

Conference paper

Alexander I. Zaitsev*

Prospective directions for development of metallurgy and materials science of steel

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Abstract: The features of current state of metallurgical technology and materials science of mass high-grade steels are viewed. A promising direction for principle improvement of the complex of properties and qualitative characteristics of steel including those, which are difficult to combine, is shown. It is the development of adequate physico-chemical methods of prediction and efficient technology methods of management of non-metallic inclusions, forms of presence of impurities, phases precipitations, structural state, including uniformity over the volume of metal. Additionally this approach allows reducing costs and expanding the raw material base. Its effectiveness is illustrated by the results of research carried out for a number of groups of mass high-quality steels.

Keywords: chemical and structural homogeneity; complex composition; forms of presence of impurities; mass high-grade steels; mechanical properties; Mendeleev XX; metal processing; metallurgical technology; non-metallic inclusions; phases precipitations; quality characteristics; service properties; structural condition.

Introduction

Currently, steel multiple keeps ahead of light and non-ferrous metal alloys, glass, ceramics, polymers and other alternative construction materials in production and consumption. This is due to not only the availability and wide occurrence of iron ores in nature, relative simplicity and non-high energy-output ratio, but also, above all, the rapid growth of complex of indicators level and stability of technology, service properties, qualitative characteristics of steel while reducing costs of production, intensification of through technology process and operation of the equipment. In particular, over the past 5–10 years indicators of technological and service properties of steels have increased several times. At the present time the problem setting for development of a wide range of common grades of steels is to achieve the extremely high levels of strength (to 2000–2200 MPa), ductility (elongation to 55–60 %), low temperature impact toughness ($KCV_{-60^{\circ}\text{C}}$ to 300–400 J/cm²), formability, corrosion resistance, and quality characteristics (the content of some types of non-metallic inclusions should be not more than 2 inc/mm², regardless of their size, the number of surface defects – not more than 1–2 per tonne of rolled steel) [1]. It is important that in most cases it is necessary to provide a high value not only of one of these parameters, but the whole complex of properties, which are usually difficult to combine, such as strength and ductility; strength, low temperature impact toughness, and corrosion resistance.

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***Corresponding author: Alexander I. Zaitsev**, I.P. Bardin Central Research Institute for Ferrous Metallurgy, Moscow, Russia, e-mail: aizaitsev1@yandex.ru

Promising directions of improving the complex of properties of steel and features of their realization in modern technologies

Pointed out circumstances require the use of innovative approaches. Results of a large amount of researches [1–3], modern manufacturing practices, and materials engineering of steel demonstrate that a key-role among them belongs to adequate physical, physico-chemical, and kinetic methods of prediction and efficient technology management techniques of following factors:

- various ways of intensive exposure during the treatment of liquid and solid metal, process interrelation;
- characteristics (the type, number, size, morphology, and distribution over metal volume) of non-metallic inclusions, precipitations of excessive phases, structure components;
- content and, above all, the forms of impurities presence;
- phase composition and structure state of steel;
- homogeneity of chemical and phase composition, structure state, and properties in the metal volume.

The implementation of each of these approaches requires the account of behavior of a large number of complex processes and phenomena that take place during the treatment of liquid and solid metal. Their direction and intensity of the flow depend on many technological parameters. Besides, these processes are becoming increasingly interconnected because of more intensive effect on the metal by the electric arc heating, processing the melt with an inert gas, ligatures, and modifiers containing active alkaline earth and rare earth metals, degassing of steel, high speed of continuous casting, the temperature-deformation treatment, including processing during the annealing of rolled steel. By means of it and due to the use of new materials the characteristics of present non-metallic inclusions, phase precipitates, forms that impurities occur, and structural components of steel have changed fundamentally [3, 4]. In particular, a natural tendency to obtain very low sulfur content (in some cases less than 0.001 %) for increasing the cold resistance and toughness of steel results in achievement of good deoxidized state of metal (active oxygen content of not more than 0.0005–0.0008 %) and slag (FeO content of not more than 0.5–1 %). Under such conditions, MgO reduction from the lining and coating slag becomes possible when its thermodynamic activity is high [5]. As a result, during ladle treatment of metal formation of inclusions based on aluminum-magnesium spinel and other $\text{MgO-Al}_2\text{O}_3$, $\text{MgO-Al}_2\text{O}_3\text{-CaO}$ compositions takes place. In many cases, this type of inclusions dominates in the modern steels. As a rule, the inclusions of this type were practically absent in steels produced more than 10 years ago. Thus, the types of non-metallic inclusions, which are present in modern steels, have changed fundamentally.

The change in the size of non-metallic inclusions is no less significant. It is well known that the above-noted intensive impact on the metal melt promotes the creation, but not the growth of already present inclusions (precipitates), and leads to a regular decrease in their sizes, which often belong to the range of nanometer values. As a result, when modern metallurgical technologies are implemented the processes of formation and evolution of nanoscale objects in steel take place already during the processing of metal melt [6]. There are all prerequisites for their use instead of or in addition to the precipitation of excessive phases, structural components, which formed with the participation of special alloying and microalloying components during the processing of solid steel and play a key role in achieving the desired structural state and high complex properties of steel [3, 4].

Special features of the formation and evolution of complex non-metallic inclusions and their influence on steel properties

Similarly, due to kinetic reasons, in many cases not independent precipitation dominates, but deposition of phases on the surface of already present precipitates is preferred. Thus, inclusions (precipitates) of a complex composition are formed. A variety of such types of inclusions is rather large, and the formation of many of

them, until recently, was considered as impossible or unlikely. For example, complex precipitates of titanium nitride on the corundum inclusions were observed in cast billets of Ti-microalloyed structural steel [7] (Fig. 1). After heating the billets for rolling, besides the well-known complex precipitates of titanium and niobium nitrides (carbonitrides) the inclusions containing the titanium nitride with manganese and calcium sulfides, aluminum-magnesium spinel were determined [7]. During hot rolling and subsequent cooling cementite deposition on the surface of these complex inclusions is possible. As will be shown below, this can have a significant positive impact on the complex properties of steel. It should be noted that until now there has been no well grounded physico-chemical, kinetic, structural and geometric methods for prediction of the forms of existence of these complex non-metallic inclusions and conditions for their formation.

The evolution of other types of non-metallic inclusions has also complicated character. For instance, deposition of calcium and manganese sulfides on the surface of inclusions based on alumina-magnesium spinel and other $\text{MgO-Al}_2\text{O}_3$, $\text{MgO-Al}_2\text{O}_3\text{-CaO}$ compositions, and further deposition of cementite, due to similarity of their crystal lattice structures [3], have been fixed during the processing of melt, crystallization, and cooling of steel.

The impact of the formed inclusions on the resulting structural state and complex of steel properties significantly vary depending on their characteristics. In particular, it is well known, that the presence of titanium nitride precipitates of large sizes (more than 8 to 10 μm) promotes the occurrence of defects detected by ultrasonic control, adversely affects the low temperature impact toughness, resistance to hydrogen cracking and other stress-corrosion fracture of rolled steel [8]. The formation of small-sized complex TiN precipitates on the corundum (Fig. 1) prevents the formation of large individual particles. Hereby their ability to inhibit the growth of austenite grains during heating of billets for rolling, austenitizing, and welding of steel is important. The ability of small-sized TiN precipitates to restrain recrystallization during rolling, owing in particular to increasing the carbon fraction in niobium carbonitride precipitates, is also relevant. In contrast, the formation of particularly large-sized complex titanium and niobium carbonitride precipitates reduces positive resource of Nb for improving the complex of properties and even leads to the occurrence of defects in steel [9].

Inclusions based on alumina-magnesium spinel and other $\text{MgO-Al}_2\text{O}_3$ compositions are not corrosive. The small-sized inclusions, in practice, do not have a negative impact on the complex of service characteristics of finished metal, and even may have some positive effect due to the inhibition of the grain growth during austenitizing and recrystallization of steel. In particular, it is well known that aluminum deoxidized steels are inherently fine grained unlike the steels deoxidized with manganese and silicon [10]. This testify the ability of corundum and corundum-based inclusions of defined dispersion to inhibit grain growth of steel during austenization. At processing, cooling, and crystallization of steel during continuous casting calcium sulphides and, mainly, manganese sulphides may deposit, as noted, on the surface of the considered inclusions, which

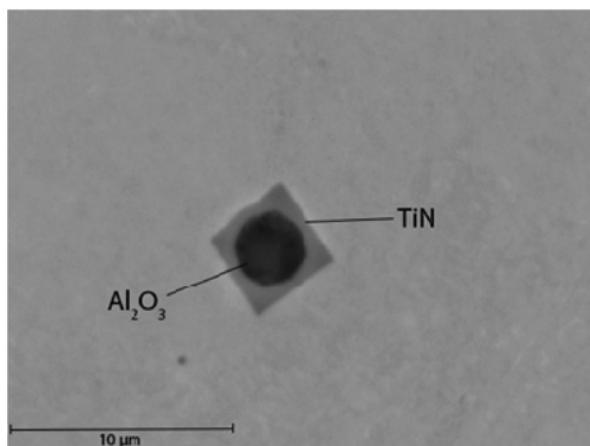


Fig. 1: Typical external view of titanium nitride precipitation on the corundum inclusion surface.

are based on alumina-magnesium spinel. As a result of formation of certain sulphide component the inclusions become corrosive. The presence of significant amounts of such complex oxide-sulfide inclusions provokes a catastrophic acceleration of local corrosion processes in chlorinated water and a number of other media [11]. Because of the ability to multiply reduce the service life of structural steels these non-metallic inclusions have been called corrosion-active non-metallic inclusions, CANI [11, 12].

During subsequent heating and thermo-deformation treatment of steel further transformation of considered inclusions takes place. It can occur in both directions: deposition on the new oxide inclusions and dissolution and subsequent transformation of sulphide component by the mechanism of coalescence with manganese sulfide transfer and increasing the size of complex inclusions. As a result, a low content of complex oxide-sulfide inclusions, which adversely effect on the resistance of steel against local corrosion, takes place at low and high temperatures and duration of heating of billets for rolling [7]. In the first case, the independent manganese sulfide precipitation does not have time to redistribute to the surface of the present inclusions, which are based on aluminum-magnesium spinel, giving them corrosivity. And, in the second case, the sulphide component has time to coalesce quite completely resulting in formation of a small number of large-sized complex oxide-sulfide inclusions with sulfide component.

Additional deposition of excessive phases (carbide, carbonitride, carbosulfide) on the surface of the sulfide, oxide-sulfide, and other complex inclusions results in formation of precipitations of complex structure and can lead to changes of mechanical properties. For instance, cementite (Fig. 2) having higher strength and hardness as compared with a metal matrix can play the role of a strengthening phase. These inclusions make a significant contribution to the strengthening of steel without lowering ductility. The results of the detailed theoretical and experimental studies [13] indicate that the attainable “seeming” volume fraction

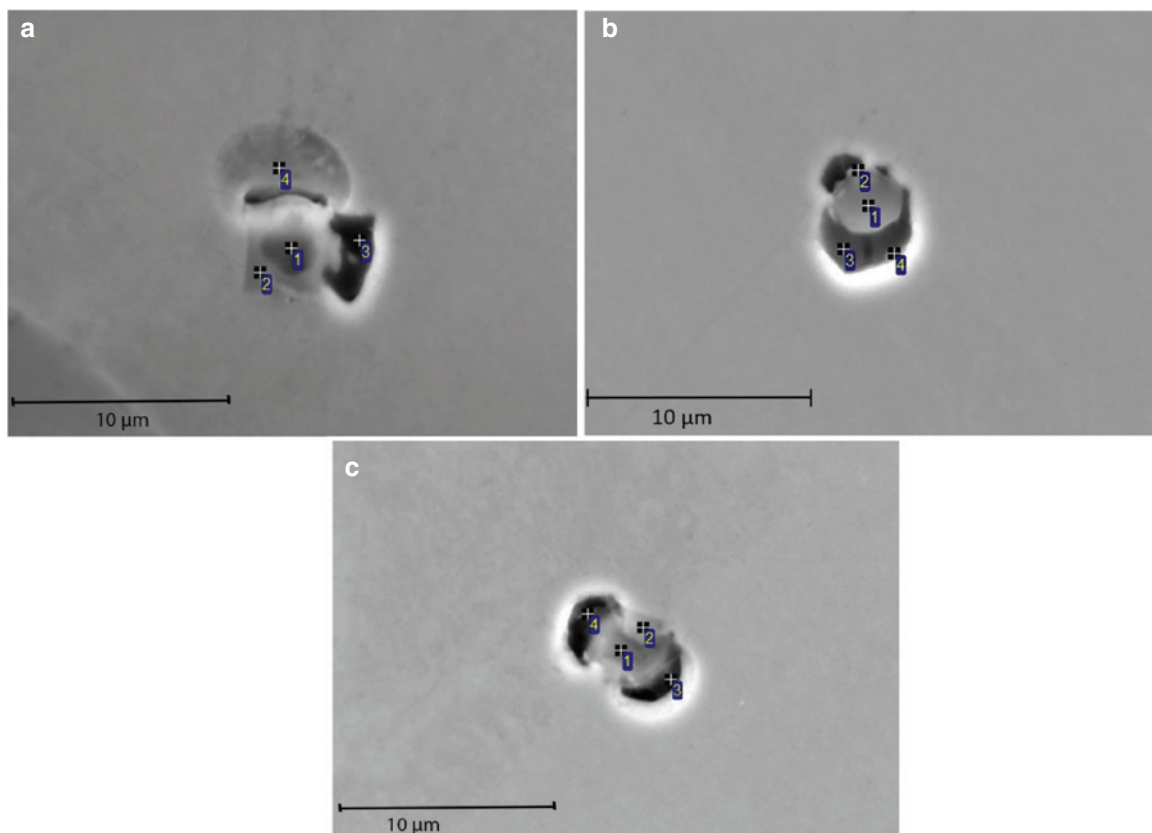


Fig. 2: Precipitation of cementite on the surface of the complex of non-metallic inclusions: (a) TiN and aluminum-magnesium spinel (1 – aluminum-magnesium spinel, 2- TiN, 3,4 – cementite), (b) MnS and aluminum-magnesium spinel (1 – MnS, 2 – aluminum-magnesium spinel, 3,4 – cementite), (c) calcium and manganese sulfide (1,2 – CaS + MnS, 3,4 – cementite).

of the strengthening phase can reach significant values and lead to a fundamental, in some cases multiple (more than 2–3 times) increase in the strength properties of steel, while maintaining high levels of plasticity. Thus, mentioned results indicate a fundamental change in the nature of the influence of non-metallic inclusions on the metal properties, depending on the parameters of their formation and evolution in the course of processing steel. Presented information reflects the regularities of influence of only a small number of probable complex non-metallic inclusions (precipitates) on the quality characteristics and properties of steel. This necessitate the creation of a fundamental knowledge database, adequate physico-chemical models for prediction of the formation and evolution of complex non-metallic inclusions (precipitates) at all stages of steel manufacturing (process stages), and the development of effective technological methods for producing metal with previously unattainable complex of properties and quality indicators. This approach offers conceptually new opportunities and mechanisms for creation of new high-graded steels with a significant reduction of material and energy costs of manufacturing. The reason is that these complex inclusions may include widespread elements, which are usually present in the steel and slag: Ca, Al, Mn, Si, C, and even so-called detrimental impurities: O, N, S [3, 4, 13]. Also significant effect is achieved by neutralizing the negative effect of impurities on the technological and service properties of steel.

Special features of impurities influence on the properties of steel depending on the form of their presence

There is another close and interconnected problem: content and form of the presence of impurities in steel. This is quite natural, in many respects, since the impurities are involved in the formation of both individual and complex inclusions (precipitates). Their influence on the properties of steel varies greatly depending on the obtained characteristics, in particular sizes. For example, forming MnS precipitates becomes possible at high temperatures due to high contents of manganese and/or sulfur in the steel. In many cases, it takes place during crystallization of last portions of the metal melt [3]. The occurring precipitates are large-sized. Due to their ability to deformation, they elongate along the direction of rolling during temperature-deformation treatment and get a threadlike shape. The presence of these inclusions is a negative factor, since it gives rise to the creation of the metal defects detected by ultrasonic testing, and leads to catastrophic reduce in cold resistance, toughness, resistance to different types of corrosion and corrosion-mechanical destruction of steel. When content of manganese (0.5–0.6 %) and sulfur (0.001–0.003 %) is balanced, MnS precipitates are formed at relatively low temperatures resulting in significant or even complete their dissolution during heating billets for rolling. This is established by the results of calculations [7, 14] for 20KSH, 13HFA steels with compositions presented in Table 1 (Fig. 3).

The presence of submicron MnS precipitates along with niobium carbonitrides in steel during hot rolling causes moderation of recrystallization that leads to structure refinement and increases the complex of mechanical properties. Indeed, analysis of production of hot-rolled 20KSH, 13HFA steels shows that when sulfur content is in the range 0.001–0.003 % the regular somewhat higher strength level and dispersion of the metal microstructure are obtained. This results in almost complete dissolution of manganese sulfide during heating billets for rolling, followed by forming MnS precipitates at hot plastic deformation. For the same reason, in many cases the yield strength drop has been detected at delivery trials of low-carbon cold-rolled steels of 08U type with requirements to the chemical composition presented in Table 2 [15].

Table 1: Results of determination of the chemical composition of the investigated steels of 20KSH, 13HFA grades.

Steel grade	Chemical composition (wt%)												
	C	Si	Mn	P	S	Cr	Ni	Cu	Al	N	V	Ti	Nb
20KSH	0.201	0.22	0.540	0.007	0.002	0.035	0.032	0.053	0.036	0.0068	0.002	0.004	0.046
13HFA	0.059	0.26	0.589	0.009	0.003	0.627	0.122	0.119	0.026	0.0063	0.055	0.0044	0.031

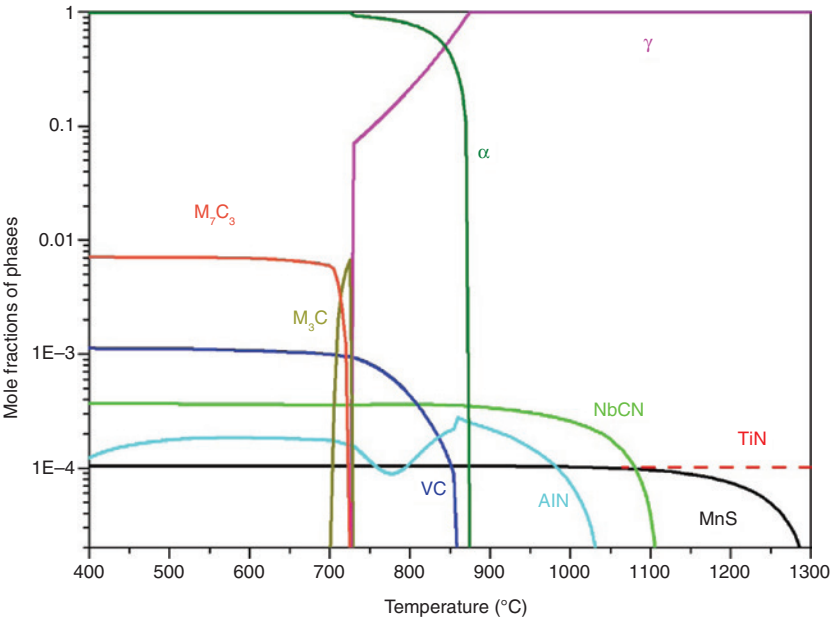


Fig. 3: The results of calculation of stability conditions of excessive phases precipitates in the steel 13HFA (Table 1) in accordance with [14].

Table 2: Requirements to the chemical composition of steels of 08U type.

Content of elements (wt%)					
C	Mn	S	P	Si	Al ^a _{as}
≤0.07	≤0.35	≤0.025	≤0.020	≤0.03	0.02-0.07

Al^a_{as}, Acid-soluble aluminum.

This is caused by to the natural progress of metallurgical technology, which has led to a reduction in the sulfur content in steel. As a result, the dispersion of MnS precipitates has increased contributed to the hardening of steel that is not desirable in this case.

An additional increase in the complex of mechanical properties of hot-rolled as well as cold-rolled products may be due to the formation of complex MnS precipitates with cementite and aluminum nitride (Fig. 4). In particular, a detailed study [16, 17] has shown that their formation leads to following processes: a decrease in the content of interstitial elements – carbon and nitrogen in solid solution; moderation of separate cementite precipitates formation and grain size variation of microstructure; facility of recrystallization of cold-rolled product.

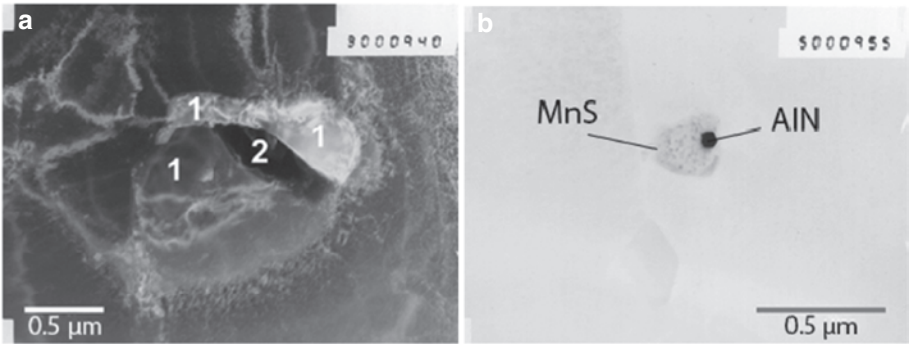


Fig. 4: Manganese sulphide precipitation in low-carbon steels with: (a) cementite (1 – Fe₃C, 2 – MnS), (b) aluminum nitride.

Thus, it results in favorable significant increase in ductility and formability, and reduce in yield strength of galvanized cold-rolled low-carbon steels. This makes it possible to use cold-rolled products of ordinary low-carbon steels of 08U-type instead of much more expensive ultra low-carbon steels for the manufacture by means of stamping, deep drawing. It is important that the number and size parameters of formed during hot rolling manganese sulfide precipitates, which are optimum for subsequent deposition of the aluminum nitride and the cementite on their surface, obtained when sulfur content in the steels of 08U-type is 0.012–0.018 % (Table 2) [16, 17]. This coincides with an optimal range of sulfur concentrations in the 08U steel that was previously found [15] in order to prevent the possibility of exceeding the maximum allowable values of yield strength.

On the other hand, the formation of complex precipitates of cementite with MnS and, as noted above, with other types of precipitates, which act as strengthening phase, is an effective way to increase strength of hot- and especially cold-rolled high-strength low-alloy steels, while ductility is maintaining or even increasing. Strengthening effect in the case of cold-rolled high-strength microalloyed steels for automobile body sheet can reach the significant values – more than 100 MPa [3, 4]. This can be comparable with the hardening effect associated with the grain refinement, which requires the use of expensive special microalloying system and manufacturing technology. The above example does not set the possible limits for improving the properties. For example, according to [13], a rise in the sulfur content from 0.009 till 0.018 %, all other conditions being equal, increases the yield strength of the steel from 200 to 500 MPa due to the growth of the volume fraction of the hardening phase precipitates. Formation of cementite precipitates, including nanoscale, during annealing cold-rolled steels is controlled by the characteristics of the initial microstructure (grain size after hot rolling, its elongation after cold rolling, number, type, size, morphology of excessive phase precipitates), and temperature-time parameters of heating, soaking, and cooling during annealing. By adjusting the ratio of places for preferred cementite precipitation (grain boundaries or surface of present particles of excessive phases) and the cooling rate, it is possible to change the morphology of the phase precipitates [4, 13], including nanoscale, and thereby affect the properties providing various parameters, in particular a unique combination of strength and ductility properties. Use of the formulated approaches allowed the development of a new class of cold-rolled ferrite-cementite steels of different strength categories (yield strength up to 500–550 MPa) with not previously achievable ductility (elongation of 30–35 %).

Positive effect on mechanical properties has been detected for complex precipitates of cementite and carbides (carbonitrides) of niobium and vanadium in the hot-rolled steel. In particular, it was found that the cementite deposition on the surface of interphase vanadium carbonitride precipitates, which formed during hot rolling in the course of $\gamma \rightarrow \alpha$ transformation, leads to their stabilization and remaining under extended annealing in bell furnaces [18]. This ultimately results in a microstructure dispersion and improving the complex of properties of annealed cold-rolled steels.

The variety of the possible directions of influence of present components and impurities on properties of boron steels is no less interesting and actual in recent years. This is caused by intensive researches and developments of high-strength steels, including hot stamping. Boron is an element, which most effectively increases the hardenability of steel at extremely low concentrations – of the order of thousandths of a percent. Its use allows not only to reduce the degree of alloying, the cost, but also greatly enhance workability, weldability, and a number of other service properties of steel. Nevertheless, for the implementation of a positive influence it is necessary to provide the boron presence in solid solution. This is a cause of its segregation at grain boundaries reducing the surface energy and as a result, complicates the formation of ferrite nuclei because of stabilizing austenite [19]. Alternative process is the formation of a complex $M_{23}(CB)_6$ borocarbide [20–22] and BN nitride [23], which, on the contrary, reduce hardenability as well as hot ductility. On the other hand, the morphology of the BN precipitates is of importance. If the boron nitride precipitation takes place on the surface of presented TiN and MnS particles, and they are uniformly distributed over the volume of the metal, this leads to improving the hot ductility, resistance to intergranular cracking and other characteristics [24]. Moreover, such complex precipitations can have nanometer sizes and participate effectively in the implementation of various mechanisms for strengthening steel.

In order to prevent the formation of unfavorable types of $M_{23}(CB)_6$ and BN precipitations and stabilization of boron state in solid solution the additional Ti, Nb, V, Mo, and Zr alloying of steel is used for carbon and

nitrogen fixation into stable nitrides, carbides, carbonitrides [20–23]. Herewith, titanium concentrations used in alloying system should result in complete nitrogen fixation in TiN that takes place during steel crystallization. During heating of billets for rolling up to commonly used temperatures (1200–1250 °C) dissolution of the titanium nitride does not take place inhibiting the growth of austenite grains. The results of the researches of carbon segregation processes testify that for effectively reducing of the carbon concentration in the grain boundaries, which controls the possibility of $M_{23}(CB)_6$ formation, it is optimum to use niobium microalloying in the range 0.03–0.06 wt.%. Owing to the ability to achieve a significant increase in hardness and strength of steel by the formation of nanosized carbide precipitates [25] it is reasonable to carry out further microalloying with vanadium. Use of these principles allowed to achieve extremely high strength characteristics, which exceed 2000–2200 MPa [19], of metal products of hot-rolled, cold-rolled, including coated rolled steel manufactured by hot stamping simulating.

The mentioned fact allows to make two important conclusions. Firstly, presence of certain impurities in steel is not always a negative factor. Secondly, the steel design principles, which were previously developed, must now be revised and modified to a great extent, because of the substantial change in the desired characteristics of the metal and its production technology. In particular, legislative desire reducing the sulfur content in the steel, in many cases, is not advisable, but on the contrary, it is desirable to satisfy its minimum limit. Unlike sulfur, reducing the nitrogen concentration in the low-carbon steels for automobile sheets unambiguously leads to increase in levels of service properties due to nitrogen conservation in solid solution during hot rolling. It promotes aluminum nitride precipitation during annealing of cold-rolled steels and stimulates improvement of grain structure and properties [26, 27]. Mentioned ambiguity of the effect of various types of conventional impurities has a supplement caused by significant change in the raw material base, especially due to the rapid growth of processing volumes of complex categories of metal junk. Thus, at the present time steels contain a number of impurities, including Mo, Zn, Sn, Pb, Cu, Cr, V, and Nb, which were previously not significant. Importantly, some of them – Mo, V, Cr, Cu, and Nb are special expensive alloying and microalloying components for modern steels of many types. However, they can negatively effect on the range of technological and service properties of other types of steel [2], for example, high stamping automobile, electrotechnical, and etc. Increase in the content of low-melting Zn, Sn, and Pb impurities, as a rule, leads to a negative impact on the complex of technological and service properties, and quality characteristics of steels of many types. An analysis of the dynamics of change in resource base clearly shows a trend of further increase in the content of impurities of these types. Caused by modern technologies the content of sulfur gives rise to possibility of precipitation of copper and zinc sulphides, which are able to strengthen steel effectively, under competition with manganese sulphide.

Presented circumstances testify to necessity of detailed research based on a fundamentally new level, which is dealing with laws of the influence of different types of impurities on the obtained structural state and the complex of properties of steels of various grade groups. Unfortunately, until now systematic studies were performed only for low-carbon steels of 08U-type [2]. It has been found that the adverse effect of impurities on ductility and formability indicators can be prevented in many cases. Among others, negative influence of presented non-ferrous metals may be inhibited by optimizing mode of recrystallization annealing. Based on the obtained results requirements have been developed for chemical composition and technological parameters of production of rolled low-carbon steel of the highest categories of drawing even with the presence of impurities, which allows to use it instead of the much more expensive rolled products of ultra low-carbon steel. The second, also important direction, which is derived from the results of the present study, is the possibility of manufacture of low-carbon high stamping automobile steels of the electric smelting metal. This opens up new opportunities to reduce costs and expand the raw material base for the steel manufacture.

Special features of formation of carbonitrides and other phase precipitates, their effect on properties of modern steels

To date, the influence of Ti, Nb, and V carbonitride precipitates on the formation of structural state and complex of properties of hot-rolled automobile body sheet, piping, structural, and other types of steel have

been studied in sufficient detail. Among other things, it is well known that nitrides and carbides of these elements have the same fcc – structure. This is favorable for their deposition on the surface of the already present particles [9, 28] to form a multilayer complex precipitates. For example, NbC and VC deposition on the surface of TiN and NbC, respectively, increases the size of the already present particles and reduces the number of independent precipitations that, in many cases, decreases the efficiency of mechanisms of steel strengthening, which are associated with the grain structure refinement and precipitation hardening. Thus, formation of complex, multilayer phase precipitates often is an unfavorable factor for desired structural state and high complex of properties of steel. To restrain recrystallization during hot rolling the most commonly niobium microalloying is used. Reducing temperature of rolling end usually increases completeness of its carbonitride precipitation, degree of containment of recrystallization and grain refinement. However, residual concentration of phase forming elements in the solid solution becomes lower resulting in the formation of smaller amounts of fine nanosized precipitates during the cooling of the strip, including in the form of the coil. As a result, the contribution of precipitation hardening reduces. Thus, by varying the parameters of temperature-deformation treatment of metal it is possible to change the ratio of the two major strengthening mechanisms, which are associated with the formation of niobium carbonitride precipitates: grain boundary and precipitation hardening. So, required indicators of strength and ductility can be achieved. Using the stated principles high-strength microalloyed steels for automobile body sheet of various strength classes with yield strength up to 700 MPa have been developed [1, 2].

Nevertheless, the choice of composition and parameters of temperature-deformation treatment of steels is carried out using thermodynamic calculations or simplified empirical relationships that do not take into account kinetic features of the reactions, do not allow obtaining of accurate information, and often lead to physically inadequate results. Therefore, experimental detailed researches of kinetics of niobium carbonitride precipitates formation have been carried out [29]. It has been found that in the absence of deformation the precipitation has significant kinetic difficulties. For the steel, which is previously subjected to complete dissolution of Nb(C,N) at 1200 °C, the formation of any significant amount of nanoscale precipitates of this phase requires extended time interval – for at least 20–40 min of isothermal heating at 900 °C, even if significant degree of supersaturation and supercooling (300 °C) of solid solution takes place. After isothermal deformation with 50 % reduction at 900 °C the formation of nanosized (3–5 nm) niobium carbonitride precipitates considerably accelerated. It begins at exposure time of approximately 10 s and ends over 250–300 s [29]. Determined interval of niobium carbonitride precipitation is quite long in comparison with commonly used modes of temperature-deformation treatment of steel in practice. This can lead to incomplete implementation of the process and the phase forming elements preservation in solid solution. This is in good agreement with the results of the study of a large number of laboratory and industrial steels [14, 30]. Additional direct experimental evidences have been obtained for the fundamental relation of the number and mechanism of nanosized niobium carbonitride precipitates formation according to the regime of preceding heat treatment. In particular, pre-cooling to room temperature and subsequent heating to exposure temperature of 700 °C leads to a significant increase in the number of formed carbonitride precipitates. Notably, their nucleation and growth occurs in ferrite in contrast to the precipitates nucleating in austenite while cooling from high temperatures.

Based on the theory of nucleation and growth of nucleuses of new phases a kinetic model of formation of excessive phases in steels has been developed [31]. The model used the original method of calculating the chemical driving force. The representation of the thermodynamic functions of phases within the framework of the modern theory of the sublattices allows taking into account the complex composition of phases. The free parameters of the model, which include surface energy, have been found using the experimental data [29]. Kinetic modeling and thermodynamic calculation of phase equilibria has been implemented for high-strength low-carbon Mo-Ti microalloyed steels. It has been found that in this case a complex fcc-carbide based on TiC is the main type of precipitates, which control mechanisms of grain boundary and precipitation strengthening. At temperatures below 800 °C molybdenum fraction in it increases. At temperatures of $\gamma \rightarrow \alpha$ transformation the fcc-carbide composition is close to $\text{Ti}_{0.43}\text{Mo}_{0.08}\text{C}_{0.49}$. Under conditions of thermodynamic equilibrium content of molybdenum in $\text{Ti}_x\text{Mo}_y\text{C}_z$ with a further decrease in temperature decreases due to

competitive Mo_2C precipitation [32]. If Mo_2C formation does not occur, e.g. for kinetic reasons, the molybdenum concentration in $\text{Ti}_x\text{Mo}_y\text{C}_z$, on the contrary, increased.

It was found that lowering the temperature of the rolling end increases the contribution of complex fcc-carbide precipitates in moderating the recrystallization and grain refinement during thermo-deformation treatment. However, it accompanies by decreasing in titanium fraction, which remains for the formation of interphase and ferritic nanosized precipitates controlling precipitation hardening. The special perspective of formation of the system of nanoscale interphase carbide precipitates during $\gamma \rightarrow \alpha$ transformation has been shown. Besides, in the case of the Mo-Ti microalloying molybdenum is mainly responsible for the containment of the phase transformation, and titanium is important for the carbide precipitates formation, which is effectively occurs only while using a relatively high temperature of the rolling end (about 900 °C). Its reduction leads to an increase in the rate of phase transformation and disruption of the mechanism of interphase precipitates formation.

Based on the obtained results the chemical composition and modes of thermo-deformation treatment of low-carbon Mo-Ti microalloyed steels have been developed that provide formation of fully ferritic microstructure and a complex of high mechanical and other service properties. The test results of manufactured rolled samples showed that the highest mechanical properties (yield strength – more than 750 MPa, tensile strength – more than 850 MPa) with good ductility (elongation – 19 %) take place while temperatures of the rolling end and coiling are 880–890 °C and 650 °C, respectively [32, 33]. The possibility of further improvement of the mechanical properties complex has been shown for steels of this type by increasing titanium content and optimizing the temperature-deformation processing of metal.

The results of the detailed investigations [34] showed that the same set of high strength characteristics with good ductility (elongation – at least 16–18 %) can be obtained for the rolled low-carbon Ti-Nb-V microalloyed steels using low (780–800 °C) as well as high (890–900 °C) temperatures of rolling end. Importantly, it is provided by forming the bulk system of nanosized carbonitride precipitates, including interphase, in case of fully ferritic steel microstructure.

It should be noted that the end of rolling at such high temperatures is favorable for producing the high-quality rolled clad steels [34] due to the high technological plasticity and uniformity of the deformation of layers. On this basis, a new class of low-carbon high-strength (tensile strength of at least 850 MPa) microalloyed steels clad by corrosion-resistant chrome-nickel austenitic steels and complex technology of their manufacture by means of electroslag facing has been developed. The steels are characterized by fundamentally improved strength level (at least 450 N/mm²), connection continuity, and thickness equality of layers.

Increasing the homogeneity of composition, structure, and properties of steel by controlling non-metallic inclusions, phase precipitates

By controlling the processes of formation of non-metallic inclusions and excessive phases precipitates, not only the complex of levels of indicators and stability of the service characteristics can be fundamentally improved, but it is possible to achieve a significant increase in the degree of homogeneity of composition, structure, and properties over the volume of metal. Among others, results of recent detailed studies [35, 36] testify that currently during ladle treatment, continuous casting of low-alloyed steels the formation of oxide inclusions, in particular the vitreous inclusions based on $\text{SiO}_2\text{--Al}_2\text{O}_3$, $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$, MnO--SiO_2 , $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MnO}$ and other compositions, takes place determining in many respects the resulting structural state and complex of properties of steel. The presence of glassy silicate-based inclusions in steel fundamentally changes the macro- and microstructure of the metal of continuous casting blank, suppresses the liquation processes. As a result, it leads to a favorable uniformity of chemical composition and structure state of the metal and extremely high complex of properties of rolled products. For example, impact toughness of rolled

steels achieved extremely high values: KCV_{-40} to 420–445 J/cm² [36]. Besides impact toughness, indicators of resistance to hydrogen cracking, and a number of other service properties increases several times.

It should be noted, that the presence of non-metallic inclusions of this type in low-alloyed structural steels deoxidized with aluminum has been determined for the first time. It is rather surprising fact, both from the theoretical and practical point of view. First of all, it is well known that if aluminum killed steels contain aluminum in the range of hundredths of a percent, and silicon concentration is of the order of tenths of a percent, which corresponds to its usual content for low-alloyed steels, then silicon acts as an alloying element and is not involved in the deoxidation processes [37]. It is important that while traditional schemes of ladle treatment of structural steels are used the formation of described non-metallic inclusions does not occur. A distinctive feature of the used regimes was addition of large masses of manganese and silicon-containing ingredients in the final stages of ladle treatment of steel.

Addition of master alloys additives and other materials into the molten steel from room temperatures leads to a sharp decrease in local temperature. Thereby initially freezing the shell of solid steel occurs on the surface of added solid particles [38]. Its geometric dimensions can be comparable with the particle sizes and even significantly exceed them depending on the ratio of the heat contents of additive and steel. Later on, as a result of equalization of the temperature field the frozen shell of solid steel removes. Herewith, total or partial melting of the particle is possible even in the presence of a solid steel shell depending on the magnitude of the melting temperature of the additive. In any case, the absorption of injected additive by liquid metal is a lengthy process, associated with the appearance of the areas of a high temperature – concentration heterogeneity. During addition of silicomanganese, manganese, and silicon containing ferroalloys, which have a lower melting temperature than the low-alloyed steels, their melting occurs even in the presence of a solid steel shell. As a result, local concentration of silicon and/or manganese can reach high values corresponding to their content in added material. To assess the impact of the noted circumstances on the type of forming non-metallic inclusions the calculation of the equilibrium products of deoxidation at 1600 °C in steels with the total oxygen content of 0.005 % has been made using model representations and the available data [36–39]. Aluminum and silicon concentration has been changed from 0.001 to 0.03 % and from 0.5 to 7 %, respectively. The calculation results have shown [36] that an increase in the silicon content leads to the transformation of oxide inclusions, which are pure corundum, into liquid silicon contained inclusions, and then – into the silicon oxide. Thus, the evidence of fundamental possibility of changing the nature of the deoxidation products due to local changes in the chemical composition of the steel has been obtained. With a decrease in the aluminum content, the appearance of silicates occurs at lower silicon concentrations.

Complex form of determined non-metallic inclusions in the metal of continuous cast steel billets [36] testifies that they are in the glassy state, and their form is produced under the influence of the growing crystals. Carbon and, possibly, nitrogen ability to transport from the cooling metal to region of oxide glassy inclusions leads to the formation of mentioned precipitates before, after, or together with titanium and niobium carbides and carbonitrides. This is favorable for their uniform distribution over the volume of metal, the lack of large-sized carbonitride precipitates in the axial zone of continuous cast billets.

Another feature of glassy inclusions is their low thermal conductivity that slows down the heat dissipation, and cooling the metal of continuous cast steel billets after crystallization. Apparently, this provides an explanation for the formation of ferrite-perlite microstructure of continuous cast billets. Thus, the formation of glassy non-metallic inclusions based on silica and other elements during the final stage of ladle treatment and/or continuous casting process leads to following: it allows improving the macro- and microstructure of continuous cast steel billets, reducing the development of liquation processes, and thereby, as noted above, increasing the quality and the level of properties of finished rolled steel.

A further significant improvement of uniformity of composition, structure, and properties of structural steels can be achieved during the hot rolling. Thus, while billets are heated for hot rolling the present precipitates of excessive phases dissolve to varying degrees. In particular, the complete dissolution of niobium and vanadium carbonitrides as well as the equalization of the component concentrations over the metal volume occurs. Thereafter, strip cooling during rolling begins from a surface that promotes, initially, formation of excessive phases precipitates just here. The resultant temperature-concentration gradient of chemical

potential causes the diffusion transfer of elements from the central region to the surface. This stimulates the change of concentration, structure, and properties of the metal over the cross-section of steel. The intensity of the transfer, obviously, depends on the chemical composition, particularly, carbon content in steel and the rolling temperature-deformation mode. Rolling start temperatures in the finishing train, which control the flow rate of described processes, are primary. As a result, a higher concentration of the components in the middle zone of the strip cross-section as well as greater enrichment of the surface area compared to the central region can be saved. This has been confirmed by structure studies and determination of the carbon content in various areas of hot-rolled strips of low-alloy high-strength structural steels with a carbon content of 0.09 % [40]. Thus, management of excessive phases precipitation during hot rolling allows elimination of the disadvantages, which have occurred at continuous casting of billets, and produce rolled steels with homogeneous composition over the cross section, structure and properties.

Conclusion

By now, high efficiency of formulated approaches has found its confirmation in the development of a number of new technical and technological solutions, technologies, and steel grades. In particular, it has been found that due to addition of certain weight of silicon and manganese-containing materials at the final stage of the ladle treatment of steel glassy silicate inclusions may form. Their presence in steel during continuous casting, to some extent, reduces the heat and mass transfer, suppresses liquation processes, leads to a substantial improvement of the macro- and microstructure of cast billets, and obtaining the extremely high indicators of low temperature impact toughness (KCV_{-60} up to 300–400 J/sm²), resistance against hydrogen cracking, and other service properties of rolled products [6]. Production technologies for pipe, structural steels with increased up to 2–3 times indicators of the resistance to total and localized corrosion, low temperature impact toughness, and operational reliability have been developed for the oil-and-gas, fuel and energy complexes. A new class of cold-rolled ferrite-cementite steels of different strength categories has been created characterized by a yield strength up to 500–550 MPa and elongation up to 30–35 %. Low-carbon high-strength microalloyed steels including the base layer of the clad rolled products have been developed. They have high level and stability of difficult to combine strength (yield strength up to 700–900 MPa) and plastic (elongation – more than 17–19 %) properties. A new generation of steels of various strength categories (tensile strength up to 2200 MPa) has been created for the manufacturing by progressive methods of hot stamping [7]. Production technologies of rolled high stamping low-carbon and ultra low-carbon steels with extremely high levels of ductility and formability for significantly difficult drawing have been developed.

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References

- [1] A. I. Zaitsev, K. L. Kosyrev, I. G. Rodionova. *Probl. Chern. Met. Materialoved.* **3**, 5 (2012).
- [2] E. Kh. Shakhpazov, A. I. Zaitsev, I. G. Rodionova, G. V. Semernin. *Russian Metallurgy (Metally)*. **2011**, 1162 (2011).
- [3] A. I. Zaitsev, V. S. Kraposhin, I. G. Rodionova, G. V. Semernin, A. S. Talis. *Complex Nonmetallic Inclusions and Steel Properties*, Metallurgizdat, Moscow (2015).
- [4] A. I. Zaitsev, A. B. Stepanov, N. A. Karamysheva, I. G. Rodionova. *Met. Sci. Heat Treat.* **57**, 531 (2016).
- [5] A. I. Zaitsev, I. G. Rodionova, G. V. Semernin, N. G. Shaposhnikov, A. Yu. Kazankov. *Metallurgist* **55**, 107 (2011).
- [6] E. Kh. Shakhpazov, A. I. Zaitsev, I. G. Rodionova, N. G. Shaposhnikov. *Probl. Chern. Met. Materialoved.* **4**, 112 (2008).
- [7] A. I. Zaitsev, A. V. Koldaev, A. V. Amezhnov, N. G. Shaposhnikov. *Metallurgist* **60**, 721 (2016).
- [8] A. I. Zaitsev, I. G. Rodionova, O. N. Baklanova, K. A. Udod, A. V. Grishin, T. S. Esiev, I. V. Ryakhovskikh, S. A. Kokhtev, A. N. Lutsenko, A. A. Nemtinov, A. V. Mitrofanov. *Probl. Chern. Met. Materialoved.* **1**, 54 (2013).
- [9] I. G. Rodionova, A. I. Zaitsev, N. G. Shaposhnikov, I. N. Chirkina, A. M. Pokrovskii, A. A. Nemtinov, P. A. Mishnev, V. V. Kuznetsov. *Metallurgist* **54**, 343 (2011).

- [10] A. P. Gulyaev. *Physical Metallurgy*, Metallurgiya, Moscow (1980).
- [11] I. G. Rodionova, A. I. Zaitsev, G. V. Semernin, N. G. Shaposhnikov, A. V. Zav'yalov, A. A. Kazankov, N. I. Endel. *Probl. Chern. Met. Materialoved.* **3**, 65 (2011).
- [12] I. G. Rodionova, A. I. Zaitsev, O. N. Baklanova, A. V. Golovanov, N. I. Endel, E. T. Shapovalov, G. V. Semernin. *Modern Approaches to Improve the Corrosion Resistance and Operational Reliability of Steels for Oilfield Pipelines*, Metallurgizdat, Moscow (2012).
- [13] A. I. Zaitsev, I. G. Rodionova, N. G. Shaposhnikov, B. M. Mogutnov, S. F. Dunaev, P. A. Mishnev, R. R. Adigamov. *Probl. Chern. Met. Materialoved.* **1**, 75 (2012).
- [14] A. I. Zaitsev, I. G. Rodionova, A. A. Pavlov, N. G. Shaposhnikov, A. V. Grishin. *Metallurgist.* **59**, 684 (2015).
- [15] E. Kh. Shakhpazov, A. I. Zaitsev, I. G. Rodionova. *Metallurgist* **53**, 187 (2009).
- [16] Yu. S. Gladchenkova, D. L. D'yakonov, I. G. Rodionova, N. G. Shaposhnikov, A. V. Koldaev, A. I. Zaitsev. *Metallurgist* **60**, 937 (2017).
- [17] Yu. S. Gladchenkova, I. G. Rodionova, A. I. Zaitsev, N. G. Shaposhnikov, D. L. D'yakonov, *Probl. Chern. Met. Materialoved.* **4**, 68 (2016).
- [18] A. I. Zaitsev, A. V. Koldaev, Yu. S. Gladchenkova, N. G. Shaposhnikov, S. F. Dunaev. *Metallurgist* **60**, 90 (2016).
- [19] N. A. Arutyunyan, A. I. Zaitsev, O. N. Baklanova. *Metallurgist* **58**, 976 (2015).
- [20] T. Hara, H. Asahi, R. Uemori, H. Tamehiro. *ISIJ Int.* **44**, 1431 (2004).
- [21] B. Hwang, D.-W. Suh, S.-J. Kim. *Scr. Mater.* **64**, 1118 (2011).
- [22] C. A. Suski, C. A. S. Oliveira. *Metallogr. Microstruct. Anal.* **2**, 79 (2013).
- [23] M. J. Kim, H. H. Cho, S. H. Ki, S. M. Nam, S. H. Lee, M. B. Moon, H. N. Han. *Met. Mater. Int.* **19**, 629 (2013).
- [24] K. C. Cho, D. J. Mun, Y. M. Koo, J. S. Lee. *Mater. Sci. Eng. A.* **528**, 3556 (2011).
- [25] A. I. Zaitsev, I. G. Rodionova, A. A. Bykov, A. A. Pavlov, T. I. Strizhakova, A. V. Amezhnov, N. V. Alalykin. *Probl. Chern. Met. Materialoved.* **2**, 70 (2012).
- [26] E. Kh. Shakhpazov, A. I. Zaitsev, I. G. Rodionova. *Probl. Chern. Met. Materialoved.* **3**, 11 (2009).
- [27] I. G. Rodionova, N. G. Shaposhnikov, N. I. Endl', B. M. Mogutnov, S. V. Zhilenko. *Probl. Chern. Met. Materialoved.* **3**, 60 (2008).
- [28] Yu. I. Matrosova, D. A. Litvinenko, S. A. Golovanenko, *Steel for Main Gas Pipelines*, Metallurgiya, Moscow (1989).
- [29] A. V. Koldaev, D. L. D'yakonov, A. I. Zaitsev, N. A. Arutyunyan. *Metallurgist* **60**, 1032 (2017).
- [30] A. I. Zaitsev, I. G. Rodionova, A. A. Pavlov, O. N. Baklanova, I. V. Lyasotskii. *Metallurgist* **58**, 909 (2015).
- [31] A. V. Koldaev, N. G. Shaposhnikov. *Probl. Chern. Met. Materialoved.* **4**, 5 (2016).
- [32] N. G. Shaposhnikov, A. V. Koldaev, A. I. Zaitsev, I. G. Rodionova, D. L. D'yakonov, N. A. Arutyunyan. *Metallurgist.* **60**, 810 (2016).
- [33] A. I. Zaitsev, O. N. Baklanova, A. V. Koldaev, A. V. Grishin, I. G. Rodionova, S. V. Yashchuk, I. V. Lyasotskii. *Metallurgist.* **60**, 491 (2016).
- [34] I. G. Rodionova, A. I. Zaitsev, A. V. Koldaev. *Metallurg.* **9**, 49 (2016).
- [35] Y.-B. Kang, H.-G. Lee. *ISIJ Int.* **44**, 1006 (2004).
- [36] A. I. Zaitsev, I. G. Rodionova, O. N. Baklanova, A. I. Kryukova, K. A. Udod, P. A. Mishnev, A. V. Mitrofanov. *Metallurgist.* **58**, 983 (2015).
- [37] A. I. Zaitsev, B. M. Mogutnov, E. K. Shakhpazov. *Physical Chemistry of Metallurgical Slags*, Interkontakt Nauka, Moscow (2008).
- [38] A. I. Zaitsev, I. G. Rodionova, A. A. Nemtinov, S. D. Zinchenko, S. V. Efimov. *Probl. Chern. Met. Materialoved.* **1**, 1 (2007).
- [39] E. K. Shakhpazov, A. I. Zaitsev, N. G. Shaposhnikov, I. G. Rodionova. *Metallurgist* **52**, 335 (2008).
- [40] E. K. Shakhpazov, A. I. Zaitsev, I. G. Rodionova. *Rare Metals.* **28**, 74 (2009).