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STRENGTH AND PLASTICITY

Microstructural Factors That Decrease the Local Strength of Grain Boundaries in Martensitic Steels

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Abstract—As a result of the phase transformation of austenite to martensite during steel quenching, weakened structural regions, specifically the boundaries of the original austenite grains, have been formed. They are weakened because of microstructural factors, such as the residual internal microstrains and segregation of embrittling impurities. The joint effect of microstructural factors, namely, residual microstrains and segregation of phosphorus and carbon at grain boundaries, on reducing the local strength of the boundaries of the initial austenite grains in martensitic steels is quantitatively evaluated, and the impacts of these microstructural factors have been separated. The dependences of the local grain-boundary strength on the ratio of various levels of residual microstrains and on the atomic concentration of phosphorus impurities at the grain boundary in segregation spots have been determined. It has been shown quantitatively that the adsorption enrichment of the austenite grain boundaries with phosphorus leads to a decrease in the intergrain adhesion and facilitates the emergence and development of cracks along the boundaries of the initial austenite grains. The quantitative dependence of the local strength of grain boundaries on the concentration ratio of carbon and phosphorus in them has been shown. Carbon in concentrations of up to 0.04% reduces the embrittlement of the boundaries due to the segregation of phosphorus and loses its neutralizing effect on the phosphorus segregation at concentrations of more than 0.04%, so the phosphorus concentration at the grain boundaries increases and the embrittlement resistance of the latter decreases. The applicability of the developed technique for the quantitative evaluation of the local strength of hardened steel grain boundaries by using tests on delayed fracture and applying the method of finite elements to determine the local strains has been shown.

Keywords: martensitic steel, grain boundary, segregation of impurities, residual microstrains, local strength, delayed fracture, threshold strain, method of finite elements

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INTRODUCTION

Delayed brittle fracture (DBF) is one of the most dangerous types of brittle fracture of critical high-strength parts made of martensite-containing steels [1–3]. In this case, the emergence of a microcrack and its subsequent growth up to fracture occur during the exposure of the sample (part) to a constant load [1, 2]. When steel is hardened as a result of the phase transformation of austenite to martensite, weakened structural regions, specifically the boundaries of the initial austenite grains (hereinafter referred to as *grain boundaries*) are formed [4, 5]. Crystals of the formed martensite emerge on them, and bulk dilatation areas that serve as sources of residual internal microstrains are formed in front of their vertices [4, 5, 8]. In addition, grain-boundary segregations of embrittling impurities of phosphorus, antimony, and tin are formed [6, 7]. This gives rise to the intercrystallite fracture. There are no quantitative data (in units of strains) about the additive (and separate) impact of these factors on reducing the local strength of grain boundaries in the literature [2, 3]. In this regard, the study of the additive (and separate) impact of the above microstructural factors on the local strength of grain boundaries is a topical issue. The characteristic ultimate strength in how it is defined is averaged over the cross section of the sample and does not describe the limiting state in the area of local fracture at the grain boundary. However, the emergence and initial growth of a microcrack at the grain boundary are local processes. Their development is determined by structural factors at the grain boundaries, such as the structural inhomogeneity of the grain boundaries and the presence of residual embrittling microstrains, segregations of impurities, and strain microconcentrators.

Therefore, during the fracture of the intercrystallite, the term *local strength* of the grain boundaries was understood as the critical value of the local tensile stress $\sigma_{11\max}$ [8]. The aim of the present study was to establish the effect of microstructural factors on reducing the local strength of the boundaries of the initial austenite grains in hardened steels and to sepa-

Table 1. Studied steels and thermal processing

Steels	Thermal processing
8Kh2N4VA with phosphorus contents of 0.005, 0.010, 0.012, 0.028, and 0.040 wt %	Quenching from 1000°C, 20 min, water

Table 2. Studied steels and thermal processing

Carbon content, wt %	Thermal processing
0.007; 0.03; 0.06; 0.16	Direct quenching from 1000°C, 1 h, water Quenching with isothermal exposure at 950°C, 1 h, water Quenching with isothermal exposure at 850°C, 1 h, water

rate their contributions to this effect. This aim is achieved by solving the following problems: (1) separating the influence of residual microstrains and phosphorus segregation and (2) analyzing the effect of the carbon and phosphorus contents on reducing the local strength of the boundaries of the initial austenite grains in martensitic steels.

EXPERIMENTAL

The effect of microstructural factors (phosphorus impurities and residual internal microstrains) on the local strength of grain boundaries in 8Kh2N4VA steel with different phosphorus contents was studied (Table 1).

The joint effect of carbon and phosphorus on the local strength of the boundaries of the initial austenite grains was studied on four low-alloyed steels with identical compositions of alloying elements and phosphorus, but with different volumetric contents of carbon (Table 2).

The only contaminant capable of segregation in these steels was phosphorus. The concentration of the phosphorus impurity at grain boundaries was varied using isothermal exposure at different temperatures. The samples were quenched in water with subsequent isothermal exposure in the γ-region (see Table 2).

To open the grain boundaries, delayed fracture tests (DBF tests) were carried out [9]. The test methodology was developed by a team of authors at Bardin Central Research Institute of Ferrous Metallurgy [6, 9]. To exclude the surface decarburization, the samples were placed in quartz ampoules prior to the thermal processing, after which the ampoules were evacuated. After the thermal treatment, the samples were exposed to air (relaxation) for 30 min, 50 h, and 100 h, then kept in liquid nitrogen until testing in order to preserve the structural state (the level of residual microstrains). Thus, samples with different levels of residual microstrains were obtained.

The used Charpy-type samples with sizes of 55 × 10 × 10 mm had a sharp notch with a depth of 2.00 mm, a radius of 0.25 mm, and an aperture angle of 45° made by a milling cutter. The tests on the active and delayed fracture were carried out by concentrated bending. The tests on the delayed brittle fracture were carried out by loading samples containing strain concentrators by concentrated bending to a given load and further holding until fracture. Delayed fracture led to the intercrystallite nature of the emergence and development of microcracks. The moment of the crack emergence (τ) was registered using the acoustic emission method. To determine the local strains in the region of the crack emergence, the method of finite elements was used. The local tensile strains ($\sigma_{11\,\max}$) in the region of local fracture at the boundary between the plastic and elastic zones in front of the notch root (Fig. 1) were calculated according to the techniques described in [10].

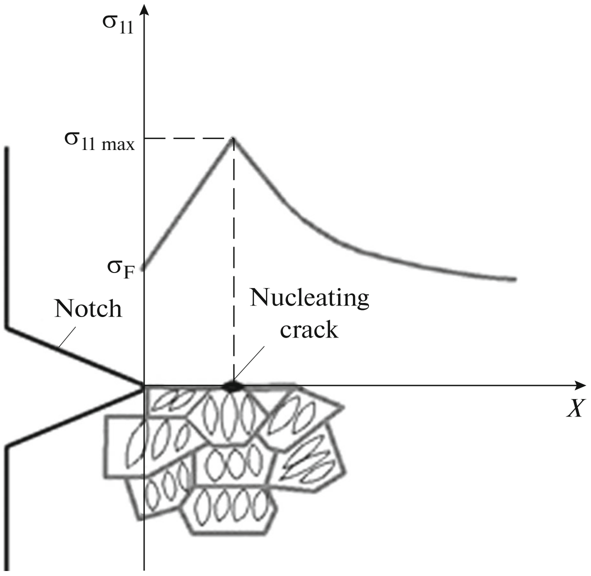

Fig. 1. Schematic representation of the emergence of a crack at the boundary of the initial austenite grain in the spot of localization of the maximum local tensile stress $\sigma_{11\max}$ in the notch root in the region of deformation constraints.

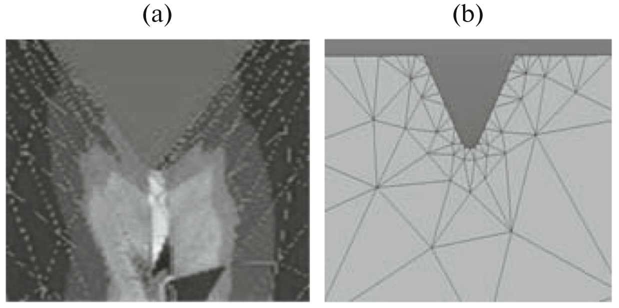

Fig. 2. Simulation of bending Charpy sample by the method of finite elements: (a) field of deformations in notch root; (b) network of finite elements that simulates the sample.

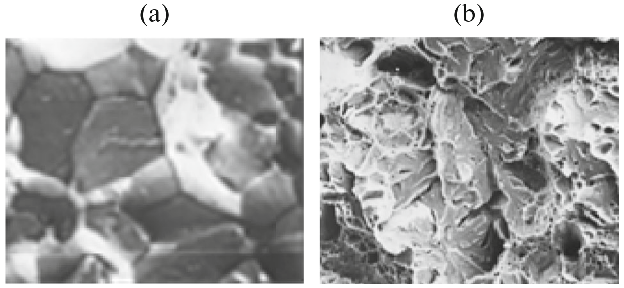

Fig. 3. Surface of fracture of 18Kh2N4VA steel (a) along grain boundaries at place of emergence and at the stage of stable crack growth, and (b) through the body of grains at the stage of rapid crack distribution (500× magnification).

The following examples are shown in Fig. 2: (a) the field of deformations at the notch root; (b) the network of finite elements that simulates a sample. The nature of sample fractures was studied by the standard methods of fractography using a JEOL electron microscope. Metallographic tests were carried out on the samples passed the tests on the delayed fracture in order to detect grain-boundary segregations of phosphorus by the method of etching the boundaries of the initial austenite grains in specially chosen reagents.

It was confirmed that the surface of fracture in the region of the emergence of a microcrack and at the stage of its stable growth during the delayed fracture is intercrystallite in nature but becomes transcrystallite at the stage of rapid distribution of the crack (Fig. 3). The content of the phosphorus contaminant on the fracture surface in the region of the emergence of a crack was determined by the method of Auger spectrometry. Using an electron spectrometer, the elemental analysis of the subsurface layer was performed with a depth resolution of 0.5–1.0 nm and a sensitivity of 0.2%.

RESULTS AND DISCUSSION

As a result of the experiments, the phosphorus concentrations in the subsurface layer of the fracture in 18H2N4VA steel with weight concentrations of phosphorus of 0.005, 0.010, 0.012, 0.028, 0.040%, as well as the corresponding grain-boundary atomic concentrations of phosphorus are determined. For four of the studied low-alloyed steels with different carbon contents (Table 2), after different thermal processing conditions, the atomic concentrations of phosphorus at the boundaries of the initial austenite grains are also determined. Using the results of the studies by the method of finite elements, the delayed fracture curves in the coordinates the local tensile stress ($\sigma_{11\max}$) versus the time prior to detection, the moment of the crack emergence (τ) is plotted (Fig. 4).

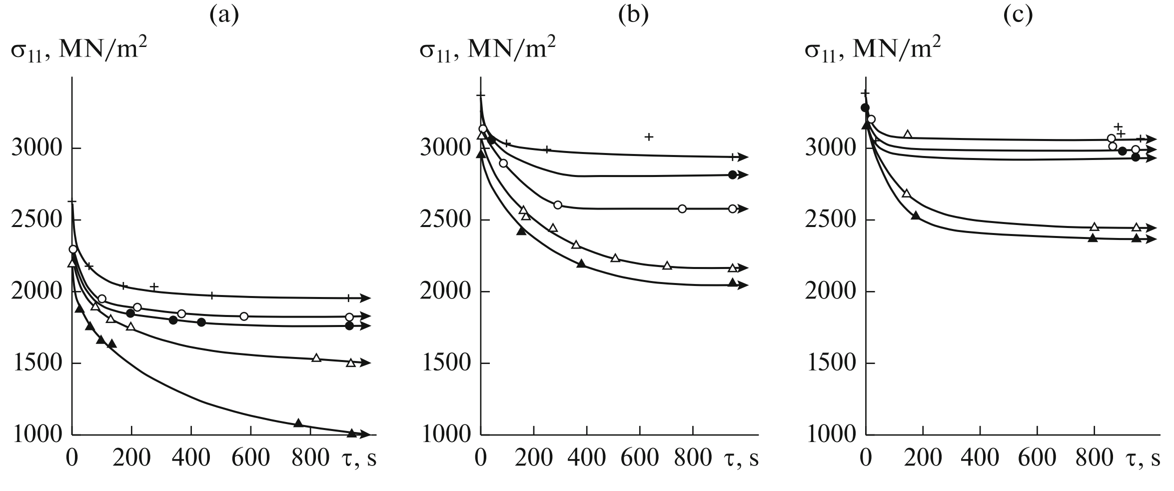

Fig. 4. Delayed fracture curves of 18Kh2N4VA steel at phosphorus contaminant contents of (+) 0.005, (●) 0.010, (○) 0.012, (△) 0.028, and (▲) 0.040 wt % after relaxation for (a) 30 min, (b) 50 h, and (c) 100 h.

The use of the threshold local tensile stress $\sigma_{11\max}$, which is a characteristic of the resistance of steel to the delayed fracture and does not depend on the geometries of the sample and strain concentrators [4], makes it possible to evaluate the embrittlement resistance of the initial austenite grain boundaries. The threshold level of the local tensile stress $\sigma_{11\max}$, below which the fracture did not occur, corresponds to a local strength of the grain boundary for each DBF curve [4].

Reducing the Local Strength of Grain Boundaries in Martensitic Steel by Segregations of Phosphorus Contaminants and Residual Microstrains

The influence of residual internal microstrains, segregations of the phosphorus contaminant, and electrolytic hydrogen saturation on the process of the local embrittlement of grain boundaries studied on structural alloyed steel 8Kh2N4VA. As a result of the delayed fracture tests by the concentrated bending of the Charpy-type samples made of structural alloyed 8Kh2N4VA steel and using the above-described techniques [4], the threshold $\sigma_{11\max}$ values after various times of relaxation were determined for steels with different contents of phosphorus (Fig. 5).

The threshold values correspond to the local strength of the grain boundaries. The intercrystallite nature of the sample fracture surface in the region of the emergence of a crack and at the stage of its steady growth along the grain boundaries is shown in Fig. 3a. It is shown in Fig. 5 that an increase in the content of the phosphorus contaminant (P, %) and a decrease in the time of relaxation after quenching give rise to a decrease in the threshold value of the local stress in the sample. The resulting surface of the threshold local stresses in martensitic steel after quenching allows one to separate the contributions of the steel relaxation after the quenching and of the mass content of phosphorus. In addition to residual internal microstrains, the cause of the embrittlement of grain boundaries in martensitic steel is the presence of segregations of embrittling contaminants at the grain boundaries. Therefore, it is important to determine the phosphorus content directly at the grain boundaries, which was accomplished using the Auger electron spectroscopy method.

The levels of the residual internal microstrains in the region of the emergence of a microcrack were determined using the method developed by the team of authors in Bardin Central Research Institute of Ferrous Metallurgy [11]. According to this method, the residual internal microstrain in the region of the emergence of a microcrack upon active loading can be estimated as the difference between the resistance to grain-boundary cleavage at a negligibly low level of residual microstrains (tempering at 100°C, 2 h) and after the related times of relaxation (30 min, 50 h, and 100 h). This made it possible to construct a three-dimensional dependence of the local strength of grain boundaries on the concentration of the phosphorus contaminant at grain boundaries and on the level of microstrains in the region of local fracture (Fig. 6).

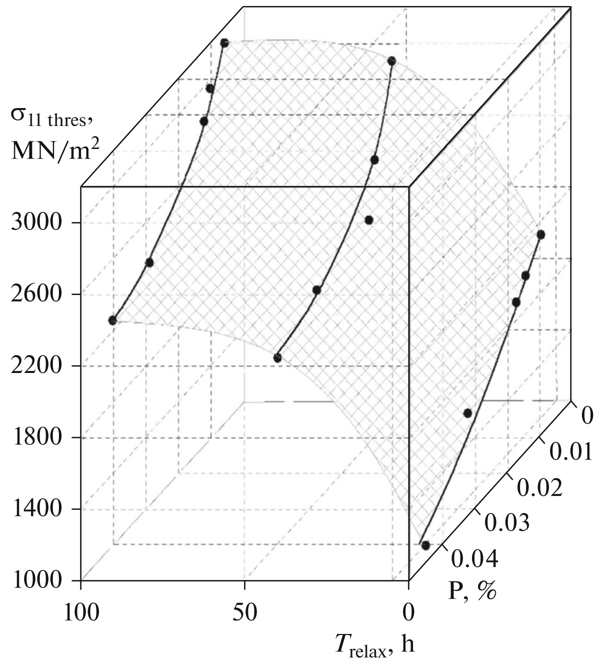

Fig. 5. Separation of influence of mass content of phosphorus (P, %) in steel and time of relaxation after quenching (T_{relax}) on threshold local stress value in 18Kh2N4VA steel.

As follows from an analysis of the experiment results, an increase in the concentration of phosphorus at grain boundaries in the form of segregations leads to a decrease in the local strength of the initial austenite grains in martensitic steel, and to a general decrease in the local strength of boundaries upon an increase in the level of residual microstrains due to a reduction in the time of steel relaxation after quenching (Fig. 6).

Thus, the effects of the grain-boundary phosphorus segregation and residual microstrains on the local strength of the boundaries of the initial austenite grains in martensitic 18Kh2N4VA steel after tempering are separated. For comparison, the local strength of the grain body free of the phosphorus contaminant at negligibly low residual microstrains (tempering at 100°C, 2 h) is determined using the method of active fracture, which is equal to $\sigma_F = 3520$ MPa.

Martensitic steels exhibit a lower strength of the grain boundaries as compared to the grain body. This is caused by the formation of bulk dilatation regions (BDRs) in the spots, in which large martensite crystals appear from the boundaries of the original austenite grains, and by the concentration of segregations (flat clusters) of the sulfur, phosphorus, and antimony con-

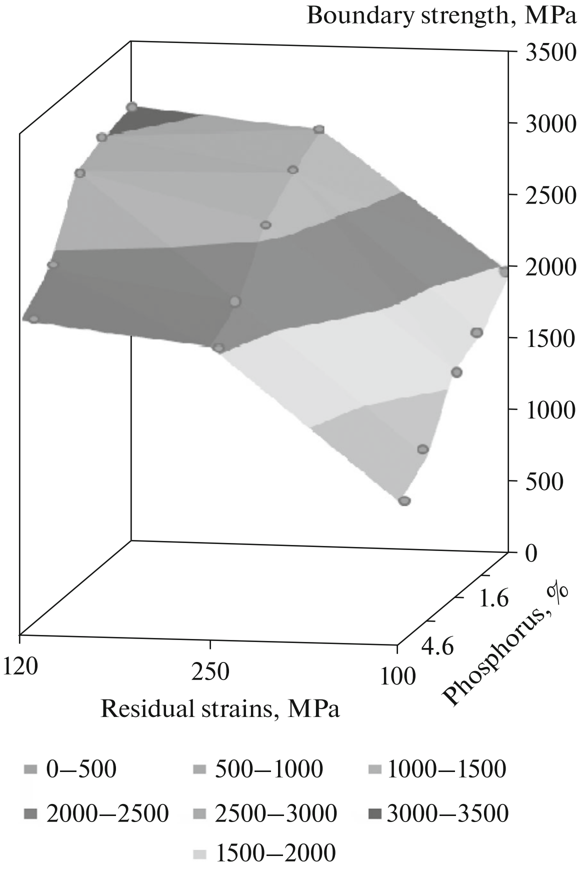

Fig. 6. Dependences of the local strength of grain boundaries on the atomic concentration of phosphorus and on the level of residual microstrains at grain boundaries of 18Kh2N4VA steel.

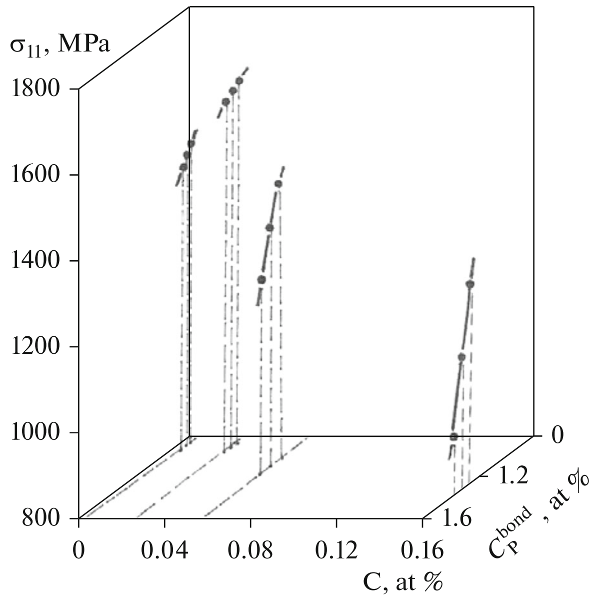

Fig. 7. Dependences of the local strength of grain boundaries on the atomic concentration of phosphorus at the boundaries of the initial austenite grains (C_P^{bond}) and on the concentration of carbon (C) in low-alloyed steels.

taminants that embrittle the boundaries [3]. These factors lead to that the emergence of microcracks and their slow growth in martensitic steels take place at the boundary of the initial austenite grains (see Fig. 3a), while their subsequent rapid distribution occurs through the grain bodies (see Fig. 3b). It has been shown that the local strength of grain boundaries in martensitic 18Kh2N4VA steel (as evidenced by the value of the threshold local stress in the DBF tests) depends on their microstructural state. The local strength of grain boundaries is reduced to the highest extent by residual internal microstrains at the martensite crystal vertices outgrown to boundary of the initial austenite grains and by phosphorus segregations.

Separation of the Effects of Carbon and Phosphorus on the Local Strength of the Boundaries of the Initial Austenite Grains

As a result of the delayed fracture tests, 12 delayed fracture curves are constructed for all combinations of the volumetric content of carbon in steel (0.007, 0.03, 0.06, and 0.16%) and atomic concentrations of phosphorus at the boundary of the initial austenite grains (three thermal processing conditions). Using the method of finite elements, then the threshold load values are converted into the threshold local stresses ($\sigma_{11\text{thr}}$). For the final analysis, 3D dependences of the local strength of grain boundaries on the atomic concentration of phosphorus at the boundaries of the initial austenite grains and on the concentration of carbon four low-alloyed steels are plotted (Fig. 7). As follows from Fig. 7, an increase in the concentration of carbon in steel leads to a decrease in the local strength of the boundaries of the initial austenite grains. In particular, the etchability of the austenite grain boundaries significantly increases, which indicates an increase in the phosphorus concentrations at the boundaries.

Carbon and phosphorus affect the local strength of the grain boundaries in different ways. It is generally agreed that carbon increases and phosphorus decreases the cohesion strength of boundaries [12]. The local strength of the boundaries of the initial austenite grains upon the combined effects of grain-boundary phosphorus and carbon is evaluated. The study of the simultaneous effects of carbon and phosphorus on the embrittlement resistance of the boundaries of the initial austenite grains, which is evaluated by the level of the threshold local tensile stresses of steel in the quenched state, showed that the dependence of the embrittlement resistance of grain boundaries on the volumetric content of carbon and on the concentration of grain-boundary phosphorus is nonmonotonic. At a volumetric carbon content of 0.007%, the concentration of grain-boundary phosphorus barely depends on the austenization conditions and equals the bulk concentration. With an increase in the volumetric carbon content from 0.007 to 0.03%, the embrittlement resistance of boundaries increases despite the simultaneous increase in the atomic concentration of grain-boundary phosphorus. A further increase in the concentration of carbon to 0.06% (the grain size does not change) leads to an increase in the concentration of grain-boundary phosphorus with a simultaneous decrease in the embrittlement strength of grain boundaries. A further increase in the concentration of carbon in the investigated range from 0.06 to 0.16% gives rise to a further decrease in the local strength of the initial austenite grains. The embrittlement strength of grain boundaries increases, even upon an increase in the phosphorus concentration at the boundaries. At higher concentrations (0.04%), carbon loses its neutralizing action on phosphorus. The local strength of grain boundaries decreases despite an increase in the concentration of carbon at the boundaries of the initial austenite grains.

CONCLUSIONS

The applicability of the developed technique for the quantitative evaluation of the local strength of grain boundaries of hardened steel has been shown using the delayed fracture tests and the methods of finite elements. The cooperative influence of microstructural factors, such as the presence of residual microstrains, segregation of phosphorus at the grain boundaries, and the carbon content on reducing the local strength of the boundaries of the initial austenite grains in martensitic steels has been evaluated quantitatively and their separate contributions have been determined.

The decrease in the local strength of the boundaries of the initial austenite grains in martensitic steel due to residual microstrains and the presence of the phosphorus contaminant has been estimated. The dependences of the local grain-boundary strength on the ratio of various levels of residual microstrains and on the atomic concentration of the phosphorus contaminant at the grain boundary in its segregation regions are determined. It has been shown quantitatively that the adsorption enrichment of the austenite grain boundaries with phosphorus leads to a decrease in the intergrain adhesion and facilitates the emergence and development of a crack along the boundaries of the initial austenite grains. The extent to which a decrease in the strength of the boundaries of the initial austenite grains leads to an increase in the tendency of quenched steel to the delayed fracture has been established.

A quantitative relationship between the concentration of carbon in steels and the embrittlement resistance of grain boundaries has been revealed. This relationship is implemented through the influence of carbon on grain-boundary phosphorus. In a narrow range of concentrations, carbon affects the formation of phosphorus segregations at the grain boundaries. The effect of carbon is positive at concentrations of up to 0.04%, since it reduces the embrittlement of boundaries by phosphorus segregations. At concentrations of more than 0.04%, carbon loses its neutralizing effect on the phosphorus segregation, so the concentration of phosphorus at the grain boundaries increases and their local strength sharply decreases.

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