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# Thermodynamic Aspects of CVD Crystallization of Refractory Metals and Their Alloys

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## 1. Introduction

The low-temperature chemical vapor deposition (CVD) of refractory metals by the hydrogen reduction of their fluorides is known as one of the perspective technique for the production of high quality metallic coatings [1]. The CVD of tungsten has been more extensively studied due to unique combination of its features such as low deposition temperature (750-900 K), high growth rate (up to 5 mm/h), a good purity and high density of tungsten deposit [2, 3]. Up to now there is a great interest to CVD tungsten alloys due to their physical-mechanical properties [4, 5].

The thermodynamic analysis of the CVD processes is useful to define the optimal deposition conditions. The understanding of the gas phase phenomena controlling the metals and alloys deposition requires the knowledge of the gaseous mixture composition and surface reaction kinetics which lead to the deposit growth. This chapter contains the calculated and known thermochemical parameters of V, Nb, Ta, Mo, W, Re fluorides, the compositions of gas and solid phases as result of the equilibrium of the hydrogen and fluorides for the metals VB group (V, Nb, Ta), VIB group (Mo, W), VII group (Re). A particular attention is paid to the theoretical aspects of tungsten alloys crystallization.

## 2. Estimation of thermochemical constants

The accuracy of thermodynamic analysis depends on the completeness and reliability of thermochemical data. Unfortunately, a limited number of the transition metal fluorides have been characterized thermochemically or have been studied by a spectroscopic technique. The experimental data were completed with the evaluated thermochemical constants for fluorides in different valent and structural states. The calculated data were obtained by the interpolation procedure based on the periodic law. The interpolation was performed on properties of a number of the compounds that represent the electron-nuclei analogies [6].

The unknown enthalpy of the fluorides formation was calculating via energy of halids atomization as following:

$$\Omega (MX_n) = \Delta_f H (M_{at}) + n \Delta_f H (X_{at}) - \Delta_f H (MX_n), \quad (1)$$

The atomization energies of isovalent fluorides, chlorides and oxides of 4, 5, 6 period metals were discussed in [7]. It can be emphasised that the chlorides and oxides are studied well by experimental way. These curves are calling as “two-hilled” curves. Quantum-mechanical interpretation of these dependences can be found in [8, 9].

$$\Omega (MX_n) = \varphi(Z_m), \quad (2)$$

$$\Delta Z_m \Omega (MF_n) / \Delta Z_m \Omega (MF_s) = \varphi(Z_m, n), \quad (3)$$

$$\Delta n_m \Omega (MF_n) / \Delta Z_m \Omega (MCl_n) = \varphi(Z_m, n), \quad (4)$$

$$\Omega (MF_n) / \Omega (MCl_n) = \varphi(Z_m, n), \quad (5)$$

$$\Omega (MF_n) / \Omega (MO_{n/2}) = \varphi(Z_m, n), \quad (6)$$

$$\Omega [M(Z_m)F_n] / \Omega [M(Z_m + 32)F_n] = \varphi(Z_m, n), \text{ where } Z_m = 39-48 \quad (7)$$

$$\Omega (MX_n) = \varphi(Z_x) = A_n \psi(Z_x) + B_n, \quad X = F, Cl, Br, I, \quad (8)$$

$$\Omega (MF_n) = \varphi(n) = \psi[\Omega (MCl_n)] : \Omega (MF_n) = C \Omega (MCl_n) + D \quad (9)$$

$$E (MF_n) = \varphi(n) = \psi[D (MF_n)] : E (MF_n) = L \Omega (MF_n) + N, \quad (10)$$

where  $A_n, B_n, C, D, L, N$  -const.

These sequences are the dependencies of energies of halids atomization (2, 8-10), one of ratio of loss of energies of fluoride and chloride atomization (3, 4) from atom number of metal  $Z_m$  (2-7), from halid  $Z_x$  (8) and from valent state  $n$  (3-7, 9, 10).

All sequences were analyzed in order to determine the probable regions for interpolation by linear function. For example, the estimation of unknown atomization energies can be performed by the use of the sequence (2) within following region:

$\Omega (MF)$  where  $Z_m$ , corresponds to (III-IV-V) and (VI-VII-VIII-I) groups;

$\Omega (MF_2)$  where  $Z_m$ , corresponds to (V-VI) and (VI-VII-VIII) groups;

$\Omega (MF_n, n \geq 3)$  where  $Z_m$ , corresponds to (V-VI-VII) groups.

The sublimation heat  $\Delta_s H (MX_n)$  and entrophy  $S (MX_n)$  were analyzed:

$$\Delta_s H (MX_n) = \varphi(Z_m, Z_x, n), \quad (11)$$

$$S (MX_n) = \varphi(Z_m, Z_x, n). \quad (12)$$

All calculated thermochemical constants together with most reliable literature data are collected in tables 1, 2. The accuracy of the estimation data is  $\pm 30$  kJ/mol for atomization energy and  $\pm 4$  J/mol K for atomization entrophy. The accurate thermochemical data of W-F-H components are collected in the table 3, due to their importance for this analysis.

The literature review shows that the formation enthalpy is determined for several fluorides enough reliable which are taken as milestone points. Among them are  $AlF_3, UF_4, UF_5, ScF_3, CrF_2, MnF_2, TiF_4, FeF_3$  and other [28, 29]. Table 1 contains also the thermochemical constants for polymer fluorides. Most reliable thermochemical data among the fluoride associations were obtained for  $Al_2F_6, Fe_2F_8, Cr_2F_4$ . The thermochemical data for tungsten fluorides are collected in table 2 because of the special importance for this investigation. Of course these data will be more full and reliable in the progress of fluoride chemistry.

No	Substance	$\Delta_f H^{\circ}_{298}$ (g)	$\Delta_f H^{\circ}$ (s)	$\Delta_s H^{\circ}_{298}$
1	V	514,1±4,2 [10]	0	514,1±4,2
2	VF	2,5±63 [11]	-	-
3	VF <sub>2</sub>	≤-514±28 [7]	≤-899±28 [7]	385±28
4	VF <sub>3</sub>	-878,0±48,1 [12]	-1263,1±48,1 [7]	385,1
5	VF <sub>4</sub>	≤-1241±8 [7]	-1412,1 [10]	169,1±8,0
6	VF <sub>5</sub>	≤-1429,7±5,0 [11]	-	-
7	V <sub>2</sub> F <sub>6</sub>	-1963,4±48,0 [13]	-	-
8	V <sub>2</sub> F <sub>8</sub>	-2746,7±20,9 [14]	-	-
1	Nb	721,9±4,2 [10]	-	721,9±4,2
2	NbF	228±25 [7]	-	-
3	NbF <sub>2</sub>	≤-226±21 [7]	-	-
4	NbF <sub>3</sub>	≤-754±16 [7]	-	-
5	NbF <sub>4</sub>	-1257±22 [7]	-1506±21 [7]	249±22
6	NbF <sub>5</sub>	-1711,7±6,3 [12]	-1813,8±0,6 [10]	102,1±6,9
7	Nb <sub>3</sub> F <sub>15</sub>	-5342,0±4,6 [15]	-	-
1	Ta	785,4±4,2 [10]	0	785,4±4,2
2	TaF	289,3±12,5 [16]	-	-
3	TaF <sub>2</sub>	-287,2±12,5 [16]	-	-
4	TaF <sub>3</sub>	-810,9±12,5 [16]	-	-
5	TaF <sub>4</sub>	-1275,7±12,5 [16]	-	-
6	TaF <sub>5</sub>	-1774,8±12,5 [16]	-1901,8±0,8 [10]	127±13,3
7	Ta <sub>3</sub> F <sub>15</sub>	-5611,2±5,4 [15]	-	-
1	Mo	655,8±3,4 [7]	0	655,8±3,4
2	MoF	271,7±9,2 [17]	-	-
3	MoF <sub>2</sub>	-168,0±12,1 [17]	-	-
4	MoF <sub>3</sub>	-591,5±14,6 [17]	-909,6±19,7 [18]	318,1±34,3
5	MoF <sub>4</sub>	-953,0±16,3 [17]	-1149,0±14,6 [18]	196,0±30,9
6	MoF <sub>5</sub>	-1240,2±35,9 [17]	-1394,4±4,6 [19]	154,2±40,5
7	MoF <sub>6</sub>	-1556,2±0,8 [10]	-	-
8	Mo <sub>3</sub> F <sub>15</sub>	-4091,0±9,6 [20]	-	-
1	W	856,1±4,2 [10]	0	856,1±4,2
2	WF	≤385 [21]	-	-
3	WF <sub>2</sub>	-86,2±13,4 [21]	-	-
4	WF <sub>3</sub>	-507,1±11,7 [21]	-	-
5	WF <sub>4</sub>	-928,8±10,5 [21]	-1206,2±7,5 [18]	277,4±13
6	WF <sub>5</sub>	-1293,3±8,4 [21]	-1446,8±8,4 [10]	153,5±16,8
7	WF <sub>6</sub>	-1721,5±0,7 [10]	-	-

N <sup>o</sup>	Substance	$\Delta_f H^{\circ}_{298}$ (g)	$\Delta_f H^{\circ}$ (s)	$\Delta_s H^{\circ}_{298}$
8	W <sub>3</sub> F <sub>15</sub>	-4244,0±8,4 [15]	-	
1	Re	775,0±6,3 [10]	0	775,0±6,3
2	ReF	343±60 [7]	-	
3	ReF <sub>2</sub>	-116±46 [7]	-	
4	ReF <sub>3</sub>	-354±36 [7]	-	
5	ReF <sub>4</sub>	-733±33 [7]	-995±33 [7]	263±26
6	ReF <sub>5</sub>	-962±29 [7]	-1142±18 [7]	180±29
7	ReF <sub>6</sub>	-1353,5±12,6 [10]	-	
8	ReF <sub>7</sub>	-1410±11 [22]	-1450,5±10,9 [22]	40,5±21,9
9	Re <sub>2</sub> F <sub>8</sub>	-1854,2±33,4 [23]		
10	Re <sub>3</sub> F <sub>15</sub>	-3337,7±17,6 [24]		
1	F	79,43±1,05 [10]	-	-
2	F <sub>2</sub>	0	-	-
1	H	217,77±0,02 [10]	-	-
2	H <sub>2</sub>	0	-	-
1	HF	-270,4±1,2 [10]	-	-

Table 1. Enthalpy of forming  $\Delta_f H$  (kJ/mol) and sublimation  $\Delta_s H$  (kJ/mol) of system M-F-H components in gas (g) and solid (s) states.

N <sup>o</sup>	Substance	$S^{\circ}_{298}$ (g)	$S^{\circ}_{298}$ (s)
1	V	182,010±0,033 [10]	28,88±0,33 [10]
2	VF	230±4 [10]	-
3	VF <sub>2</sub>	254,4 [12]	76,220 [25]
4	VF <sub>3</sub>	283,05 [12]	96,99 [10]
5	VF <sub>4</sub>	305±4 [7]	126,13 [10]
6	VF <sub>5</sub>	331,0±2,9 [10]	-
7	V <sub>2</sub> F <sub>6</sub>	397,0±17 [13]	-
8	V <sub>2</sub> F <sub>8</sub>	456±17 [14]	-
1	Nb	186,000±0,033 [10]	36,53±0,21 [10]
2	NbF	241,4 [12]	-
3	NbF <sub>2</sub>	281,6 [12]	-
4	NbF <sub>3</sub>	296,2 [12]	-
5	NbF <sub>4</sub>	325,5 [12]	100±4 [10]
6	NbF <sub>5</sub>	323,8 [12]	157,3±2,1 [10]
7	Nb <sub>3</sub> F <sub>15</sub>	683,0±16,7 [15]	-
1	Ta	184,927±0,033 [10]	41,47±0,17 [10]
2	TaF	240,8 [12]	-

No	Substance	$S^{\circ}_{298}$ (g)		$S^{\circ}_{298}$ (s)
3	TaF <sub>2</sub>	290,9	[12]	-
4	TaF <sub>3</sub>	308,1	[12]	-
5	TaF <sub>4</sub>	336,1	[12]	-
6	TaF <sub>5</sub>	332,7	[12]	169,7±16,7 [10]
7	Ta <sub>3</sub> F <sub>15</sub>	720,6±14,6	[15]	-
1	Mo	181,663±0,029	[10]	28,59±0,21 [10]
2	MoF	243,53	[12]	-
3	MoF <sub>2</sub>	275,9	[12]	-
4	MoF <sub>3</sub>	301,3	[12]	93±12 [7]
5	MoF <sub>4</sub>	319,3	[12]	100±12 [7]
6	MoF <sub>5</sub>	327,7±1,7	[10]	125±12 [10]
7	MoF <sub>6</sub>	350,3±1,2	[10]	-
8	Mo <sub>3</sub> F <sub>15</sub>	580,6±16,7	[20]	-
1	W	173,675±0,029	[10]	32,65±0,33 [10]
2	WF	250,6±4,2	[10]	-
3	WF <sub>2</sub>	285,8	[12]	-
4	WF <sub>3</sub>	314,2	[12]	-
5	WF <sub>4</sub>	330,1	[12]	103,3±8,4 [10]
6	WF <sub>5</sub>	343,1	[12]	146±13 [10]
7	WF <sub>6</sub>	353,5±1,3	[10]	-
8	W <sub>3</sub> F <sub>15</sub>	631±12	[15]	-
1	Re	188,643±0,029	[10]	36,49±0,33 [10]
2	ReF	251±4	[7]	-
3	ReF <sub>2</sub>	285±4	[7]	-
4	ReF <sub>3</sub>	308,8	[12]	-
5	ReF <sub>4</sub>	333,9±6,3	[10]	146,4±8,4 [10]
6	ReF <sub>5</sub>	337,6±6,3	[10]	175,7±8,4 [10]
7	ReF <sub>6</sub>	363,6±2,1	[10]	-
8	ReF <sub>7</sub>	360	[22]	-
9	Re <sub>2</sub> F <sub>8</sub>	497±17	[23]	-
10	Re <sub>3</sub> F <sub>15</sub>	736±17	[24]	-
1	F	158,489±0,021	[10]	-
2	F <sub>2</sub>	202,52±0,25	[10]	-
1	H	114,494±0,021	[10]	-
2	H <sub>2</sub>	130,395±0,021	[10]	-
1	HF	173,512±0,033	[10]	-

Table 2. Entropy data  $S^{\circ}_{298}$  (J/K mol) of system M-F-H components in gas (g) and solid (s) states.

Kom- ponents	$\Delta H_f^{298}$ , kJ/mol	$S_{298}$ , J/mol·K	$C_p = \alpha + \beta T + \gamma T^2 + \delta T^{-2}$ , J/mol·K				References
			$\alpha$	$10^3 \beta$	$10^5 \gamma$	$10^{-5} \delta$	
H <sub>2</sub>	0,0	130,4	32,02	-7,36	0,58	1,34	[10, 26]
H	217,8	114,5	20,77	0,0	0,0	0,0	[10, 26]
F <sub>2</sub>	0,0	202,5	26,42	22,36	-1,25	-0,63	[10, 26]
F	79,4	158,5	25,08	-7,86	0,42	-0,33	[10, 26]
HF	-270,4	173,5	30,01	-3,47	3,47	-0,25	[10, 26]
WF <sub>6</sub>	-1719,9	357,2	117,46	83,60	-5,02	-16,93	[10, 21, 26]
WF <sub>5</sub>	-1292,0	342,8	114,95	54,76	-3,26	-14,13	[12, 21]
WF <sub>4</sub>	-928,0	329,8	80,67	56,85	-3,43	-7,98	[12, 21]
WF <sub>3</sub>	-506,6	313,9	65,63	36,28	-2,21	-7,57	[12, 21]
WF <sub>2</sub>	-86,1	285,5	53,92	26,41	-1,59	-3,85	[12, 21]
WF	384,6	250,4	30,72	13,92	-0,79	-1,55	[12, 14]
W <sub>2</sub> F <sub>8</sub>	-2042,4	414,5	166,36	112,86	-6,81	-22,40	[7, 27]
W <sub>2</sub> F <sub>10</sub>	-2829,4	497,0	202,31	142,12	-8,61	-28,34	[7, 27]
W <sub>3</sub> F <sub>15</sub>	-4244,0	631,2	295,00	247,94	-15,29	-42,39	[7, 15]
HWF <sub>5</sub>	-1383,9	352,2	98,65	103,25	-5,60	-15,01	[27]

Table 3. Standart thermochemical constants of W-F-H components.

### 3. Equilibrium states in M-F systems

Temperature dependencies of equilibrium compositions in the M-F systems (M = V, Nb, Ta, Mo, W, Re) are presented at the Fig.1. The data represent the thermodynamic stability of the refractory metal fluorides with different valencies both monomer and polymer states depending on the place of the metal in the Periodic table. The gas phase composition depends on both the heat of the fluoride formation and the vaporation heat of the fluorides. The thermodynamic analysis of M-F systems shows that the highest fluorides of the metals are stable at temperatures up to 2000 K. The exceptions contain the fluorides VF<sub>5</sub>, MoF<sub>6</sub>, ReF<sub>6</sub> that decompose slightly at the high temperature range and their thermal stability increase according to the following order: VF<sub>5</sub> > MoF<sub>6</sub> > ReF<sub>6</sub>.

The gas low-valent fluoride concentrations, which depend upon the metal place in the periodic system, rise with the increase of atomic number within each group and decrease with the increase of atomic number within each period. Thus tantalum fluorides are most strongly bonded halids and vanadium fluorides are most unstable among considered fluorides. It is necessary to note that partial pressures of low valent fluorides in Re-F system are close to each other but low valent fluorides in Ta-F system have very different concentrations.

Nevertheless the vaporation temperature of fluorides varies depending upon the metal place in the periodic system in opposite direction than the gas low-valent fluorides concentration. The most refractory fluorides are VF<sub>2</sub> and VF<sub>3</sub> (above 1500 K), the low-valent fluorides of Nb and Mo possess the mean vaporation temperature (900-1100 K). Th low-

valent fluorides of tantalum, tungsten, rhenium have the lowest vaporation temperature (500-550 K).

The peculiarity of the fluorides is the possibility of their polymerization. It is known that dimers or threemers are observed in gas state but tetramer clusters of Nb, Ta, Mo, W fluorides and chains of V, Re fluoride polymers are forming in solid state [30]. For example, fluorides  $W_2F_8$ ,  $W_2F_{10}$  and  $Mo_2F_6$ ,  $Mo_2F_8$ ,  $Mo_2F_{10}$  exist in W-F and Mo-F system, correspondingly. The main structural state of Nb, Ta, Mo, W, Re fluoride polymers are threemers but vanadium pentafluoride does form polymer state.  $M_3F_{15}$  polymers are forming by the single M-F-M bonds but the fluoride dimers have double fluorine bridge bonds. The exception are dimer molecules  $V_2F_6$ ,  $V_2F_8$ ,  $Re_2F_8$  with the M-M bonds. All polymer states are presented in tables 1-3.

#### 4. Equilibrium states in M-F-H systems

The equilibrium analysis of the metal-fluorine-hydrogen (M-F-H) systems for the temperature range 400-2000 K, total pressure of  $1.3 \times 10^5$  Pa and 2 kPa and for fluoride to hydrogen ratio from 1:3 to 1:100 have been calculated using a special procedure based on the search of entropy extremum for the polycomponent mixture [7, 31]. All experimental and calculated thermochemical constants of the fluorides and the characteristics of the fluoride phase transitions were involved into the data set. The equilibrium compositions of M-F-H systems (M=V, Nb, Ta, Mo, W, Re) for the optimal total pressure and the optimal reagent ratio are presented at the Fig.2.

The comparison of the results presented at the Fig. 1 and Fig.2 shows that the addition of hydrogen to VB metal pentafluorides decrease concentrations of the highest fluorides in monomer and polymer states (except of  $V_2F_6$ ) and rise the concentration of lower-valent fluorides. The large difference is observed for V-F-H system and small difference - for Ta-F-H system.

The hydrogen addition to tungsten, molibdenium and rhenium hexafluorides leads to the decrease of  $MF_x$  concentration,  $7 \leq x \geq 3$ , and to a small increase of di- and monofluorides concentration.

The source of VB group metals formed from M-F-H systems are highest fluorides and polymers. The VI group metals are the product of hexa-, penta- and terafluoride decomposition, but all known rhenium fluorides produce the metallic deposit. The variation of the external conditions (total pressure and fluoride to hydrogen ratio) influence on the gas phase composition according to the law of mass action and Le Chatelier principle.

Fig. 3 presents the equilibrium yield of solid metallic deposit from the mixtures of their fluorides with hydrogen as a function of the temperature. It is shown that metallic Re, Mo, W may be deposited from M-F-H system at temperatures above 300 K. Yields of Nb and Ta were varied in the temperature range from 800 K to 1300 K. Metallic V may be not deposited from M-F-H system until 1700 K due to the high sublimation temperature of  $VF_2$  and  $VF_3$ . It was established that the moving force (supersaturation) of the metal crystallization in M-F-H system increase in the order for following metals: Re, Mo, W, Nb, Ta, V. These thermodynamic results are in agreement with experimental data reviewed in [7, 32, 33].

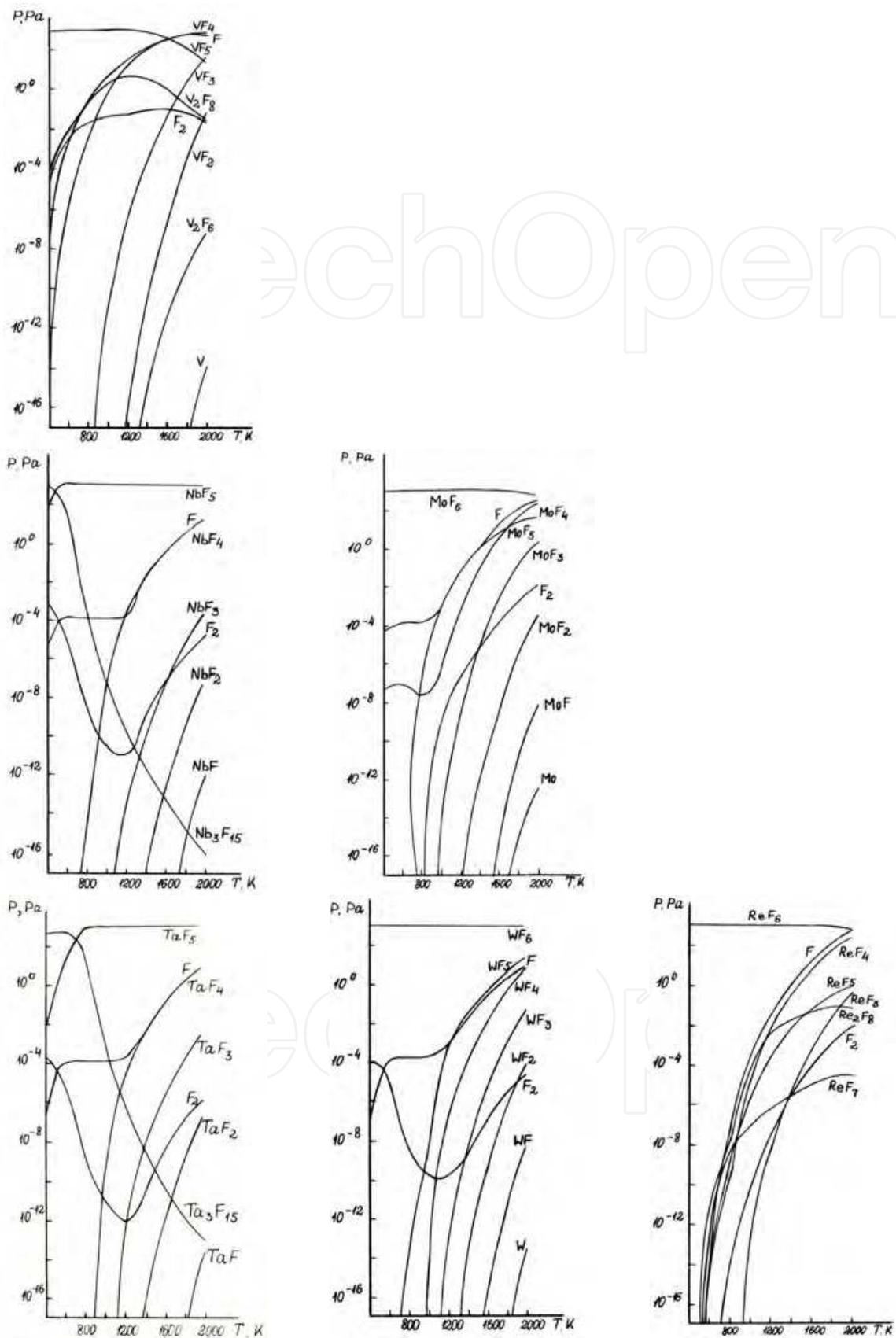


Fig. 1. Equilibrium gaseous composition in M-F systems at total pressure of 2 kPa [7].

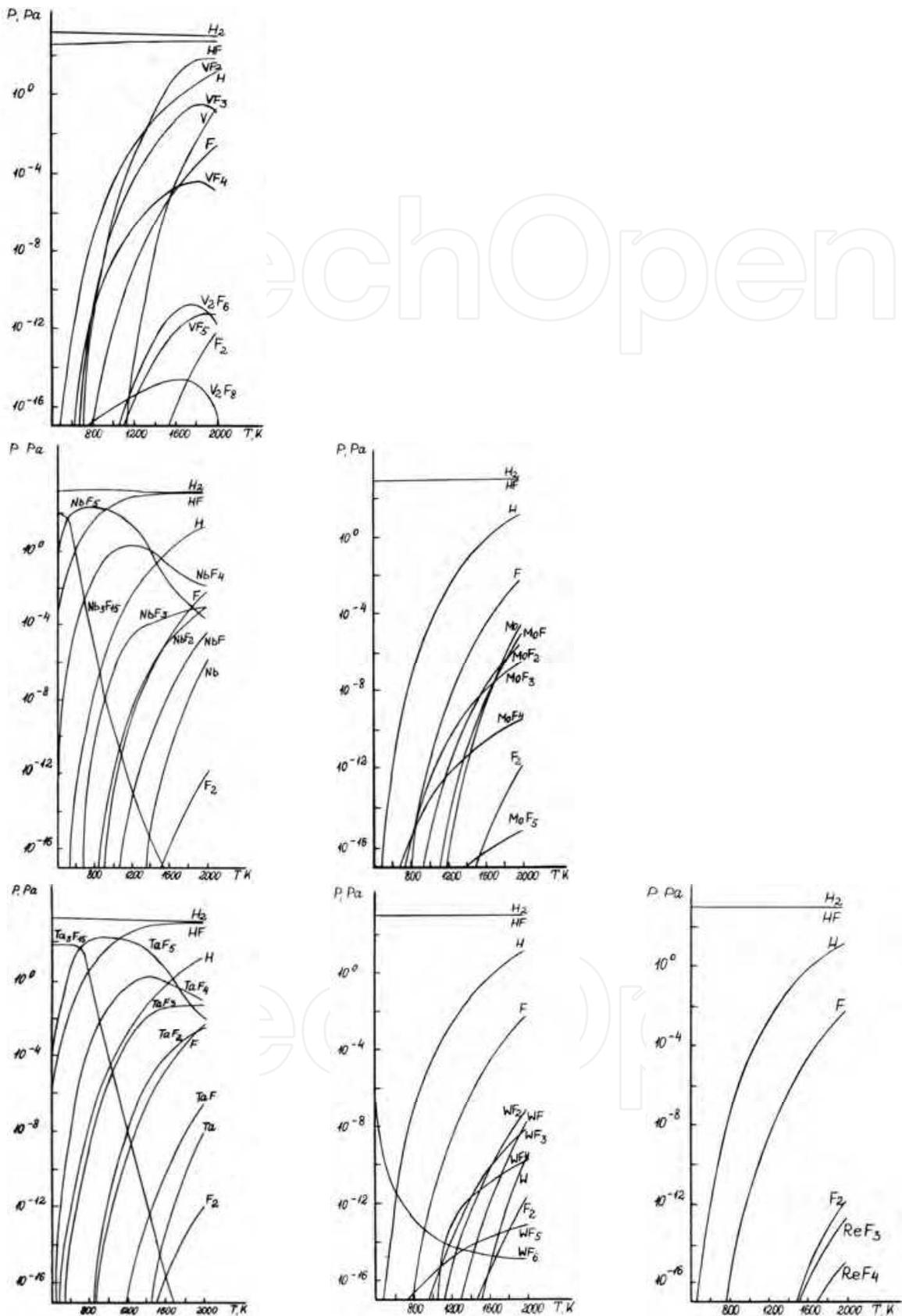


Fig. 2. Equilibrium gaseous composition in M-F-H systems at total pressure of 2 kPa and hydrogen to highest fluoride initial ratio of 10 [31].

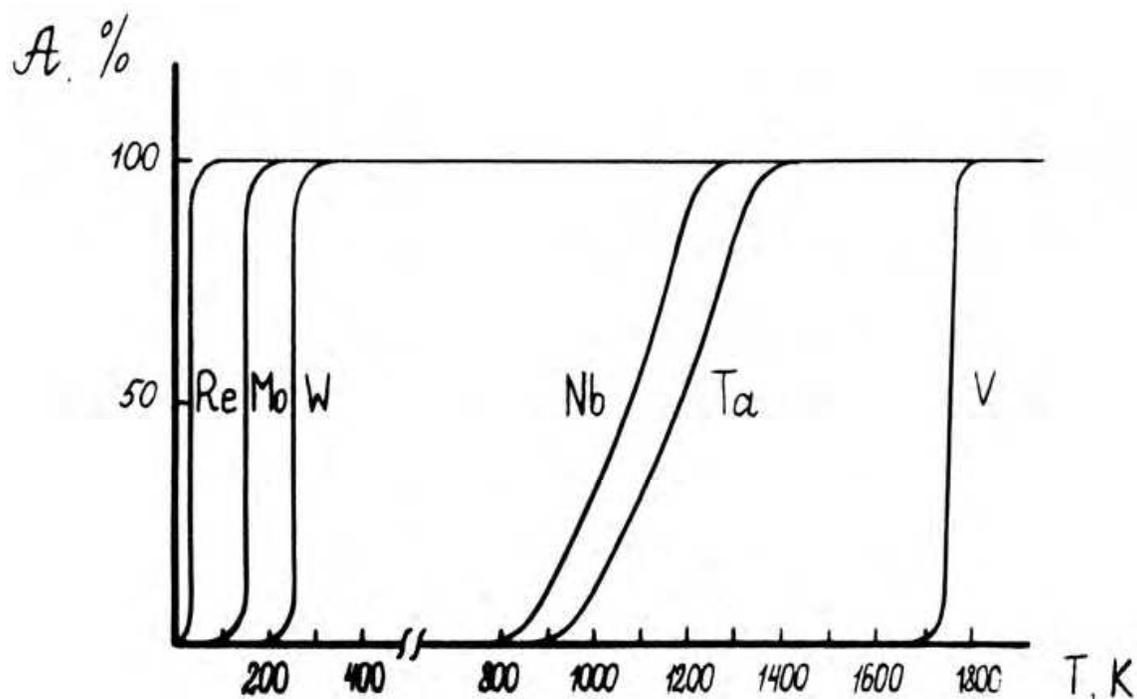


Fig. 3. Yield of metals (V, Nb, Ta, Mo, W, Re) from the equilibrium mixtures of their fluorides with hydrogen (1:10) as a function of the temperature [31].

### 5. Equilibrium composition of solid deposit in W-M-F-H systems

A thermodynamics of alloy co-deposition is often considered as a heterogeneous equilibrium of gas and solid phases, in which solid components are not bonded chemically or form the solid solution. The calculation of the solid solution composition requires the knowledge of the entropy and enthalpy of the components mixing. The entropy of mixing is easily calculated but the enthalpy of mixing is usually determined by the experimental procedure. For tungsten alloys, these parameters are estimated only theoretically [34]. A partial enthalpy of mixing can be approximated as the following:

$$\Delta H_m = (h_{1,i} + h_{2,i} T + h_{3,i} x_i) \times (1 - x_i)^2,$$

where  $h_{1,i}$ ,  $h_{2,i}$ ,  $h_{3,i}$  – polynomial's coefficients,  $T$  – temperature,  $x_i$  – mole fraction of solution component.

The surface properties of tungsten are sharply different from the bulk properties due to strongest chemical interatomic bonds. Therefore, there is an expedience to include the crystallization stage in the thermodynamic consideration, because the crystallization stage controls the tungsten growth in a large interval of deposition conditions. To determine the enthalpy of mixing of surface atoms we use the results of the desorption of transition metals on (100) tungsten plane presented at the Fig. 4. [35]. The crystallization energy can be determined as the difference between the molar enthalpy of the transition metal sublimation

from (100) tungsten surface and sublimation energy of pure metal. These values are presented in the table 4 in terms of polynomial's coefficients, which were estimated in the case of the infinite dilute solution. The peculiarity of the detail calculation of polynomial's coefficients is discussed in [7]. The data predict that the co-crystallization of tungsten with Nb, V, Mo, Re will be performed more easily than the crystallization of pure tungsten. The crystallization of W-Ta alloys has the reverse tendency. Certainly the synergetic effects will influence on the composition of gas and solid phases.

$N_0$	M	$\Delta H_m^0 @ 298\text{ K}$ $x_i = 0$	$h_{1, i}$ kJ/mol	$h_{2, i}$ kJ/mol	$h_{3, i}$ kJ/mol	$x_i$
1	W	0	0	0	0	1,0000-0,9375
	Ta	36,4±10,9	36,4	-0,00042	72,7	0,0000-0,0625
2	W	0	0	0	0	1,0000-0,9375
	Nb	-225,7±50,2	-225,7	-0,00025	-451,4	0,0000-0,0625
3	W	0	0	0	0	1,0000-0,9375
	V	-434,7±50,2	-434,7	-0,00017	-1304,2	0,0000-0,0625
4	W	0	0	0	0	1,0000-0,9375
	Mo	-467,7±10,9	-467,7	-0,00117	-935,5	0,0000-0,0625
5	W	0	0	0	0	1,0000-0,9375
	Re	-220,3±10,9	-220,3	-0,00058	-440,5	0,0000-0,0625

Table 4. Excess partial "enthalpy of mixing" atoms for crystallization of W-M binary solid solution and  $h_i$  polynomial's coefficients for  $x_i = 0 - 0.0625$  and  $T = 298 - 2500\text{ K}$  [7, 31].

Therefore the thermodynamic calculation for gas and solid composition of W-M-F-H systems were carried out for following cases:

1. without the mutual interaction of solid components;
2. for the formation of ideal solid solution
3. for the interaction of binary solution components on the surface.

The temperature influence on the conversion of VB group metal fluorides and their addition to the tungsten hexafluoride – hydrogen mixture is presented at the Fig.5 a,b,c. If the metal interaction in the solid phase is not taken into account, the vanadium pentafluoride is reduced by hydrogen only to lower-valent fluorides. It should be noted that metallic vanadium can be deposited at temperatures above 1700 K. Equilibrium fraction of  $\text{NbF}_5$  conversion achieves 50% at 1400 K, and of  $\text{TaF}_5$  – at 1600 K (Fig. 5 a,b,c, curves 1).

The thermodynamic consideration of ideal solid solution shows that tungsten-vanadium alloys may deposit at the high temperature range ( $T \geq 1400\text{ K}$ ) and metallic vanadium is deposited in mixture with lower-valent fluorides of vanadium (Fig. 5 a, curves 2). The beginnings of formation of W-Nb and W-Ta ideal solid solutions are shifted to lower temperature by about 100 K (Fig. 5 b,c, curves 2) in comparison with the case (1).

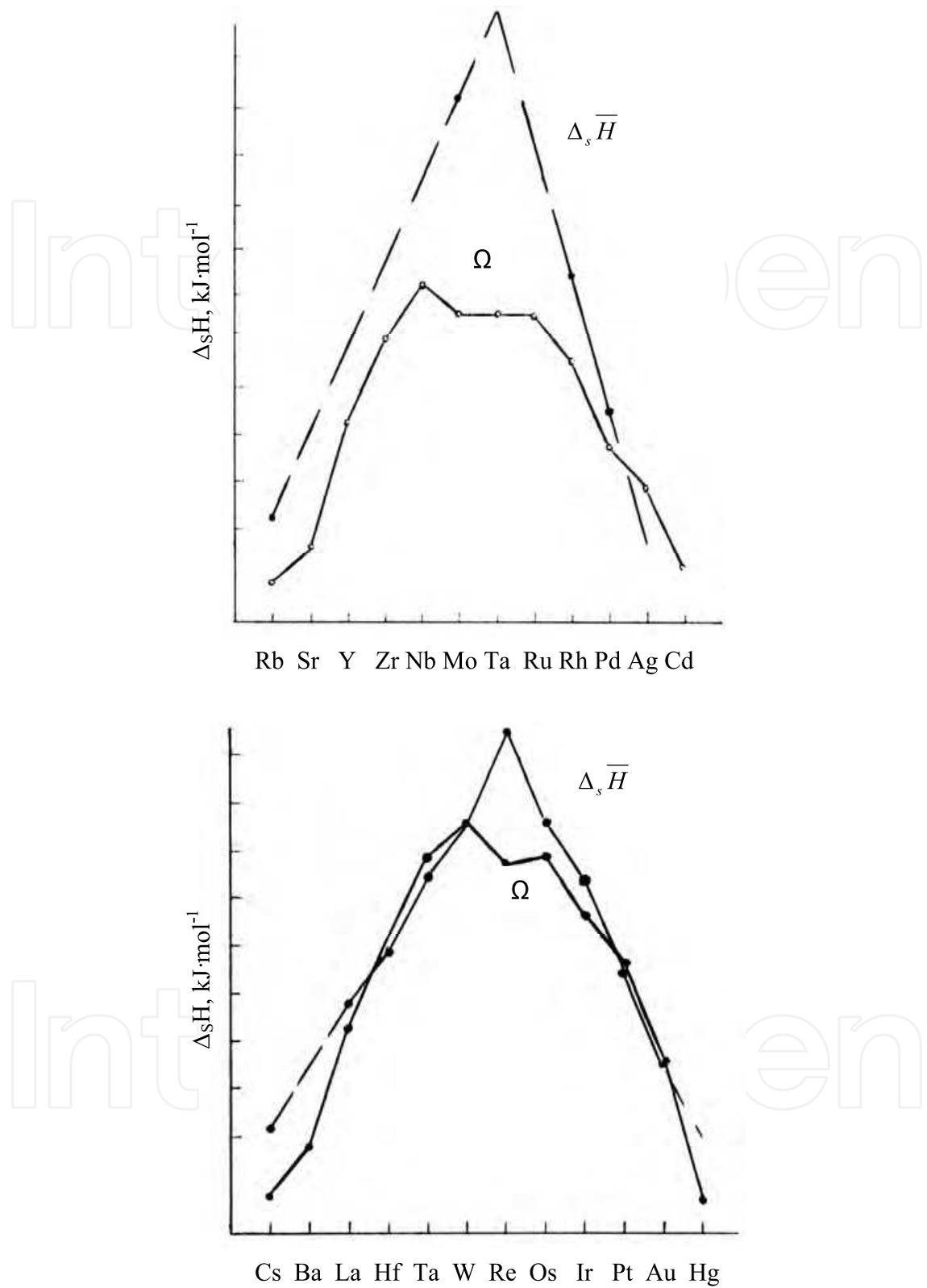


Fig. 4. Partial molar enthalpy of 4d и 5d atoms sublimation ( $\Delta_s \bar{H}$ ) from tungsten plane (100) and atomization energy ( $\Omega$ ) of transition metals in dependence on their place in periodic table [35]

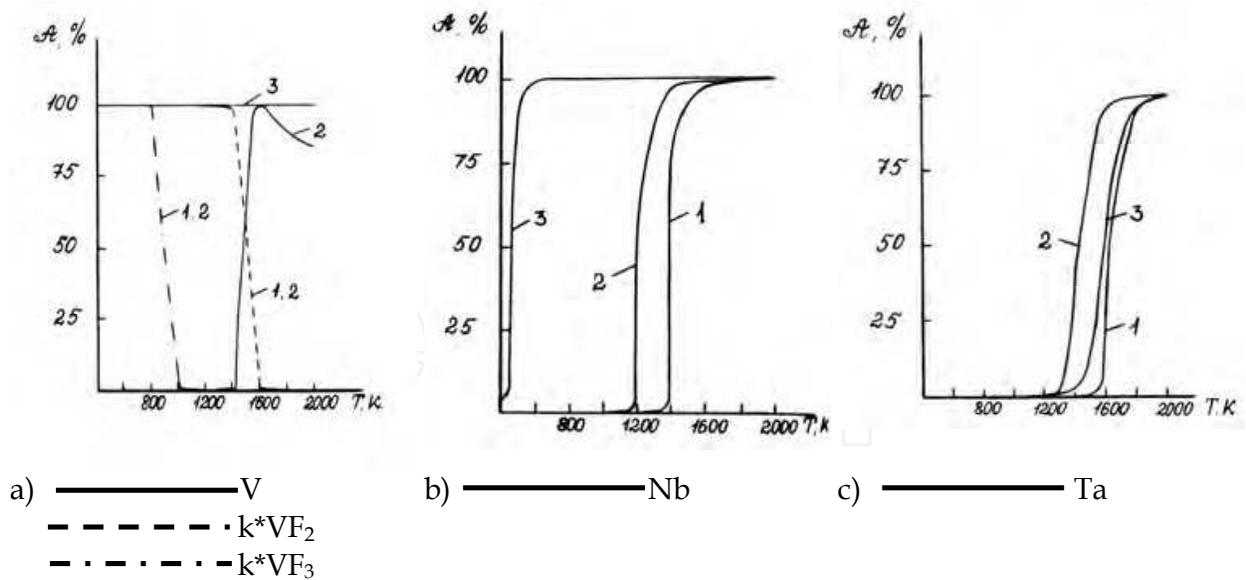


Fig. 5. Equilibrium yield of VB metals during crystallization with tungsten at initial ratio  $WF_6:MF_5:H_2=10$ , total pressure of 2 kPa calculated for following cases:  
 1. without the mutual interaction of solid components;  
 2. for the formation of ideal solid solution  
 3. for the interaction of binary solution components on the surface.

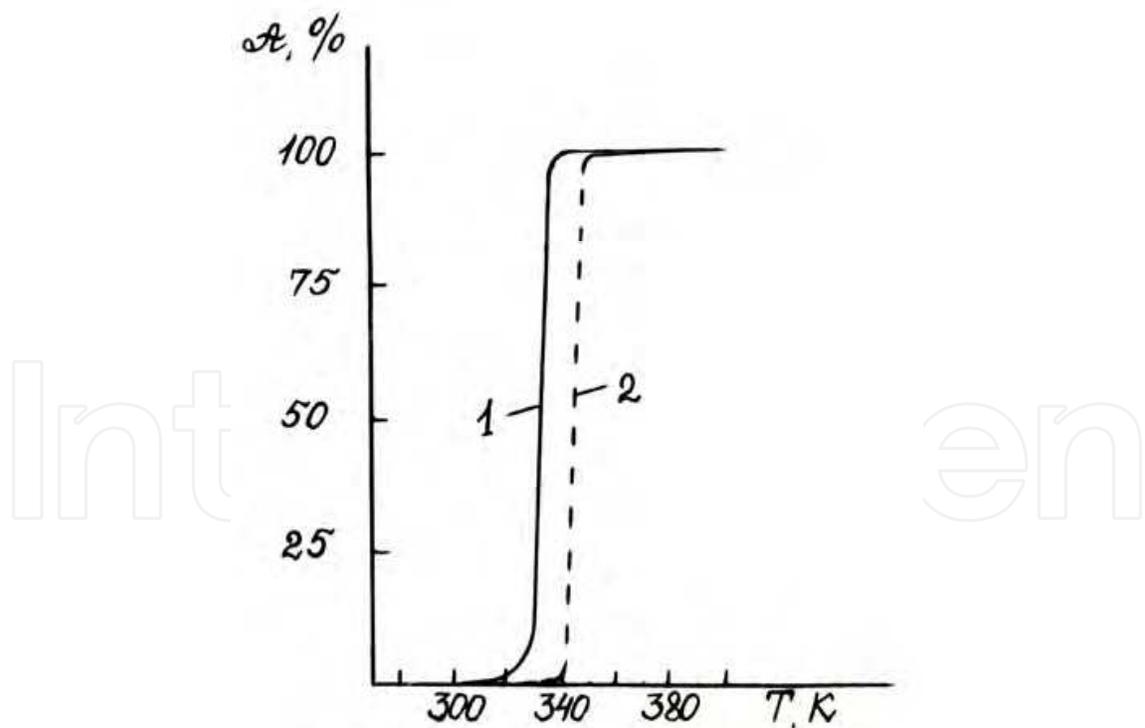


Fig. 6. Temperature influence on equilibrium yield of tungsten in W-Re-F-H (1) and W-F-H (2) systems at total pressure of 2 kPa and gaseous composition of  $(WF_6+6\% ReF_6) : H_2 = 10$

Taking into account the interaction of component of alloys during crystallization, the formation of W-V and W-Nb alloys possibly takes place at the temperatures above 300 K

(Fig. 5 a,b, curves 3). Temperature boundary shown at the Fig. 5 is shifted in reverse direction for the W-Ta system (Fig. 5 c, curves 3). It should be noted, that the calculation results performed for cases (2) and (3) (for ideal and nonideal solid solution) for the W-Ta system are almost identical due to the small enthalpy of mixing [35].

The influence of rhenium and molybdenum on the equilibrium yield of tungsten in the M-W-F-H systems is observed for W-Re and W-Mo alloys deposition. The  $\text{ReF}_6$  addition to the gas mixture with  $\text{WF}_6$  increase insignificantly the yield of tungsten in spite of strong atom interaction during the crystallization according to thermodynamic calculations (Fig. 6). This effect is still smaller for the case of W-Mo co-deposition. However equilibrium yield of metals for their co-deposition with tungsten and the energy of the interaction of metallic components during the crystallization have the common tendency. The knowledge of refined data of process energies will allow us to obtain a more realistic situation.

## 6. The application fields of the coatings

The thermodynamic background presented above is very useful for production of the coatings based on tungsten, tungsten alloys with Re, Mo, Nb, Ta, V and tungsten compounds (for example tungsten carbides). The tungsten coatings have found wide application in thin-film integral circuits when preparing the Ohmic contacts in the production of the silicon-, germanium-, and gallium-arsenide-based Schottky-barrier diodes. The tungsten selective deposition technology is perspective in the production of conducting elements at dielectric substrates [36]. Tungsten films are used for covering hot cathodes, improving their emission characteristics, and as protective coatings for anodes in extra-high-power microwave devices. The CVD-tungsten coatings are used as independent elements in electronics.

The X-ray bremsstrahlung in modern clinical tomographs and other X-ray units is obtained by using tungsten or W-Re coatings at rotating anodes made of molybdenum or carbon-carbon composite materials. In the nuclear power engineering, tungsten was shown to be a good material for enveloping nuclear fuel particles because of low diffusion permeability of the envelope for the fuel. The tungsten- and W-Re alloy-coatings [2, 3, 5] are extremely stable in molten salts and metals used as coolants in high-temperature and nuclear machinery, e.g., in heat pipes with lithium coolant and in thermonuclear facilities. Tungsten emitters with high emission uniformity, elevated high-temperature grain orientation and microstructure stability are of interest for their use in thermionic energy converters.

High-temperature technical equipment cannot go without tungsten crucibles, capillaries, and other works that can be easily prepared by the CVD techniques. Tungsten is used as a coating for components of jet engines, fuel cell electrodes, filters and porous components of ion engines, etc. [2] The CVD-alloying of tungsten coatings with rhenium allows to improve significantly their operating ability, especially under the temperature or load cycling. Tungsten compounds have a wide field of application. The tungsten-carbide composites deposited by using the fluoride technology occupy a niche among coatings with a thickness of 10 to 100  $\mu\text{m}$ ; they are unique in respect of strengthening practically any material, starting with carbon, tool, and stainless steels, titanium alloys, and finishing with hard alloys. CVD method permits to coat complicated shape components (which cannot be coated using PVD-method or plasma sputtering of carbide powders with binder). Below we list the most promising fields of applications [37].

In the first place we can mention the strengthening of the oil and gas and drilling equipment (pumps, friction and erosion assemblies). The problems of hydrogen- sulfide corrosion,

wear of movable units, and erosion of immobile parts of drilling bits operating underground take special significance because their replacement is very expensive. The carbide coatings can be deposited inside cylinders and on the outer surfaces of components of rotary or piston oil pumps. Numerous units in the oil and gas equipment, for example, block bearings, solution-supplying channels in drilling bits, backings directing the sludge flow, etc. require the strengthening of their working surfaces.

Another application in this field is the coating of metal-metal gaskets in the high- and ultrahigh-pressure stop and control valves. In addition to intense corrosion, abrasion and erosion wear, the working surfaces of ball cocks and dampers are subject of seizing under high pressure; W-C-coatings prevent the seizure. An important advantage of the carbide coatings is their accessibility for the quality of surface polishing, due to the initial smooth morphology. The examples mentioned above relate not only to oil and gas but also to chemical industry. The W-C-coatings are promising for working in contact with hydrogen-sulfide-rich oil, acids, molten metals, as well as chemically aggressive gases. Due to their high wear and corrosion resistance, these coatings can be use instead of hard chromium.

The abrasion mass extrusion and the metal shape draft require expensive extrusion tools; the product price depends on the working surface quality and life time. The extrusion tools must often have sophisticated shape inappropriate for coating with PVD or PACVD methods. Therefore, W-C-coating prepared by a thermal CVD-method is promising in strengthening these tools. Strengthening of spinneret for drawing wires or complicated section of steel, copper, matrices for aluminum extrusion, ceramic honeycomb structures for the porous substrate of catalytic carriers may give the same effect. Also, very perspective is the deposition of strengthening coatings onto components of equipment for the pressing of powdered abrasion materials. One may also mention the strengthening of knife blade used for cutting paper, cardboard, leather, polyethylene, wood, etc [38].

In addition to the surface strengthening, the W-C-coatings can function as high-temperature glue for mounting diamond particles in a matrix when preparing diamond tools or diamond cakes (conglomerates) in drilling bits [39]. The above-given examples demonstrate the variety of applications for tungsten, its alloys and carbides in mechanical engineering, chemical, gas and oil industry, metallurgy, and microelectronics.

## 7. Conclusion

1. A number of unknown thermochemical constants of refractory metal fluorides were calculated and collected in this chapter.
2. The systematic investigation of equilibrium states in the M-F, M-F-H (M = V, Nb, Ta, Mo, W, Re) systems was carried out. It was demonstrated that the equilibrium concentrations of highest fluorides in the M-F systems are determined by the place of metal in the periodic table. They rise with the increase of atomic number within each group and decrease with the increase of atomic number within each period. The low valent fluoride concentrations have the opposite tendency. It was shown that the equilibrium yield of Re, Mo, W deposition from the M-F-H systems achieve 100% at room temperature, equilibrium yield of Nb, Ta and V deposition - at temperatures above 1300 K, 1600 K and 1700 K, respectively.
3. The solid compositions of the W-M-F-H systems were calculated by taking into account the formation of ideal, nonideal solid solution, the mechanical mixture of solid

components and the atom interaction on the growing surface during the crystallization. It was established that only an introduction in the thermodynamic calculation of atom interaction on the growing surface, which increase in the following sequence: Ta, W, Re, Nb, V, Mo, results in a rise of yield of VB group metals under their co-deposition with tungsten, excepting W-Ta system. This may explain the experimentally observed tungsten yield rise under its alloying with rhenium and molibdenium.

4. The thermodynamic analysis, performed by taking into account the formation of solid lower-valent fluorides and excess enthalpy of atom interaction during crystallization, showed that the moving force of CVD of the alloys from the W-M-F-H systems (the supersaturation in these systems) increase in order: Ta, Nb, V, Mo, W, Re.
5. A lot of applications of tungsten coatings, deposited from tungsten hexafluoride and hydrogen mixture at low temperature, as well as tungsten alloys and carbides are reviewed in this chapter.

## 8. Acknowledgments

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## 9. Appendix 1

Description of symbols used in the text

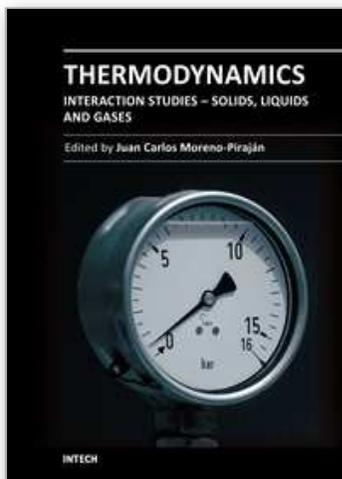
Symbol	Description
$\Omega$	Atomization energy
M	Metal
X	Halid
n	Valency of metal
$\Delta_f H$	Formation enthalpy
at	Atom
$\varphi$	Function
$Z_m$	Atomic number of metal
$Z_x$	Atomic number of halid
$\psi$	Functional
$\Delta_s H$	Sublimation enthalpy
S	Entropy
$\Delta_f H^{\circ}_{298} (g)$	Standart formation enthalpy at 298 K at gaseous state
$\Delta_f H^{\circ} (s)$	Standart formation enthalpy at 298 K at solid state
$\Delta_s H^{\circ}_{298}$	Standart sublimation enthalpy at 298 K
$S^{\circ}_{298} (g)$	Standart entropy at 298 K at gaseous state
$S^{\circ}_{298} (s)$	Standart entropy at 298 K at solid state
$C_p$	Specific heat at constant stress
$\Delta H_m$	Partial enthalpy of mixing
$\Delta_s \bar{H}$	Partial molar enthalpy
$\Delta H^0_m$	Standart mixing enthalpy

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