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Non-stable structure of high-chromium and high-nitrogen iron-based alloy

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The structure of an iron alloy containing 18% Cr and 0.72% N after different treatments was studied by X-ray and electron microscopy. It was shown that the γ-structure of the alloy after quenching is non-stable at all temperatures of isothermal holding, especially at high tempering temperatures. The C-shaped hypothetical diagram of the alloy was constructed from the experimental results.

1. Introduction

At the present time, there is a wide-spread tendency towards full or partial replacement of carbon by nitrogen in steel. It is justified by the fact that nitrogen provides a better combination of mechanical characteristics as well as higher fatigue strength, improved corrosion resistance and weldability of steels. The replacement of carbon by nitrogen for steels containing a large amount of chromium allows the formation of $M_{23}C_6$ carbide to be avoided. The employment of nitrogen as an element forming interstitial phases is undoubtedly one of the prospective trends in the development of steels with improved properties.

Another prospective trend is to use nitrogen as a stabilizer of γ-phase iron at room temperature. The introduction of a large quantity of nitrogen atoms into iron could decrease or completely exclude the employment of γ-phase stabilizers such as nickel or manganese. In this case, however, ageing of nitrogen-containing iron-based alloys resulting in nitrides precipitation should be considered as an undesirable phenomenon promoting the γ–α transition. In order to shift the onset of nitrides precipitation to higher ageing temperatures it is possible to make use of the well-known properties of carbide- and nitride-forming elements in steels, such as the delay of the onset of solid-solution decomposition, caused by them, i.e. to use high-alloy steels, particularly high-chromium ones. The latter are known to have high corrosion-resisting properties. It is rather difficult, however, to produce an austenite structure in high-chromium steels using nitrogen introduction, because chromium is an element which contracts the γ-region of iron in the phase diagram.

In the present paper, results of the investigation of high-chromium steels are presented, where carbon is almost completely replaced by nitrogen.

2. Experimental procedure

The iron-based alloy containing 0.05% C, 18.0% Cr, 0.72% N (impurities being in amounts within the standard for high chromium steels) was produced by melting armco iron and extralow-carbon ferrochrome in the laboratory furnace under a nitrogen pressure of 1.8 MPa; the ingot was forged and homogenized. The forging was cut into the specimens for research. The specimens were exposed to different heat treatments: the varieties of the heat treatments are indicated in the text and in the tables. The properties of the alloy after different modes of heat treatment have been determined by measurement of the Rockwell hardness. The structure was investigated using transmission diffraction electron microscopy. The quantity of γ- and α-phases in the structure was measured by X-ray phase analysis.

3. Results and discussion

The replacement of carbon by nitrogen in the high-chromium steel is not simply the replacement of one interstitial element by another, and thus the replacement of carbides by nitrides within the same structures, but, in fact, it is the rearrangement of the whole phase diagram of the alloy. This may be seen in Table I, where the results on hardness measurements and X-ray determination of the γ/α phase relationship after different modes of heat treatment are summarized. From the table it can be seen that after quenching from 900 °C at any cooling rate, the hardness has high values (50 H_{Rc} and even higher) and the structure represents 100% ferrite (the lattice parameter is about 0.2886 nm) having high fragmentation and a high density of dislocations (Fig. 1). After quenching at any rate (into water, oil or air) from temperatures between

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TABLE I Rockwell hardness and relationship of α- and γ-phases after quenching

Quenching parameters	Rockwell hardness	γ-phase in structure (%)
900 °C, water, oil or air	50–53	0
1150 °C, water	43	93
1150 °C, oil	29–33	85–100
1150 °C, air	31–43.5	85–100
1200 °C, water	34–42	86–95
1200 °C, air	36–43	91–92
1250 °C, air	28–41	95–100
1250 °C, oil	32–36	98–99
1250 °C, air	32–37	91–97

Note: Some specimens were tested at every position.

Figure 1 The structure of high-temperature nitrous ferrite after quenching from 900 °C, ×36 000.

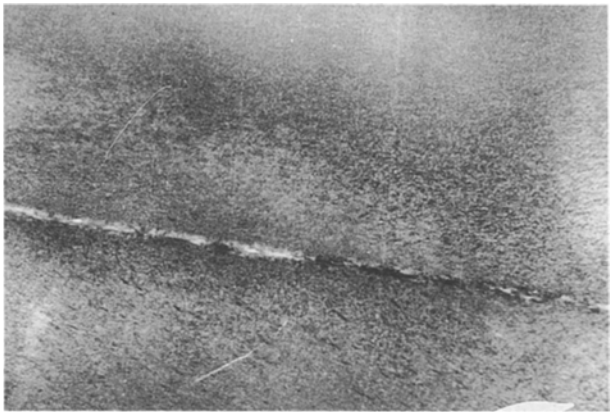

Figure 2 The structure of nitrous austenite after quenching from 1150 °C; ×36 000.

TABLE II Hardness and phase composition after heating at 1150 °C, cooling to temperatures given below and quenching in air

Quenching temperature (°C)	Rockwell hardness	γ-phase in structure (%)
1150	33	97
1050	37	97
950	47	67
850	51	0

1150 and 1250 °C, the structure is preferentially austenite (Fig. 2) with the lattice parameter being equal to 0.3619 nm. The amount of austenite increases with heating temperature before quenching. It should be noted that there is no direct dependence between the amount of γ-phase present in the structure, and hardness, i.e. it is not possible to determine the amount of γ-phase from the hardness value. In addition, there is no direct dependence either between the heating temperature before quenching and the rate of cooling, on the one hand, and the γ-phase amount, on the other.

The presence of 100% α-phase in the structure after quenching from 900 °C could be explained by the fact that at relatively low heating temperatures before quenching, the CrN particles are not fully dissolved in the solid solution and the latter circumstance is displayed on depletion of the solid by nitrogen; therefore, during quenching, the martensite γ–α transformation of the depleted solid solution occurs. The transformation temperature is found to be considerably higher than room temperature. To verify this supposition, several specimens were heated to 1150 °C, held for 30 min at this temperature, and further cooled, together with the furnace to 1050, 950, 850 °C. Then they were held for 30 min at the above temperatures, taken out of the furnace and cooled in air. The results are given in Table II. The presence of a large amount γ-phase after quenching from 1150 °C (Table II) and the absence of any visible undissolved CrN particles, as is clearly seen in the electron micrographs (Fig. 2), suggests that all the chromium nitrides are dissolved in the solid solution at 1150 °C. The same fact is evinced by the measurements of the lattice parameter of γ-solution (0.3619 nm), the value of which corresponds to the Fe–18% Cr solid containing 0.72% N.

Two reasons could lead to the appearance of either amount of α-phase in the structure of the specimens quenched from 950 and 850 °C:

1. for a temperature decrease from 1150 °C down to 950 or 850 °C, the γ-solid solution transforms into α through the γ + α intermediate region of the phase diagram and, during further quenching from 950 or 850 °C, the structures of the high-temperature region of the phase diagram are fixed, i.e. γ + α or α;
2. on decreasing the temperature from 1150 °C down to 950 or 850 °C the CrN precipitation in γ-solid occurs, and therefore austenite is depleted by nitrogen. In the process of quenching the martensite γ–α transformation occurs and α + CrN structure is fixed.

The experimental results, however, confirm the first supposition only. Firstly, the chromium nitrides are known to begin to dissolve in the solid on heating to relatively low temperatures, e.g. about 850 °C [1]. Secondly, the α-solid solution lattice parameter after quenching from 900 °C is high enough, being 0.2885 nm. Supposing that chromium atoms influence inconsiderably the α-Fe lattice parameter and the introduction of 1 at % nitrogen increases the α-Fe parameter by 0.0008 nm, the conclusion may be drawn that if the lattice parameter is equal to 0.2885 nm, all the nitrogen remains in the solid solution. The electron microscope data confirm this conclusion (extra reflections from any CrN particles are completely absent after quenching from 900 °C). The phase analysis indicates the absence of CrN particles in the anodic residue. Thus there is a rather wide region of α and γ co-existence in the phase diagram, approximately in the temperature range between 950 and 1250 °C.

To determine the initial point of the γ–α martensite transformation, several quenched specimens were cooled to temperatures lower than room temperature. Other quenched specimens were kept at room temperature and somewhat higher temperatures to study the stability of the austenite structure. All the results are listed in Table III.

As was expected, at subzero temperatures, the partial transformation of nitrous austenite into ferrite occurs. The structure of such ferrite (Fig. 3) differs essentially from the ferrite structure formed after quenching from 900 °C into water (Fig. 1). This fact shows that the mechanisms of the formation of these structures are different, and the α-phase structure fixed after quenching from 900 °C and below, is not the product of γ–α martensitic transformation, but represents the structure of the α-phase existing at 900 °C. The α-structure formed as the result of deep cooling of the quenched specimens, resulted from the γ–α transformation according to the martensitic mechanism. However, typical martensite structures characteristic of carbon steels were not observed (Fig. 3) because the lattice of the Fe–Cr–N martensite is not tetragonal. On studying Fig. 3 one can see that the initial point of martensite transformation, M_s, lies over the range 0 to − 50 °C. A certain increase of hardness and decrease of the amount of γ-phase after the quenched specimen was kept for several days at room temperature, can be explained by nitrogen atom segregation processes at the boundaries, dislocations and other defects of the crystalline lattice of the alloy. Mittemeijer and Wierszyllowski [2], for example, have drawn the same conclusion concerning nitrogen-atom segregation at the crystalline lattice defects at low ageing temperatures.

Figure 3 The structure of martensite after holding the quenched alloy in liquid nitrogen; × 24 000.

Similar segregation processes reduce the nitrogen concentration in the non-defect microzones of solid solution and the partial γ–α martensite transformation seems to occur in those microzones. This process is accompanied by an increase in hardness of the alloy due to the growth of the coherent stresses at the austenite–ferrite boundaries. The nitrogen segregation process at defects at room temperature is so slow that only 1%–4% of nitrous austenite transforms into ferrite over 4 days.

Holding at higher temperatures (for example, at 100–300 °C) leads to a certain increase in hardness and to the reduction of austenite in the structure (Table III). This process seems to be provided by inhomogeneity of the nitrogen-atom distribution in the γ-solid solution occurring at these temperatures, i.e. by the same segregation processes as in the previous case. It seems that decomposition of nitrous ferrite and nitrous austenite at the temperatures when diffusion mobility of substitutional atoms is sufficiently high, proceeds in different ways. Fig. 4 shows that the character of the hardness curves is different for ferrite and austenite decomposition.

TABLE III Hardness and phase composition at subzero and low-temperature ageing of specimens quenched from different temperatures

Quenching parameters	Treatment after quenching	Rockwell hardness		γ-phase in structure (%)	
		After quenching	After treatment	After quenching	After treatment
1150 °C, oil	− 196 °C, 1 h	31	47	90	74
1150 °C, oil	− 50 °C, 3 h	33	48	97	79
1150 °C, air	− 50 °C, 3 h	37	48	97	66
1150 °C, oil	+ 20 °C, 10 days	33	36	85	83
1150 °C, air	+ 20 °C, 10 days	31	35	89	87
1150 °C, oil	+ 20 °C, 3 days	29	30	100	100
1150 °C, air	+ 20 °C, 3 days	37	41	99	98
1200 °C, air	+ 20 °C, 10 days	36	39	91	87
1250 °C, oil	+ 20 °C, 3 days	33	37	99	98
1250 °C, air	+ 20 °C, 3 days	32	35	96	95
1250 °C, water	+ 100 °C, 5 h	39	41	100	89
1250 °C, water	+ 200 °C, 5 h	40	42	100	92
1250 °C, water	+ 300 °C, 5 h	41	44	100	90
1250 °C, water	+ 400 °C, 5 h	38	37	100	91

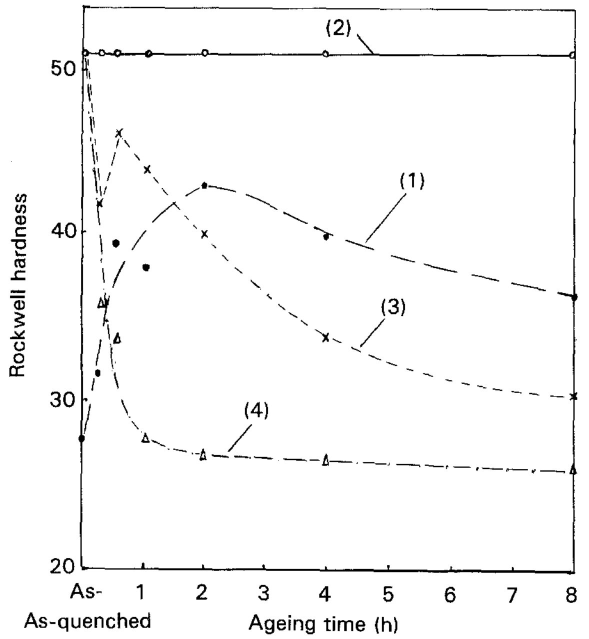

Figure 4 Rockwell hardness changes at isothermal ageing at different temperatures: (1) austenite structure obtained after quenching aged at 500 °C; (2–4) ferrite structure obtained after quenching aged at 500, 550 and 600 °C, respectively.

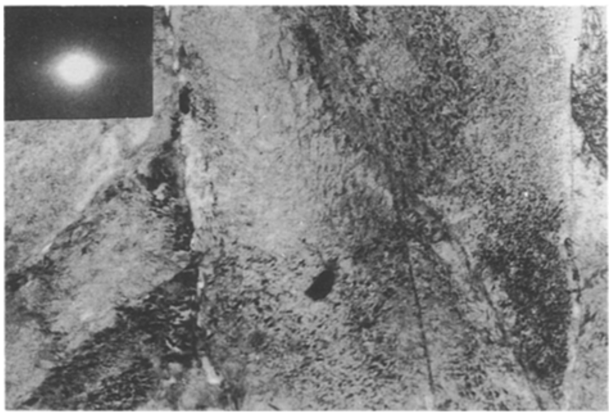

Figure 5 Austenite structure obtained after quenching aged at 500 °C, 0.25 h. Diffusion streaks in $\langle 1\,0\,0\rangle_\alpha$ directions; × 60 000.

The decomposition of the alloy having austenite structure after quenching begins with nitrogen cluster formation and therefore, $\gamma \rightarrow \alpha$ transformation in regions of the austenite depleted by N atoms takes place. X-ray phase analysis confirms that the $\gamma \rightarrow \alpha$ transformation occurs as only ageing temperature reaches 500 °C. With longer ageing times (for example, 0.25 h) the highly dispersed regular structure, which is revealed due to deformation contrast of the matrix, is observed (Fig. 5). This structure is characteristic of alloys having high elastic coherent stresses. Apparently, these stresses arise in the coherent boundaries between precipitates and matrix. Diffusion streaks parallel to the [1 0 0] direction and associated with the (2 0 0) main reflection maximum are detectable in the electron diffraction patterns (Fig. 5, inset). No additional reflections of a new phase are observed. It can be supposed that the dispersed regular structure visible in Fig. 5 does not seem to be new phase precipitates in the solid solution but represents mixed zones simultaneously enriched by chromium and nitrogen. Earlier, the analogous mixed zones of alloy elements atoms and carbon were observed during secondary hardening of the alloy steels [3].

The structure at the peak of hardness represents particles of precipitates in solid solution (Fig. 6a). The particles lie on the $(1\,0\,0)_\alpha$ planes of the matrix. The electron diffraction pattern of this stucture is shown in Fig. 6b. The orientation relationship of precipitate–ferrite was found to correspond to that originally proposed by Baker and Nutting for bcc and fcc structures: $(1\,0\,0)_\alpha \parallel (1\,0\,0)_p$ and $[0\,1\,1]_\alpha \parallel [0\,0\,1]_p$ (where p indicates precipitate, Fig. 6c). The electron

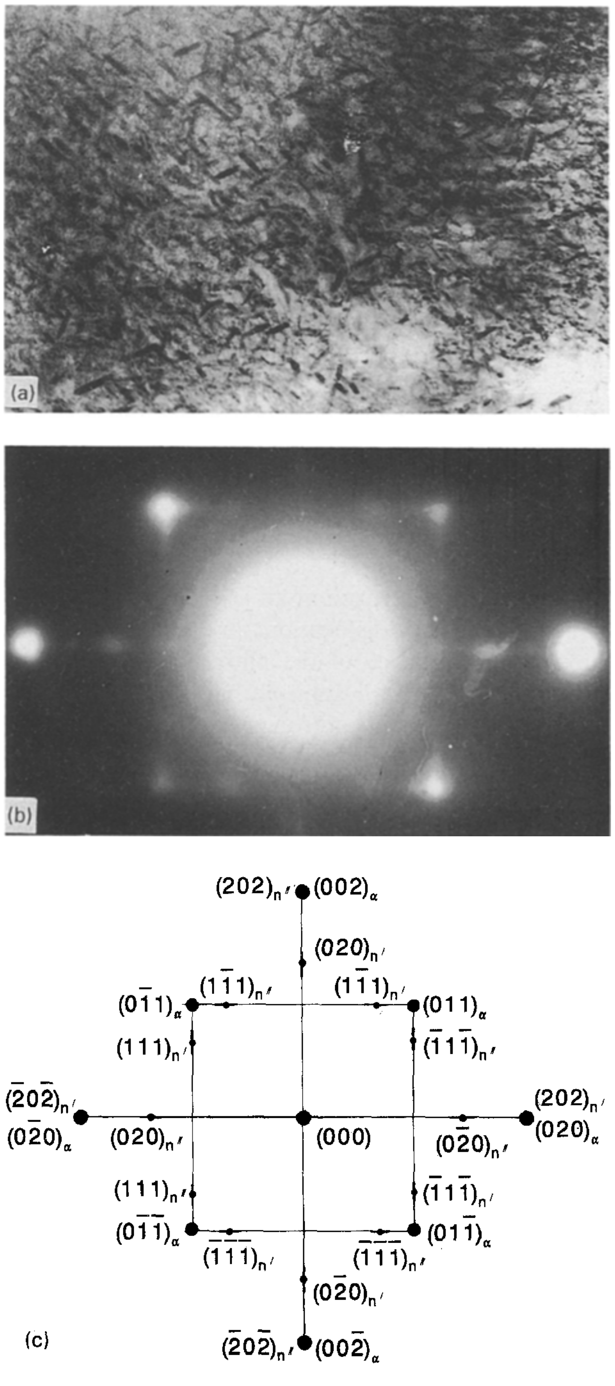

Figure 6 (a) Austenite, structure obtained after quenching aged at 500 °C, 2 h peak of hardness; × 80 000. (b) Electron diffraction pattern from $(1\,0\,0)_\alpha$ orientation; (c) schematic representation of (b) n′ and n″, reflections of two nitride systems.

diffraction pattern and its identification in Fig. 6 show that particles of precipitates at the peak of hardness are CrN having fcc structure of NaCl type with a lattice parameter of 0.414 nm. Elastic distortions of the matrix at the boundaries between it and precipitates are caused by the great difference between the specific atomic volumes of the fcc CrN particles ($\sim 17.7 \times 10^{-3}$ nm) and the bcc matrix ($\sim 11.8 \times 10^{-3}$ nm). The scattered effects in the electron diffraction patterns occurring during the stages of hardness increase and hardness peak, support the idea that the matrix is greatly distorted elastically. Further ageing leads to loss of coherence between the CrN particles and the matrix and, therefore, to the hardness decrease of the alloy (Fig. 4).

If the structure of the alloy after quenching is ferrite the hardness curves at 550 and 600 °C ageing show a sharp decrease at the first periods of ageing and then after achievement of a certain level of H_{Rc} they no longer change (500 °C ageing is insufficient for CrN precipitation). In the hardness curve at 550 °C–0.5 h, a small peak can be observed which could be interpreted as the result of the secondary hardening process due to the precipitation of CrN highly dispersed particles (by analogy with the previous case). The structural changes in the process of ageing are also similar to the previous case. At the beginning of ageing (550 °C, 0.5 h) the highly dispersed regular structure is observed (Fig. 7); after 550 °C, 4 h ageing, the CrN particles do not differ in size, position and dispersion from those which precipitate on ageing of the solid solution formed after quenching at 1250 °C.

The results obtained are summarized in the form of a hypothetical C-shaped diagram (Fig. 9) which is suitable for interpretation of all the processes observed during quenching and ageing. It should be noted that the lines shown in the diagram are quite conventional and require some verification but, on the whole, the diagram reflects adequately the state of the alloy after it has been exposed to various heat treatments.

For example, during quenching from 900 °C and below (denoted by 1 in Fig. 9), the α-Fe monophase structure is fixed. Ageing of this structure at temperature higher than 500 °C results in the precipitation of CrN particles from the solid solution. On quenching of the alloy from temperatures equal to or higher than 1250 °C into water, oil and air, the γ-Fe monophase structure can be obtained (denoted by 2). Further cooling of the quenched structure to subzero temperatures partially transforms the austenite into ferrite. Holding of the austenite, obtained after quenching from 1250 °C, at temperatures up to 400 °C promotes the transformation of up to 10% austenite into ferrite. If the holding is performed at 500 °C or above, the austenite decomposes into a mixture of ferrite and CrN. The mixed γ + α structure is fixed on quenching the alloy from the temperature range between 950 and 1250 °C (not indicated in Fig. 9).

Figure 7 Ferrite structure obtained after quenching aged at 550 °C, + 0.5 ; × 60 000.

Figure 8 Ferrite structure obtained after quenching aged at 550 °C, + 4 h; × 36 000.

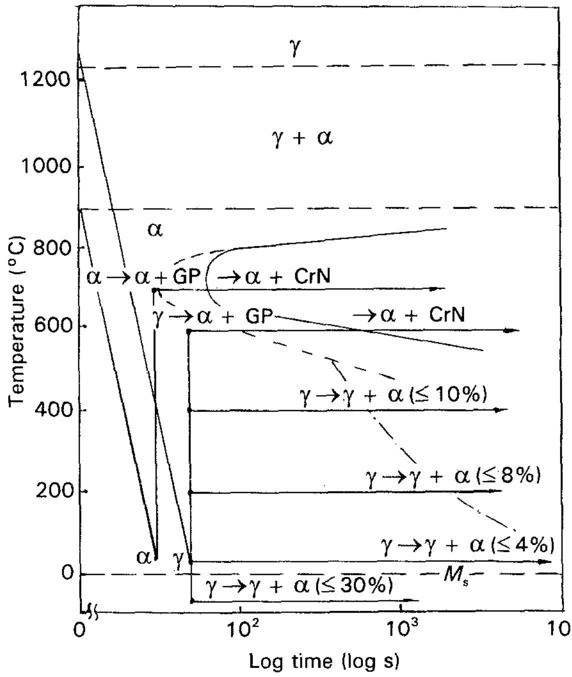

Figure 9 Hypothetical C-shaped diagram of the alloy.

4. Conclusion

The nitrous austenite structure formed in high-chromium and high-nitrogen iron-based alloys after quenching from 1250 °C and higher, is not stable. At temperatures below 0 °C it transforms into a ferrite structure according to the martensite mechanism only. In the temperature range 20–400 °C, the nitrogen atoms partially segregate at defects, deplete some microzones of the solid, and provoke the martensite γ–α transformation in these nitrogen-depleted non-defect microzones. Between 500 and 800 °C, the decomposition of austenite into ferrite and chromium nitrides occurs, which begins analogously to the previous case. Chromium nitrides are fully dissolved in the structure after heating at 850 °C and above. The nitrous ferrite structure formed after quenching from 950 °C and below, is decomposed on ageing through the mixed-zone stage.

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