

INVESTIGATION OF GRAIN BOUNDARY CHEMICAL COMPOSITION IN MARTENSITIC CLASS LOW-CARBON STEELS AFTER PROLONGED TEMPERING

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Nickel concentration at grain boundaries is studied in martensitic steels by Auger electron spectroscopic analysis after various heat treatment operations. Absence of a directly proportional relationship between nickel content within grain boundaries and impurity element concentration in these boundaries after quenching and long-term high-temperature tempering is established. The role of nickel in transformations occurring during high-temperature tempering in steels is demonstrated on the basis of existing ideas about the mechanism and driving forces for these transformations.

Keywords: martensitic steel, heat treatment, grain boundaries, Auger electron spectroscopy.

Introduction

A key area of technological breakthrough in various branches of industry is the steady development of structural materials with an improved set of physical and strength properties [1, 2].

Currently in aviation engineering there is active use of low-carbon steels of the martensitic class for critical components. The problem of improving transport system component manufacturing technology is one of the most important in contemporary engineering. First it is important for aviation component gear wheels, helicopter transmissions, vessel reactors, caterpillar machines, and also high-speed railway transport bearings, and many other mechanisms [3].

One of the main safety and operational reliability conditions for gas turbine components at elevated temperatures is retention of material structural stability. In this case there is practical interest in analyzing results of studying the structure of heat-resistant steels of the martensitic class after prolonged high-temperature heating [4, 5].

The operating conditions of contemporary machine components requires steels used for their manufacture with retention of high-strength properties at elevated temperature i.e., heat resistance. Use of steels of the martensitic class with a specific carefully selected alloy system resolves this problem. Various forms of chemical heat treatment used for preparing the optimum structure propose holding for a long time within temperature ranges close to those within the zone for development reverse temper brittleness. Concerning the effect of

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Table 1
Steel Chemical Composition

| No. | Steel | Element content, wt.% | | | | | | | | | | | | |
|-----|------------------|-----------------------|------|------|-------|-------|------|------|------|------|------|------|------|------|
| | | C | Mn | Si | P | S | Cr | Ni | Cu | Mo | V | Al | N | Nb |
| 1 | 10Kh4G1N1MF | 0.11 | 1.01 | 0.23 | 0.015 | 0.027 | 3.76 | 0.99 | 0.13 | 0.31 | 0.18 | – | – | – |
| 2 | 10Kh4G1N2MF | 0.10 | 0.98 | 0.22 | 0.016 | 0.024 | 3.64 | 1.99 | 0.12 | 0.31 | 0.18 | – | – | – |
| 3 | 10Kh4G1N3MF | 0.10 | 0.91 | 0.20 | 0.013 | 0.21 | 3.47 | 3.15 | 0.15 | 0.33 | 0.08 | – | – | – |
| 4 | 16Kh2N3MFBAYu-Sh | 0.18 | 0.49 | 0.33 | 0.011 | 0.015 | 1.85 | 2.90 | – | 0.44 | 0.13 | 0.04 | 0.01 | 0.14 |
| 5 | 15Kh3G1MFB-Sh | 0.15 | 1.88 | 0.35 | 0.031 | 0.024 | 3.00 | 0.16 | 0.25 | 0.35 | 0.16 | – | – | 0.16 |
| 6 | 20Kh3N3MFB-Sh | 0.18 | 0.53 | 0.28 | 0.023 | 0.022 | 2.86 | 3.02 | 0.24 | 0.47 | 0.16 | – | – | 0.18 |

non-carbide forming elements such as nickel many authors have expressed an opinion on these processes (for example [6-10]), but information is often contradictory and is not of a systematic nature. Some research indicates that the role of alloying elements is very significant [11 12].

In view of this a detailed study is made in the present work of the effect of nickel on transformations within low-carbon steels of the martensitic class during prolonged exposure in the temperature range close to that for development reverse temper brittleness.

Work was completed within the scope of implementing complex direction 8.2: High-temperature construction and corrosion resistance of weldable steels with high fracture toughness (“Strategic area for development of materials and their processing technology in the period up to 2030”) [13].

Research Procedure

A study is conducted in the work of experimental steels containing a different amount of nickel, i.e., about 1, 2, and 3% (Table 1, lines 1, 2, and 3 respectively). These steels were not subjected to cleaning by electroslag remelting. Steel of the series 16Kh2N3MFBAYu-Sh (see Table 1, line 4) was also studied, undergoing electroslag remelting. Specimen fractures were studied, tempered according to the regime: 500°C, 24 h + 540°C, 40 h, simulating exposure during two-stage nitriding.

Electron microscope study by the carbon replica extraction method with trans-illumination was conducted on specimens of steels 15Kh3G1MFB-Sh and 20Kh3N3MFB-Sh (lines 5 and 6 in Table 1).

Within this work chemical analysis of steel mono-atomic surface layers was performed by Auger electron spectroscopy (AES). Research was accomplished in a special

Auger-spectrometer from JEOL (Japan) grade JAMP-10S. Analysis of Auger electron spectra was conducted with recording them after electrical differentiation $dN(E)/dE$ that overcomes the considerable background, caused by scattered primary electrons and inelastically-scattered Auger electrons. Then the spectra obtained were analyzed in a computer by means of a special program in which weight concentration of each of the elements detected was calculated within a given surface region. A program for calculating these was proposed on the basis of an external standard method. According to this method Auger-spectra for the specimens studied were compared with standard spectra, containing the elements of interest in a known concentration.

Table 2
Results of Analyzing Spectra Obtained by EAS from experimental Steel Specimen Fractures
with a Different Nickel Content not Subjected to Electroslag Remelting

| Chemical element | Average nickel content in steel, wt.% | | | | | |
|------------------|---------------------------------------|---------------|-------------|---------------|-------------|---------------|
| | 0.99 | | 1.99 | | 3.15 | |
| | \bar{x}^* | δ^{**} | \bar{x}^* | δ^{**} | \bar{x}^* | δ^{**} |
| Ni | 4.6 | 1.8 | 18.3 | 5.6 | 21.4 | 9.3 |
| P | 1.3 | 0.5 | 0.4 | 0.1 | 0.2 | 0.05 |
| S | 0.1 | 0.05 | 0.3 | 0.1 | 0.2 | 0.1 |

Comments: * \bar{x} – mathematical expectation; ** δ – dispersion.

In addition, in JAMP-10S Auger spectrometer images of the test objects were obtained by means of recording secondary electron radiation in a scanning regime (SEI). As necessary, by using this image the surface section of interest was selected and an the analyzer electron beam was applied to it. These images were produced on a monitor screen.

Atomization of target (object) material was used as necessary in studying the chemical element distribution at a depth from a fracture surface. Material atomization was accomplished by Ar ions directly within the analyzer chamber.

Objects failed at -194°C (79 K) with the aim of obtaining grain boundary fracture. Spectra were recorded at 7-8 randomly selected points within a fracture surface.

Research Results and Discussion

Results are provided in Table 2. Examples of Auger spectra recorded from a fracture surface of experimental steels with a different average nickel content are provided in Fig. 1. Research results were treated by mathematical statistics methods. The average element content at a fracture surface was represented by mathematical expectation, and the region of experimental values obtained around the median determines dispersion. It is apparent from research results that the average nickel concentration at boundaries depends on the average content of this element within steel. This dependence is not directly proportional: the greater the nickel content on average within a steel composition, the higher is its concentration at a boundary and a greater interval is observed with respect to concentration of this element within a boundary. In steel specimens containing about 3% nickel, even in the area of a fracture, a zero concentration was detected. Phosphorus and sulfur concentration at a fracture surface in all cases exceeds the average concentration by several factors. A connection between nickel content within a fracture surface and impurity elements (phosphorus and sulfur) is lacking.

AES study of specimens of nickel-containing steel 16Kh2N3MFBAYu-Sh (VKS-7) was performed with the aim of studying nickel redistribution during various heat treatment operations. The objects for study were cut from a single lump of metal each time after performing one of the following operations: water quenching 920°C , 0.5 h; tempering at 580°C , 2 h; tempering at 520°C , 24 h + 540°C , 35 h. Fractures were prepared at a temperature of -194°C (79 K).

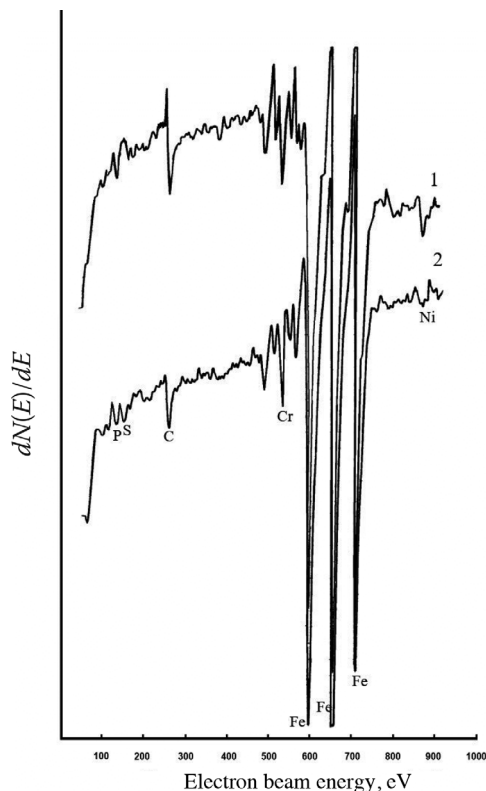


Fig. 1. Auger spectra recorded for the surface of experimental steel fractures with a different nickel content: 1 — steel 10Kh4G1N2MF; 2 — steel 10Kh4G1N1MF.

Curves for distribution and amount of nickel in relation to atomization depth are provided in Fig. 2. Assuming that a crack opening at a fracture surface proceeded through the crystallographic boundary of a grain we consider a fracture surface as a collection of uncovered austenite grain boundaries.

In a quenched condition nickel concentration at grain boundaries is 1.5%, i.e., this is less than the average concentration and increases at a depth up to 2.9%, i.e., it emerges into the average nickel concentration established according to chemical analysis data. During subsequent high-temperature tempering (580°C, 2 h) the nickel concentration increased at grain boundaries to 1.8%. An even greater increase in the amount of Ni up to 2.7% at a boundary proceeds after prolonged tempering, simulating nitriding process temperature conditions, and it actually emerges at the level of the average nickel content.

This nickel behavior may be due to the different sign of absorption activity of this alloying element with respect to grain boundaries of different phases. By comparing values of surface tension the author of the work suggests that Ni is negatively adsorption-active with respect to γ -iron [14]. In studies based on calculating the ratio of surface tension according to measurement data for dihedral angle at ternary junctions for different phases it was concluded that nickel is unfavorably active with respect to austenite grain boundaries since it reduces the $\sigma_{\gamma}^{\text{carb}}/\sigma_{\gamma}^{\gamma}$ ratio. Here $\sigma_{\gamma}^{\text{carb}}$ is surface tension at a cementite-austenite boundary, and σ_{γ}^{γ} is surface tension at an austenite-austenite boundary [14]. In addition, nickel has increased solubility in γ -phase. In this case when steel is in an austenitic condition and has an FCC-lattice, a nickel lattice is isomorphic, and energetically its outflow into the depth of a grain is suitable. Quenching secures the picture of Ni atom redistribution in an austenitic condition, which is seen in Fig. 2a. During tempering as a result of a concentration gradient there is equalizing diffusion in primary pores (Fig. 2b).

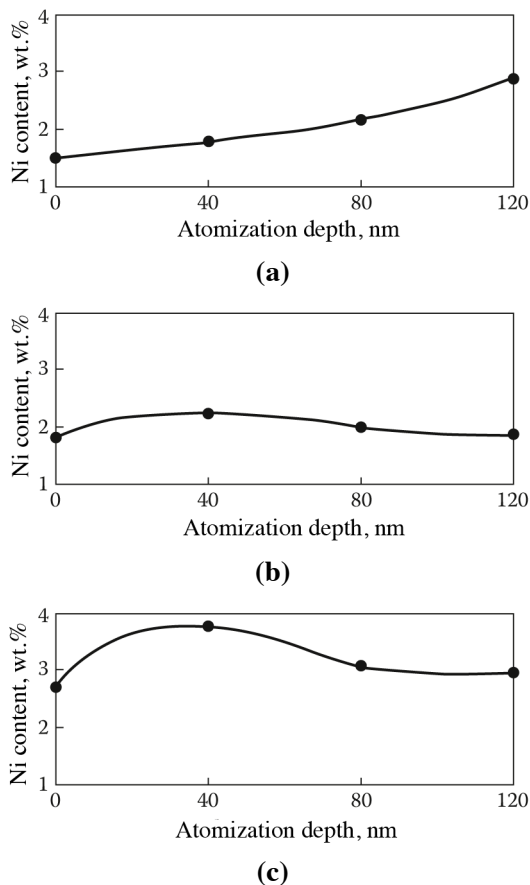


Fig. 2. Dependence of Ni content upon distance from fracture surface after different steel VKS-7 heat treatment operations: (a) 920°C, 1 h, oil quenching; (b) quenching + 580°C, 2 h; (c) quenching + 580°C, 2 h + 500°C, 26 h + 540°C, 33 h.

Within α -phase nickel is a diffusion pair with iron, which leads during tempering to formation of clusters, and accumulation of this alloying element. Formation of nickel accumulations at grain boundaries will proceed significantly more rapidly than within the grains themselves since the element substitution diffusion coefficient at boundaries is significantly higher than within crystals. According to radiographically obtained data for substitution of Ni^{62} isotope, the diffusion coefficient over a grain boundary is higher by two orders of magnitude than for grains [15].

Therefore, individual parts of large angle boundaries will contain an increased amount of Ni, and others with unite with alloying element. In Fig. 2c the Ni distribution is shown within the depth of these boundary areas. Output of Ni into accumulations may be explained by the introduced content immediately at the surface of a fracture compared with a material layer at a depth of 40 nm. An increase in Ni content at this depth compared with the average concentration is governed to all appearances by the tendency of this element to emerge at a boundary since it does not exhibit significant solubility within α -iron.

A gradual reduction in Ni concentration close to a fracture surface proceeds as a result of its ever increasing mobility as it approaches a crystallographic boundary. An increase in substitution atom mobility is determined by an increase in the degree of crystal lattice imperfection.

The nickel redistribution described above in favor of grain boundaries is possible, and therefore nickel does not participate in reactions with carbon as a carbide-forming element. In addition, this alloying element is expelled from cementite [16], which also facilitates an increase in its content at a boundary. Attention is drawn to

the very high branching of small- and high-angle boundaries in steels of the martensitic class. To all appearances, there is a considerable amount of Ni atom rapid movement paths, and this explains its high content within individual areas (see Table 2). However, since Ni diffusion mobility as a substitution element within a crystal at high temperature is not high, redistribution will proceed within quite local boundary regions of a crack in tenths or hundredths of nanometer not affecting the deep intragranular volumes.

In order to explain reasons for the differences described above within the structure of nickel-free and nickel-containing steels it is necessary to consider its sequence, i.e., structure changes during tempering. A number of hypotheses exist about moving forces and kinetics of these movements. In the current study concepts of Yu. I. Ustinovchikov are used laid down by him in a series of works, most significant of which are [17, 18]. Within the concepts developed in this work an attempt is made to use an exceptionally classical understanding connecting all processes of secondary phase formation from solution, redistribution within it of substitution and interstitial elements, and also phenomena leading to occurrence of temper brittleness, and to explain them on a single theoretical basis.

Traditional ideas include the fact that if in any way an unstable solid solution is obtained at a given temperature, then it should undergo two-phase breakdown with formation of phases having the least bulk free energy. This decomposition may proceed in two fundamental ways; *by a sinusoidal mechanism and by a nucleus formation and growth mechanism.*

In essence the approach proposed by Yu. I. Ustinovchikov includes the fact that a sinusoidal breakdown mechanism for non-stoichiometric composition alloys is considered as a uniquely possible mechanism of specific diffusion phase transformations. In [18] it has been demonstrated that classical theory of nucleus generation and growth is not fulfilled, and that alloys of all compositions, with the exception of stoichiometric, break down by a spinodal mechanism.

In contrast to nucleus generation and growth theory, where crystal structure defects play a governing role in the process of generation, being regions where the probability of forming new phase rarely increases compared with defect-free sections of a matrix, for generation by a spinodal mechanism presence within alloys of crystal structure defects is not entirely obligatory. In accordance with these ideas vacancies during decomposition play a purely kinetic role, and the role of dislocations and grain boundaries is determined by decomposition kinetics and thermodynamics.

Kinetics of these defects are directly affected by acceleration of alloying element diffusion. For example, the rate of interstitial element diffusion through dislocations is two orders of magnitude faster than with respect to defect-free areas of a crystal. Dislocations and boundaries affect decomposition thermodynamics in relation to the nature of dissolved chemical elements. Dissolved atom behavior depends upon the contribution of chemical energy E_{mi}^{chem} and elastic energy E_{mi}^{elas} to total mixing energy E_{mi}

$$E_{mi} = E_{mi}^{chem} + E_{mi}^{elas} , \quad (1)$$

So, for interstitial elements $E_{mi}^{elas} \gg |E_{mi}^{chem}|$. In view of the fact that primarily they form precipitates at dislocations and grain boundaries, thereby forming the start of a Cottrell atmosphere, and then phases. Phase generation with respect to defect-free areas proceeds in the case when places of preferential generation are exhausted, and interstitial elements remain unbonded into precipitates.

Substitution elements for which $E_{mi}^{elas} \gg |E_{mi}^{chem}|$ also tend to precipitate at dislocations and grain boundaries (mainly this concerns impurity elements within steel S, P, Sb, Sn, As, etc.).

Separation occurs first at grain boundaries and then at dislocations. In relation to defect-free areas these elements only separate in the case of a considerable concentration after filling areas of preferred precipitates.

For substitution elements, for which $E_{mi}^{elas} \ll |E_{mi}^{chem}|$, which is normally carbide forming elements Cr, Mn, V, W, Mo, etc., precipitate location is almost indifferent. However, some preference for precipitates at dislocations and boundaries as a result of more intense occurrence of diffusion.

During high-temperature tempering atoms of different elements form diffusion pairs. In [18] interactions are revealed whose energy in the opinion of the authors is quite high.

Mainly this is diffusion pairs of dissolved elements with iron atoms: iron carbide forming elements, iron non-carbide forming element, iron impurity substitution atom, iron-carbon, and carbide-forming element-carbon.

Drawing attention to all of the picture above of solid solution decomposition during tempering of heat-resistant steel of the martensitic class it is presented in the following form. As a result of chemical interaction for an Fe–C diffusion pair there will be cementite Fe_3C . As noted previously, crystal structure defects have a marked effect on interstitial elements since the elastic component of their substitution energy is higher. In view of this within the scope of Fe–C diffusion interaction there is formation a diffusion pair of a carbon-grain boundary and carbon-dislocation. The result of this type of interaction is cementite precipitation on different unidimensional and two-dimensional defects.

We consider a carbide-forming element-carbon diffusion pair. On heating as a result of considerable interaction energy between a carbide-forming element and carbon, compared with iron-carbon interaction, some carbon atoms are collected around statistically distributed free atoms of carbide-forming elements. It should be noted that stable carbon and alloying element chemical compounds do not form on heating, since at temperatures below 450–500°C there is a strong increase in diffusion mobility of carbon alone, and the diffusion mobility of carbide-forming elements remains almost unnoticeable.

On reaching a tempering high temperature and holding at this temperature a carbide-forming element–carbide pair breaks down. This proceeds as a result of an increase in diffusion mobility of carbon and the substitution element itself. Carbon leaves the vicinity of statistically distributed carbide-forming element atoms and participates in forming cementite. A carbide-forming element in turn forms a diffusion pair of a iron-carbide-forming element, as a result of which formation of a cluster of this element commences within the iron lattice. After forming this cluster the possibility develops of forming special carbides. Since special carbide formation is thermodynamically more suitable than forming cementite, during formation of alloying element carbides not only free but also bonded carbon participates in compounds, but also carbon emerging from the cementite composition, i.e., as a result of forming special carbides there may be partial dissolution of cementite.

A carbide-forming element-non-carbide-forming element diffusion pair is not nominated among diffusion pairs having reaction energy. However, according to some data (for example [19]) this interaction has a considerable effect on transformation proceeding during steel tempering. In discussing chemical element redistribution during high-temperature tempering in low-carbon steels of the martensitic class it should be considered that nickel reduces carbide-forming element diffusion mobility. This in turn leads to retardation of alloying element cluster formation.

Formation of an iron-non-carbide forming element diffusion pair, in this case iron-nickel, leads to occurrence of clusters. Since the elastic component of displacement energy for nickel as a substitution element is low, the probability of forming accumulations within a matrix and at grain boundaries should differ strongly. In spite of this a considerable amount of clusters might be expected at grain boundaries and a higher nickel concentration within them as a result of greater diffusion mobility of atoms over these boundaries.

According to the Fisher model lodged in [20, 21] at low temperature there is overriding diffusion of carbon atoms at boundaries where there is also formation of its segregation. With an increase in temperature some C atoms of these segregations emerge at boundaries within the volume and others form grain boundary carbides. Apparently emergence of carbon atoms from boundaries at high tempering temperature is stimulated by nickel, reducing carbon bond energy with lattice defects. As a result of this the amount of cementite precipitated at grain

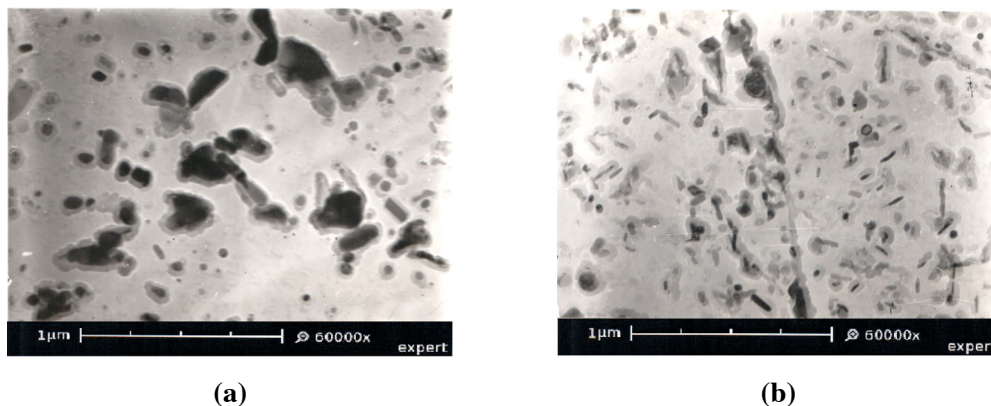


Fig. 3. Structure of steels 15Kh3G1MFB-Sh (a) and 20Kh3N3MFB-Sh (b) revealed by a replica extraction method (83×120 mm).

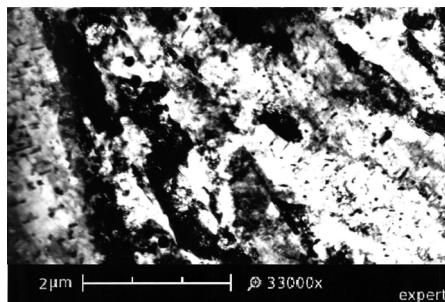


Fig. 4. Structure of steel 16Kh2N3MFBAYu-Sh after quenching and tempering, electron microscopy, light field image (78×135 mm).

boundaries in nickel steels is significantly less than in steels not having this alloying element within the composition, and therefore in steel containing nickel there is no preferential grain boundary precipitation of cementite; these precipitates are arranged comparatively uniformly throughout the whole volume of a crystal (which is seen in Fig. 3).

We have already drawn attention to presence of a comparatively large amount of acicular precipitates after high-tempering in steels containing about 3% nickel (see Fig. 3b). Generation and growth of these precipitates proceeds undoubtedly by a mechanism similar to that of supersaturated solid solution decomposition during ageing. They have the shape of disks lying within planes perpendicular to the replica plane. Presence of these “needles” or more correctly disks after quite prolonged exposure at high temperature points to the very considerable stability towards coagulation. The spatial arrangement of these precipitates is such that the direction along which individual neighboring “needles” are extended is between some sharp angle estimated as $53\text{--}60^\circ$ (see Fig. 3b).

It has been demonstrated in [18] that special carbides within steels generally and within steels containing Cr, Mo, V in particular, form through a stage of mixed zones of atoms of carbide-forming elements and carbon, and preferentially they have an FCC structure B1. This is due to the fact that the minimum deformation energy during separation of a new phase within the ferrite lattice is only achieved in the case when new phase particles have the shape of disks arranged within an α -matrix over direction $\langle 100 \rangle$. At the same time, as noted above, an electron microscope method has detected carbide precipitates within nickel-containing steel extended along the $\langle 111 \rangle$ α -phase direction (Figs. 4, 5). The Bagaratskii orientation relationship [22] makes it possible to identify these carbide precipitates as cementite, fulfilled during cementite precipitation within untwinned martensite

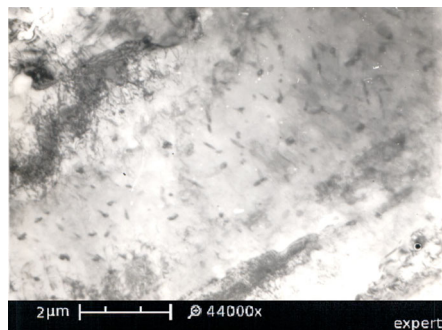


Fig. 5. Structure of steel 20Kh3N3MFB-Sh after quenching and tempering, electron microscopy, light field image (80 × 120 mm).

crystals:

$$[100]_c \parallel [011]_f; \quad [011]_c \parallel [111]_f; \quad [001]_c \parallel [211]_f. \quad (2)$$

In this case plates are extended along the $\langle 111 \rangle_f \parallel [010]_c$ direction where there is good conformity of the position of iron atoms within martensite and cementite [22].

After simple calculations, proceeding from crystal lattice geometry, the angle between crystallographic directions $\langle 100 \rangle$ and $\langle 111 \rangle$ is obtained equal to $54^\circ 48'$. Based on conformity of the angle between crystallographic directions in the range of angles between directions of precipitates within the nickel-containing steel matrix, and also considering the last reasoning, it is possible to conclude presence within experimental steel containing about 3% Ni after prolonged high-temperature tempering of both special carbides and iron carbides formed by a mechanism similar to an ageing mechanism and not subject to coagulation.

Some difference in chemical composition of the steels compared, expressed in presence of about 1% Mn in nickel-free steel, and absence of this in nickel-containing steel, cannot lead to marked correction of the reasoning provided since in spite of similarity of Ni and Mn in the periodic table the effect of them on structure and properties is often contradictory. For example, in [11] it is noted that nickel accelerates diffusion within ferrite, but manganese slows it down as a carbide-forming element. Mn enters into the composition of $(\text{Fe}, \text{Mn})_3\text{C}$ carbides, and nickel is expelled from them [14], etc. In view of this the effects detected demonstrate even more the degree of the effect of Ni on martensitic class steel structure after prolonged high-temperature tempering.

Cementite precipitates mainly formed over grain boundaries, are predominantly equiaxed, that is they are not directed along boundaries. Nickel reduces the magnitude of a ferrite-ferrite boundary free energy, which facilitates accelerated spheroidization of grain boundary cementite. All of the transformations described are apparently accelerated with flow there of additional nickel atoms from grain boundary spaces during high-temperature tempering.

Possibly presence not only of special carbides, but also cementite precipitates in the form of platelets or discs, uniformly distributed throughout a grain explain the reduction cementite deposited within grain boundaries, and as a result the nickel content and its partial dissolution with transfer of carbon from boundaries into a grain volume. The fact that a matrix contains cementite in the form platelets and not globules, points to formation of cementite in the later stages of tempering.

As has been shown, the nickel concentration at boundaries depends upon its average content within steel. Therefore, a connection may be proposed for the grade content of steel Ni and the intensity of carbide formation during tempering. This assumption is confirmed by the difference recorded in the experimental steel structure. Within images of a steel fracture containing less than 1% Ni, obtained in secondary beams by the Auger-spectroscopy scanning method (Fig. 6a), dark veins of cementite phase are observed over grain boundaries. Within

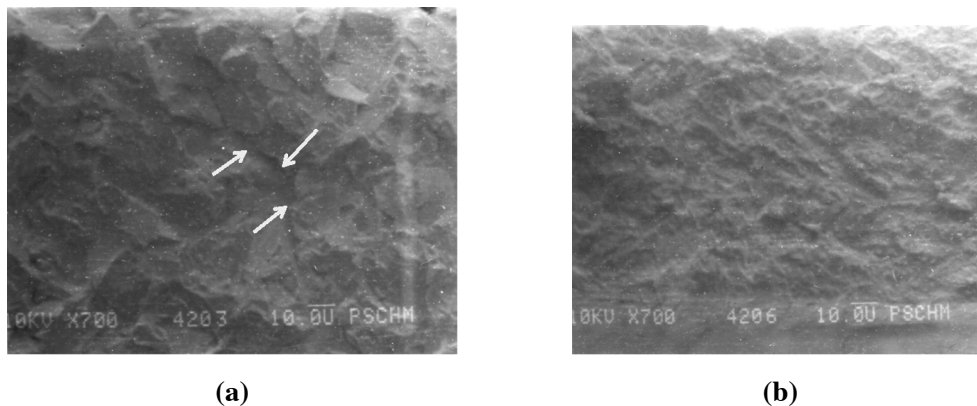


Fig. 6. Images of steel 15Kh3G1MFB-Sh (a) and 20Kh3N3MFB-Sh (b) fractures in secondary electrons. Arrows show cementite precipitates; $\times 700 \times 1.25$.

a fracture of steel containing 3% of this alloying element these precipitates are not detected (Fig. 6b). The appartenance of these veins to carbide phase is confirmed by the shape of the Auger carbon peak (Fig. 7), which on introducing carbide into an electron beam has a typical saw-like form (marked by a circle in Fig. 7). With the aim of excluding random effects energy spectra they were recorded several times in succession: with suggested cementite precipitate after careful application and with neighboring regions for comparison.

In order to explain all of the situations connected with tempering of thermally stable nitrated steel of the martensitic class consideration should be given to an iron-impurity element diffusion pair. It is well-known that impurity element segregation such as S, P, Sb, Sn, and As leads to occurrence of reverse temper brittleness.

Drawing attention to the temperature and duration of exposure for nitriding, occurrence might be expected of steel temper brittleness during occurrence of the production process.

According to opinions lodged in [17, 18] when steel temperature becomes adequate for diffusion of impurity atoms (350–550°C), a carbide-forming element impurity element diffusion pair arises. This leads to the situation that impurity atoms diffuse towards carbide-forming atoms dissolved within solid solution. As noted previously, carbon atoms at this time start to move into defects and carbide-forming elements develop free bonds [23], which are balanced by impurity atoms. The latter are retarded by carbide-forming elements and in a cluster formation stage. During formation of special carbides based on clusters, they cease to be an area of impurity atom attraction and do not tend towards boundaries.

Experiments conducted on steels with a different nickel content (see Table 2) showed that after prolonged high-temperature tempering at grain boundaries there is not a strong increase impurity element content, i.e., P and S, in spite of the fact that these steels are not cleaned by electroslag remelting and the level of impurities within them is quite high. In [24] on the example of vanadium-containing and molybdenum-containing steels it was demonstrated that when these carbide-forming elements are in solid solution or in the form disk-shaped precipitates over α -phase [100] planes, in which carbon atoms only occupy a bond partially, phosphorus atoms are also within a grain not forming boundary precipitates. How special carbides Mo_2C and VC are recorded within a steel structure and solid solution is connected with carbide-forming elements, brittle failure becomes intercrystalline, and at a fracture surface a high phosphorus concentration is observed.

A relatively low level of P and S grain boundary content in experimental steels (see Table 2) after prolonged high-temperature tempering is apparently determined by the fact that impurity elements are bonded into a grain of some carbide-forming elements not forming special carbides. In test experimental steels the highest value of relative chemical reaction energy with phosphorus for molybdenum ($\beta_{\text{MP}}^{\text{B}} = 33.0 \text{ kJ/mole}$) [18] and

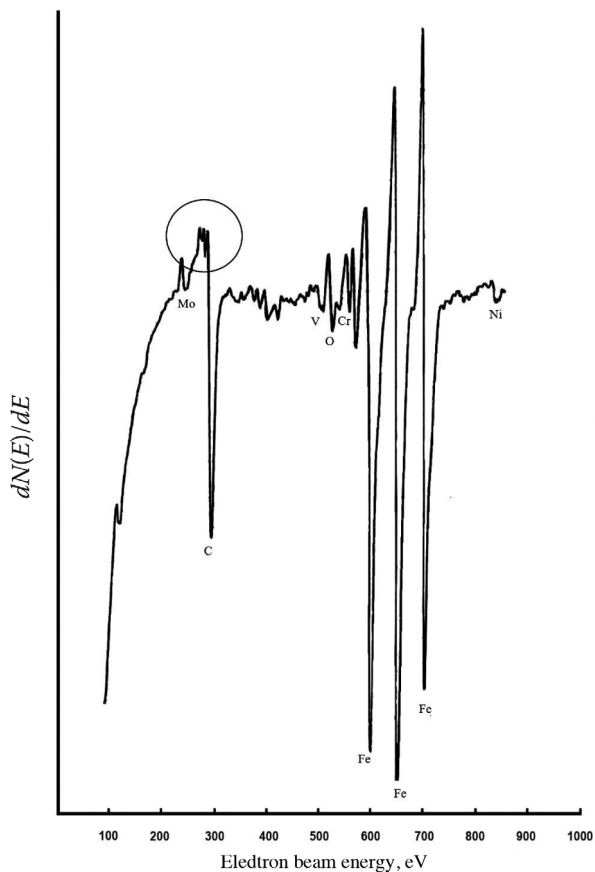


Fig. 7. Spectrum obtained by AES method from a nickel-containing steel 16Kh2N3MFBAYu-Sh (VKS-7) specimen fracture surface recorded from cementite precipitate.

vanadium ($\beta_{MP}^B = 27.0$ kJ/mole) [25]. Here β_{MP}^B is the metal-phosphorus relative interaction coefficient determined within the volume $(Fe, Mn)_3C$ phosphides. For comparison: for nickel $\beta_{MP}^B = 5.6$ kJ/mole, and for manganese $\beta_{MP}^B = 12.5$ kJ/mole. Other alloying elements have low reaction energy and in an inadequate amount within steels for preventing grain boundary precipitation of impurities.

Based on the reasoning provided above it may be concluded that role of an element, bonding impurity elements within a grain, is played mainly by Mo. This element has the least affinity for phosphorus among all of those present within the test steels. In addition, formation of equilibrium Mo_2C carbide requires considerable carbide-forming element accumulation at carbide forming atoms, and consequently a considerably greater time shall we say for forming VC carbide. Vanadium in contrast forms special carbides and participates weakly in impurity stabilization within a grain. The substitution energy of 17 kJ/mole is considerably lower than the substitution energy for phosphorus at 38 kJ/mole [26], which determines the tendency of phosphorus atoms, freed from bonding with molybdenum atoms, to be present at grain boundaries, and also uniform distribution of molybdenum atoms between grain boundaries and a grain body.

This conclusion may be confirmed by data in [11]. In steel 34KhN3MF after tempering at 350°C for 6 h 23% V, 100%Mo, and 73% Cr of their total amount remain in solid solution after quenching.

Among a number of factors reducing temper brittleness it is possible to relate a small amount of carbon in all of the nitrated steels studied. A reduction in the amount of carbon should reduce the probability of all carbide-forming elements to be bonded into special carbides.

As a result of the studies of chemical composition of experimental steel grains no correlation is detected between nickel and phosphorus concentration within boundaries. Consequently, with an increase in nickel content the amount of phosphorus decreases somewhat (see Table 2).

Since in a number of works the reinforcing effect of Ni is confirmed on impurity atom precipitation at a boundary the greater its concentration within steel, and in [12] Ni is even excluded from the composition of heat-resistant steels aimed at explaining the role of nickel in embrittlement resting on conducting research.

Previously an assumption has been made about the relative effect of nickel on transformations taking place during tempering steel of known compositions, which in particular includes the fact that an alloying element reinforces carbon atoms with structural defects, including grain boundaries in different stages of tempering, and possibly facilitates partial dissolution of grain boundary carbides in later stages.

Both of these phenomena facilitate an increase in carbon content within the volume of a grain. As a result of number of reasons described this carbon with high-temperature tempering may be within the solid solution composition. It attempts to be supplemented having an accumulation of carbon atoms around clusters of carbide-forming elements and reduces the possibility of existence in subsequent free bonds for holding impurity atoms within grains. Therefore, additional discharge of carbon from boundaries generates critical movement of impurity atoms towards boundaries. In fact, in our view this represents a mechanism of "embrittling effect reinforcement" by nickel in alloy steels. Consequently, it is not connected with synergetic cosegregation of N and P atoms, as proposed in [12, 6].

Absence within the nickel-containing steel studied after prolonged high-temperature tempering of phosphorus and sulfur precipitates in the form of monolayers over grain boundaries is connected to all appearances with release in steels of V and Mo simultaneously in optimum amounts on one hand, and with the low content of carbon within them on the other hand. Vanadium and molybdenum form carbides with different crystal lattices and stoichiometric composition, and they are also found within steels in an amount complicating rapid cluster formation. Nickel, somewhat reducing diffusion mobility of carbide-forming element atoms slows down special carbide formation.

So, after holding at the temperatures and times indicated only vanadium forms visibly in a stable condition, and formation of stable molybdenum carbide is in the stage of forming accumulations within which impurity atoms is retained. This delay in Mo carbide formation with respect to VC is apparently explained by the required presence of twice as much carbide-forming element in order to separate stable carbide.

The possibility of forming Mo_2C carbide in the temperature range for this time points to the fact noted previously of presence within grains of fine not coagulated cementite platelets apparently separated in the last stages of tempering. Separation of cementite in the last tempering stages is energetically less suitable process than formation of stable Mo_2C carbide. Consequently, occurrence of the first of these processes confirms the impossibility in this stage of occurrence of the second. Therefore, material condition after high-temperature tempering for tens of hours may be considered as intermediate and unstable. It is apparent that with an increase in holding time all of the carbide forming elements within steel enter into the carbide composition and free impurity atoms form their own precipitates at boundaries.

CONCLUSIONS

On the basis of Auger spectroscopic studies of the chemical composition of surface fractures flow-carbon steels of the martensitic class it has been established than nickel exhibits negative adsorption activity with respect to austenite grain boundaries (horophobicity) when steel is in an austenitic condition and tends to emerge at grain boundaries when the matrix has an FCC-lattice. For example, within steel 16Kh2N3MFBAYu-Sh after quenching from 920°C the nickel concentration at grain boundaries is less by a factor of 2 to 2.5 than within

their volume. In addition, Ni atoms form accumulations at grain boundaries. After tempering by a regime: 580°C, 2 h + 500°C, 24 h + 540°C, 40 h for martensitic class low-carbon class the maximum nickel content in accumulations at grain boundaries increases from 6.4 to 30.7%, and with an increase in average nickel content in steel from 0.99 to 3.15 wt.%, and the total content of sulfur and phosphorus atoms varies from 2 to 0.6 wt.%. Absence has been established of a directly proportional relationship between the nickel content at boundaries and the concentration there of impurity elements.

On the basis these experiments and existing ideas about the mechanism and moving forces of transformations proceeding during high-temperature tempering steels the double effect of nickel is shown by expelling carbon from grain boundaries and increasing its mobility in

α -phase nickel facilitates accelerated replacement of impurity element atoms and their bonds with carbide-forming elements. As a consequence of this there is quite rapid formation of impurity atom monolayers over grain boundaries. Simultaneously nickel slows down diffusion of carbide forming elements and consequently formation of special carbides. This prevents accelerated formation of monolayers of impurity atoms at grain boundaries. As a consequence presence within low-carbon steels of the martensitic class of such carbide-forming elements Mo, W, Nb, etc., the occurrence of phenomena connected with the process of reverse temper brittleness slows down and carbon expelled from boundaries forms fine carbides with iron.

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