PHYSICAL CHEMISTRY

E. Z. VINTAIKIN

1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. Z. VINTAIKIN

THE VAPOR PRESSURE OF CHROMIUM OVER CHROMIUM-IRON ALLOYS IN THE SOLID STATE

(Presented by Academician G. V. Kurdyumov, 12 VII 1957)

A thermodynamic study of chromium-iron alloys is of interest not only from the standpoint of their practical importance, but also because it can provide new information for the development of the theory of solid solutions. The chromium-iron system in the solid state has unlimited solubility. At temperatures below 800°, in alloys of approximately equiatomic composition, a σ-phase is formed, which is a chemical compound. In stainless chromium steels, annealing at 475° leads to embrittlement, concerning the nature of which various and even contradictory opinions have been expressed ($^{1-4}$). In particular, in the work (^{3}), carried out with the aim of investigating the nature of the brittleness of chromium steels, it is asserted that at a temperature of 475° decomposition of the solid solution occurs, which leads to embrittlement. The authors consider that the decomposition process is an intermediate one, preceding the formation of the σ-phase. In the work (^{2}), a second phase was detected in an iron-chromium alloy with 27% Cr after prolonged (4-year) annealing at a temperature of 482°. The second phase is a chromium-iron solid solution having a body-centered lattice with a chromium content of 80%.

The decomposition of solid solutions that have a tendency to form a chemical compound is unusual, since usually, upon formation of a chemical compound, as also upon ordering, there is a negative deviation from ideality with a negative heat of mixing, whereas the necessary condition for decomposition upon lowering the temperature is a positive heat of mixing. Knowledge of the thermodynamic properties of the chromium-iron system may to some extent help to form a correct idea of the behavior of the solid solution in this case. In addition, a thermodynamic study of systems with such unusual behavior may provide new information for creating a more exact theory of real solid solutions.

There are works in the literature devoted to the study of the thermodynamic properties of the chromium-iron system. A study of the iron-chromium system (^{5}) showed that this system in the liquid state has small positive deviations from the laws of ideal solutions. In the work (^{6}), values of the activity of iron were obtained, and the heats of sublimation in iron-chromium alloys were also determined in the temperature range 1100-1300°. Consideration of the results of this work from the standpoint of general thermodynamic regularities leads to the conclusion that the data obtained in it are erroneous. Indeed, according to the results of work (^{6}), for an alloy with 10% Cr the activity of iron exceeds unity and reaches a value of 2 at 1100°. If this were so, then the partial vapor pressure of iron over the alloy would have to be greater than the vapor pressure over the pure metal at ···

at the same temperature. The presence of several maxima and minima on the curves of the dependence of thermodynamic activity on concentration also contradicts the general theory of solutions. Finally, the assertion that the heat of sublimation of iron at 50% Cr reaches 156 kcal/g-atom is implausible, since this would imply a greater chemical affinity between iron and chromium than actually exists.

The purpose of the present work was to measure the saturated vapor pressure of chromium over chromium—iron alloys in the temperature range 1100-1400°C in order to calculate the thermodynamic functions of these solutions. The work employed the Knudsen effusion method with radiometric determination of the amount of chromium condensed on the targets. A diagram of the apparatus is given in article (^{10}); a more detailed description of the method was given in work (^{7}). Electrolytic iron and chromium purified in hydrogen were used to prepare the alloys; the latter contained the radioactive isotope Cr^{51}. Melting was carried out in alundum crucibles in a helium atmosphere. In all measurements, close attention was paid to preventing depletion of the alloy surface in chromium, for which purpose the sample was taken in the form of fine filings. In addition, measures were taken to reduce the degassing time. As the experiments showed, the depletion of the surface was so insignificant that it could be neglected. The results of determining the vapor pressure of chromium over chromium—iron alloys can be expressed by the following empirical equations:

$$\lg P_{\text{bar}} = -\frac{18430}{T} + 11.653 \qquad \text{for 21.3 at. \% chromium}$$

$$\lg P_{\text{bar}} = -\frac{18500}{T} + 11.990 \qquad \text{for 41.4 at. \% chromium}$$

$$\lg P_{\text{bar}} = -\frac{18670}{T} + 12.122 \qquad \text{for 55.2 at. \% chromium}$$

$$\lg P_{\text{bar}} = -\frac{18730}{T} + 12.234 \qquad \text{for 75.5 at. \% chromium}$$

$$\lg P_{\text{bar}} = -\frac{18940}{T} + 12.388 \qquad \text{for pure chromium.}$$

Fig. 1. Curves of thermodynamic activity in the chromium—iron system

Fig. 1. Curves of thermodynamic activity in the chromium—iron system

Figure 1: Fig. 1. Curves of thermodynamic activity in the chromium—iron system

Fig. 2. Thermodynamic functions of the chromium—iron system

Figure 2: Fig. 2. Thermodynamic functions of the chromium—iron system

The vapor-pressure results for pure chromium agree well with the data of works ([8], [9]).

Using the vapor-pressure data, we calculated the thermodynamic activity of chromium and the heats of solution. Figure 1 presents the dependence of chromium activity on its mole fraction in chromium—iron alloys at a temperature of 1667°K. The same figure gives the activity curve for iron at 1667°K, calculated with the aid of the Gibbs—Duhem equation. The heats of sublimation, as well as the partial heats of solution of chromium, are given in Table 1. From the values of the heat of solution of chromium, the heats of solution of iron were calculated by means of the Gibbs—Duhem equations.

From the values of the activity and heat of solution, the integral molar thermodynamic functions—the change in heat content ΔH and the change in free energy ΔF—were calculated:

$$\Delta H = x_{\mathrm{Cr}}\overline{\Delta H}_{\mathrm{Cr}} + x_{\mathrm{Fe}}\overline{\Delta H}_{\mathrm{Fe}},$$

$$\Delta F = RT\left(x_{\mathrm{Cr}}\ln a_{\mathrm{Cr}} + x_{\mathrm{Fe}}\ln a_{\mathrm{Fe}}\right).$$

The entropy ΔS was calculated by the well-known formula: $\Delta F = \Delta H - T\Delta S$. These functions are shown in Fig. 2. As can be seen from this figure, solid Cr—Fe solutions exhibit a positive deviation from ideal solutions, the excess of the thermodynamic potential over the ideal one being due mainly to the positive heat of mixing, since the entropy of mixing, as is evident from the figure, is very close to the ideal value. It should be noted that the curve for the change in heat of mixing is asymmetric with respect to the equiatomic composition; the maximum is shifted toward chromium.

Table 1

Mole fraction of chromium, x_{Cr}	Heat of sublimation of chromium, kcal/g-atom	Heat of dissolution of chromium $\overline{\Delta H}_{\mathrm{Cr}}$, kcal/g-atom
0.214	84.4	+2.3
0.414	84.7	+2.0
0.552	85.5	+1.2
0.755	85.8	+0.9
1.000	86.7	0

Fig. 2. Thermodynamic functions of the chromium—iron system

In alloys, as is evident from Fig. 2, there is a positive heat of mixing; therefore the chromium—iron solid solution is prone to segregation. Extrapolation of the concentration dependence of the free energy to low temperatures makes it possible to estimate the critical temperature of decomposition, which proved to be 600°C. It should be noted that, from the data of our work, it follows that the maximum of the decomposition curve is shifted toward chromium.

Thus, in light of the results obtained in the present work, it should be considered that embrittlement in the temperature range around 475° is a consequence of the segregation process ($^{2-4}$).

On the basis of literature data and the results of the present work, it may be assumed that at a temperature of 475° the solid α-solution can either transform into the σ-phase or decompose into two solid solutions. Since the process of formation of the σ-phase proceeds extremely slowly, in practice only the second path occurs.

The author expresses deep gratitude to Academician G. V. Kurdiumov and Prof. L. A. Shvartsman for their attention to this work, as well as for a number of valuable comments.

Institute of Metallurgy and Physics of Metals
Central Scientific-Research Institute of Ferrous Metallurgy

Received
10 VIII 957

CITED LITERATURE

1. H. S. Link, P. W. Marshall, Trans. Am. Soc. Metals, **44**, 549 (1952).
2. R. M. Fisher, E. J. Dulis, K. G. Carroll, J. Metals, **5**, 690 (1953).
3. A. J. Lena, M. F. Hawkes, J. Metals, **6**, 607 (1954).
4. E. Baerlecken, H. Fabritius, Stahl und Eisen, **77**, 1774 (1955).
5. A. P. Lyubimov, A. A. Granovskaya, *Application of Radioactive Isotopes in Metallurgy*, **34**, 95 (1955).
6. L. I. Ivanov, M. P. Matveeva, DAN, **111**, 1271 (1956).
7. Yu. V. Kornev, V. N. Golubkin, *Physics of Metals and Metallography*, **1**, 286 (1955).
8. R. Speiser, H. L. Johnston, P. Blackburn, J. Am. Chem. Soc., **72**, 4142 (1950).

9. E. A. Gulbransen, K. F. Andrew, J. Electrochem. Soc., **99**, 402 (1952).

10. E. Z. Vintaikin, DAN, **117**, No. 4 (1957).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.