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Fig. 1

Figure 1: Fig. 1

Abstract

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EQUILIBRIUM IN THE SYSTEM V_2C–H_2–CH_4–V

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Data on the free energies of formation of carbides of transition metals are important for clarifying a number of questions in theoretical physical metallurgy. In particular, they can be used to predict the solubility of carbides of alloying elements in solid solutions based on iron and other metals.

Transition metals in the fourth row of the periodic system to the left of iron are distinguished by a very high affinity for carbon. As a result, the study of equilibria involving carbides of such elements is associated with great difficulties.

Fig. 1

The literature contains data mainly on the heats of formation of the carbides indicated. In a number of cases these data are highly contradictory. It should also be emphasized that carbides of transition metals, as a rule, are phases of variable composition (^{1}). Meanwhile, in many studies on the thermodynamics of these carbides there are no indications of the structure and composition of the equilibrium phases. For the reasons listed, reliable data on the thermodynamics of carbides of such elements as Ti, V, Cr, and Mn are limited.

The available data on vanadium carbide are based on measurements of the equilibrium pressure of CO over a mixture of vanadium, vanadium carbide, and vanadium monoxide.

···of vanadium at one temperature, 1613° K. It was assumed in this case that the carbide corresponds to the composition VC. Using the heat-capacity data and the indicated measurement, Richardson (^{2}) found the following approximate equation for the free energy of formation of VC from the elements:

$$\Delta G^0_{298\text{—}2000^\circ\mathrm{K}} = -12500 + 1.6T. \qquad (1)$$

The purpose of the present communication is to describe the results of experiments to determine the free energy of formation of vanadium carbide, close in composition to V_2C and in equilibrium with metallic vanadium. The structure of the carbide was monitored by X-ray structural analysis. The equilibrium studied was

$$V_2C_{(s)} + 2H_{2(g)} = CH_{4(g)} + V_{(s)}. \tag{2}$$

The equilibrium constant of this reaction,

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

was determined with the aid of an apparatus whose schematic is shown in Fig. 1: *A*—electrolyzer; *B* and *C*—vessels for storing gases; 3—furnace for preliminary treatment of the sample under hydrogen and in vacuum; 5—calibration vessel; 6—electromagnetic circulation pump; 7—valve device ensuring continuous motion of the gas in one direction; 8—McLeod manometer; 9—vacuum lamps; 10 and 11—mercury U-manometers; 12—diffusion oil pump; 13—transfer vessel; 14—forevacuum cylinder.

Into a quartz tube located in furnace 1 with adjustable temperature was placed the powder of the carbide under study, over which hydrogen circulated, and then, as reaction (2) proceeded, an H_2—CH_4 mixture. After equilibrium was reached, the hydrogen was burned in tube 2, containing copper oxide heated to 300°. The water vapor was frozen out with liquid nitrogen in trap 4. For kinetic reasons, methane does not burn over copper oxide at the indicated temperature ([3],[4]); its pressure was measured with a McLeod manometer. Since the equilibrium of reaction (1) is shifted very strongly to the left, the partial pressures of methane were very small—of the order of 10^{-3}—10^{-2} mm Hg. For this reason, in calculating K_p, the equilibrium pressure of hydrogen, of the order of 190—300 mm, was taken as equal to the total pressure in the circulation circuit, measured with a U-shaped mercury manometer (10) with microscopic reading of the level.

Figure 2 presents the X-ray diffraction pattern of the sample studied, showing the presence of two phases—metallic vanadium and a carbide of hexagonal structure with lattice periods: $a = 2.875$ kX and $c = 4.530$ kX. According to the data of work ([1]), this carbide corresponds to the composition V_2C. The experiments were carried out in the temperature range 700—1000°.

It was established that equilibrium of reaction (1), depending on the temperature, is reached in 75 to 20 h. The experimental results are presented in Fig. 2 in the coordinates

$$\lg K_p — \frac{1}{T}.$$

Fig. 3

Figure 2: Fig. 3

The equation of the straight line in Fig. 3, found by the least-squares method, has the form

$$\lg K_p = \frac{2201.9}{T} - 5.825 \tag{3}$$

and for the free energy

$$\Delta G^0_{973—1273^\circ\mathrm{K}} = -10050 + 26.65\,T. \tag{4}$$

To the article by V. I. Alekseev and L. A. Shvartsman, p. 1331

Fig. 2

To the article by V. F. Gachkovsky, p. 1358

Fig. 1. Fluorescence spectra: 1 —polystyrene, 2 —serum albumin, 3 —poly-para-carboxyphenylmethacrylamide, 4 —solution of polyphenylacetylene (mol. wt. 1500) in benzene, 5 —solution of polyphenylacetylene (mol. wt. 1100) in benzene, 6 —deoxyribonucleic acid (DNA)

For the methane formation reaction, according to (2)

$$\mathrm{C_{(s)}} + 2\mathrm{H_{2(g)}} = \mathrm{CH_{4(g)}}; \tag{5}$$

$$\Delta G^0_{500-2273^\circ\mathrm{K}} = -21550 + 26.16\,T. \tag{6}$$

Combining reactions (2) and (5) and the corresponding equations for ΔG^0 gives

$$2\mathrm{V_{(s)}} + \mathrm{C_{(g)}} = \mathrm{V_2C_{(s)}}. \tag{7}$$

$$\Delta G^0_{973-1273^\circ\mathrm{K}} = -11500 - 0.49\,T. \tag{8}$$

Thus, in the temperature range studied, the value of ΔH of formation of V_2C is -11500 ± 500 cal/g-mol. The entropy change $\Delta S_{973-1273^\circ\mathrm{K}} = 0.49$ cal/g-mol $\cdot$ deg, which is within the experimental error.

The value obtained for the heat of formation of vanadium carbide is somewhat smaller than that estimated in work (2) for VC (—12500 cal/g-mol, according to equation (1)).

Fig. 3

Meanwhile, the heat of formation of the carbide with the lower carbon content should have been greater. This discrepancy is apparently due to the inaccuracy in determining the value of ΔH for VC, which, as indicated above, is based on experimental results at a single temperature only. In addition, there is no certainty that this carbide actually had the composition VC. Taking into account the value of ΔH found by us for V_2C, it may be assumed that the value of the heat of formation of VC given in the literature ([5]), equal to −28000 cal/g-mol, is considerably too high.

In steels alloyed with vanadium, the excess carbide phase is a compound close in composition to VC. The equation obtained in the present work for the free energy of formation of V_2C can be used to calculate limiting carbon concentrations in solid solutions in those cases where this carbide is the excess phase, similarly to the way in which the solubility of carbon in α-Fe was calculated ([6]). In addition, equation (7) makes it possible to calculate other equilibria involving V_2C.

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