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Abstract

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FREE ENERGY OF FORMATION OF MANGANESE CARBIDE

$Mn_{23}C_6$

(Presented by Academician G. V. Kurdyumov, June 12, 1961)

Manganese is a constituent of almost all structural grades of steel and, in addition, is used as an alloying element. The influence of manganese on the properties of steel is to a considerable extent due to its interaction with carbon (1). However, the data on the thermodynamic properties of manganese carbides are at present insufficient. According to work (2), five carbides exist in the Mn–C system: $Mn_{23}C_6$ (stable up to 1025°C), Mn_7C_2 (stable between 850 and 1000°), Mn_3C (stable between 950 and 1050°), Mn_5C_2 (stable up to 1050°), and Mn_7C_3 (stable up to 1100°). In earlier works not all of these carbides had been detected, and the existence of only the carbide Mn_3C was assumed.

In connection with the uncertainty that existed regarding the composition and nature of the manganese carbides, there was also uncertainty in the results obtained in studying their thermodynamic properties. Thus, for example, Ulich and Simonsen (3), by determining the heat of combustion, found the heat of formation (ΔH) of Mn_3C to be −3.6 kcal. (±1.0 kcal.). At the same time, according to Rota' s measurements (4), this quantity is −17.0 kcal. It may be supposed that this discrepancy is due to uncertainty in the phase composition of the specimens with which these authors worked.

Let us note that the heats of formation (ΔH) of the carbides of the two elements neighboring manganese—chromium and iron ($Cr_{23}C_6$ and Fe_3C)—are respectively −13.6 kcal and +5.4 kcal per gram-atom of carbon. In this connection it appears that the result of Ulich and Simonsen is closer to the true value than Rota' s result.

Recently a paper was published (5) in which data are given on the free energy of formation of manganese carbide Mn_7C_3. By measuring the vapor pressure of manganese over a mixture of this carbide and graphite, in combination with the data for the vapor pressure of pure manganese in work (5), for the reaction

$$^7/_3\mathrm{Mn}(\beta) + \mathrm{C}_{(\mathrm{graphite})} =^1 /_3\mathrm{Mn}_7\mathrm{C}_{3(\mathrm{solid})}$$

the following expression was found for the change in free energy:

$$\Delta G^0_{1075—1235^\circ\mathrm{K}} = 5130 - 11.64T.$$

Thus, up to the present time, only two manganese carbides (Mn_3C and Mn_7C_3) of the five existing ones had been the objects of thermodynamic studies.

In the present communication we give the results of determining the free energy of formation of the manganese carbide with the lowest carbon content, $Mn_{23}C_6$. The equilibrium in the system $Mn_{23}C_6$—H_2—Mn—CH_4 was studied by means of the circulation method described earlier (^{6}). The carbide was prepared by sintering a mixture of powders of metallic manganese (99.77% Mn, 0.08% C, and 0.103% S) and lampblack carbon at a temperature of 1050°C for 24 hours, in an argon atmosphere.

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Fig. 1. X-ray diffraction pattern of a specimen consisting of two phases—carbide $Mn_{23}C_6$ and metallic manganese. Lines 1, 3, 8, 9, 10, 11, 12, 15, 17, 18, 20 correspond to the carbide phase; the remaining lines to metallic manganese (taken in chromium radiation), without filter

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Fig. 3. Microphotographs of crystalline methyl methacrylate spherulites during polymerization. a —spherulite before the onset of polymerization; b —boundary between the polymerized and unpolymerized parts of the crystalline spherulite; c —the same spherulite as in a, after completion of polymerization. Magnification 70×

Figure 1 shows the X-ray diffraction pattern of the sample with which the experiments were carried out (the diffraction pattern was taken in chromium radiation without a filter). The interference lines 1, 3, 8, 9, 10, 11, 12, 15, 17, 18, 20 belong to the carbide $Mn_{23}C_6$; the remaining lines (2, 5, 6, 7, 13, 14, 16, 19, 21, 22) belong to metallic manganese. Some of the interference lines of the diffraction pattern presented (for example, lines 1, 3, and 6) may, to an equal extent, be assigned both to the carbide phase and to metallic manganese. Identification of the lines in the diffraction pattern of Fig. 1 was carried out using the tabulated data of work (^{7}) (for the carbide $Mn_{23}C_6$). The interplanar spacings for metallic manganese were first calculated from the diffraction pattern of electrolytic Mn.

X-ray phase examination of the sample after the experiments also showed the presence in the sample of two phases, namely $Mn_{23}C_6$ and Mn. Thus, it may be considered that in the experiments the equilibrium constant

$$K_p = \frac{P_{\mathrm{CH4}}}{P^2_{\mathrm{H2}}}$$

Fig. 2. Dependence of $\lg K_p$—$1/T$ for the reaction
$^1/_6\mathrm{Mn}_{23}\mathrm{C}_{6(\mathrm{solid})} + 2\mathrm{H}_{2(\mathrm{gas})} = {}^{23}/_6\mathrm{Mn}_{(\mathrm{solid})} + \mathrm{CH}_{4(\mathrm{gas})}$

Figure 1: Fig. 2. Dependence of $\lg K_p$—$1/T$ for the reaction $^1/_6\mathrm{Mn}_{23}\mathrm{C}_{6(\mathrm{solid})} + 2\mathrm{H}_{2(\mathrm{gas})} = {}^{23}/_6\mathrm{Mn}_{(\mathrm{solid})} + \mathrm{CH}_{4(\mathrm{gas})}$

was determined for the reaction:

$$^1/_6\mathrm{Mn}_{23}\mathrm{C}_{6(\mathrm{solid})} + 2\mathrm{H}_{2(\mathrm{gas})} = {}^{23}/_6\mathrm{Mn}^{+}_{(\mathrm{solid})} + \mathrm{CH}_{4(\mathrm{gas})}. \tag{1}$$

The value of K_p was determined in the temperature range 650-900° C. The experimental results are presented in Fig. 2 in the coordinates $\lg K_p$—$1/T$. The study of equilibrium (1) is associated with difficulties due to the fact that metallic manganese volatilizes intensely and condenses on the cold parts of the apparatus. This may lead to some change in the composition of the gas phase as a result of adsorption of methane and hydrogen by the condensate. In addition, the high volatility of manganese hindered thorough degassing of the sample at the temperature required for this purpose. Apparently, for these reasons, a certain scatter of the experimental data is observed.

Fig. 2. Dependence of $\lg K_p$—$1/T$ for the reaction

$$^1/_6\mathrm{Mn}_{23}\mathrm{C}_{6(\mathrm{solid})} + 2\mathrm{H}_{2(\mathrm{gas})} = {}^{23}/_6\mathrm{Mn}_{(\mathrm{solid})} + \mathrm{CH}_{4(\mathrm{gas})}$$

Processing of the experimental data presented in Fig. 2 by the method of least squares leads to the equations

$$\lg K_{p\,923—1173^\circ\mathrm{K}} = \frac{4000(\pm 380)}{T} - 6.45(\mp 0.45); \tag{2}$$

$$\Delta G^\circ_{923—1173^\circ\mathrm{K}} = -18300(\pm 1700) + 29.51(\mp 2.0)T. \tag{3}$$

Combining equation (3) with the equation for the free energy of the reaction of methane formation from carbon and hydrogen ([8]) gives, for the reaction

$$^{23}/_6\mathrm{Mn}_{(\mathrm{solid})} + \mathrm{C}_{(\mathrm{graphite})} = {}^1/_6\mathrm{Mn}_{23}\mathrm{C}_{6(\mathrm{solid})} \tag{4}$$

$$\Delta G^\circ_{973—1173^\circ\mathrm{K}} = -3300(\pm 1700) - 3.35(\mp 2.0)T. \tag{5}$$

It follows from this that the heat of formation of $\mathrm{Mn}_{23}\mathrm{C}_6$ (−3300 cal.) is very close to that found by Ulich and Simonsen ([3]) for a carbide whose composition these authors considered to correspond to the formula $\mathrm{Mn}_3\mathrm{C}$. Since X-ray structural analysis was not used in work ([3]), it may be assumed that the results of that work refer to the very same carbide that was the object of the present investigation. In this case the agreement between the values of the heat of formation of $Mn_{23}C_6$ found by Ulich and Simonsen and by us may be regarded as quite satisfactory.

It is of interest to compare the thermodynamic data obtained for $Mn_{23}C_6$ with the corresponding data for Mn_7C_3 (^{5}).

Whereas carbide $Mn_{23}C_6$ is formed with the evolution of heat, the carbide with a higher carbon content, Mn_7C_3, is an endothermic compound. This fact can be interpreted on the basis of the following considerations. According to the views existing in the literature, in the formation of carbides of transition metals of the fourth period, the *d* shell of the metal atoms is partially filled by the valence electrons of the carbon atoms. Since the electrons experience mutual repulsion, as the vacant places in this shell are filled, the energy of the electrons being added increases. Therefore the heat of formation of carbides decreases as the degree of filling of the *d* shell by electrons increases. Such an increase in the degree of filling occurs both with increasing atomic number of the metal in the series Ti → Ni and with increasing ratio of the number of carbon atoms to the number of metal atoms in carbides. In support of the first of these considerations is the well-known fact that the affinity of metals for carbon decreases in the series Ti → Ni.

The second consideration is in agreement with the result of the comparison made above of the heats of formation of the two manganese carbides $Mn_{23}C_6$ and Mn_7C_3.

Let us note that in the series Ti → Ni, chromium is an exception with respect to its affinity for carbon. Thus, the heat of formation of chromium carbide $Cr_{23}C_6$, equal to -13600 cal per 1 g-atom of carbon (^{9}), exceeds the heat of formation of vanadium carbides (for example, the heat of formation of V_2C is -11500 cal. (^{6})). The presence of such an anomaly makes it possible to advance a supposition concerning the relative role of the *s*- and *d*-electrons of transition-metal atoms in carbide formation. The electronic structure of the free chromium atom differs from that of the atoms of its neighbors in the periodic system (manganese and vanadium) in that it contains only one electron at the 4*s* level instead of two in Mn and V. At the same time, the *d* shell of the chromium atom contains as many electrons as the *d* shell of the manganese atom and, accordingly, two electrons more than in the same shell of the vanadium atom. In this connection it may be assumed that, in the formation of chromium carbides, a covalent bond may be realized through pairing of one of the valence electrons of carbon with the 4*s* electron of chromium. Apparently for this reason the heat of formation of $Cr_{23}C_6$ exceeds both the heat of formation of vanadium carbides and, significantly, the heat of formation of the manganese carbide $Mn_{23}C_6$, which is isomorphous with $Cr_{23}C_6$.

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REFERENCES CITED

1. L. I. Kogan, R. I. Entin, DAN, **94**, No. 4 (1954).
2. K. Kuo, L. E. Persson, J. Iron and Steel Inst., part I, **78**, 39 (1954).
3. H. Ulich, H. Siemonsen, Arch. Eisenhüttenwesen, vol. 14, 27 (1940).
4. W. A. Roth, Zs. angew. Chem., vol. 42, 981 (1929).
5. C. McCabe, R. Hudson, J. Metals, No. 1a (1957).
6. V. I. Alekseev, L. A. Shvartsman, DAN, **133**, No. 6 (1960).
7. Ya. S. Umanskii, *X-ray Diffraction of Metals*, Moscow, 1960, p. 441.
8. F. D. Richardson, J. Iron and Steel Inst., 175 (1953).
9. V. I. Alekseev, L. A. Shvartsman, *Physics of Metals and Metallography*, **11**, issue 4, 545 (1961).

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