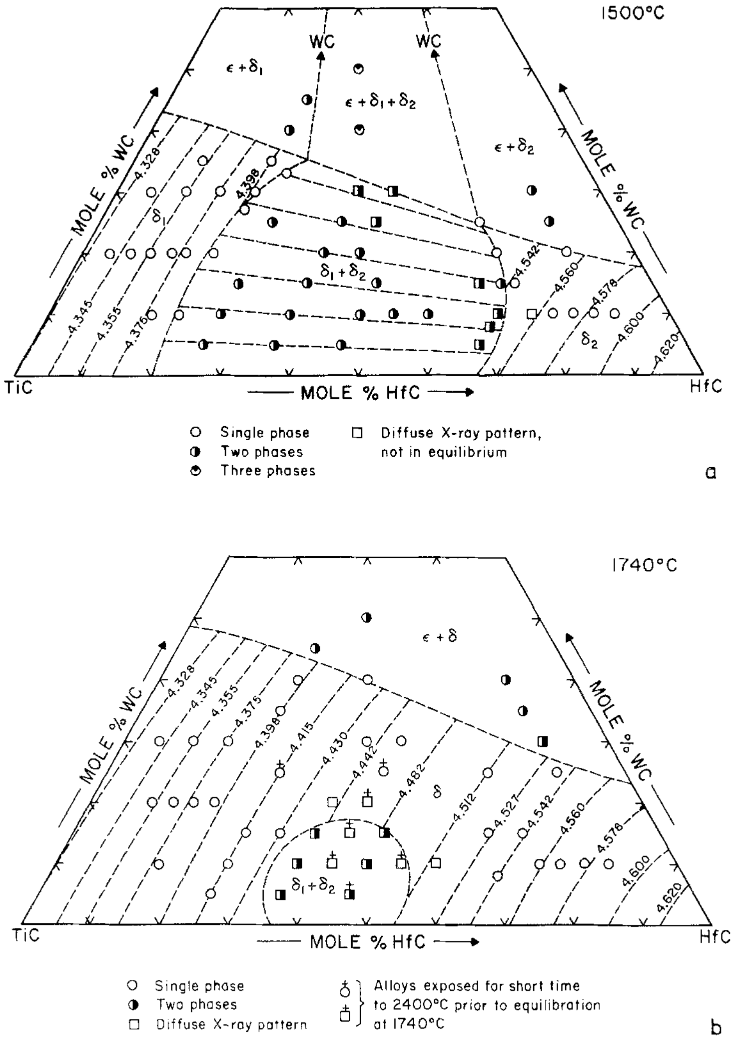

Fig. 3. Location and qualitative (X-ray) phase evaluation of alloy samples equilibrated at 1500 °C (*a*) and at 1740 °C (*b*). Dashed lines are isoparametric lines

the solvus curve and opens into an $\varepsilon + \delta_1 + \delta_2 + C$ field involving hexagonal WC (ε).

Carbon as a phase has been removed from the diagram* (Fig. 3*a*) for easier interpretation and because of the very small amounts in-

---

* As well as in all other isothermal sections in solid state.

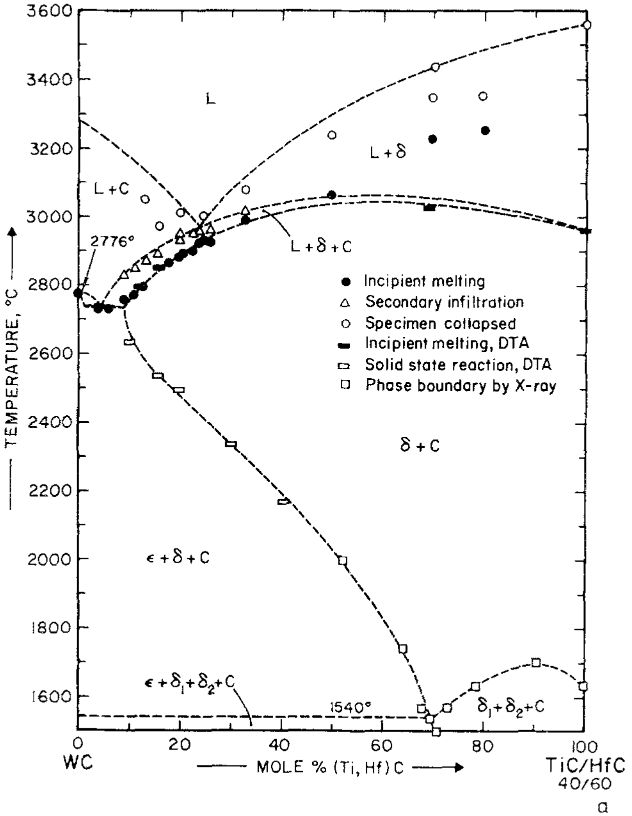

Fig. 4. *a* Melting temperatures and phase distribution along the join WC—$(Ti_{0.4}Hf_{0.6})C$

volved (≈ 1 at% C). Isoparametrical lines have been drawn on the basis of averaged lattice parameter values.

A series of isothermal sections have been similarly studied at 1540, 1560, and 1600 °C in order to find the unique point where the miscibility gap closes (critical point on binodal) and is touched by the solvus curve. Fig. 5*a* shows the phase equilibria within the isothermal section at 1540 °C as well as the location of the critical point P_c at $(TiC)_{0.27}(HfC)_{0.41}(WC)_{0.32}$ where the $\varepsilon + \delta_1 + \delta_2 + C$ field degenerates into one limiting tie line originating at P_c. The two phase fields $\delta_1 + C$ and $\delta_2 + C$, which were separated at lower temperatures by the presence of the miscibility gap, join at that point (1540 °C).

According to the angles under which the miscibility gap meets the TiC—HfC binary, Fig. 3*b* (isothermal section at 1740 °C) shows

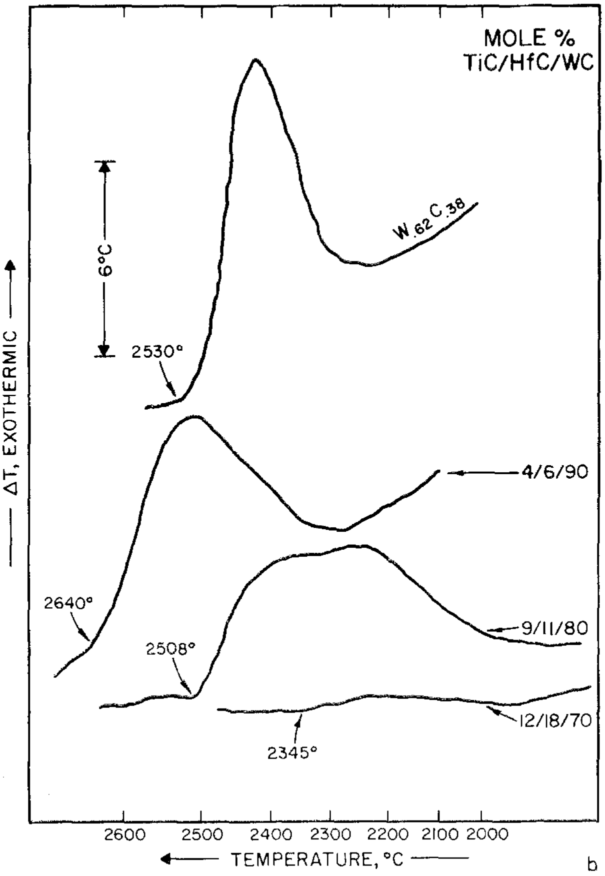

Fig. 4. *b DTA*-thermograms showing the disproportionation of the cubic phase in binary W—C and ternary TiC—HfC—WC alloys. Cooling rates at 2 °C per second

indication of a separation of the miscibility gap from the TiC—HfC binary at higher temperatures and formation of an isolated ternary miscibility gap. This behaviour was studied in isothermal sections at 1780, 1800, and 2000 °C. The isolated ternary critical point was determined at ≈ 1800 °C at an approximate composition of $(TiC)_{\approx 0.50}(HfC)_{\approx 0.45}(WC)_{\approx 0.05}$ (Fig. 5*b*).

In a recently reported study on the WC-precipitation from supersaturated ZrC—WC solid solutions it was shown by *Brun*[13], that hexagonal WC precipitates in form of rods. The crystallographic relation between the precipitated phase and the cubic B 1-matrix was established by electron diffraction technique: $[100]_{WC}$ // $[110]_{ZrC}$ and

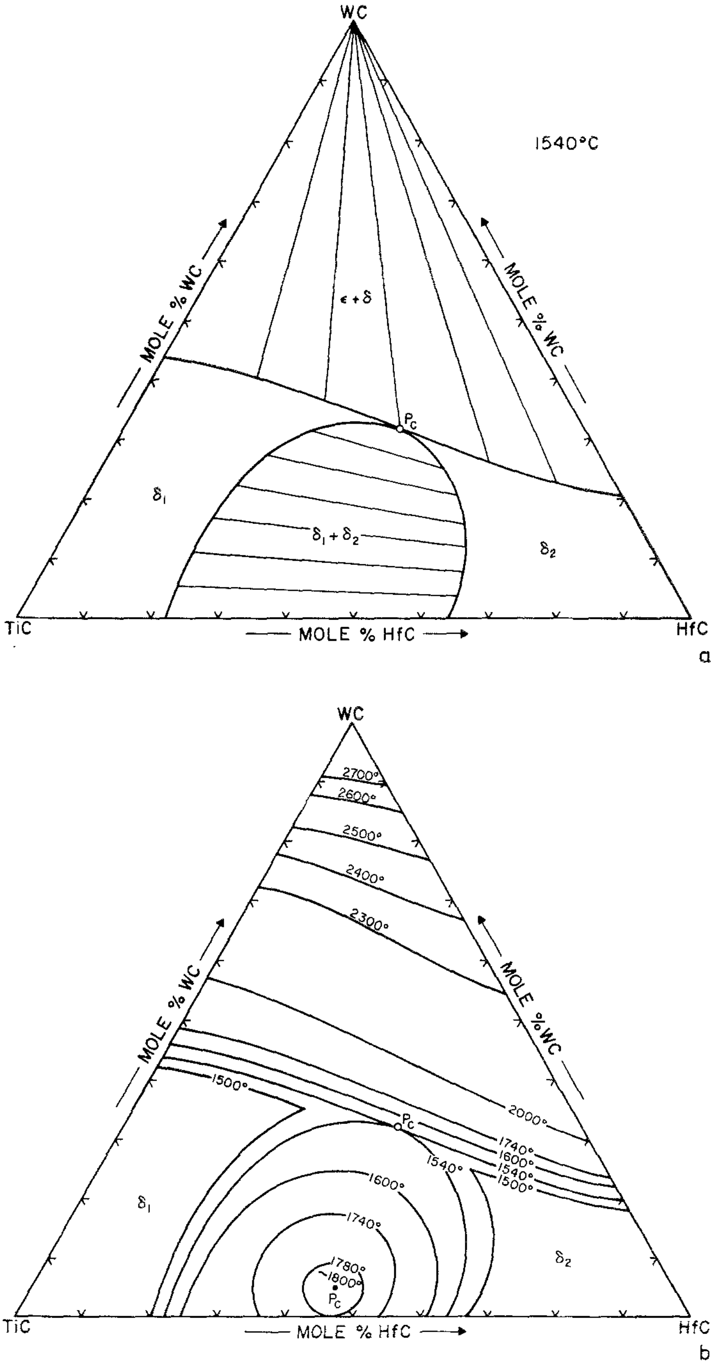

Fig. 5. Isothermal sections of the TiC—HfC—WC system, Figs. 5*a* through 5*f*: *a* 1540 °C. *b* Phase boundaries at different temperatures

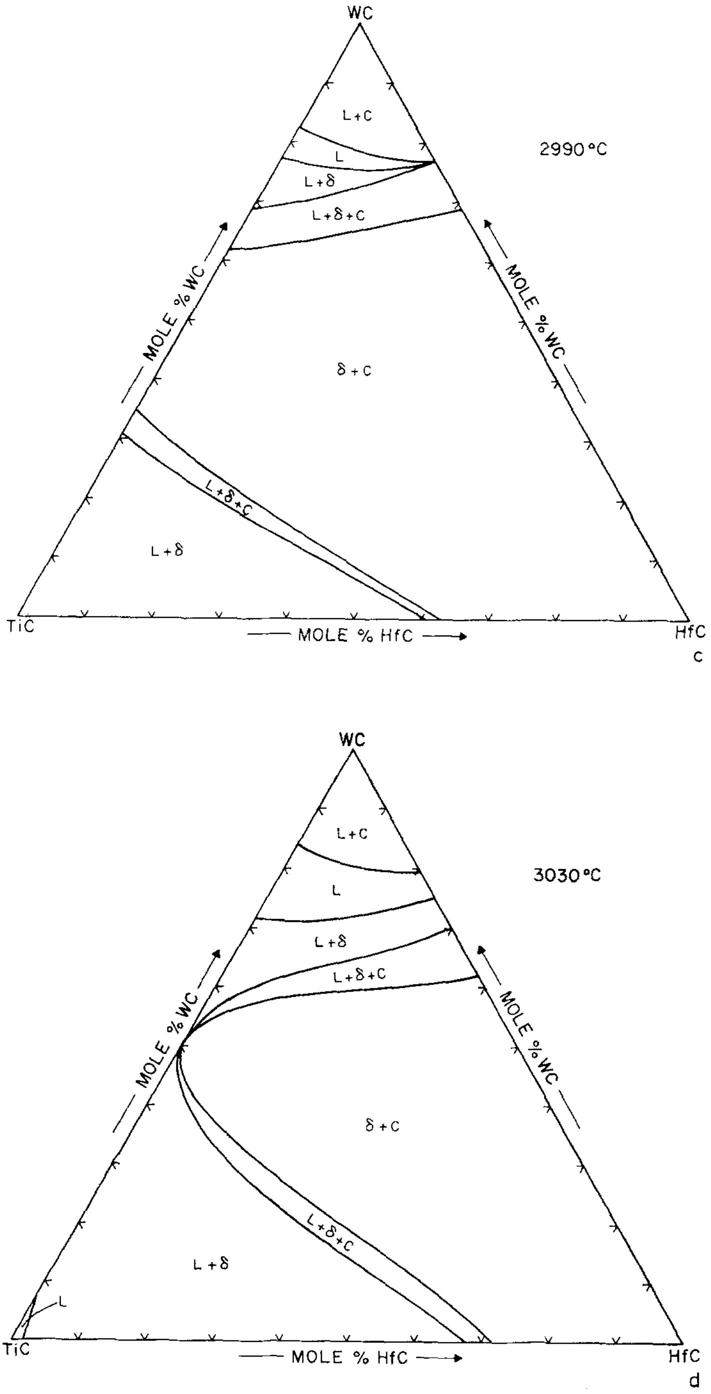

Fig. 5. *c* Isothermal sections at 2990 °C. *d* 3030 °C

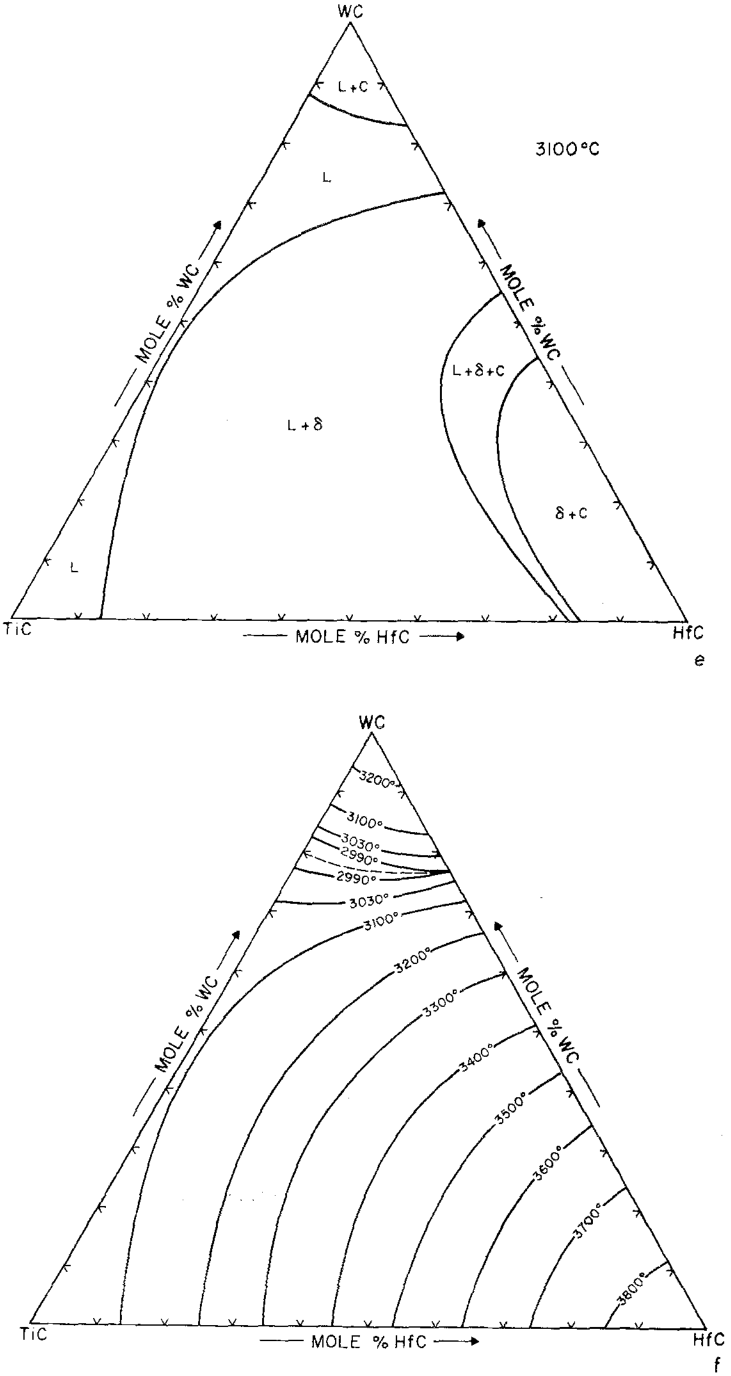

Fig. 5. *e* Isothermal section at 3100 °C. *f* Liquidus projection in the TiC—HfC—WC system at 50 at% carbon

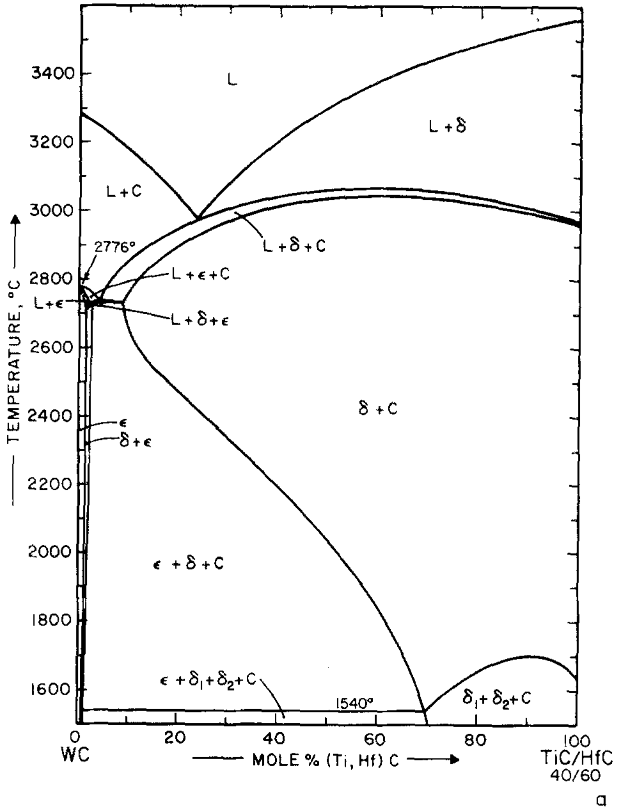

Fig. 6. *a* Isopleth WC—($(Ti_{0.4}Hf_{0.6})C$)

$[010]_{WC}$ // $[011]_{ZrC}$. The interfacial planes were (001) for the hexagonal WC and (111) for ZrC. It can be assumed, that the precipitation of WC in case of the (Ti, Hf, W)C solid solution exhibits the same crystallographic relationship; furthermore the lattice parameter mismatch in case of the (Ti, Hf, W)C-ss (3.14/2.91 Å) is even less than in case of the (Zr, W)C-ss (3.22/2.91 Å).

Phase Equilibria at High Temperatures

The Isopleth WC—$(Ti_{0.4}Hf_{0.6})C$

The isopleth WC—$(Ti_{0.4}Hf_{0.6})C$ (Fig. 6*a*) contains the limiting tie line of the degenerating $\varepsilon + \delta_1 + \delta_2 + C$ phase field (see also Figs. 5*a* and 4*a*).

For some alloys in the WC-rich corner Fig. 4*b* shows *DTA*-thermograms (cooling 2 °C/sec). The peaks are produced by the decomposi-

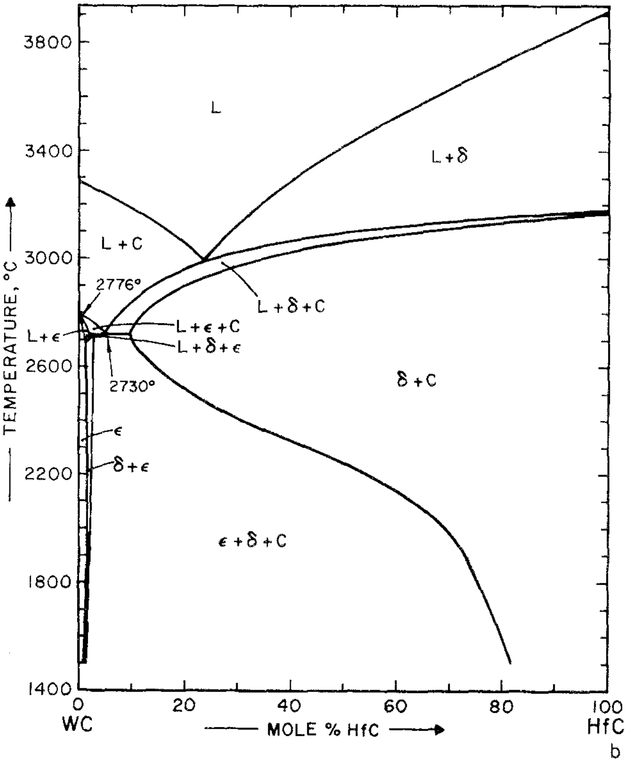

Fig. 6. *b* Isopleth WC—HfC

tion of the cubic monocarbide solution and rejection of hexagonal WC in crossing the phase fields on cooling. The decomposition reaction is very fast at high WC concentrations and reveals relatively sharp onset of narrow peaks but gets very sloppy and sluggish at smaller WC concentrations. The phase behaviour in the WC-rich corner is characterized by the class II reactions within TiC—WC and HfC—WC and exhibits an additional $L + \delta + \varepsilon + C$ phase field of extremely narrow range within the TiC—HfC—WC ternary.

Approximately 75 alloy specimens have been investigated in the melting point furnace in order to determine the liquidus as well as solidus of TiC—HfC—WC (Fig. 5*f*). Starting from the metal—carbon binaries Ti—C and Hf—C the monocarbide—carbon eutectic proceeds as a bivariant reaction into the ternaries: Ti—W—C and Hf—W—C (see Ref. [5]). Both eutectic valleys intersect with the isopleths TiC—WC and HfC—WC thus creating a melting trough within TiC—HfC—WC.

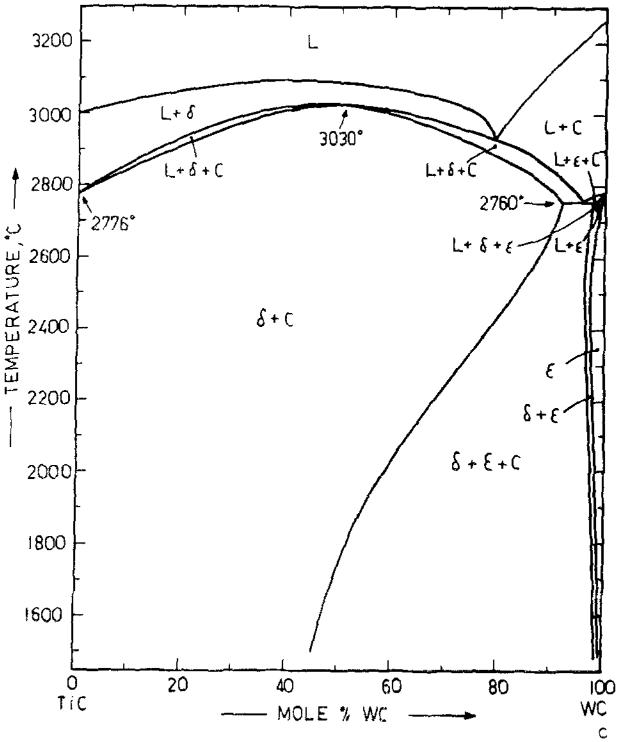

Fig. 6. c Isopleth TiC—WC

The bottom line of this melting through (in the WC-rich corner) is represented by a dashed line (Fig. 5*f*), separating the $L + C$ and $L + \delta$ field of primary crystallization (see also section III).

Assembly of the Phase Diagram

All available experimental data have been combined to construct a phase diagram of the TiC—HfC—WC system. For a convenient use of the constitutional diagram a number of concentration and temperature sections is shown in Fig. 5*a* through Fig. 6*c*. A three dimensional space model is represented in Fig. 6*d* (see also section III).

V. Thermodynamic Calculations

Thermodynamic description of segregation in regular ternary solutions were extensively studied by *Meijering*[14] and spinodal—solvus interaction could be calculated with very satisfactory results in case of the Ni—Cr—Cu phase diagram. The regular solution model was

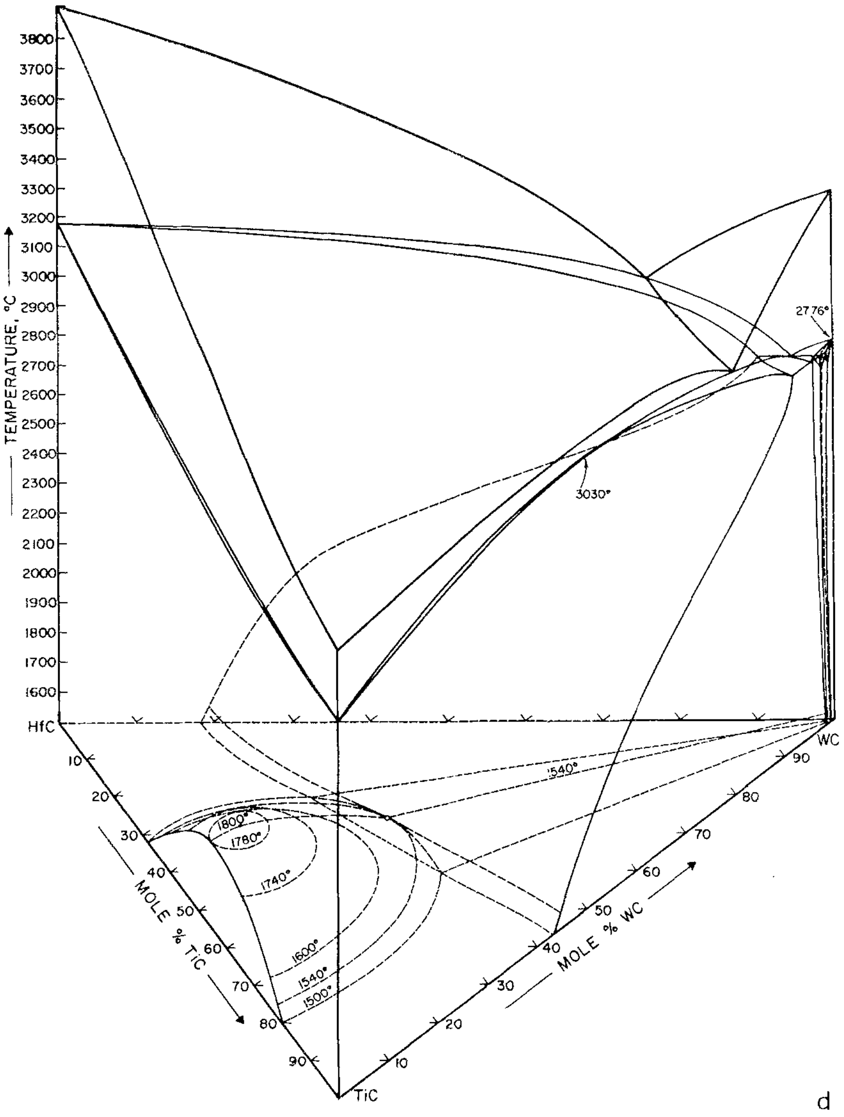

Fig. 6. *d* Space model of TiC—HfC—WC at ≈ 50 at% C

also employed by *Rudy*[7] in thermodynamical calculations of miscibility gaps in pseudoternary carbide systems.

In spite of its lack of asymmetric features the easy to handle one parameter description of the regular solution model offers striking advantages in computing and was also employed in our calculations.

The interaction parameters (ε, cal/mole) of the pseudobinary solutions have been evaluated by the slopes of the experimentally observed tie lines across the miscibility gap, the slope of the tangent at the solvus—binodal interaction point (1540 °C) as well as from the phase behaviour of the boundary systems [i.e., maximum melting point of the (Ti, W)C solid solution] and the critical evaluation of ternary metal—metal—carbon equilibria.

The transformation energy of $WC_{hex.} \rightarrow WC_{cub.}$ (stoichiom.) was averaged from the observed solid solubility of WC in TiC and HfC at different temperatures in form of a linear temperature dependency within the temperature range 1500–2200 °C. Because of the very low solubility of TiC and HfC in $WC_{hex.}$ the transformation energies for TiC and HfC have been taken 20,000 cal/mole and constant within the temperature range of 1500–2200 °C.

The interaction parameter of the TiC—HfC solid solution was derived from the critical temperature $T_c = 1780$ °C of the miscibility gap (Table 1).

Table 1

ε (cal/mole)		$\Delta F_{cub. \rightarrow hex.}$ (cal/mole)	
TiC—WC	— 3000	TiC	20,000
HfC—WC	5500	HfC	20,000
TiC—HfC	8160	WC	$-7{,}800 + 2.15\,T$

A FORTRAN II program was developed to calculate the ternary spinodal and binodal curve, the critical point at each temperature as well as the tie lines within the miscibility gap and the coordinates and temperature of a possible ternary isolated critical point or a ternary saddle point. A second part of the program calculates the ternary solvus curve. The calculations of the binodal, the solvus and the critical points are carried out by means of the *Newton—Raphson* iteration method. A detailed description of the computer program will be published[15].

Fig. 7*a* shows the comparison between the calculated and observed phase equilibria in an isothermal section of TiC—HfC—WC at 1500 °C. Considering the fact that the binary TiC—HfC miscibility gap showed deviation from the regular solution approach by its asymmetry (see Fig. 1*b*), observed and calculated values are in fairly good agreement. The opening of the binary TiC—HfC miscibility gap by small additions of WC due to a negative or very small interaction parameter ε_{TiC-WC}

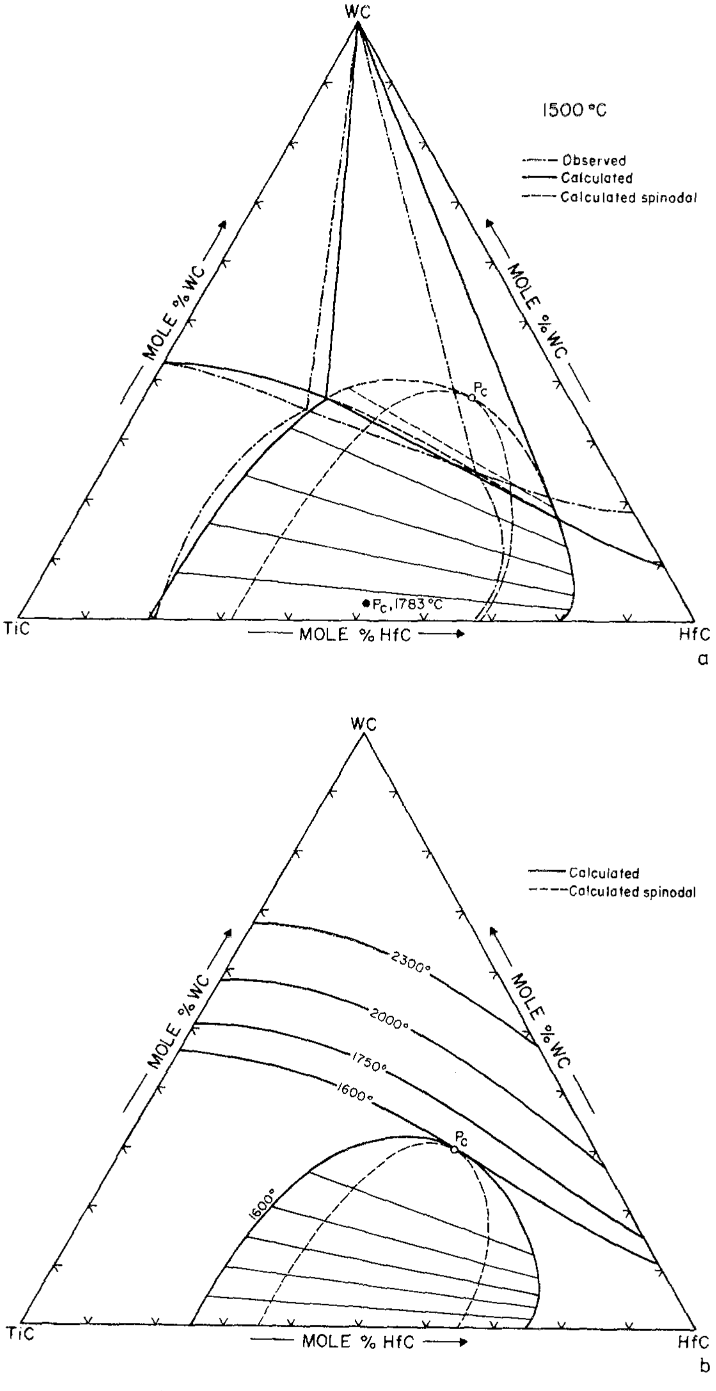

Fig. 7. *a* Comparison between observed and calculated temperature section of the system TiC—HfC—WC at 1500 °C. Regular solutions. *b* Calculated isothermal section TiC—HfC—WC at 1600 °C and calculated solubilities of WC in (Ti, Hf)C at temperatures variing from 1600 to 2300 °C

is clearly shown in the experimental observation as well as the *S* shape of the solvus curve.

With the interaction parameters used (Table 1) a ternary isolated critical point is calculated at 1783 °C and $(Ti_{0.47}Hf_{0.50}W_{0.03})C$ which is in fairly good agreement to the experimentally observed critical point at $\approx$ 1800 °C and $(Ti_{\approx 0.50}Hf_{\approx 0.45}W_{0.05})C$.

Calculations and especially precalculation of higher temperature sections proved to be very helpful and time saving in establishing the solvus—binodal contact point (Figs. 5*a*, 7*b*).

The shape of the solvus curve reported earlier[10] is in contradiction to the phase behaviour of the TiC—WC solution (maximum congruent point at substoichiometric compositions) which in terms of a regular solution can only be described by a negative interaction parameter value. Furthermore the limiting tie line of the miscibility gap (isothermal section at 1600 °C, parallel to the TiC—HfC boundary[10]) would not allow a correct description of the phase behaviour in the TiC-rich corner regarding the thermodynamic laws governing the intersection of phase boundaries.

From the consideration above, it becomes obvious that the precalculation of isothermal sections can be done with good accurracy provided the binary interaction parameters are known or available*. Furthermore the precalculation of uninvestigated systems can be of great importance in gaining valuable information on the phase behaviour at different temperatures and provides a quick and easy method for a selection of proper diagrams as a starting point to experimental investigations or development of high quality cutting tool materials on the basis of spinodal decomposition.

Acknowledgment

One of the authors, *P. Rogl*, wants to express his gratitude to Prof. *H. Nowotny* (Institute of Physical Chemistry, University of Vienna) for valuable criticism and fruitful discussions.

Research sponsored by National Science Foundation grant DMR-74-23256 and by a grant by General Electric Company and Teledyne, Inc.

References

[1] *R. Kieffer* and *F. Benesovsky*, Hartmetalle. Wien: Springer. 1963.

[2] *E. Rudy*, Compendium of Phase Diagram Data. AFML-TR-65-2, 5, 1969.

---

* It shall be noted that the interaction parameter values of the boundary systems are in excellent agreement with values earlier derived by *Rudy*[5].

[3] *E. Rudy*, AFML-TR-65-2, 2,2, 1966.

[4] *E. Rudy*, J. Less Common Metals **33**, 43 (1973).

[5] *E. Rudy*, J. Less Common Metals **33**, 245 (1973).

[6] *H. Nowotny, R. Kieffer, F. Benesovsky, C. Brukl,* and *E. Rudy*, Mh. Chem. **90**, 669 (1959); *H. Nowotny, R. Kieffer, F. Benesovsky,* and *C. Brukl*, Mh. Chem. **90**, 86 (1959); *H. Nowotny, F. Benesovsky,* and *R. Kieffer*, Planseeber. Pulvermet. **7**, 78 (1959).

[7] *E. Rudy, H. Nowotny, F. Benesovsky, R. Kieffer,* and *A. Neckel*, Mh. Chem. **91**, 176 (1960).

[8] *C. Brukl* and *D. Harmon*, AMFL-TR-65-2, 2 (1966).

[9] *R. Kieffer, H. Nowotny, A. Neckel, P. Ettmayer,* and *L. Usner*, Mh. Chem. **99**, 1020 (1968).

[10] *R. Kieffer, G. Trabesinger,* and *N. Reiter*, Planseeber. Pulvermet. **17**, 25 (1969).

[11] *G. Jangg, R. Kieffer,* and *L. Usner*, J. Less Common Metals **14**, 269 (1968).

[12] *E. Rudy* and *G. Progrulsky*, Planseeber. Pulvermet. **15**, 13 (1967).

[13] *M. Brun* and *V. Stubican*, J. Amer. Ceram. Soc. **57**, 117 (1974).

[14] *J. Meijering*, The Physical Chemistry of Metallic Solutions and Intermet. Compounds, Nat. Phys. Sympos., HMSO, London, 1958.

[15] *P. Rogl*, to be published.

Correspondence and reprints:
Dr. P. Rogl
Institut für Physikalische Chemie
Universität Wien
Währinger Straße 42
A-1090 Wien
Austria