THERMODYNAMICAL PROPERTIES OF ALLOYS CARBONCONTAINING SYSTEMS

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Introduction

The thermodynamical properties of alloys binary and ternary system have important means for determination optimal conditions realization of some technological processes: alloying, welding, deoxidation, desulfuration, soldering, tinning of details. . For reception of materials with unique-properties it is necessary to know thermodynamic properties of alloys of binary and ternary carbon-containing systems.

Results and discussion

The partial and integral enthalpies of mixing of binary liquid alloys of Si (Ni)-C systems are determined by method of isoperibolic calorimetry at 2000 K in the interval of concentration 0<xc<0,1.Findings data given in table 1.

Table 1
Enthalpies of mixing of binary liquid alloys of Si (Ni)-C systems at 2000 K (in kJ/mol).

System Si-C					
x_c	0,02	0,04	0,06	0,08	0,1
$-\Delta_s H$	1,0	1,8	2,4	3,1	4,0
$-\Delta H$	2,8	5,6	7,9	10,5	13,2

System Ni-C						
x_c	0	0,02	0,04	0,06	0,08	0,1
$\Delta_s H$	0	0,9	1,9	3,1	4,5	6,5
$-\Delta H$	0	0,9	1,8	2,5	2,9	2,5
$\Delta\overline{H}_C$	-48	-45	-41	-31	-11,4	13,6

We also investigated thermochemical properties of the diluted solutions of system Al-C at 1773 K. In the investigated interval of composition of system Si-C partial enthalpies of dissolution and mixing of graphite are constant within the limits of a mistake of experiment (-38±2 and -132±6 kJ/mol accordingly).

For systems with strong interpartial interaction in a solid state (silicon-, boron-, sulfur, phosphorcontaing) have established, that from standard enthalpies the formation compounds can be predicted thermochemical properties of liquid alloys. In this work we try to expand this method for predict enthalpies of mixing carboncontaining alloys. Predicted and experimentally established enthalpies of mixing for these systems in extremum points (in kJ/mol):and mole part of carbon are given in table 2.

One can see that experimental enthalpies of mixing of melts of Si-C system and predicted ones are in good agreement with one another. It allows to assume, that for other metal-carbon systems it is possi ble to predict correct values of enthalpies of mixing.

Experimentally established enthalpies of mixing of binary carbon-containing melts with chromium, manganese are more negative, than predicted ones. The $\Delta_f H_{298}0$ values of Fe_3C are positive that don't agree with experimentally established values of mixing enthalpies. This fact can be explained by metastable state of this compound. Our calculations show that mixing enthalpies values can not be predicted with enough accuracy for systems in which only low temperature compounds are stable. On the contrary, for systems with congruently melting refractory compounds data on $\Delta_f H_{298}$solid compounds correlate with data on $\Delta_s H$ liquid alloys. Simulated enthalpies of mixing of ternary alloys systems from similar data for binary boundary systems on equation Bonnier-Kaboz have appeared close to experimental.

Enthalpies of mixing of melts of the d binary systems lantanoid (actinoid) of -carbon experimental not is. Therefore from enthalpies of formation of carbides of lantanoids (actinoids) it was calculatedenthalpies of mixing of melts, which are resulted in табл.3, 4.

Our method of prediction of thermodynamical properties of liquid alloys is very useful for systems with difficulties in experimental investigation and for multi-component systems. But because of aggressive, heigh melting and heigh boiling of components investigated not always succeed.

The thermodynamics properties of alloys and them the diagram state are very connect. The diagrams states of many binary and some ternary system well-known, therefore can used them for forecast of the Thermodynamic Properties of Alloys, if one or both components are aggressive or refractory. For region of diagram state which characterize with equilibrium liquid solution-solid component the best is equation:

$$\mu_1^l = \mu_1^{S_0};\ \mu_1^l + RT_P \ln a_1 = \mu_1^{S_0};$$

$$RT_P \ln a_1 = \mu_1^{S_0} - \mu_1^l;$$

$$\Delta\overline{G}_1^{надл.} = -\Delta\overline{G}_n - RT \ln x_1$$

Calculated activities components binary systems Si(Ge, Al)-metall from this equations agreement with experimental

From the diagrams states which have regions of equilibrium liquid solution - solid component (solid solution) we elaborated the methods witch allow of calculation the thermodynamics properties of alloys binary and ternary system with satisfactory precision, used coordinate of liquidus corresponding heat melt of components and in some cases thermodynamical parameters of solid and liquid phases.

For regions of diagram state with congruent melted compounds more efficient is improvement of Hauffe-Wagner method with the help to calculate activity of components in liquid alloys.

For the first time activities of components binary system C-metall and C-B - metall have been predicted in wide interval of composition. For this we used one or two fragments of diagram state

Conclusions

1.The partial enthalpies of mixing of carbon of binary liquid alloys of Si (Ni)-C systems are determined by method of isoperibolic calorimetry at 2000 K in the interval of concentration 0<xc<0,1.

2. Enthalpies of mixing of binary alloys simulated from standard enthalpies of formation compounds and of ternary alloys systems from similar data for binary boundary systems on equation Bonnier-Kaboz.

Table 2

Enthalpies of mixing of binary liquid alloys of M-C systems (in kJ/mol)

System	Be-C	B-C					
-ΔH	57.4 (0.66)	14.3 (0.2)					
System	Mg-C	Al-C	Si-C				
-ΔH	29.3 (0.66)	18.0 (0.42)	36.0 (0.5) 20.2 (0.2)*				
System	Ca-C	Sc-C	Ti-C	V-C	Cr-C	Mn-C	Fe-C
-ΔH	19.8 (0,66)	45.5 (0,33)	115.8 (0.5)	59.2 (0.5)	19.6 (0.4) 47.0 (0.35)*	4.1 (0.15) 23.5 (0.3)*	-7.0 (0.33) 10.0 (0.2)*
System	Sr-C	Y-C	Zr-C	Nb-C	Mo-C		
-ΔH	28.2 (0,66)	37.7 (0.66)	100.0 (0.5)	70.0 (0.5)	15.0 (0.33)		
System	Ba-C	La-C	Hf-C	Ta-C	W-C		
-ΔH	25.1 (0.66)	23.7 (0.66)	113.0 (0.5)	72.4 (0.5)	17.6 (0.5)		

Table 3

Enthalpies of mixing of binary liquid alloys of systems lanthanoid - carbon (in kJ/mol)

Me	Ce	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho
x_B	0,6	0,66	0,66	0,66	0,6	0,66	0,66	0,66	0,6
Δ H	19,4	20,9	20,3	17,4	23,7	20,9	41,8	16,4	46,9
Me	Ho	Er	Tm	Yb	Lu				
x_B	0,66	0,66	0,66	0,66	0,66				
-Δ H	36,3	25,8	27,9	25,1	25,1				

Table 4

Enthalpies of mixing of binary liquid alloys of systems actinoid - carbon (in kJ/mol)

Me	Th	U	U	U	Pu	Pu	Pu
x_B	0,5	0,5	0,6	0,66	0,5	0,6	0,66
-Δ H	61,9	48,5	41,0	30,5	25,1	40,8	11,2