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DISTRIBUTION OF SMALL AMOUNTS OF CARBON IN ALLOYED IRON

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The problem of the distribution of alloying elements, and in particular carbon, in microscopic regions of the α- and γ-solid solution in iron alloys—a problem that is receiving ever increasing attention in metallurgical studies—has not yet obtained a convincing experimental solution.

In the present work, the character of the redistribution of carbon in alloyed iron was investigated by the method of autoradiography, with the aid of the radioactive isotope of carbon C^{14}. The effectiveness of this method for studying the distribution of certain elements in ferrous and nonferrous alloys has been established in a number of works ($^{1-7}$).

Low-carbon iron alloys, alloyed separately with chromium, nickel, silicon, and molybdenum, were investigated. The composition of the alloys is given in Table 1.

Table 1

System investigated	C	Cr	Ni	Mn	Si	Mo
Iron—chromium	0.05	4.6	–	0.10	0.10	–
Iron—nickel	0.04	0.08	4.8	trace	0.11	–
Iron—silicon	0.03	0.09	–	trace	4.4	–
Iron—molybdenum	0.03	0.08	–	0.08	0.10	12.5

Radioactive carbon was introduced into the alloys under investigation by "cementation" in a medium of radioactive barium carbonate. Since the source of radiocarbon was only barium carbonate without the addition of carbon, no increase in the total carbon content in the "cemented" specimens above the 0.03-0.05% already present in them occurred. The penetration of radioactive carbon (which we shall denote conventionally by C^*) from BaCO into the steel took place by isotopic exchange, evidently according to the following scheme:

$$2BaC^*O_3 \rightarrow 2BaO + 2C^*O_2$$

$$2C^*O_2 + 2C_{\text{from steel}} \rightarrow 2C^*O + 2CO$$

$$2C^*O + 2CO \rightarrow C^*O_2 + CO_2 + \underbrace{C^* + C}_{\text{into steel}}$$

After the radioactive specimens had undergone the specified heat treatment, they were radiographed. For exposure, NIKFI nuclear film of the MR type was used.

From consideration of the autoradiograms corresponding to annealed alloys (Figs. 1*a*-4*a*), it follows that the annealed state is characterized by a sharply expressed nonuniformity in the distribution of carbon within the bounds

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 1. Autoradiograms of an iron alloy with 4.6% chromium; 65×; *a* –annealing at 970°, 50 h; *b* –quenching in water from 1200°; *c* –tempering at 590°, 10 h.

Fig. 2. Autoradiograms of an iron alloy with 4.8% nickel; 65×; *a* –annealing at 970°, 50 h; *b* –quenching in water from 1200°; *c* –tempering at 590°, 10 h.

Fig. 3. Autoradiograms of an iron alloy with 4.4% silicon; 65×; *a* –annealing at 970°, 50 h; *b* –quenching in water from 1200°; *c* –tempering at 590°, 10 h.

Fig. 4. Autoradiograms of an iron alloy with 12.5% molybdenum; 65×; *a* –annealing at 970°, 50 h; *b* –quenching in water from 1200°; *c* –tempering at 590°, 10 h.

grains; this is especially noticeable in iron-silicon and iron-molybdenum alloys, in which the carbon is concentrated mainly along the grain boundaries.

Autoradiograms corresponding to alloys quenched in water from a temperature of 1200° (Figs. 1 –4) have, within the limits of the adopted magnification, a completely uniform darkening; an analogous picture was also obtained as a result of quenching from a temperature of 950°. This indicates that at temperatures of 900 and 1200° in the alloys under consideration there is no enrichment of the grain boundaries of austenite (in Fe–Cr and Fe–Ni alloys) or ferrite (in Fe–Si and Fe–Mo alloys) with carbon.

If in the quenched and annealed states all the alloys show, in the character of the carbon distribution, a certain general tendency (homogeneity with respect to carbon after quenching and its redistribution as a result of annealing), then tempering of the quenched alloys (590°, 10 h) makes it possible to distinguish two groups of alloys that differ sharply in the degree of inhomogeneity of the carbon distribution: the iron-chromium alloy (Fig. 1), which shows no tendency toward redistribution of carbon, and the iron alloys with nickel, silicon, and molybdenum (Figs. 2 –4), in which, during tempering, a sharp redistribution of carbon occurred in the direction of enrichment of the grain boundaries.

This clearly confirms the proposition that carbide-forming elements are capable of retaining carbon in ferrite up to elevated tempering temperatures, and that processes of carbon segregation are intensified by non-carbide-forming elements* (8).

It is also clearly illustrated that silicon is a more vigorous intensifier of the processes of redistribution and segregation of carbon than nickel (8): comparison of autoradiograms of the tempered iron-nickel (Fig. 2) and iron-silicon (Fig. 3) alloys makes it possible to establish that in the latter case the carbon, as a result of tempering, proves to be more intensively "pushed back" toward the grain boundaries than in the former.

The uniform character of the darkening of the autoradiogram of the tempered iron-chromium alloy (Fig. 1) indicates that at temperatures above AC_3 the distribution of chromium within the grain is uniform. Indeed, if an inhomogeneous distribution of chromium had occurred in austenite, then, as a result of tempering after quenching, carbon would have moved to places enriched with this element, owing to the inequality of the diffusion rates of carbon and chromium in ferrite (6).

The fact that in the iron-chromium alloy no redistribution of carbon occurred as a result of tempering (Fig. 1) testifies to the uniform distribution of chromium in austenite at 1200° (relative to the grain boundaries).

By analogy with the Fe–Cr alloy, one might have expected that in the Fe–Mo alloy as well the character of the carbon distribution as a result of tempering would undergo no changes in comparison with the state fixed by quenching; in reality, however, in the tempered iron-molybdenum alloy there is the most sharply expressed concentration of carbon along the grain boundaries (Fig. 4).

The explanation of this fact should be sought in the phase composition of the alloy under consideration. If, in a binary system, the concentration of one of the elements exceeds its limiting solubility in the solid solution, then its excess amount separates out in the form of a separate phase, predominantly along the grain boundaries of the solid solution. If an impurity of a third element is present in the system, the latter will either diffuse to the grain boundaries, if the forces of its bonding with the atoms of the segregated element are greater than the forces of its bonding with the atoms of the solvent element, or, conversely, diffuse into the interior of the grain, if the forces of bonding with the atoms of the solvent exceed the forces of bonding with the atoms of the segregated element (8).

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* The question of the probable causes of carbon segregation during tempering of the iron-molybdenum alloy will be considered below.

In the iron—molybdenum alloy under consideration, containing 12.5% Mo, the presence in the structure, along with the α phase, of some amount of the ε phase is inevitable, since the maximum concentration of molybdenum in the α phase already at 600° is 8%. Since the lowest concentration of molybdenum in the ε phase is 50%, it is natural that the concentration of this phase along the boundaries of the ferrite grain should cause carbon to diffuse toward them during tempering, owing to the known affinity between molybdenum and carbon.

Thus, the process—identical in its radiographic effect—of carbon concentration along the boundaries of the ferrite grain in Fe—Si alloys (Fig. 3) and Fe—Mo alloys (Fig. 4) has a different nature: in the Fe—Si alloy, carbon is displaced to the grain boundaries by silicon uniformly distributed in the iron; in the Fe—Mo alloy, containing 12.5% molybdenum, carbon diffuses to the grain boundaries as a result of the separation at these boundaries of an excess phase enriched in molybdenum.

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