Investigation of a Mechanism of Structural Transformations in High-Strength Steel

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Abstract. Mechanical, technological and operational properties of metal materials are largely influenced by changes of concentrations, morphology, dimensions, localization, elemental and phase composition of dispersed precipitates. This paper is devoted to a study of dispersed carbides of submicron size at tempering of high-strength medium-carbon steel. The main emphasis is on comparing the data obtained by small-angle neutron scattering and transmission electron microscopy. As a result of the analysis, it was found that carbide growth begins in the investigated steel immediately after quenching when the tempering temperature increases. First, it is fixed by a transmission electron microscopy and a small-angle neutron scattering and then above ~ 300 °C carbide growth is fixed by neutron diffraction. The residual austenite is also completely dissolved by the time the temperature reaches ~ 300 °C. A good matching has been reached for the methods used. It has been shown that a complex use of integral and local methods allows to obtain fully information about the structure and properties of the investigated material.

1. Introduction

In modern conditions, in order to create new structural materials and improve existing ones, it is impossible to do without studying and subsequent determining parameters of dispersed precipitates of a submicron and/or nanometer size range. Changes in concentrations, morphology, sizes, localization, element and phase composition significantly affect mechanical, technological and operational properties of metal materials. Various techniques are used to control the state of dispersed phases: directed crystallization, deformation, heat treatment, quenching followed by tempering, aging [1]. Understanding the mechanisms of dispersion formation is an important problem because it is one of the most effective hardening mechanisms in metal alloys.

The required combination of strength and plastic properties is achieved by a microscopic defective structure determined, among other things, by dispersed particles of submicroscopic size. So this paper is devoted to their study during tempering [2], [3].

The main focus of this study is on comparing and specifying data obtained by different methods. In order to obtain a picture reflecting the state of the dispersed particles, an integral method, small angle neutron scattering (SANS), was used. Due to the fact that the final result of SANS depends on the parameters of the particle distribution model used, preliminary information on the processes occurring in the metal is needed to select the optimal calculation model and further adjust it. For this purpose, transmission electron microscopy (TEM) is used, which provides direct observation of fine particles, but at very local areas of the test sample. The complex use of methods makes it possible to compare
the sizes of the dispersed precipitates obtained by SANS and by TEM and to obtain information about changes in the metal with greater accuracy. In papers [4] and [5] and earlier studies of dispersed particles in high-strength medium carbon B1700 steel grade subjected to various tempering conditions were carried out, but no direct comparison of TEM and SANS data on the same samples was carried out.

2. Materials and experimental methods

Chemical composition of investigated high-strength medium-carbon B1700 steel grade is as follows: C – 0.45%; Si – 0.36%; Mn – 1.13%; Ni + Cu – 1.3%; Cr + Mo – 1.66%; Ti + V + Nb – 0.11%; Al – 0.04%; and also 0.03% Ca, 0.003% B, 0.012% N, 0.010% S and 0.010% P is determined by calculation methods [6].

Electron microscopy studies were performed using a Tecnai G2 30 S-TWIN transmission electron microscope with an accelerating voltage of 200 kV. Thin foils of metal are made by means of Struers “Tenupol-5” electrolytic thinning unit in chlorine-alcohol electrolyte at a temperature of +8°C and a voltage of 20 V.

Experiments on small-angle scattering of neutrons using time-of-flight spectrometer YuMO [7], [8] were carried out on pulse reactor IBR-2 in JINR (Dubna) [9], at the distance sample - detector 5.28 and 13.04 m, providing the range of obtained values of scattering vector Q from 0.007 to 0.5 Å⁻¹. Diameter of irradiated area of the sample was 14 mm. Neutron scattering intensities on the obtained spectra are given to absolute units cm⁻¹ by correcting the scattering intensity for absorption, sample thickness, background scattering on the substrate and on the control sample from vanadium using SAS software [10], [11]. In the samples under investigation, changes in the scattering vector are approximated by the Porod's law see (1) corresponding to scattering from objects with a smooth surface [12].

\[ I(Q) = A \cdot Q^{-4} = 2\pi \Delta \rho^2 \cdot \frac{S}{V} \cdot Q^{-4} \]

\[ \rho_p = \frac{\sum_{i=1}^{m} N_j \cdot b_i}{\sum_{i=1}^{m} N_j \cdot v_i} \cdot \frac{M_i}{\rho_m \cdot N_a} \]

where \( \Delta \rho = \rho_p - \rho_{mat} \) – contrast, \( \rho_p \) – scattering density of the particle, \( \rho_{mat} \) – scattering density of the matrix surrounding particle, \( N_j \) – number of components, \( b_i \) – scattering amplitudes, \( v_i \) – molar volume, \( M_i \) – molar mass, \( \rho_m \) – density, \( N_a \) – Avogadro constant. Size and concentration of carbide particles are evaluated by value of coefficient A.

3. Experimental results and discussion

As is known, quenching results in a non-equilibrium structure with carbon supersaturation, increased defect density and lattice distortion caused by martensite formation. Martensite unlike the volume-centered cubic lattice of α-Fe has a tetragonal lattice and the smaller the amount of carbon in steel, the closer it is to a BCC lattice α-Fe. One of the most commonly used methods for obtaining the required level of combination of strength and plastic properties is tempering. Depending on tempering time and temperature, various new carbide phases are formed that affect the properties of metal. This problem calls significant interest of researchers for a long time starting with papers [13] continuing [14], [1] including modern papers on this topic [3], [15], [16]. A number of modern papers are aimed at the study of low-temperature tempering with ε-carbide formation [17], [2], [18].

When a tempering temperature increases, a sample is "compressed" (carbon exits a grid and a martensite tetragonality parameter c/a tends to one) in the case of this steel detected dilatometrically [4]. This process is limited to a temperature of 150 °C. Martensite is decomposed with excess carbon release and formation of carbide of variable composition FeₓC, coherent to the main phase α-Fe. Such
martensite is called released [13]. Further, in the temperature range of \( \sim 150 – 300 \, ^\circ C \) there is a slight increase in steel volume caused by a degradation of residual austenite (transformation of FCC-lattice to BCC-lattice occupying a larger volume), as indicated by the results of dilatometry and X-ray phase analysis [4]. Cementite-type carbides are also formed. Above 300 \( ^\circ C \) compression occurs again caused by the final release of carbon from \( \alpha \)-Fe lattice with the resulting carbides losing coherence with matrix and fixing their inherent lattice with the corresponding properties of the resulting carbide. At the same time micro-distortions of crystal lattice caused by previous transformations are removed, detected by X-ray diffractometry method, as well as coagulation of formed carbide particles occurs and martensite decay ends.

In this paper a comparative study of the parameters of dispersed precipitates obtained both by means of a widespread but rather labour-intensive high-local analysis by TEM method and by means of an integral SANS method, which significantly simplifies sample preparation for research, high expression of obtaining initial scattering data, but the implementation of measurements requires high-intensity neutron fluxes and special equipment located at the outlet of channels from nuclear reactors.

Using TEM, the fine structure of three samples after tempering was analyzed at: 150 \( ^\circ C \), 300 \( ^\circ C \), 500 \( ^\circ C \), typical images of the observed dispersed phases are shown in Figure 1. Figure 2 shows the primary SANS data for the corresponding temperatures, although it should be noted that the total number of studies carried out in the tempering range of 150-600 \( ^\circ C \) was 12 measurements: after quenching, after quenching and tempering at 150, 200, 250, 300, 330, 360, 390, 420, 450, 500 and 600 \( ^\circ C \).

![Figure 1. Images of dispersed phases obtained on samples after tempering at the above temperatures](image)

Figure 3 and Table 1 show TEM data on size and concentrations of the carbide particles. According to [13], [6] at a tempering temperature below 200 \( ^\circ C \) cementite \( Fe_3C \) has not yet formed, intermediate carbides \( Fe_2C \) stoichiometries are isolated, crystal lattice of which is coherent with the matrix lattice (BCC – Fe). In the temperature range up to 300 \( ^\circ C \) the carbide particles grow and partially coagulate, with coagulation being the leading mechanism the average size growing. It should also be noted that at the initial stage conversion is uneven and somewhere martensite needles already lose carbon to form intermediate carbides, and somewhere else there is no, in which case complex analysis of the material by means of SANS together with TEM is particularly useful. The use of intermediate \( Fe_2C \) carbide with a slightly lower scattering density than \( Fe_3C \) in the calculation results leads to a better correspondence between the TEM and SANS data. A drop in the average size of the dispersed precipitates at a tempering temperature of more than 300 \( ^\circ C \) can be associated with a further increase in the average size of carbides and beyond the applicability of the SANS method, which obtains only centers that effectively scatter neutrons of less than 100 nm. At the same time, the value of the volume occupied by carbides determined by TEM decreases curiously more slowly due to the large range of measured dimensions. For particles larger than 100 nm, small-angle neutron scattering can hardly be
obtained. At a tempering temperature of 500 - 600 °C sufficiently large carbides obtained by neutron and X-ray diffraction methods (ND and XRD) have already been formed, and the amount of fine carbides is quite small due to coagulation and formation of larger particles. As a result, a concentrations of the particles is reduced.

Figure 2. SANS of samples after tempering at a temperature of 150, 300 and 500 °C

Figure 3. Size of dispersed precipitates according to TEM (♦), SANS at approximation of Fe$_2$C (■), Fe$_3$C (▲).
4. Conclusions

Based on the analysis of small-angle scattering and transmission electron microscopy data, the mechanism of structural transformations of carbide particles in steel during tempering was revealed. When the tempering temperature increases, the amount of residual austenite decreases and after tempering above 300 °C, Fe₃C carbide increases markedly. However, taking into account the TEM data and calculating the size of the dispersed precipitates from the SANS data, the growth of carbides begins immediately after the start of tempering and continues up to 600 °C. Thus, after quenching and tempering at 150 °C a growth of Fe₂C carbide particles begins, then as the tempering temperature increases Fe₂C is transformed into a more stable Fe₃C. At the tempering temperature of 300 °C carbide coagulation begins, resulting in a decrease in the average particle size of the recorded particles in the investigated range of SANS. At the same time, TEM gives a wider range of measured dimensions of dispersed precipitates. Increasing the tempering temperature causes the total amount of cementite to increase so that the phase can be indicated by ND and XRD methods. In addition, the neutron diffraction method records not only the appearance of cementite, but also the dissolution of residual austenite.

A comprehensive study of dispersed precipitates based on X-ray and neutron diffraction data, as well as TEM data, made it possible to refine the behavior model of dispersed carbide particles in high-strength medium-carbon steel.

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Acknowledgments

The work has been performed with financial support of the Ministry of Education and Science of the Russian Federation within Subsidy Agreement No. 14.579.21.0003 (the Unique Project Identifier is RFMEFI 57914X0003). Experimental studies were carried out on the equipment of the Core shared research facilities "Composition, structure and properties of structural and functional materials” of the NRC «Kurchatov Institute» - CRISM "Prometey” with the financial support of the state represented by
the Ministry of Education and Science of the Russian Federation under agreement No. 13.CKP.21.0014. The unique identifier is RF----2296.61321X0014.