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Metallochemistry of chromium in ternary systems formed by chromium with d-metals and carbon☆

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Abstract

The results of the experimental investigation of phase equilibria at solidus temperatures of the Cr–Nb(Ta,Re)–C systems are given. They add much to the information on the Cr–dM–C systems. Certain regularities have been revealed for the phase diagram constitution, particularly detailed for those formed with high valence d-metals and applied as a basis for prediction of the Cr–Tc–C phase diagram at high temperatures yet unstudied experimentally.

Keywords: Ternary alloy; Phase diagram; Chromium; d-metal; Carbon

1. Introduction

The phase structure and phase equilibria for ternary Cr–M–C systems (M is a d-metal of groups IV–VII of the Periodic system) are studied rather comprehensively. Alloy phase diagrams for most of these systems are constructed within the whole range of concentrations and within a wide range of temperatures, including the melting–solidification region. The wide-scale study of these systems has permitted the authors [1] to classify them according to the type of phase equilibria at certain homological temperature, the solidus temperature being chosen as such. The type of equilibria of bcc metal phase based on chromium with carbides served as a main classification criterion.

Equilibrium between 'fcc'-carbide[1] (the NaCl structure type) and chromium-based bcc-phase has permitted not only well studied Cr–(Ti,Zr,Hf)–C systems to be attributed to the first classification group, but also Cr–(Nb,Ta)–C systems, for which preliminary data on phase equilibria at high temperatures have been published [2,3]. A dominating phase in equilibria in these systems is presented by 'fcc'-carbide which is in equilibria with almost all other phases of ternary systems.

The second classification group includes well studied Cr–V(Mo,W)–C systems together with the Cr–Re–C and Cr–Tc–C systems. Preliminary data on phase equilibria at high temperatures for the Cr–Re–C system were published [4], while there were neither such data for the Cr–Tc–C system. A change in direction of reactions is observed for this group. A dominating phase is presented by 'hcp'-carbide[2] with structure deriving from the Mg-type metal sublattice.

Partition of the systems into the two classes reflects different levels of d-metal carbide stability (Gibbs energies of formation). The stability correlates with such electron-dimensional characteristic of d-metal as the ratio of the total number of external electrons (of s- and d-levels) of d-metals to the atomic radius e_M/r_M [5–7] given in Table 1. The first classification group of Cr–M–C systems is formed by metals of groups IV and V for which $r_C(e_M/r_M)<2.7$ (multiplier r_C, atomic radius of carbon, is inserted to the ratio e_M/r_M for the dimensionless quantity of the ratio). The second group is formed by those metals of groups V to VII for which $2.7<r_C(e_M/r_M)<4.0$. For

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☆In respectful memory of Professor Alan Prince.

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[1] The term 'fcc'-carbide will be used for the interstitial phase based on the metal fcc-sublattice in which carbon atoms and vacancies are statistically distributed in octahedral free spaces.

[2] Designation 'hcp'-carbide is introduced for high-temperature L'_3-modifications of carbides (of the M_2C composition and carbon-deficient) with disordered location of carbon atoms and vacancies in octahedral free spaces.

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Table 1
Influence of the atomic dimension and electronic factors of d-metals on the constitution of the Cr–M–C phase diagrams

Classification	The first classification group					The second classification group						
M	Zr	Hf	Ti	Nb	Ta	V	W	Mo	Cr	Re	Tc[c]	Mn
Interstitial phases	▥[d]	▥	▨	▥	▥	▨	▨	▨	–	▨	▨	
r_M, pm [8]	160.2	158.0	146.2	146.8	146.7	134.6	140.8	140.0	128.2	137.5	136.0	126.4
r_C/r_M[a]	0.481	0.487	0.527	0.525	0.525	0.572	0.547	0.550	0.601	0.560	0.566	0.609
$(r_M - r_{Cr})/r_M$	0.200	0.189	0.123	0.127	0.126	0.048	0.089	0.084	0	0.068	0.057	−0.014
e_M[b]	4	4	4	5	5	5	6	6	6	7	7	7
$(e_M/r_M)\times 10^2$, pm^{-1}	2.50	2.53	2.74	3.41	3.41	3.71	4.26	4.29	4.68	5.09	5.15	5.54
$r_C(e_M/r_M)$	1.92	1.95	2.11	2.62	2.62	2.86	3.28	3.30	3.60	3.92	3.96	4.26
$n_e \times 10^9$, pm^{-3}	172	179	226	279	280	362	380	386	518	476	492	613

[a] $r_C = 77$ pm; r_M for $Z = 12$ (as in the preceding row).

[b] e_M is general external (s+d)-electrons number.

[c] Predicted.

[d] ▨, Chromium substitutes about 50% of the d-metal and more in the interstitial phase on the basis of close packed metal sublattice; ▥, chromium substitutes less than 30% of the d-metal in the interstitial phase on the basis of close-packed metal sublattice.

brevity, those metals will be referred to as high-valency metals, thus acknowledging that the notion of ‘valency’ in metal chemistry should take into account not only the number of external electrons, but also the size of atoms participating in chemical reactions. This paper presents peculiarities of the metal-chemical behavior of chromium in the ternary systems formed by chromium with high-valency metals and carbon taking into account the specified results of the experimental examination of phase equilibria in the Cr–Nb(Ta,Re)–C systems. Refined prediction of phase equilibria in the Cr–Tc–C system which is not studied experimentally is a natural result of the analysis carried out.

2. Experimental investigation of the ternary Cr–Nb(Ta,Re)–C systems

2.1. Experimental procedure

The flake-like chromium (99.9%), bar niobium (99.7%), sheet tantalum (99.8%), powder rhenium (≥99.8%), and nuclear graphite (ash content 0.05 wt.%) were used to prepare samples. Master alloys $Cr_{90}C_{10}$, $Cr_{59.3}C_{40.7}$, $Nb_{49}Cr_{49}C_2$, $Ta_{49}Cr_{49}C_2$ and $Re_{82}C_{18}$, made of the same materials and under the same conditions as alloys, were also used. Master alloys and ingots for the investigations were obtained by melting in the arc furnace with copper water-cooled hearth in argon (pressure 50–80 kPa) purified by preliminary melting of titanium getter for 3 min. A tungsten nonconsumable electrode was used. Initial mixtures weighing 10–15 g were sintered under a weak arc and then remelted three times, each time being turned over. After melting, ingots were crushed and remelted again by the same method. The cooling rate of the samples was ~100°C/s.

Selective chemical analysis of the alloys has shown that oxygen percentage in alloys of the Cr–Nb(Ta)–C systems is ~0.01 wt.%, in alloys of the Cr–Re–C system it is 0.03–0.04 wt.% (nitrogen content in all alloys was less than 0.001 wt.%). In most cases the weight expenditures during preparation of the alloys did not exceed 0.5%, so their composition was charge-admissible. In case of greater loss of weight (rhenium-rich alloys of the Cr–Re–C system) the composition of the alloys made was checked by chemical and X-ray spectral analyses.

Temperatures of phase transformations were determined by the method of differential thermal analysis using a device with a string thermocouple of tungsten/80 W–20 Re (wt.%) in a protective atmosphere of high-purity helium (a tungsten-made heater). Heating and cooling rates were 1.2–1.4°C/s. Specimens were put into ceramic Sc_2O_3, Al_2O_3, Y_2O_3 or HfO_2 crucibles.

The temperature of the solidus was determined also by the Pirani-Alterthum method in a protective argon medium using an optical pyrometer with an instrumental error within 900–1400°C as ±2.8; 1400–2000°C as ±4; 2000–3000°C as ±12°C. Immediately after measurement the specimens were annealed in the same chamber at temperatures lower by 5–30°C than the solidus temperature during, as a rule, 30 min followed by quenching at a rate of 150–300°C/s.

Alloys as cast and annealed at subsolidus temperature were investigated by the method of X-ray phase analysis (the Debye–Scherrer method), light and electron microscopy and electron microprobe analysis. Data obtained from measurements of the temperature and patterns have been statistically processed with allowance for errors of the methods. Confidence intervals of the values are given for $\alpha = 0.95$.

The investigation methods used are described in detail in Ref. [9].

2.2. Binary systems

The binary Nb–C, Ta–C, Re–C and Cr–Ta systems from Ref. [10] and Cr–Nb from Ref. [11] are accepted. Invariant equilibrium temperatures of Ref. [12] were preferable for the Cr–C system. The Cr–Re phase diagram was reinvestigated [13]. Experimental data obtained at solidus temperatures differ from Ref. [10] in the homogeneity regions for phases (Cr) (up to 43 at.% Re), σ (50–72 at.% Re), and (Re) (up to 17 at.% Cr), as well as in temperatures of invariant equilibria l+σΔ (Cr) and l+(Re) Δσ (2150±15°C and 2335±15°C, respectively). The solid phases observed in binary systems are given in Table 2.

2.3. The Cr–Nb–C and Cr–Ta–C systems

The compositions of the alloys and the results obtained on the basis of experimental investigation of the alloy are presented in Figs. 1 and 2 and Tables 3 and 4. These results were used as the basis for construction of the Cr–Nb–C and Cr–Ta–C solidus surfaces projection given in Figs. 1 and 2.

Ternary phases with the crystal structure that differs from the lattice structure of phases forming in boundary systems are not found (Table 2). Solubility of chromium in niobium and tantalum carbides at subsolidus temperatures is approximately three times higher than that reported in the literature at 1000 and 1350°C [14,15]. At the same time the type of phase equilibria in the systems remains unchanged within the whole range of temperatures studied (from 1000°C to the solidus). It was observed that ‘fcc’-carbides (Nb,Cr)C_{1-x} and (Ta,Cr)C_{1-x} coexist in equilibria with all other phases, except for niobium- and tantalum-based solid solutions. The above ‘fcc’-carbides possess the highest thermodynamic stability (as shown in the thermodynamic data [16,17]) and are the most significant in the systems mentioned in the process of the phase equilibria formation. Maximal folds of ruled solidus surfaces and quasi-binary eutectics have been observed in two-phase fields formed by the ‘fcc’-carbides with both congruently melting compounds (Laves phases and Cr_7C_3) and chromium phase.

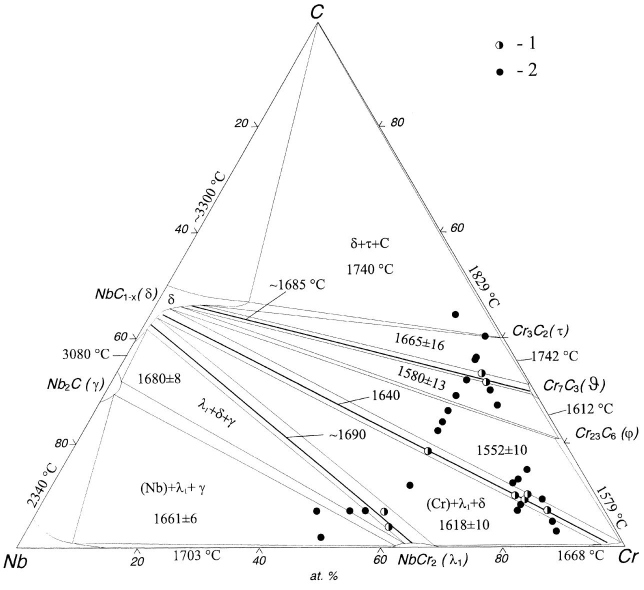


Fig. 1. Projection of solidus surface of the Cr–Nb–C system: 1, two phase; 2, three phase alloys.

Solubility of niobium and tantalum in chromium carbides at solidus temperatures were determined by electron microprobe analysis and for both metals were as follows: 1–2 at.% for $Cr_{23}C_6$; about 0.5 at.% for Cr_7C_3 and Cr_3C_2. These values are close to those described for lower temperatures [14,15]. Composition and lattice parameters of the solid phases which are in equilibria at solidus temperatures are listed in Tables 3 and 4.

2.4. The Cr–Re–C system

The composition of the alloys and the results obtained on the basis of experimental investigation of the alloys are

Table 2
Crystal structure of the phases related to solidus regions for the Cr–M–C systems [10,18]

Phase	Pearson symbol	Space group	Prototype	Close-packed metallic lattice (sublattice)
βTi, βZr, βHf, V, Nb, Ta, Cr, Mo, W	*cI2*	$Im\bar{3}m$	W	–
αTi, αZr, αHf, Tc, Re	*hP2*	$P6_3/mmc$	Mg	hcp
V_2C, Nb_2C, Ta_2C, Mo_2C, W_2C (HT)	*hP3*	$P6_3/mmc$	Fe_2N[a]	hcp
TiC_{1-x}, ZrC_{1-x}, HfC_{1-x}, VC_{1-x}, NbC_{1-x}, TaC_{1-x}, αMoC_{1-x}, αWC_{1-x}, TcC_{1-x}	*cF8*	$Fm\bar{3}m$	NaCl	fcc
ηMoC_{1-x}	*hP8*	$P6_3/mmc$	TiAs	–
WC	*hP2*	$P6m2$	WC	–
C	*hP4*	$P6_3/mmc$	C (Graphite)	–
$Cr_{23}C_6$	*cF116*	$Fm\bar{3}m$	$Cr_{23}C_6$	–
Cr_7C_3	*oP40*	*Pnma*	Cr_7C_3	–
Cr_3C_2	*oP20*	*Pnma*	Cr_3C_2	–
λ_1-$ZrCr_2$, λ_1-HfC_2, λ_1-$NbCr_2$, λ_1-$TaCr_2$	*hP12*	$P6_3/mmc$	$MgZn_2$	–
λ_2-$NbCr_2$, λ_2-$TaCr_2$	*cF24*	$Fd\bar{3}m$	$MgCu_2$	–
σ(Cr,Tc), σ(Cr,Re)	*tP30*	$P4_2/mnm$	σCrFe	–

[a] Structurbericht designation L'_3.

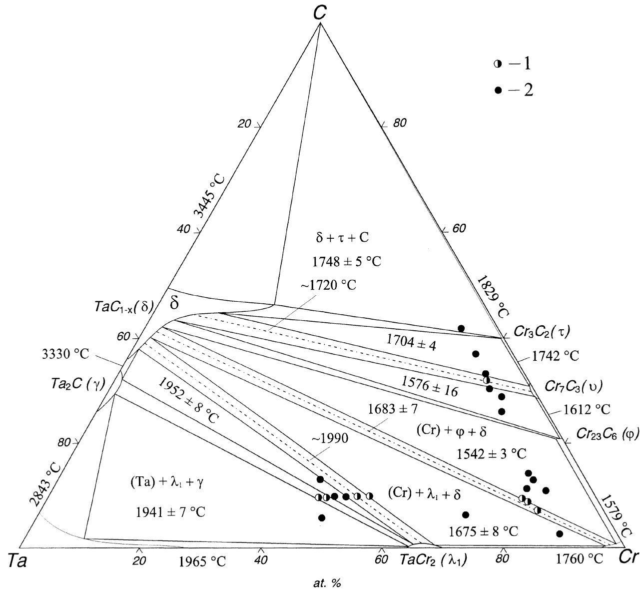


Fig. 2. Projection of solidus surface of the Cr–Ta–C system: 1, two phase; 2, three phase alloys.

given in Fig. 3 and Table 5. The constitution of the Cr–Re–C solidus surface projection is given in Fig. 3.

No phases with the crystal structure differing from phases of boundary systems were found in the Cr–Re–C system, as well as in the Cr–Ti(Zr,Hf,Nb,Ta)–C systems. An interesting property of this system is surprisingly high combined solubility of chromium and carbon in rhenium on the solidus surface: it comprises 36 at.% C and 53 at.% Cr at the temperature of 1764±16°C. This significantly exceeds maximal solubility of chromium and carbon in rhenium in corresponding binary systems and their combined solubility in rhenium at 1300°C according to data [19]. Solid solution on the basis of rhenium which is in equilibrium with phases on the basis of chromium carbides Cr_7C_3 and Cr_3C_2 at the solidus temperature 1718±11°C has composition $Cr_{54}Re_{12}C_{34}$ and lattice constants $a=283.3(1)$, $c=444.3(6)$ pm (Table 5), which are significantly higher than those for pure rhenium and similar to lattice constants of hypothetical chromium carbide 'Cr_2C' ($a=283.5$ and $c=446.0$ pm; Fig. 4). So, the phase of this composition may be treated as solid solution of rhenium in

Table 3

Coordinates of invariant points on solidus surface and lattice parameters of phases of the Cr–Nb–C system

Equilibrium	Phase	Composition, at.%			Lattice parameters, pm		
		Cr	Nb	C	*a*	*b*	*c*
~1740°C	C	0	0	100	–	–	–
C+δ+τ	δ	15	43	42	442.2(2)		
	τ	~59.1	~0.7	~40.2	553.0(2)	283.0(1)	1147.0(2)
1665±16°C	δ	~7.5	~46.2	~46.3	443.9(3)	–	–
δ+τ+ϑ	τ	~59.1	~0.7	~40.2	553.2(5)	283.8(1)	1148.5(7)
	ϑ	~69.9	~0.2	~30.9	1402.9(3)	–	453.1(4)
~1685°C (max)	δ	5.3	48	46.2	444.1(5)	–	–
δ+ϑ	ϑ	69.5	0.6	29.9	1403.5(1)	–	453.9(1)
1580±13°C	δ	4	50	46	444.6(6)	–	–
δ+ϑ+φ	ϑ	~70.5	~0.4	~29.1	1403.3(2)	–	452.4(1)
	φ	~78.8	~0.5	~20.7	1066.7(5)	–	–
1552±10°C	δ	3	51.3	45.7	444.9(1.0)	–	–
δ+φ+(Cr)	φ	~78	~1.3	~20.7	1067.8(5)	–	–
	(Cr)	~98.8	~0.2	~1	288.6(1)	–	–
1640°C (max)	δ	1.5	54	44.5	444.3(1)	–	–
δ+(Cr)	(Cr)	~97.7	~2	~0.3	288.4(4)	–	–
1618±10°C	δ	1.3	54.5	44.2	443.0(4)	–	–
$\delta+(Cr)+\lambda_1$	(Cr)	~96.3	~35	~0.2	289.7(4)	–	–
	λ_2^a	~68.3	~31.5	~0.2	696.2(6)	–	–
~1690°C (max)	δ	~1.2	~55.8	~43	442.8(1)	–	–
$\delta+\lambda_1$	λ_1	~66.2	~37	~0.8	495.0(2)	–	808.8(2)
1680±8°C	δ	1	57	42	442.6(3)	–	–
$\delta+\lambda_1+\gamma$	λ_2^a	~64.2	~35	~0.8	698.2(1)	–	–
	γ	~2	~76	~32	311.8(4)	–	496.0(9)
1661±6°C	(Nb)	~9	~90	~1	324.6(2)	–	–
$(Nb)+\lambda_1+\gamma$	λ_2^a	~62.8	~47	~0.2	702.8(2)	–	–
	γ	~2	~69	~29	312.5(1)	–	496.6(2)

[a] The high temperature modification λ_1 was not detected.

Table 4
Coordinates of nonvariant points on solidus surface and lattice parameters of phases of the Cr–Ta–C system

Equilibrium	Phase	Composition, at.%			Lattice parameters, pm		
		Cr	Ta	C	*a*	*b*	*c*
~1748±5°C	C	0	0	100	–	–	–
C+δ+τ	δ	~19	~34.5	~46.5	440.7(2)	–	–
	τ	~59.3	~0.5	~40.2	553.2(2)	283.2(1)	1148.2(3)
1704±4°C	δ	~10	~45	~45	441.5(1)	–	–
δ+τ+ϑ	τ	~59.3	~0.5	~40.2	553.2(6)	284.0(4)	1149.0(1.0)
	ϑ	~68.5	~0.5	~31	1402.6(1)	–	453.1(2)
~1720°C (max)	δ	~7	~53	~40	441.6(1)	–	–
δ+ϑ	ϑ	~69.5	~0.5	~30	1403.0(2)	–	452.8(4)
1576±16°C	δ	~4	~52.5	~43.5	442.7(6)	–	–
δ+ϑ+φ	ϑ	~71	~0.5	~28.5	1403.5(2)	–	452.7(3)
	φ	~78.5	~0.5	~21	1068.1(3)	–	–
1542±3°C	δ	~25	~55.5	~42	442.2(2)	–	–
δ+φ+(Cr)	φ	~78	~1	~21	1069.1(1)	–	–
	(Cr)	~98	~1	~1	288.5(3)	–	–
1683±7°C (max)	δ	~2	~56.5	~41.5	441.2(3)	–	–
δ+(Cr)	(Cr)	~97.3	~2	~0.7	288.5(3)	–	–
1675±8°C	δ	~1.8	~58	~40.2	440.5(2)	–	–
δ+(Cr)+λ_1	(Cr)	~96.5	~3	~0.5	288.3(9)	–	–
	λ_1	~68.5	~31	~0.5	490.4(3)	–	804.5(1.0)
~1990°C (max)	δ	~1.5	~59.5	~39	441.2(3.0)	–	–
δ+λ_1	λ_1	~66	~33	1	492.6(2)	–	808.1(3)
1952±8°C	δ	~1	~61	~38	441.7(3)	–	–
δ+λ_1+γ	λ_1	~65	~34.5	~0.5	496.0(2)	–	814.8(3)
	γ	~1	~76	~33	310.7(1)	–	493.7(1)
1941±7°C	(Ta)	~10	~88	~2	326.9(1)	–	–
(Ta)+λ_1+γ	λ_1	~64	~35.6	~0.4	498.6(2)	–	819.6(2)
	γ	~1.5	~69.3	~29.2	310.1(2)	–	493.7(6)

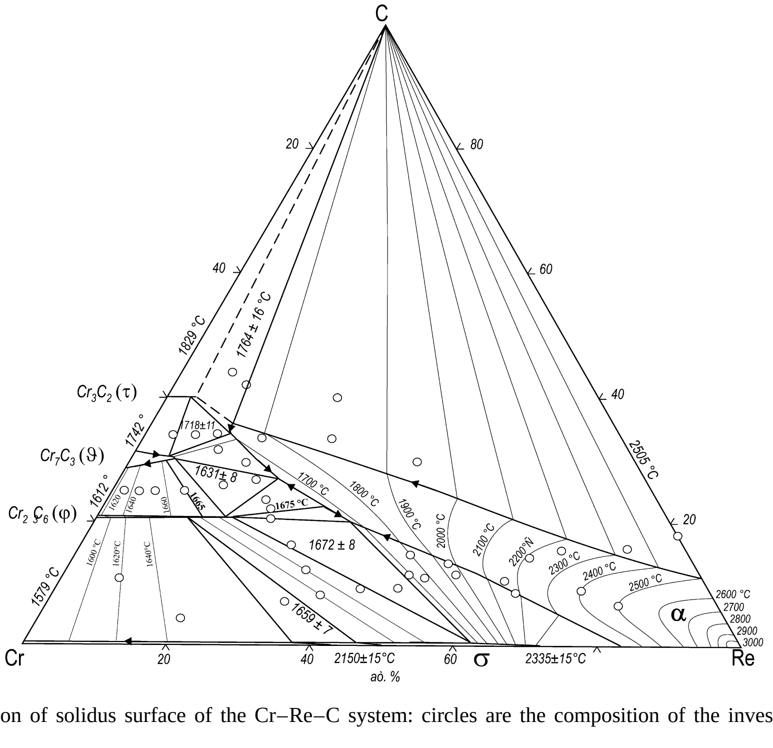
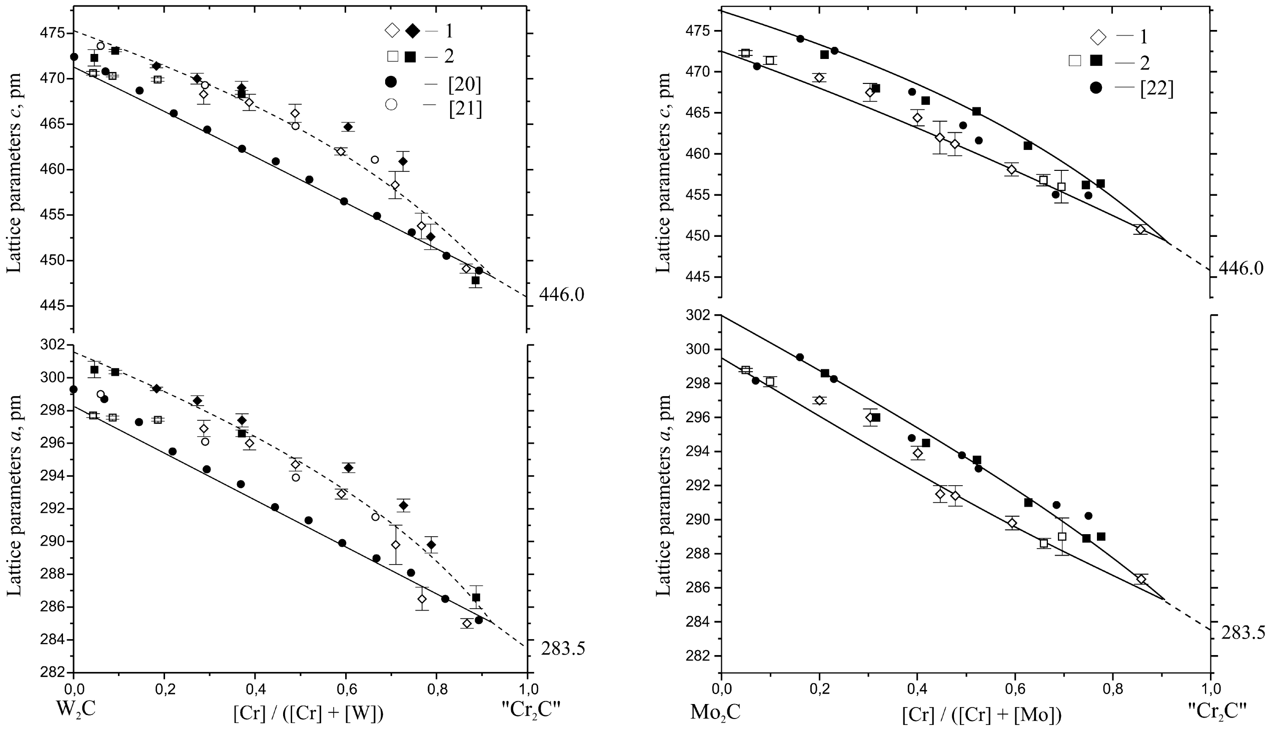


Fig. 3. Projection of solidus surface of the Cr–Re–C system: circles are the composition of the investigated alloys.

Table 5
Coordinates of invariant points on the solidus surface and lattice parameters of phases of the Cr–Re–C system

Equilibrium	Phase	Composition, at.%			Lattice parameters, pm		
		Cr	Re	C	*a*	*b*	*c*
1631±8°C	α	51	22	27	280.55(8)	–	444.3(6)
$\alpha+\varphi+\vartheta$	φ	61.3	18	20.7	1082.6(4)	–	–
	ϑ	64	6	30	1412.4(3)	–	456.6(3)
1764±16°C	α	53	11	36	285.34(7)	–	448.4(4)
$C+\alpha+\tau$	τ	56	4	40	556	285	1148
	C	0	0	100	–	–	–
1718±11°C	α	54	12	34	283.3(1)	–	444.3(6)
$\tau+\alpha+\vartheta$	ϑ	65	5	30	1409.3(4)	–	455.8(5)
	τ	57	3	40	556(2)	283.5(9)	1150(8)
1672±8°C	α	44	36	20	278.97(7)	–	444.3(3)
$\alpha+\sigma+\varphi$	σ	37.5	62.0	0.5	928.5(2)	–	482.6(4)
	φ	60.3	19.0	20.7	1081.4(5)	–	–
1659±7°C	(Cr)	62.0	37.8	0.2	297.2(4)	–	–
$\sigma+(Cr)+\varphi$	σ	53.0	46.5	0.5	919.1(4)	–	478.0(2)
	φ	12.4	67.0	20.7	1075.1(2)	–	–
1675°C (max)	α	47	31	22	278.9(4)	–	444.4(5)
$\alpha+\varphi$	φ	60.3	19.0	20.7	1082.6(4)	–	–
1665°C (max)	φ	63.3	16.0	20.7	1076.8(2)	–	–
$\varphi+\vartheta$	ϑ	64.5	5.5	30.0	1408.2(4)	–	454.5(4)
~1680°C, φ (max)	φ	62.3	17	20.7	1079.7(4)	–	–



a) b)

Fig. 4. Lattice parameters of 'hcp'-carbide solid solutions versus chromium content in ternary systems Cr–Mo–C (a) and Cr–W–C (b), based on data at 1350°C [20,21], 1400°C [22] and solidus temperatures [23]: 1, for as cast alloys [23]; 2, for annealed at subsolidus temperature alloys [23]. Full and empty points sign upper and below boundaries of homogeneity range on carbon content.

this 'fcc'-carbide 'Cr_2C' or as ternary 'hcp'-carbide, $(Re_{0.18}Cr_{0.82})_2C$, isostructural to high-temperature L'_3-modifications of Mo_2C, W_2C, V_2C, Nb_2C or Ta_2C carbides, their metal sublattice being the same as the rhenium lattice. The wide field of solid solutions $(Re,Cr)_2C_{1-x}$, which is in equilibrium with all other phases, except for a chromium-base phase, determines the constitution of the alloy phase diagram of the ternary system on the whole.

Among the chromium carbide phases, the $Cr_{23}C_6$ solid solution has the maximal extension of the homogeneity range at the solidus temperature: 19 at.% Re at 1675°C. It has been found out that there is a maximum point on its solidus surface at 17 at.% Re and ~1680°C. Two other carbides, Cr_7C_3, and Cr_3C_2, dissolve 6 and ~4 at.% Re, respectively, at temperature 1631±8 and 1764±16°C (Table 5).

3. Regularities of the constitution of alloy phase diagrams for ternary systems formed by chromium with high-valency d-metals and carbon

A particular feature of the Cr–V(Mo,W,Re,Tc)–C ternary systems is that the 'fcc'-carbides of d-metals forming this group of systems are characterized by lower (as compared with carbides of Nb, Ta and d-metals of IV group) thermodynamic stability. For some metals a result is that their concentration of saturation with carbon does not reach stoichiometry 1:1, for other (Cr and Re) such carbides are obtained only in the metastable state [24,25].

Solid solutions on the basis of 'hcp'-carbides V_2C, Mo_2C and W_2C are dominating phases in the Cr–V(Mo,W)–C systems. They have the largest extension of homogeneity range at the solidus temperature. For example, over 90% of molybdenum or tungsten atoms are replaced by chromium atoms [23]. So, this points to stabilization of the virtual phase, 'hcp'-carbide 'Cr_2C', by vanadium, molybdenum or tungsten additives. These phases are in equilibrium with almost all other phases of the ternary Cr–V(Mo,W)–C systems. In the Cr–Re–C system $(Cr_{0.18}Re_{0.82})_2C$, solid solution on the rhenium base, where over 80% of rhenium atoms are replaced by chromium atoms, is similar to the 'semicarbides'. It is precisely this existence of an extended homogeneity range of the interstitial phase on the basis of hcp-sublattice of a metal makes the Cr–Re–C system similar to the Cr–V(Mo,W)–C systems. Extrapolations of the lattice constants for solid solutions $(Mo,Cr)_2C$ and $(W,Cr)_2C$ on the zero contents of Mo or W give $a=283.5$ and $c=446.0$ pm for 'hcp'-carbide 'Cr_2C' (the carbon content being about 32–33 at.%), based on data at 1350°C [20,21], 1400°C [22] and solidus temperatures [23] (Fig. 4).

The 'fcc'-carbides also have a rather large extension of homogeneity range at high temperature in the Cr–V(Mo,W)–C systems. They are solid solutions on the basis of VC_{1-x}, α-MoC_{1-x} and α-WC_{1-x}, in which chromium replaces almost 70% of vanadium, molybdenum or tungsten at the solidus temperatures. In this case also we may say on stabilization of the virtual phase — 'fcc'-carbide 'CrC_{1-x}' — by vanadium, molybdenum or tungsten. Extrapolation of data on the lattice constant for solid solution of cubic carbides in the ternary Cr–Ti(V,Mo)–C systems gives lattice parameters and composition of this phase: $a\approx411$ pm and composition ~40 at.% C, (Fig. 5). Bouzy et al. [25] obtained the 'fcc'-carbide CrC_{1-x} in the metastable state during solidification of amorphous alloys which contained from 38 to 50 at.% C. The lattice constant of the 'CrC_{1-x}' $a=402$ pm has been obtained in the alloy which contained 45% C. The authors [25] leave room for a possibility that the alloy contained free carbon. Quite possibly it is precisely carbon deficiency of the lattice of this carbide that is responsible for the rather lower value of its lattice constant as compared with the results of data extrapolation (Fig. 5) for ternary systems.

There is a certain analogy in the topology of solidus surfaces of the Cr–V(Mo,W)–C and Re–V(Mo,W)–C [28] systems. Both rhenium and chromium in these systems are able to replace V, Mo or W atoms in 'fcc'-carbides (up to 80%). Hcp-rhenium with 'hcp'-carbides M_2C forms a continuous series of solid solutions. Similarity of these systems as to behavior of interstitial phases is demonstrated visually in Fig. 6.

Discussions of the reasons for the surprising (at first glance) shape of the homogeneity field boundary of 'fcc'-carbides (of the NaCl type) in the ternary systems with rhenium have led to the conclusion on a decisive effect of the electron-dimensional factor on the behavior of ternary phases [5]. That factor was used earlier to explain carbon deficiency on the upper boundary on carbon of homogeneity ranges of binary carbides of such high-valency metals as vanadium, molybdenum and tungsten. The

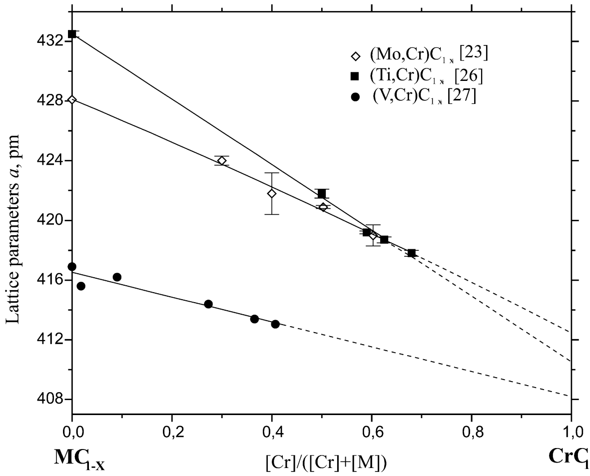


Fig. 5. Lattice parameters of 'fcc'-carbide solid solution in equilibrium with carbon versus chromium content in ternary systems Ti–Cr–C, Mo–Cr–C (based on solidus surfaces data [23,26]) and V–Cr–C (at 1300°C [27]).

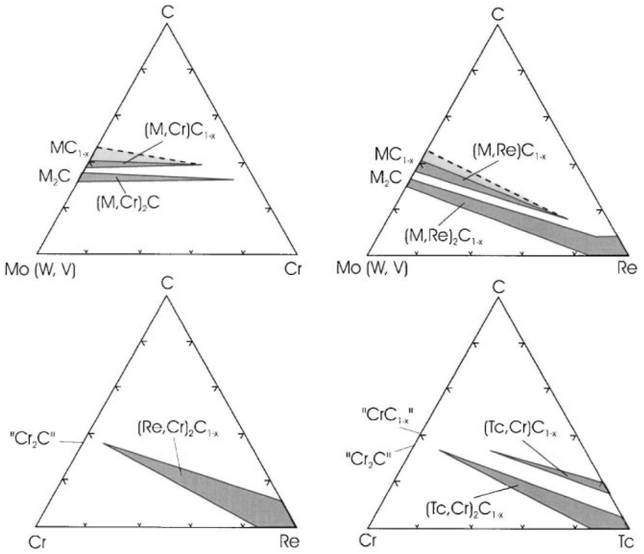


Fig. 6. 'Fcc' and 'hcp' interstitial phases in ternary systems formed by d-metals with carbon for which $r_C(e_M/r_M)>2.7$ (dash lines are boundaries of (V,Cr)C_{1-x} or (V,Re)C_{1-x} solid solutions) (scheme).

analysis of chemical behavior of these d-metals relative to carbon in binary M–C systems and phase equilibria in the ternary M′–M″–C systems has permitted a conclusion to be made that there are rather simple correlations between metal-chemical behavior of d-metals in these systems and certain simple functions of dimensional and electronic characteristics of these metals and their carbides. It has been shown that both binary and ternary 'fcc'-carbides lose stability when volume concentration of valent electrons (referred to as density of valence electrons for carbide), which is estimated as a relation of a sum of external s-, p- and d-electrons of metal (metals) and carbon atoms in an elementary cell of carbide to its volume:

$$n_e = \frac{\sum e_{MC_{1-x}}}{a^3_{MC_{1-x}}}$$

attains a definite critical value. A range of critical values of n_e in the account for one formula unit was determined as 480±20 electrons/nm^3. Table 1 and Fig. 7 show that this limit is attained by already pure fcc Re and Tc, and fcc chromium exceeds it. It completely correlates with the absence of stable phases of the NaCl type in the Cr–C and Re–C systems and with strong deficiency of carbon in the 'fcc' Tc$C_{0.21}$ [29].

The essence of the criterion mentioned may be comprehended by expanding positions of the statistical-thermodynamic theory of the chemical bond in interstitial phases

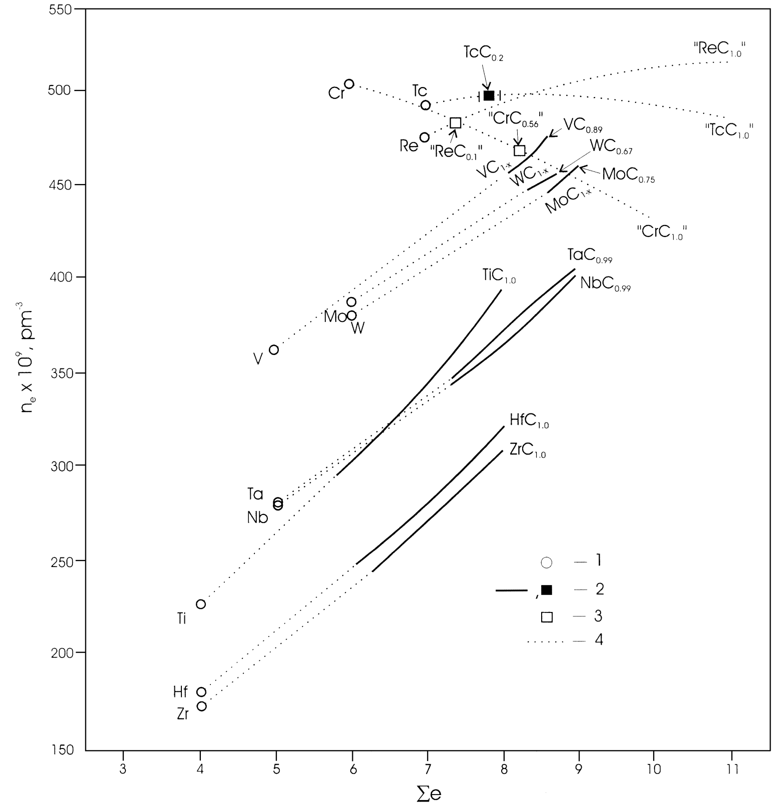


Fig. 7. Density of valence electrons (n_e) for 'fcc'-carbides of d-metals versus composition shown as the number of valence electrons per formula unit: 1, calculation for virtual fcc-modifications of d-metals; 2, calculation using experimental data; 3, calculation based on data obtained with extrapolation in ternary systems; 4, hypothetical.

of the NaCl type formed by d-transition metals of group IV and V with nonmetal components developed by Tskhai and Gel’d [30,31] for the systems formed by d-metals of higher valency (VI, VII groups) [5]. This theory explains why the criterion mentioned is a specific property of carbide systems and cannot be used for other M–X systems in which there are interstitial phases of the NaCl type (e.g. M–N and M–O). Not dwelling on this fact, we pay attention to the fact that not exceeding a critical value of n_e makes a solid solution of rhenium in vanadium, molybdenum and tungsten ‘fcc’-carbides decrease the carbon concentration in this phase in equilibrium with graphite with an increase of rhenium concentration in this phase. As a result, when rhenium substitutes group V and VI metals n_e does not grow and remains within the limits from 473, 460 and 455 electrons/nm^3 for $VC_{0.89}$, $MoC_{0.75}$ and $WC_{0.67}$, respectively, to 487 electrons/nm^3 for $ReC_{0.11}$, which exceeds the n_e value for pure rhenium only slightly (see Tables 1 and 6, Fig. 7). Likewise, when chromium dissolves in cubic vanadium, molybdenum and tungsten carbides, n_e remains within the limits which do not exceed the critical value: it only slightly grows for $(Cr,Mo)C_{1-x}$ and $(Cr,W)Cr_{1-x}$ ‘fcc’-carbides and even falls for the $(Cr,V)C_{1-x}$ carbide. In this case carbon concentration in the ‘fcc’-carbide remains almost unchanged. Taking into account that the n_e value for pure chromium exceeds the critical one, this result may be treated as having proceeded from the substantial positive deviation of the concentration dependence of lattice constants of a solid solution from the Veggard law or (which is the same) we may suppose that the efficient atomic radius of chromium in $(M,Cr)C_{1-x}$ solution has certain other values, differing from r_{Cr} of pure chromium and exceeding it. The limit concentration of chromium in solid solutions $(V,Cr)C_{1-x}$, $(Mo,Cr)C_{1-x}$ and $(W,Cr)C_{1-x}$ at the solidus temperatures is restricted by a criterion related to the known Hägg criterion for binary phases of the NaCl type, namely, by a critical value of the ratio between sizes of carbon and metal atoms which for binary systems looks like: $r_C/r_M \leq 0.59$. If we assume $r_C = 77$ nm as in Hägg, and $r_{\text{‘M’}} = x_{Cr} r_{Cr} + (1 - x_{Cr}) r_M$, where $x_{Cr} = [Cr]/([Cr] + [M])$ ([Cr] and [M] are at.%), then $r_C/r_{\text{‘M’}}$ for chromium-saturated ‘fcc’-carbides in systems with V, Mo and W (Table 6) is a constant value equal to about 0.58. It is interesting that for the Cr–Ti–C, system which also demonstrates high solubility of chromium in ‘fcc’-carbide, the $r_C/r_{\text{‘M’}}$ value is similar to that mentioned above and is equal to 0.575.

So, it appears that if the difference between atomic radii of d-metal and chromium is within the limits which are favorable to form extended series of solid solution by these metals and, thus, replacement of M atoms by Cr atoms in carbide is not confined to excessive difference in radii of these metals, then the critical value $r_C/r_{\text{‘M’}}$ that has been found is the criterion which restricts chromium solubility in the ‘fcc’ MC_{1-x} carbide.

Thus, chromium in systems with d-metals where atomic radii differ not more than by 13% is able to replace a certain number of d-metal atoms in their ‘fcc’ and ‘hcp’ carbides. The ability of d-metals to replace chromium in its carbides is significantly less. Carbides $(Cr,M)_{23}C_6$ have the largest extension of homogeneity ranges (Tables 3–5). Maximal solubility of V, Nb, Ta, Mo, W and Re in $Cr_{23}C_6$, which corresponds to the solidus temperatures, is compared in Fig. 8. It is interesting that atomic radii of molybdenum and tungsten almost coinciding in their

Table 6
Data on ‘fcc’-carbides MC_{1-x} (NaCl structure type) saturated with carbon and saturated with carbon and chromium

d-metal (M)	With C saturated				With C and Cr saturated	
	$1-x$	$a_{MC_{1-x}}$ pm	$n_e \times 10^9$, pm^{-3}	$\frac{a_{dMC_{1-x}} - a_{CrC_{1-x}}}{a_{CrC_{1-x}}}$[a]	$\frac{[Cr]}{[M]+[Cr]}$	$r_C/r_{\text{‘M’}}$
Zr	1.00	470.2	308	0.144	0.03[a]	0.484
Hf	1.00	465.3	318	0.132	0.09[a]	0.496
Ti	1.00	433.2	394	0.054	0.68[a]	0.575
Nb	0.99	447.1	401	0.088	0.28	0.544
Ta	0.99	445.6	406	0.084	~0.27	0.543
V	0.89	416.5	473	0.013	~0.44	0.584
W	0.67	424	455	0.032	0.69[b]	0.583
Mo	0.75	428.1	460	0.042	0.68[b]	0.583
Cr	~0.67[c]	~411	499	–	–	–
Re	0.11[d]	394	487	−0.041	–	–
Tc	0.21	398.2	497	−0.031	0.55[e]	0.58[e]

[a] Given according to data in Ref. [26].

[b] Given according to data in Ref. [23].

[c] Composition and lattice parameters for virtual chromium ‘fcc’-carbide was estimated by extrapolation of experimental data for solid solution $(Mo,Cr)C_{1-x}$ [23] and $(Ti,Cr)C_{1-x}$ [26] (Fig. 5).

[d] Composition for metastable rhenium ‘fcc’-carbide was estimated [6] on the basis of its lattice parameters in Ref. [24].

[e] Predicted.

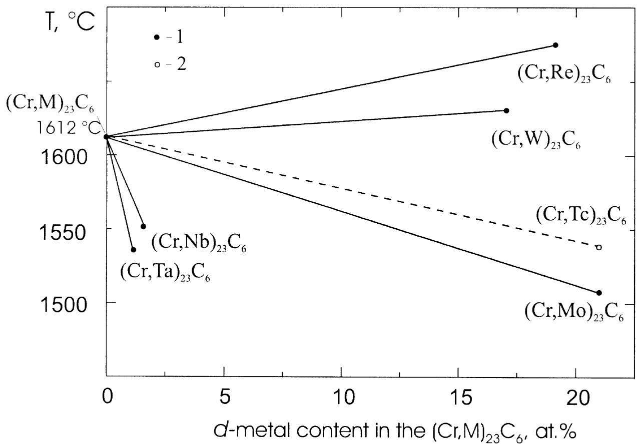


Fig. 8. Relationship between solubility of d-metals in $Cr_{23}C_6$ and solidus temperature of saturated with d-metal solid solutions $(Cr,M)_{23}C_6$: 1, experiment; 2, prediction.

values, but solubility of molybdenum (4d-metal) in this phase on the solidus and of tungsten (5d-metal) differs by more than 10%.

In the Tc–C system there are both interstitial phases based on close-packed metal lattices — hcp and fcc: solid solution based on hcp-technetium and ‘fcc’-carbide deficient in carbon [29,32]. That is why there are reasons to treat this system as an analogue of binary V(Mo,W)–C systems and to attribute the ternary Cr–Tc–C system to the same classification group as Cr–V(Mo,W,Re)–C systems. Regularities of the constitution of alloy phase diagrams for the Cr–M–C systems mentioned above make it possible to transfer with confidence to prediction of the alloy phase diagram for the Cr–Tc–C system at high temperature.

4. Prediction of the alloy phase diagram of the Cr–Tc–C system

The Cr–Tc and Tc–C alloy phase diagrams which are boundaries for the ternary Cr–Tc–C system have not yet been studied experimentally. The σ-phase has been found experimentally in the Tc–Cr [33]. Probable phase equilibria in this system are presented proceeding from the expected analogy with the Cr–Re system [10].

The alloy phase diagram of the Tc–C system is from Refs. [34,35], where it is described by the results of the assessed data [29,32,36] and differs from that given in Ref. [10] as it has taken into account the experimental data [29] on the existence of ‘fcc’-carbide TcC_{1-x}. In compliance with these data the $Tc_{82.5}C_{17.5}$ cast alloy annealed at 1400°C was a single-phase alloy. When carbon concentration was higher, the alloys were two-phase [29,32]. They contained ‘fcc’-carbide and graphite and melted at 1835±50°C [32].

Proceeding from chemical likeness and similar atomic radii of rhenium and technetium, the latter, as well as rhenium, should solve a significant amount both of chromium and carbon. In this case the homogeneity range of the $(Tc,Cr)_2C_{1-x}$ solid solution is to be directed to the ‘Cr_2C’ composition (Fig. 9) precisely as the $(Re,Cr)C_{1-x}$ solid solution is in the Cr–Re–C system, achieving at the

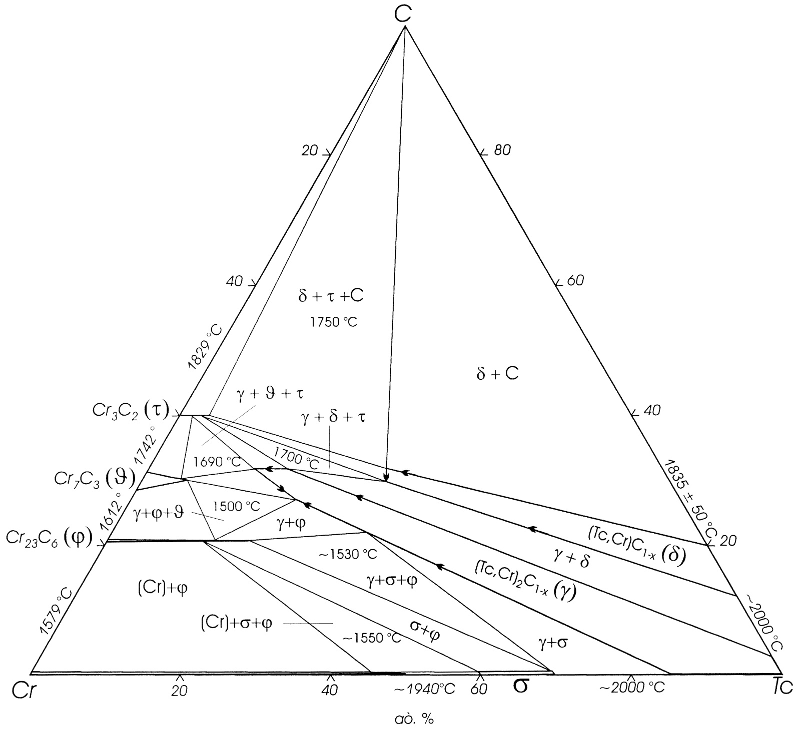


Fig. 9. Projection of solidus surface of the Cr–Tc–C system (prediction).

solidus temperature approximately the same stoichiometry which occurs in the respective system with rhenium, namely, $(Tc_{0.2}Cr_{0.8})_2C$.

The existence of ‘fcc’-carbide $(Tc,Cr)C_{1-x}$ differs the ternary Cr–Tc–C system from the Cr–Re–C one and demonstrates its likeness to the Cr–Mo(W)–C systems. A slight difference in atomic radii of Cr and Tc (6%) gives reason to expect that Cr can isomorphously replace rather a large amount of Tc in ‘fcc’-carbide $TcC_{0.2}$, probably, as well as it can replace V, Mo and W in their ‘fcc’-carbides. In this case the homogeneity range of this solid solution should be extended towards ‘$CrC_{0.67}$’ and its upper boundary on carbon should not exceed the boundaries which are limited by a critical value of n_e, i.e. should be in compliance with a monotonous change in n_e from 497 nm^{-3} for $TcC_{0.21}$ to 473 nm^{-3} for ‘$CrC_{0.67}$’. Proceeding from the criterion $r_C/r_{\text{'M'}} \leq 0.58$ for ‘fcc’-carbides in the ternary Cr–M–C systems, the concentration of chromium carbide in technetium ‘fcc’-carbide $TcC_{0.2}$ may be estimated as 55 mol.% at solidus temperature, i.e. it is consistent with the ratio $[Cr]/([Cr]+[Tc])=0.55$ ([Cr] and [Tc] are at.%).

Maximal solubility of technetium in chromium carbides at the solidus temperatures was estimated by the analysis of data on solubility of groups VI to VII metals in these phases (Fig. 8). The solidus temperature of ternary $(Tc)+(Cr_3C_2)+(Cr_7C_3)$ alloys that should be ~1690°C and $(Tc)+(Cr_7C_3)+(Cr_{23}C_6)$ that should be ~1500°C has been predicted coming from the correlation found between the solidus temperatures of three-phase alloys and a melting point of d-metals (Fig. 10) [37].

New results obtained for the Cr–Re–C system have permitted a deeper insight into the metal-chemical behavior of chromium in the Cr–M–C ternary systems. Proceeding from the conclusions made, a substantiated prediction has been given for the alloy phase diagram of the Cr–Tc–C systems at high temperatures. The prediction [34] made from the analogy with the Cr–Re–C system and based on data as to the isothermal section of the Cr–Re–C system at 1300°C [19] should be regarded as referring to comparatively low temperatures.

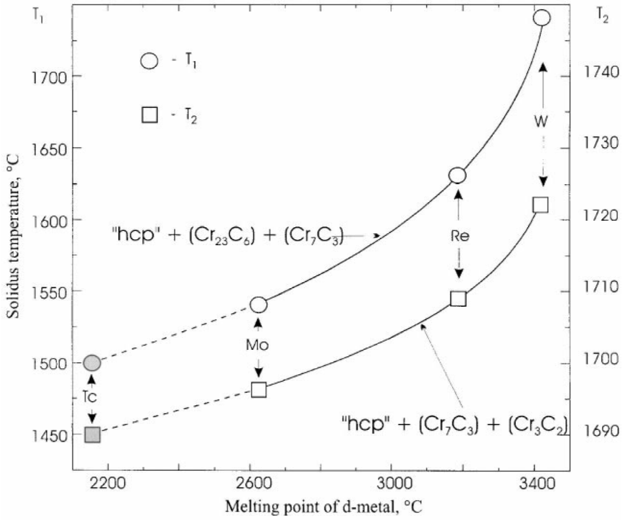


Fig. 10. Correlation between solidus temperatures of three-phase ‘hcp’-carbide$+(Cr_3C_2)+(Cr_7C_3)$ and ‘hcp’-carbide$+(Cr_7C_3)+(Cr_{23}C_6)$ alloys in the systems Cr–M–C and melting points of d-metals.

5. Conclusion

As distinct from d-metals of groups IV–VI of the Periodic system, chromium does not form stable carbide interstitial phases on the basis of close-packed metal sublattices. It is motivated by a relatively small atomic radius of chromium for which the Hägg criterion is exceeded: $r_C/r_{Cr}=0.60$. But in the ternary Cr–M–C systems chromium is able to replace considerable amounts of atoms of d-metals both in ‘hcp’- and in ‘fcc’-carbides in those cases when there is no unfavourable ratio of geometrical dimensions of metals. In such a manner chromium demonstrates its metal-chemical affinity to vanadium, rhenium, technetium and d-metals of group VI of the Periodic system.

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