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Abstract

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METASTABLE PHASE DIAGRAM OF THE IRON–CHROMIUM SYSTEM

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In the present communication a quantitative estimate is given of the energy of interatomic interaction in alloys of the iron–chromium system, obtained using the results of work [1] and experiments specially carried out for this purpose to determine the position of the alpha-gamma phase-equilibrium curves in this system.

According to work [1], the equilibrium curves of the alpha and gamma phases are described by the equations

$$RT \ln \frac{C_{A\alpha}}{C_{A\gamma}} = \Delta G_A + \frac{z_\alpha \varepsilon_\alpha}{2} C_{B\alpha}^2 - \frac{z_\gamma \varepsilon_\gamma}{2} C_{B\gamma}^2;$$

$$RT \ln \frac{C_{B\alpha}}{C_{B\gamma}} = \Delta G_B + \frac{z_\alpha \varepsilon_\alpha}{2} C_{A\alpha}^2 - \frac{z_\gamma \varepsilon_\gamma}{2} C_{A\gamma}^2; \quad (1)$$

provided that the atoms are distributed randomly over the lattice sites of the coexisting phases. Here $C_{A\alpha}$, $C_{B\alpha}$, $C_{A\gamma}$, $C_{B\gamma}$ are the concentrations of atoms A (iron) and B (chromium) in the α and γ phases, respectively; z_α and z_γ are the coordination numbers of the α- and γ-phase lattices; $\varepsilon_\alpha = \varepsilon_{AA}^\alpha + \varepsilon_{BB}^\alpha - 2\varepsilon_{AB}^\alpha$ and $\varepsilon_\gamma = \varepsilon_{AA}^\gamma + \varepsilon_{BB}^\gamma - 2\varepsilon_{AB}^\gamma$ are parameters characterizing the interatomic interaction in the alpha and gamma phases; the quantity $\Delta G_A = G_A^\gamma - G_A^\alpha$ is the difference in the free energies of the γ- and α-phases of pure iron; ΔG_B is a parameter of the theory depending only on temperature.

In the work mentioned it was shown that equations (1) make it possible to explain the presence of a minimum on the equilibrium curves of the α- and γ-phases of certain systems; in particular, for the Fe–Cr system, equations (1) were compared with the averaged experimental results of various authors. In doing so, it proved possible to determine the difference

$$\frac{z_\gamma \varepsilon_\gamma}{2} - \frac{z_\alpha \varepsilon_\alpha}{2},$$

as well as the parameter ΔG_B, which proved to be a linearly increasing function of temperature throughout the entire range of existence of the γ-loop. Separately, the quantities

$$\frac{z_\gamma \varepsilon_\gamma}{2}$$

and

$$\frac{z_\alpha \varepsilon_\alpha}{2}$$

were not found, because their reliable determination requires more precise data on the position of the γ-loop than those available in the literature.

The literature gives data for alloys of technical purity and, moreover, without allowance for the possible influence on the position of the equilibrium curves of the high-temperature treatment of the alloys preceding the experiment. We have established that preliminary "homogenizing" annealing of alloys can noticeably shift the equilibrium curves, which

is apparently associated with the establishment of short-range order in the phase subjected to prolonged heating.

To estimate, by equations (1), ε_γ and ε_α, we repeated the experiments on determining the position of the equilibrium curves of the alpha and gamma phases in the Fe–Cr system*. The starting materials were electrolytic chromium refined in a stream of hydrogen, containing 0.003% O_2, 0.0266 N_2, 0.03% Si, and electrolytic iron (in the form of flakes), initially containing 0.02% C, 0.0009% Mn, 0.017% Si, 0.003% P, degassed in a high vacuum at 1400–1500° for 13 hours, followed by melting and holding in the molten state for about 2 hours. After this melting procedure, only traces of carbon ($< 0.003\%$) were found in the iron. The temperature of the $\alpha \rightarrow \gamma$ transformation of the alloys was determined from the sharp break in the curves of electrical resistivity versus temperature. Fig. 1 shows the curves, obtained in this way, for the beginning and end of the $\alpha \rightarrow \gamma$ transformation of the investigated alloys. It should be noted that the end of the transformation was recorded with some lag, as is seen from the fact that the curves for the beginning and the end of the transformation do not touch at the minimum point. Therefore, in determining the quantities of interest to us we used only data relating to the beginning of the transformation. We also note that our data refer to alloys that were not subjected to prolonged high-temperature heating, i.e., in the experiment conditions were maintained that ensure [2] a random arrangement of atoms at the lattice sites.

Fig. 1. Curves of the beginning and end of transformation (on heating) in the Fe–Cr system.

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In comparing equations (1) with the experimental data we used, for ΔG_A, values taken from work [3].

Using the condition that ΔG_A and ΔG_B are independent of composition, with the aid of relations (1), we find (graphically) that it is satisfied only when

$$\frac{z_\gamma \varepsilon_\gamma}{2} - \frac{z_\alpha \varepsilon_\alpha}{2} = 2570 \text{ cal/g-at.}$$

Further, at the minimum point ($C_{B\alpha} = C_{B\gamma}$) the following relations must be satisfied:

$$\Delta G_A(T_{\min}) = \left(\frac{z_\gamma \varepsilon_\gamma}{2} - \frac{z_\alpha \varepsilon_\alpha}{2}\right) C_{\min}^2;$$

$$\Delta G_B(T_{\min}) = \left(\frac{z_\gamma \varepsilon_\gamma}{2} - \frac{z_\alpha \varepsilon_\alpha}{2}\right) (1 - C_{\min})^2. \quad (2)$$

According to our data $T_{\min} = 830^\circ$C; according to the data of work [3], $\Delta G_A(830^\circ\text{C}) = 19$ cal/g-at.; thus, using (2), we find $C_{\min} = 8.6$ at. % (or about 8 wt. %), $\Delta G_B(830^\circ\text{C}) = 2147$ cal/g-at. It would have been simpler to proceed in the reverse way: take from the experimental curve of the beginning of transformation the value $C_{\min}$, and from relations (2) determine the difference

$$\frac{z_\gamma \varepsilon_\gamma}{2} - \frac{z_\alpha \varepsilon_\alpha}{2}.$$

But in this case a large error could be obtained in determining

$$\frac{z_\gamma \varepsilon_\gamma}{2} - \frac{z_\alpha \varepsilon_\alpha}{2},$$

since the position of the minimum on the curve (Fig. 1) cannot be determined sufficiently accurately. Further, equations (1) are used to determine

* The experiments were carried out jointly with G. V. Kharkova.

$\frac{z_\gamma \varepsilon_\gamma}{2}$ and $\frac{z_\alpha \varepsilon_\alpha}{2}$ separately. For this it is sufficient to make use of the data for some one more temperature, for example 840°C. According to Smith' s data

Fig. 2. Metastable diagram of the Fe–Cr system (theoretical).

Figure 2: Fig. 2. Metastable diagram of the Fe–Cr system (theoretical).

([3]), $\Delta G_A(840^\circ\text{C}) = 16$ cal/g-at.; according to our data, the straight line $T = 840^\circ$C intersects the curve for the beginning of the transformation at two points, $C'_{B\alpha} = 10.67$ at. % and gives $C''_{B\alpha} = 5.88$ at. %. The graphical solution of equations (1) under these conditions gives

$$\frac{z_\alpha \varepsilon_\alpha}{2} = -3530 \text{ cal/g-at.}$$

$$\frac{z_\gamma \varepsilon_\gamma}{2} = -960 \text{ cal/g-at.}, \tag{3}$$

while the quantity $\Delta G_B(840^\circ\text{C})$ proves to be equal to 2165 cal/g-at., i.e., it increases with increasing temperature, as was also established in work ([1]).

The negative sign of ε_α and ε_γ indicates that both phases belong to the class of decomposing solid solutions of the Becker type. In reality, however, decomposition should be observed only for the α-phase, since the γ-phase exists in a very limited range of concentrations. The theoretical curve of decomposition of solid solutions of the γ-phase, constructed from the equation borrowed from ([4]), with use of (3), is shown in Fig. 2.

Fig. 2. Metastable diagram of the Fe–Cr system (theoretical).

The results obtained make it possible to understand the nature of the so-called 475°C brittleness—a phenomenon long known, but investigated most thoroughly only in the recent work ([5]), in which direct experiments proved that the 475°C brittleness is associated with decomposition of the initial solid solution (Fig. 2).

The diagram shown in Fig. 2 depicts metastable, although very stable, states. Indeed, as indicated above, the experimental conditions were such that they excluded the possibility of the occurrence of short-range ordering in the alloys—the necessary stage on the path to formation of the metallic compound (σ-phase) during equilibrium decomposition.

The negativity of the quantity $\varepsilon = \varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB}$ (the positivity of the mixing energy, $-\frac{1}{2} C_A C_B z \varepsilon$) indicates that the mean value of the interaction energy of like atoms is greater in absolute value than the interaction energy of a pair of unlike atoms. In the equilibrium case, in solid solutions of this kind short-range order should arise, in which unlike atoms avoid one another and each atom tends to surround itself with like atoms. Meanwhile, in the equilibrium case chromium ferrite decomposes with the precipitation of a metallic compound; therefore one would expect that in the initial solid solution there should exist

short-range order in which each atom tends to surround itself with atoms of the other kind.

The contradiction noted indicates that, in the Fe–Cr system, the interatomic interaction cannot be fully described by the quantity ε determined by us. During short-range ordering of the alloy, some additional forces must manifest themselves in the form of an added energy of negative sign, which more than compensates the positive mixing energy of the alloy in the chaotic state, $-\frac{1}{2}C_A C_B z\varepsilon_\alpha$, and it becomes thermodynamically advantageous for atoms to surround themselves with atoms of the other kind.

According to work [2], a possibility of this kind is found in systems in which, in addition to the ordinarily understood metallic bond, there exists an additional interatomic bond of ionic character, arising as a result of the redistribution of electronic charge between unlike atoms in the alloy.

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