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Abstract

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ON THE THERMODYNAMICS OF COMPLEX CARBIDES $(Fe_xMo_y)_2C$

(Presented by Academician G. V. Kurdyumov on III 4, 1964)

Thermodynamic investigations of transition-metal carbides up to the present time have been almost completely limited to simple carbides. However, thermodynamic data on complex carbides, containing atoms of two or more metals in their composition, are also important both for practice and for theory.

In the present communication we give the results of experiments studying equilibria between complex carbides $(Fe_xMo_y)_2C$ and hydrogen–methane gas mixtures. The reaction of hydrogen with the carbon of a carbide may be expressed as follows:

$$C\,(\text{in carbide}) + 2H_2(g) = CH_4(g). \tag{1}$$

The investigation was carried out by the circulation method described earlier ([1]). Since the amount of methane formed at equilibrium is negligibly small, it may be assumed that the composition of the initial carbide does not change during the experiments. Therefore the equilibrium state may be characterized by the ratio

$$r = \frac{P_{CH4}}{P_{H2}^2}, \tag{2}$$

where P_{CH4} and P_{H2} are the partial pressures of methane and hydrogen.

Determining experimentally the values of r and using the data known from the literature on the equilibrium of methane–hydrogen gas mixtures with pure graphite ([2]), for which the equilibrium constant r^0 has been determined with a high degree of accuracy, one can find the activity of carbon in carbides relative to graphite from the equation

$$a_C = r/r^0. \tag{3}$$

From this, in turn, the partial molar quantities for carbon in complex carbides can be calculated.

The carbides were synthesized from pressed powder mixtures by sintering in vacuum at 1400°C for 10 h. The impurity content in the starting materials was as follows: carbonyl iron (0.86 wt.% C), molybdenum (0.001% C; 0.243% O_2; 0.004% Fe; <0.001% Si); lamp black (ash content 0.57%, S 0.24%). During sintering of the charge in vacuum, oxygen was removed and slight carbon burnout occurred.

The results of X-ray structural analysis (Cr–Kα radiation, asymmetric exposure, d = 57.3 mm) and the compositions of three synthesized carbides are given in Table 1. All three specimens have the structure of Mo_2C.

Table 1

No.	Composition, wt.% C before experiments	Composition, wt.% C after experiments	Composition, wt.% Fe	Composition, wt.% Mo	Carbide formula	Lattice parameters a, Å	Lattice parameters c, Å	Lattice parameters c/a
1	5.65	5.60	0.97	93.1	$(Fe_{0.02}Mo_{0.98})_2C$	2.994	4.729	1.579
2	5.55	5.60	2.01	92.05	$(Fe_{0.036}Mo_{0.964})_2C$	2.994	4.729	1.579
3	5.70	5.65	3.01	91.00	$(Fe_{0.05}Mo_{0.95})_2C$	3.000	4.719	1.573

The experimental data on the study of the equilibrium of reaction (1) are given in Table 2. From these data, by the least-squares method, the following was found for the temperature dependence of the quantity r:

$$\text{for } (Fe_{0.02}Mo_{0.98})_2C \qquad \lg r = \frac{4190}{T} - 7.83, \tag{4}$$

$$\text{for } (Fe_{0.036}Mo_{0.964})_2C \qquad \lg r = \frac{4140}{T} - 7.81, \tag{5}$$

$$\text{for } (Fe_{0.05}Mo_{0.95})_2C \qquad \lg r = \frac{2720}{T} - 6.39. \tag{6}$$

On the basis of equation (3), from data (2) and equations (4), (5), (6), expressions were found for the relative partial free energies of carbon in the carbides ($\Delta\bar{G}_C = \bar{G}_C - G^0_{\text{graphite}} = RT\ln a_C$):

$$\text{for } (Fe_{0.02}Mo_{0.98})_2C \qquad \Delta\bar{G}_C = -2360 - 9.66T \quad (873\text{–}1123°K), \tag{7}$$

$$\text{for } (Fe_{0.036}Mo_{0.964})_2C \qquad \Delta\bar{G}_C = -2610 - 9.56T \quad (873\text{–}1173°K), \tag{8}$$

$$\text{for } (Fe_{0.05}Mo_{0.95})_2C \qquad \Delta\bar{G}_C = -9090 - 3.10T \quad (873\text{–}1173°K). \tag{9}$$

The root-mean-square error in determining $\Delta\bar{G}_C$ from these equations is about 2%; the error in determining the first term is ±1500 cal, and that of the coefficient at T is about ±2 cal/deg. Within the accuracy of the measurements, it may be considered that the first terms in equations (7)–(9) are the relative partial heat contents of carbon $\Delta\bar{H}_C$, and the coefficients at T are the relative partial entropies $\Delta\bar{S}_C$ in the range 873–1173°K.

Consideration of equations (7)–(9) shows that, as the iron content in the complex iron–molybdenum carbides increases, the thermodynamic characteristics of carbon change substantially. Namely: with increasing iron content in the carbide, the exothermicity of the reaction of transfer of carbon from graphite to the carbide increases. The entropy of carbon in the carbide decreases in this case.

Table 2

No. of experiment	T-ra, °C	Duration of experiment, h	Equilibrium gas pressure, mm Hg: p_{H2}	Equilibrium gas pressure, mm Hg: $p_{CH4} \cdot 10^2$	$r \cdot 10^4$, atm^{-1}	No. of experiment	T-ra, °C	Duration of experiment, h	Equilibrium gas pressure, mm Hg: p_{H2}	Equilibrium gas pressure, mm Hg: $p_{CH4} \cdot 10^2$	$r \cdot 10^4$, atm^{-1}
Sample No. 1 $(Fe_{0.02}Mo_{0.98})_2C$											
1	850	53	297	1.18	1.02	6	700	63	298	2.79	2.39
2	850	29	341	1.37	0.90	7	650	93	296	5.09	4.42
3	800	72	285	1.27	1.19	8	600	135	313	13.52	10.48
4*	800	7	271	0.915	0.95						
5*	750	7	354	2.98	1.81						
6	700	75	291	3.08	2.76						
7	650	96	290	4.37	3.95						
8	625	88	284	7.15	6.74						
9	600	94	248	10.62	13.12						

No. of experiment	T-ra, °C	Duration of experiment, h	Equilibrium gas pressure, mm Hg: p_{H2}	Equilibrium gas pressure, mm Hg: $p_{CH4} \cdot 10^2$	$r \cdot 10^4$, atm^{-1}	No. of experiment	T-ra, °C	Duration of experiment, h	Equilibrium gas pressure, mm Hg: p_{H2}	Equilibrium gas pressure, mm Hg: $p_{CH4} \cdot 10^2$	$r \cdot 10^4$, atm^{-1}
Sample No. 2 $(Fe_{0.036}Mo_{0.964})_2C$						Sample No. 3 $(Fe_{0.05}Mo_{0.95})_2C$					
1	900	16	332	0.85	0.58	1	900	23	292	1.00	0.90
2*	850	7	298	1.01	0.87	2*	900	24	273	0.87	0.89
3*	800	9	283	1.00	0.95	3*	850	15	364	2.11	1.21
4	800	54	322	1.47	1.08	4	800	44	300	1.79	1.51
5*	750	9	316	2.39	1.82	5	800	56	296	1.37	1.19
						6	750	70	247	0.90	1.47
						7*	750	20	244	1.40	1.79
						8	700	47	295	1.54	1.76
						9	700	71	165	1.01	2.81
						10	675	48	240	1.79	2.36
						11	650	90	302	6.93	5.77
						12	600	72	285	5.87	5.50

* The equilibrium of reaction (1) was reached from the side of carburization of the sample.

Let us note that an analogous effect of iron on the activity of carbon has also been found experimentally for carbides of the type $(Fe_xCr_y)_{23}C_6$. Such a result appears unexpected if one takes into account that the affinity of iron for carbon is substantially less than that of molybdenum (and still more so than that of chromium) for carbon.

Similar facts concerning the influence of a third component on the thermodynamic properties of a complex carbide, as far as we know, have not been described in the literature.

At present, a theoretical interpretation of the new facts noted above presents considerable difficulties.

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REFERENCES

1. V. I. Alekseev, L. A. Shvartsman, DAN, **133**, No. 6, 1331 (1960).
2. F. D. Richardson, J. Iron and Steel Inst., **175**, 45, 1953.

Note: Figure translations are in progress. See original paper for figures.