Physical Chemistry

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1962

SovietRxiv

Abstract

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ON THE THERMODYNAMICS OF SOLID SOLUTIONS IN THE SYSTEM Fe–Ni–C

(Presented by Academician G. V. Kurdyumov, 14 II 1962)

In the work of R. Smith (^{1}) it was found that at 1000°C in solid solutions of the Fe–Ni system there is a minimum in the solubility of carbon at approximately 75 at.% nickel. Correspondingly, at this same composition the maximum value of the activity coefficient of carbon is observed. The observed increase in the activity coefficient of carbon upon adding nickel to iron can be interpreted qualitatively both from the standpoint of quasi-chemical theory and from the standpoint of the theory of free electrons. In the first case it may be attributed to the fact that the energy of the nickel–carbon interaction is less than the corresponding value for the iron–carbon interaction. In the second case the effect can be explained by an increase in the number of electrons in the *d*-band of the solid solution as the nickel concentration increases. However, neither of the theories mentioned can explain the fact that the activity coefficient of carbon increases and its solubility decreases when iron is added to nickel.

In (^{1}) the determinations were carried out only at one temperature, and therefore it was impossible to evaluate separately the influence of nickel concentration on the enthalpy and entropy of the process of carbon dissolution in iron-nickel alloys. In this connection it seemed advisable to determine the temperature dependence of the activity or solubility of carbon at least for an alloy of one composition, in order to calculate the heat and entropy of dissolution of carbon.

For this purpose we selected an alloy containing 73.5% nickel, i.e., close in composition to that at which the minimum solubility of carbon is observed. In addition, for comparison, experiments were carried out with pure nickel.

By the method described earlier (^{2}), the temperature dependence of the equilibrium

$$C + CO_{2(g)} = 2CO_{(g)}, \tag{1}$$

was studied, where C is carbon dissolved in the metal (in nickel or in the iron–nickel alloy). For comparison with literature data obtained by metallographic methods, the results found were used to calculate the solubility of carbon in the metal in the following way.

Fig. 1

Figure 1: Fig. 1

The equilibrium constant of reaction (1) has the form:

$$K = \frac{P_{\mathrm{CO}}^2}{P_{\mathrm{CO2}}[\%\,\mathrm{C}]} = \frac{r}{[\%\,\mathrm{C}]}, \tag{2}$$

where P_{CO} and P_{CO2} are the partial pressures of CO and CO_2 (in atm.) and $[\%\,\mathrm{C}]$ is the wt.% of carbon in the solid solution at equilibrium.

Since in the experiments the concentration of carbon in the metal did not exceed 0.01 wt.%, the solutions may be regarded as ideally dilute and the activity coefficient of carbon may be taken as constant.

Owing to the instability of nickel carbide, when nickel-based solid solutions are saturated with carbon, from them as the excess phase there separates—

graphite is precipitated. In this case the composition of the gas phase must satisfy the equilibrium

$$\mathrm{C_{(gr)}} + \mathrm{CO_{2(g)}} = 2\mathrm{CO_{(g)}}, \tag{3}$$

whose constant is expressed by the equation

$$r^0 = \frac{P_{\mathrm{CO}}^2}{P_{\mathrm{CO2}}}. \tag{4}$$

Taking into account that, when graphite is precipitated from the metal, equilibria (1) and (3) must be satisfied simultaneously, we obtain an equation for determining the solubility of carbon by substituting r^0 for r in (2):

$$[\%\,\mathrm{C}] = \frac{r^0}{K}. \tag{5}$$

Fig. 1

The magnitude r^0 and its temperature dependence have been reliably determined by many investigators.

According to (3), the change in free energy in reaction (3) is expressed by the equation:

$$-RT\ln r^0 = \Delta G^0_{298-2273^\circ\mathrm{K}} = 405000 - 41,25T. \tag{6}$$

In the present work the magnitude K was determined at 850; 900; 950; 1000 and 1050° C (for pure nickel and the alloy 73.5% Ni and 26.5% Fe), and the solubility of carbon was calculated from equation (5).

The data obtained are shown by points in Fig. 1 in the coordinates lg[% C]–$1/T$. The upper straight line refers to pure nickel. It was drawn from data obtained over a wide temperature range by metallographic methods (4). It is evident from Fig. 1 that the agreement between the results of the present work and the literature data is quite satisfactory.

The upper straight line in Fig. 1 is described by the equation:

$$\ln[\%\,\mathrm{C}] = -\frac{2120}{T} + 1,08, \tag{7}$$

from which it follows that the change in the free energy of dissolution of graphite in pure nickel is expressed by the equation

$$-RT\ln[\%\,\mathrm{C}] = \Delta G^0 = 9700 - 4,95T. \tag{8}$$

Consequently, in the indicated temperature range the heat of dissolution of graphite in nickel is 9700 cal/g-at., and the quantity associated with the change in entropy is 4.95 cal/deg • g-at.

As can be seen from Fig. 1, the experimental points relating to the iron–nickel alloy of the indicated composition lie satisfactorily on the lower straight line, which differs appreciably in slope from the line for pure nickel and corresponds to the equation:

$$\lg[\%\,\mathrm{C}] = \frac{1830}{T} + 0,784. \tag{9}$$

Accordingly, the free energy of dissolution of carbon is

$$-RT\ln[\%\,\mathrm{C}] = \Delta G^0 = 8370 - 3,60T, \tag{10}$$

i.e., the heat of dissolution of carbon is 8370 cal/g-at.

Thus, the heat of dissolution of carbon in the iron–nickel alloy proves to be appreciably lower than in nickel. This could have been expected, proceeding

because carbon has a greater affinity for iron than for nickel. A decrease in the heat of solution of carbon in the alloy should have led to an increase in the solubility of carbon as compared with nickel. The actually observed decrease in solubility leads to the conclusion that this effect, as can be seen from a comparison of equations (8) and (10), is due to a decrease in the entropy of solution of carbon in the alloy.

Such a decrease in the entropic component of the free energy can be interpreted on the basis of ideas about the interaction between nickel and iron, which leads to a certain ordering of the alloy and to a decrease in the number of sites in the lattice for the incorporation of carbon atoms.

Thermodynamic confirmation of this assumption is provided by the results of work (^5), in which the activities of nickel and iron were determined in single-phase solid solutions of the binary iron—nickel system. It turned out that, for nickel, negative deviations from Raoult' s law are observed over the entire concentration range from 0 to 100%, while for iron such negative deviations occur up to nickel contents of about 30%.

At nickel concentrations close to 70%, the integral excess free energy of formation of the iron—nickel alloy is minimal. Thus, at compositions in which the interaction between nickel and iron is maximal, the solubility of carbon is minimal.

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Institute of Ferrous Metallurgy
named after I. P. Bardin

Received
12 II 1962

CITED LITERATURE

^1 R. P. Smith, Trans. Met. Soc. AIME, **218**, 62 (1960). ^2 E. F. Petrova, L. A. Shvartsman, *Problems of Metallurgy and Physics of Metals*, Collection 6, 1959. ^3 F. Richardson, J. Iron and Steel Inst., **175**, 257 (1953). ^4 M. Hansen, *Constitution of Binary Alloys*, N. Y., 1958. ^5 B. Fleischer, J. F. Elliott, *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds*, Nat. Phys. Lab. Symposium, No. 9, 1, paper 2F, London, 1959.

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