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MODIFICATION AND MICROALLOYING OF THE METAL OF WELDS ON HSLA STEELS PRODUCED BY FUSION WELDING METHOD (REVIEW)

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ABSTRACT

The paper considers various aspects of the modification and microalloying of weld metal of high-strength low-alloy (HSLA) steels with dispersed particles of various compounds. The essence and relationship of the processes is highlighted in the context of improving the mechanical properties of the weld metal. The methods and technologies of modification of the structure of HSLA steels and their welded joints were analyzed. The use of various technologies and methods of introducing modifiers into the liquid weld pool is considered, with determination of their effectiveness and impact on the quality of the final product. The influence of different types of modifiers on structure formation, features of the kinetics of phase transformations, structural and chemical liquation and mechanical properties of the resulting welded joints have been analyzed. Particular attention is paid to the aspects of nanomodification of weld metal, determining its advantages and disadvantages.

KEYWORDS: high-strength low-alloy steels, modification, microalloying, microstructure, mechanical properties, automatic welding, weld metal, liquation, nanoparticles

INTRODUCTION

Welding in modern industry is an indispensable part of production processes, which creates an integral element of construction and manufacture. The ability to produce joints ensuring the strength and ductility, makes welding a critical stage of the production cycle. However, with advance of technology and expansion of quality requirements, the need to improve the techniques and materials used in the welding process becomes greater.

In particular, welding of high-strength low-alloy (HSLA) steels with a low content of alloying elements, faces the challenge of ensuring not only strength, but also toughness of the weld metal structure.

Controlling the formation of primary microstructure of the weld metal is given a lot of attention in literature. Grain refinement [1], solid solution alloying and microalloying [2], as well as formation of nonmetallic inclusions of a certain size, composition and morphology (also by addition of dispersed high-melting particles into the weld pool) [3] are the main factors, allowing providing of weld metal strength and toughness. Among these methods, application of weld metal modification by second phase particles is becoming and integral part for achieving optimal results.

"Microalloying" term should be understood as a method to influence the structure and properties of the metal (alloy) only by adding small quantities (≤0.1 %) of elements or their compounds to its composition, which have a considerable impact on the processes running in the solid phase.

"Modification" term should be understood as a set of any chemical, physical or complex processes, influencing the end structure and properties of the metal (alloy). This is a process of active regulation of primary crystallization and/or changing the degree of dispersity of the crystallizing phases. Metal modification can be conducted by adding modifiers to the melt, or by active influence of various physical (mechanical) methods on the melt.

"Nanomodification" term should be understood to mean adding nanoparticles or nanomaterials of less than 100 nm size to the liquid weld pool with the purpose of influencing the formation of weld metal microstructure to improve its properties.

Dispersion strengthening, where second phase particles are used, as a mechanism of grain growth prevention, similar to the mechanism of refinement of microstructural components, is particularly important for weldable steels. Refinement of the structure of the majority of steels and alloys has a favourable impact on the entire complex of their mechanical properties [4].

There is a large number of materials and methods for realization of modification in modern technological processes. One of them is addition of high-melting exogenic inclusions into the liquid melt (inoculation). Two main mechanisms of the influence of exogenic inclusions on melt crystallization are usually considered [5]. In keeping with the first one, the particles are independent crystallization centers, performing "direct" heterogeneous nucleation, or form such centers as a result of interaction with the melt. By the second mechanism, the particles block the growth of crystallites or structural elements, which form during cooling.

Modification results in refinement of the grains or structural components. In a number of cases, direct combination of both the processes is possible, which leads to transformation of the phases with an acicular or lamellar structure into a more equilibrium globular one that increases the metal strength, ductility and toughness, preventing internal stress concentration and cracking.

Over the recent years, application of specially prepared nanopowder inoculators or modifiers to increase the cast metal quality is attracting a lot of interest. These are nanopowders with particle sizes of <100 nm from refractory compounds (oxides, nitrides, carbides, borides, etc.) [6, 7]. At addition to the melt, they are distributed over the liquid metal volume, and serve effective crystallization centers.

Wide prospects of dispersed powder application for modifying influence on the melt in metallurgy allow looking in a new way at the possibilities of controlling the process of liquid pool crystallization in arc processes of fusion welding [8, 9].

Modification is widely used in production of materials for construction, transportation, mechanical engineering and other industries, as a result of improvement of the strength, ductility and impact toughness of metal products operating under high loads and extreme service conditions [4].

Alongside the indubitable advantages of application of the modification method, however, use of modifying for welded joints may face certain challenges and potentially negative consequences. This is, primarily, formation of macro- and microdefects, cavities, pores, cracks and other defects, appearance of regions of chemical heterogeneity and liquation in the weld. Secondly, the particles can completely dissolve in the liquid pool without any modifying effect that necessitates application of additional specific requirements to control of temperatures and technical parameters of welding. Thirdly, nonuniform distribution of particles in the weld metal will lead to heterogeneity in the microstructure, and, consequently, to lowering of the mechanical properties in individual regions of the weld.

The objective of this work is analysis of literature data on modification and microalloying of the metal of welds, influence of modifying particles of different compounds on the structure and mechanical properties, as well as of the prospects for nanoparticle application for welding high-strength low-alloy steels.

MODIFICATION AND MICROALLOYING OF THE WELD METAL

Addition of powderlike material into the weld pool (Figure 1) may lead to different consequences, namely primary modifier particles remain in the weld metal (modification); the particles may dissolve completely, changing the solid solution composition (microalloying) [10]; new particles precipitate in the form of dispersed nonmetallic inclusions (dispersion hardening); the particles coagulate and/or stick to each other, forming complex phase precipitates (coagulation); particles change the morphology and composition of nonmetallic inclusions already existent in the metal.

Changes of chemical composition of weld metal and particles can also influence the kinetics of transformation in the solid state, transformation temperature and the forming microstructure. Influence of modifiers at liquid metal crystallization may influence the primary dendritic structure of the weld metal, the width and type of the weld dendritic structure [11]. The microstructure will be influenced by the composition, distribution and size of modifying and secondary particles [12].

As a result of the dispersed particles interacting with the liquid metal, when they are used for modification, their complete or partial dissolution is possible, leading to metal microalloying in individual regions of the weld. Therefore, at modification by fine particles this process cannot be considered without regard to microalloying.

It is widely known that the microcontent of chemical elements or their compounds in the metal or the welded joint can have an essential influence on the nature of metal crystallization, shape and composition of nonmetallic inclusions, structure of grain boundaries and near-boundary zones, weldability, hardening, heat- and wear resistance, etc., i.e. on a whole set of technological and service properties [13].

One of the effective methods to control the liquid metal composition during electric arc welding is

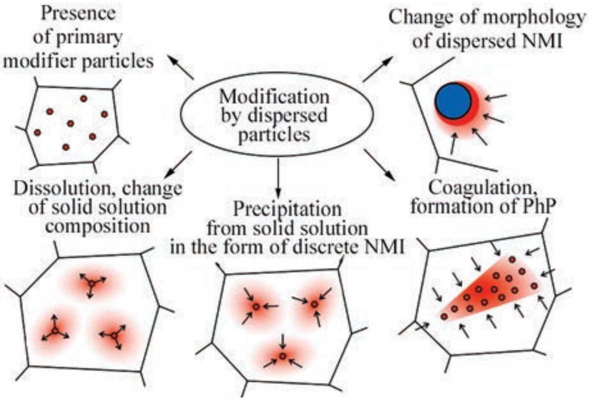


Figure 1. Modification influence on the nature of transformations of dispersed particles [31]

its modification and microalloying through welding consumables which is effective in terms of cost and technology. Literature sources quite widely cover the problem of microalloying of steels and their welded joints [14].

Although the content of individual elements at microalloying is not higher than 0.1 wt.%, they have a considerable effect on the processes running in the solid phase (structural-phase transformations, phase composition, size of the primary austenitic grain, structure and cleanliness of the boundaries and near-boundary zones, etc.) [15].

So, microalloying with chromium increases the hardness, strength, toughness, wear resistance, improves the corrosion resistance, as well as ductility, but decreases the heat conductivity. Vanadium improves the hardness, strength, toughness, resistance to dynamic stresses and wear, reduces temper brittleness, refines the structure and improves the resistance to overheating at quenching. Molybdenum increases the hardness, strength, hardenability, treatability by cutting, heat resistance; promotes formation of a fine-grained structure, improves the weldability and mechanical properties of the welded joints. Titanium microadditive improves the hardness, strength, and wear resistance, but lowers the hardenability. Titanium is used in the form of its compounds with carbon, nitrogen and boron. Titanium carbonitrides Ti(C, N) are the most often used as modifiers, leading to grain refinement. Application of WC tungsten carbide in the metal of low-alloy steel leads to formation of a more homogeneous microstructure, increasing the ductile characteristics [16]. Boron microadditives are used to improve the set of mechanical properties of steels, subjected to hardening with tempering. Here, boron influence is associated with increase of hardenability and refinement of austenitic grain. In some cases not free boron, which is difficult to add to the liquid metal, but its compounds TiB_2, LaB_6, CaB_6, etc. are used.

Recently, such nanomaterials, as nanoparticles of carbon [17, 18], graphene [19] or fine oxides of refractory metals [20] also began to be used for modification.

Modification of welded joint metal allows effective use of the modes of postweld heat treatment to produce the desired structural components and mechanical properties.

In the general case it can be noted, that application of microalloying and modification leads to grain refinement and to producing a more homogeneous structure that has a positive impact on the toughness and ductility characteristics of the welded joints, and influences the technological and other properties of the metal [20, 21].

TECHNOLOGIES OF ADDING MODIFIERS

Different modification technologies are traditionally used in metallurgical production, namely: chemical, electrochemical and physical (microcoolants) and combined, by adding modifiers into the solution, or applying different physical (mechanical) methods to the solution. Widely applied among the modification technologies are the chemical methods, using the chemical state of the modifiers for modifying the metal structure. This is achieved by adding powders of different chemical compounds to the liquid pool in the form of flux-cored wires, bands, aerosols or predeposition of powder onto the surface (adhesion bonding). This approach allows refining the metal structure and forming new strengthening phases, which, in its turn, promotes an improvement of its service properties [22, 23].

The physical impact methods having a modifying effect include the following: ultrasonic treatment, high-frequency peening, temperature-time treatment, superposition of an electromagnetic field on the melt, etc. Of great interest are the processes related to pressure application to the metal of crystallizing castings. In particular, in the technological schemes of casting with alloy crystallization under pressure (die casting — DC) the pressure applied to the melt during solidification, has a significant influence on the nature of crystallization.

At present there are few references in literature to the use of combined technologies of adding modifiers, which influence the metal structure components and thus improve its performance [24].

Among the modern methods of adding modifiers to cast iron and steel melt, the following should be singled out: method of processing with balls of the matching master alloys; submerged block method; processing with lump ferroalloys, processing by powderlike wire and blowing with powderlike ferroalloys.

Application of combined ultrasonic methods of welded joint surface modification using nanosized modifiers can improve the modification effectiveness. Reduction of the dimensions of modifying particles leads to reduction of mean dimensions of weld metal grains and stress intensity factor [24]. Use of nanodispersed particles having higher specific surface energy increases the probability of chemical interaction between the particles and the metal, leading to formation of strong bonds and more effective refinement of the deposited metal structure (Figure 2).

Similar to metallurgical production, the methods of modification of welded joint metal can also be divided into three main groups: chemical (addition of modifiers), physical (application of external physical

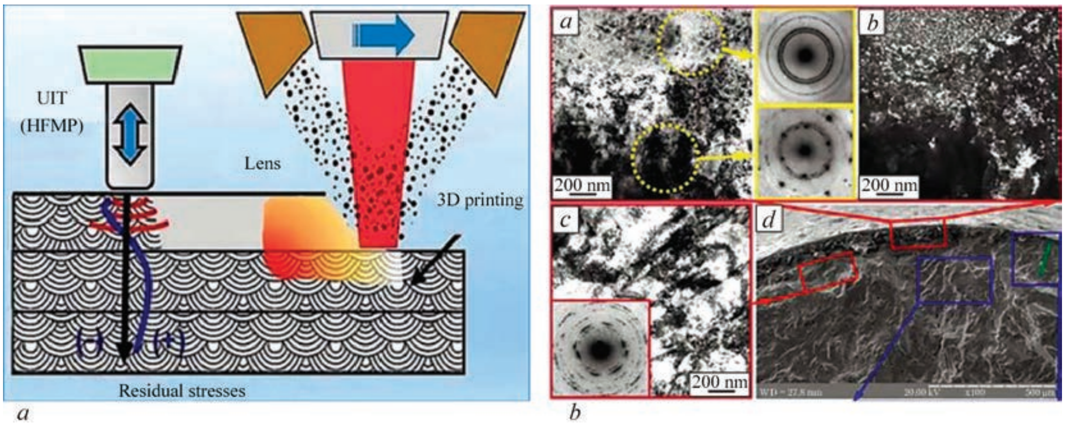


Figure 2. Scheme of combined application of ultrasonic methods of surface modification: *a* — ultrasonic impact treatment (HFMP); *b* — surface microstructure and X-ray patterns of the studied regions [24]

impacts) and combined [14], while all the modifiers can be divided into three classes, depending on the manner of their influence on weld metal crystallization [22].

Modifiers of the first kind improve the wettability of one alloy component by another one, i.e. they reduce the energy of surface tension on the interface, thus facilitating the nucleation of the new solid phase, contacting the liquid (Figure 3). Modifiers of the 2nd kind are directly the crystallization nuclei. They, however, can be such rather conditionally — in the case, when the melt temperature is so close to that of modifiers solidification that it will be insufficient for melting the modifiers added to the liquid pool. Modifiers of the 3rd kind (inoculators) change the weld metal structure by lowering the temperature of overheating of the liquid metal being solidified [14]. The higher cooling rate increases the crystallization rate and promotes an increase in development of the liquation processes which is favourable for the weld metal microstructure.

Moreover, the modifiers can be divided into two types: those, which do not change the surface properties of the crystallizing phase, and those changing the surface tension on the melt-particle interface [14]. Additives of the second type are usually called surface-active, and they are selectively concentrated on the surface of the crystals (dendrites). Surfactants are capable of creating a continuous adsorption layer. It means that at practical absence of surface-active modifier solubility in the solid phase a shell of a liquid enriched in modifier elements forms around it [14].

Complex modifiers are a system consisting of two and more modifiers of the same or different types of elements from those given above. Such a complex application of modifiers allows significantly decreasing the liquation processes in the weld metal and the HAZ, which will lead to a more uniform distribution of the alloying elements, lowering of concentration gradients and homogenizing of the properties (Figure 4) [25]. The effect of such modifiers, depending on their type, is usually manifested in a more inten-

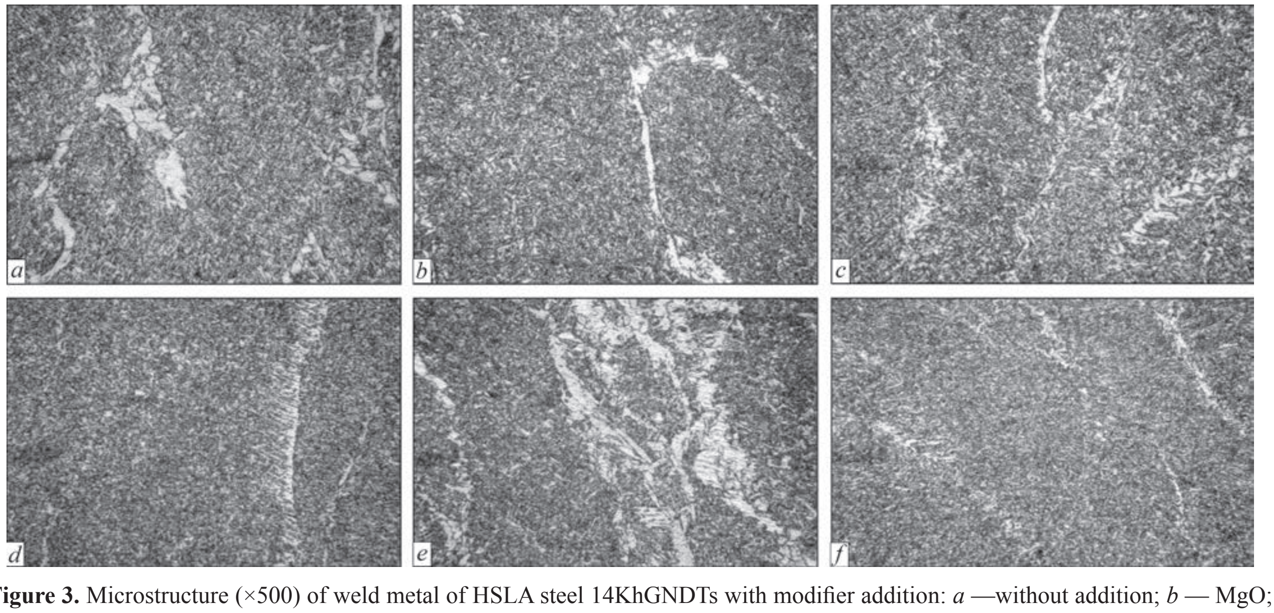


Figure 3. Microstructure (×500) of weld metal of HSLA steel 14KhGNDTs with modifier addition: *a* —without addition; *b* — MgO; *c* — ZrO_2; *d* — TiO_2; *e* — Al_2O_3; *f* — SiC

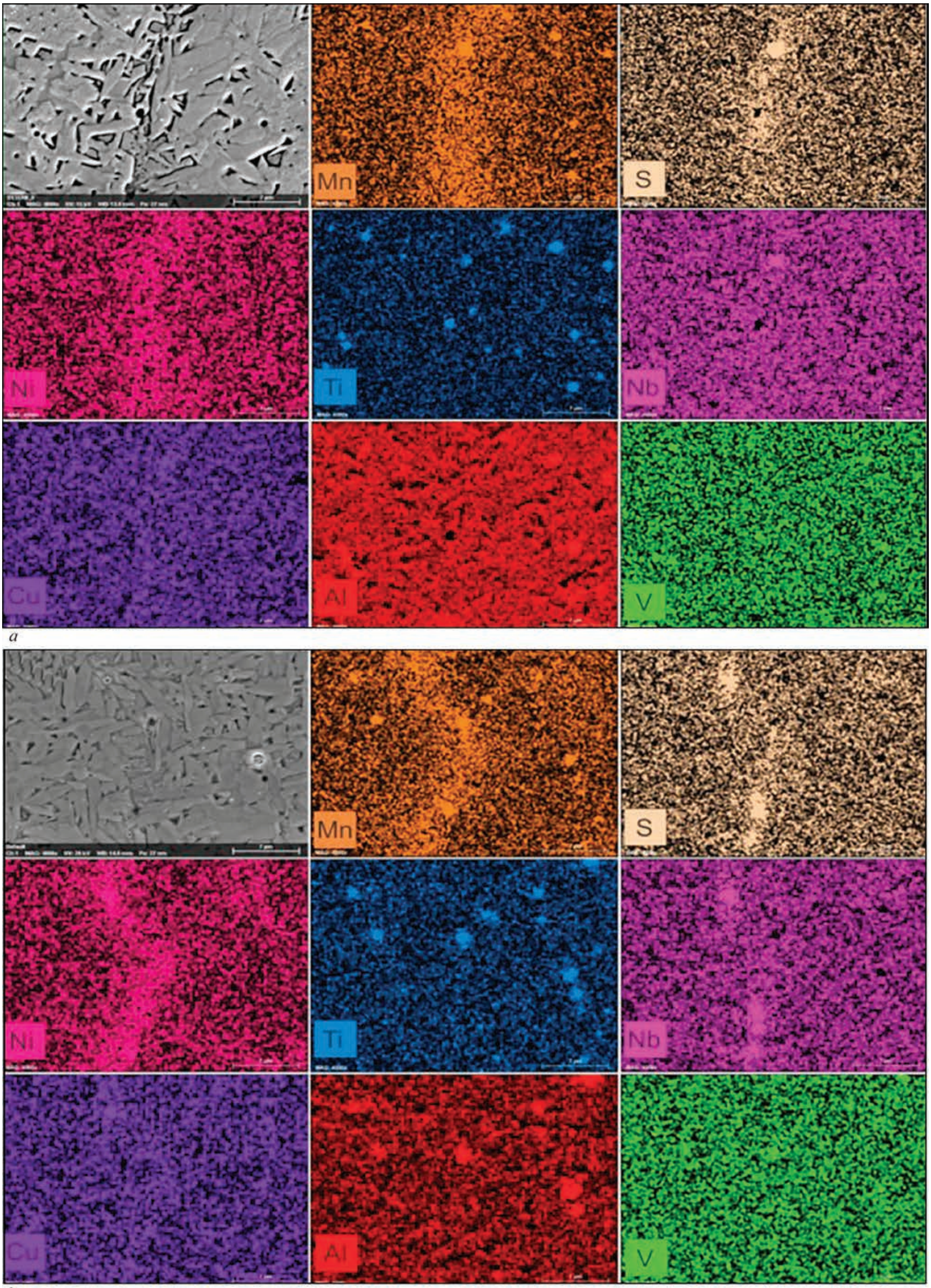


Figure 4. Influence of modifying additives (Nb, V, Ti, Ni) on alloying element liquation in weld metal of HSLA steels: *a* — A572 G50; *b* — A656 G80 steel [25]

sive and complex way, simultaneously influencing the mechanical, technological and service properties of the weld metal [26].

The physical methods of modification include those, which are based on the influence of physical processes on the processes of crystallization and formation of the weld metal structure. This is, in particular, application of vibrations during welding, pulsed application of energy from the heat source; pulsed feed of electrode or filler wire; application of sources with welding current modulation, as well as in a number of cases use of additional heat sources influencing the HAZ close to the weld fusion line; external electromagnetic influence, etc. [14, 27]. In work [28] the authors used a combined method of treatment of welded joints of 40Kh steel. The nitride layer was applied by plasma nitriding, and then treated by a scanning electron beam. It was found that hardness (850 *HV*) increased more than three times, compared to the initial material. Application of this combined method (PN + EBT) improves the steel wear resistance at abrasive wear by more than two times, compared to plasma nitriding.

INFLUENCE OF MODIFIERS ON THE STRUCTURE AND PROPERTIES OF WELD METAL OF HSLA STEELS

Flux-cored wires with different degree of filling with particles of oxides, carbides and nitrides of predominantly refractory metals are often used as modifiers in welding HSLA steels. The following compounds are often used for these purposes: TiC, SiC, NbC, TiO_2, Al_2O_3, ZrO_2, MgO, TiN, TiB. Appearance of modifier powders is given in Figure 5.

In work [29] it was established that carbide modifiers (TiC, SiC, NbC) influence the transformation kinetics and formation of secondary crystalline structure due to their dissolution and change of the metal chemical composition, while oxide modifiers (TiO_2, Al_2O_3, ZrO_2, MgO) and modifiers based on titanium compounds dissolve and precipitate on the surface of nonmetallic inclusions, as well as in the form of individual nonmetallic inclusions and phase precipitates, influencing structure formation and mechanical properties of the modified weld metal.

It was shown [29] that at modification by particles based on titanium compounds new nonmetallic inclusions are formed, appearing inside the weld metal grains with high dislocation density (10^{-10}–10^{-11} cm^{-2}) around the inclusions, which has a negative impact on the ductility indices of the welded joint metal.

Oxide-based modifiers have a complex impact on structure formation processes and they can be recommended for industrial applications. Proceeding from the obtained results the authors ranged by the degree of modifiers influence on weld metal strength and ductility: ZrO_2–MgO–TiO_2–Al_2O_3. It was found that modification by ZrO_2 powders should be recommended to improve the ductility and impact toughness, and Al_2O_3 powders should be used for higher strength.

In work [30] it was established that modification with ZrO_2 and MgO particles leads to a certain increase of the temperatures of the beginning of transformation for cooling rates below 17 °C/s. Modification by TiC, SiC, NbC, TiO_2, Al_2O_2 and TiN particles leads to lowering of critical transformation temperatures. Modification by carbide modifiers and TiN leads to formation of a pronounced martensite phase at dilatometric and metallographic investigations. The highest martensite content and the highest values of metal microhardness were produced for samples modified by TiN particles.

Dependence of transformation temperature on the cooling rate demonstrates a lowering of the transformation temperature for all the studied samples. It should be noted that modification by ZrO_2 and MgO

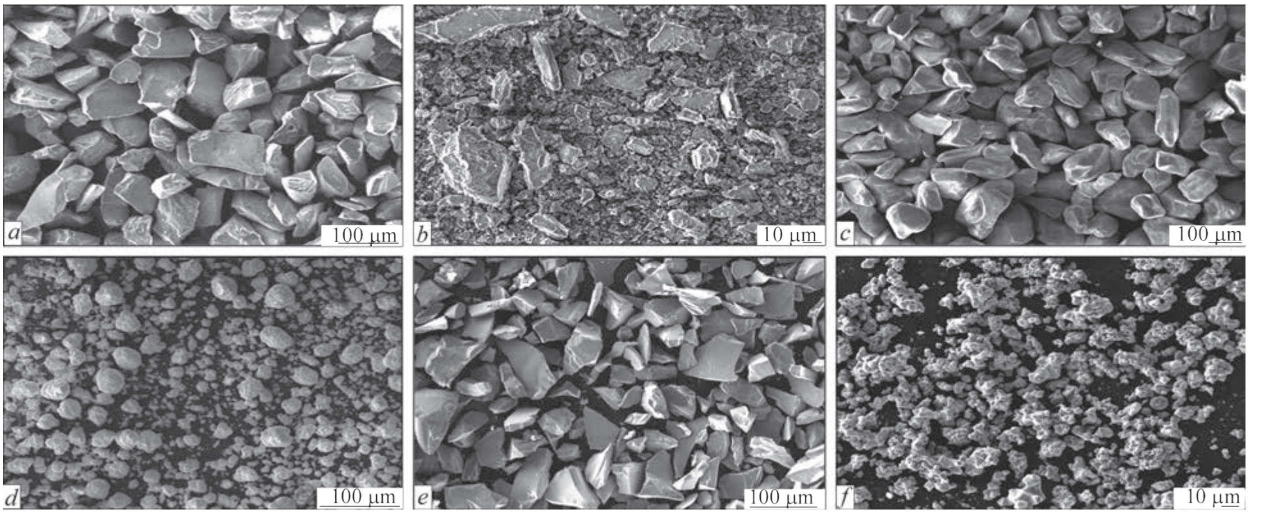
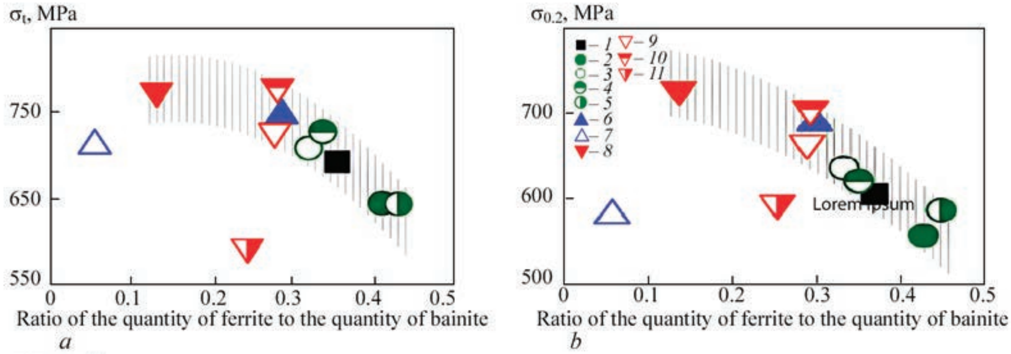


Figure 5. Appearance of modifier powders: *a* — Al_2O_3; *b* — MgO; *c* — TiO_2; *d* — ZrO_2; *e* — SiC; *f* — TiC



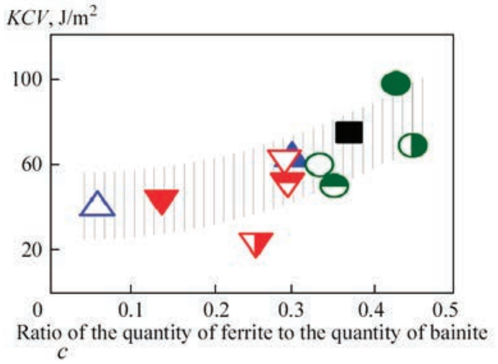


Figure 6. Influence of structural composition on mechanical properties of modified weld metal: *a* — ultimate strength; *b* — yield limit; *c* — fracture toughness [29]; *1* — without modification; *2* — ZrO_2; *3* —TiO_2; *4* —Al_2O_3; *5* —MgO; *6* —FeTi; *7* —TiN; *8* —SiC; *9* —TiC; *10* —VC; *11* —NbC

particles leads to improvement in the transformation temperature by 50–75 °C, and on the whole the values of transformation temperature for MgO, ZrO_2, TiO_2, Al_2O_3 oxide modifiers are higher than those for SiC, VC, NbC carbide particles. The lowest temperature transformation values are observed for a sample modified by TiN titanium nitride [30].

Influence of modifying particle type on the mechanical properties of weld metal of HSLA steels (Figure 6) shows a lowering of strength and increasing of ductility characteristics at increase of the ratio of the quantity of ferrite phase to that of bainite phase.

At the same time, an opposite dependence was established at weld metal modification by TiN and NbC particles, which was accounted for by the presence of a martensite phase in the structure of weld metal of these samples, as a result of dissolution of carbide-forming modifiers.

NANOMODIFICATION. ADVANTAGES AND DISADVANTAGES

Application of finer particles or powders of refractory metals became a further development of the technology of metal structure modification. Use of such particles of less than 100 nm size on the one hand allows controlling the metal structure already at the micro- or even atomic level, and on the other hand it requires development of special technologies and equipment for their realization. Application of such nanoparticles allows more thoroughly influencing the growth of primary grains during liquid metal crystallization; controlling the grain-boundary processes; forming a complex subgrain microstructure; influencing the distribution of dislocations, impurities and level of chemical heterogeneity, i.e. improving the metal structure in some way and increasing its metal properties.

At the same time, scientists are faced serious difficulties of both technological and research nature. From the view point of technology, equipment should be developed for adding nanopowders into the weld pool and for preventing their dissolution at the stage of weld metal crystallization. Their dissolution has to be prevented that is a more complex task, compared to traditional particles of larger size, used for modification. Moreover, a uniform distribution of the nanoparticles should be ensured, disregarding their tendency to combine — to form clusters and aggregations.

Therefore, the majority of the works, devoted to welded joint modification by nanoparticles are devoted to solid-phase welding, i.e. welding, where no melting occurs. Now, in those works, where fusion welding methods (TIG, MIG/MAG) are used, the nanoparticles solubility is almost not controlled.

In work [29] an attempt was made to assess the change in nanoparticle size during welding of HSLA steel. Analysis of the distribution of particles and size of inclusions in the metal of welds without modifiers and with their application reveals a reduction of the fraction of fine inclusions, and increase of the fraction of inclusions large than 0.36 μm.

An important technological aspect of nanomodification is addition of nanoparticles to the weld pool. The high specific surface energy of the nanoparticles associated with a large overall surface area, leads to nonuniform distribution of the nanoparticles (Fig-

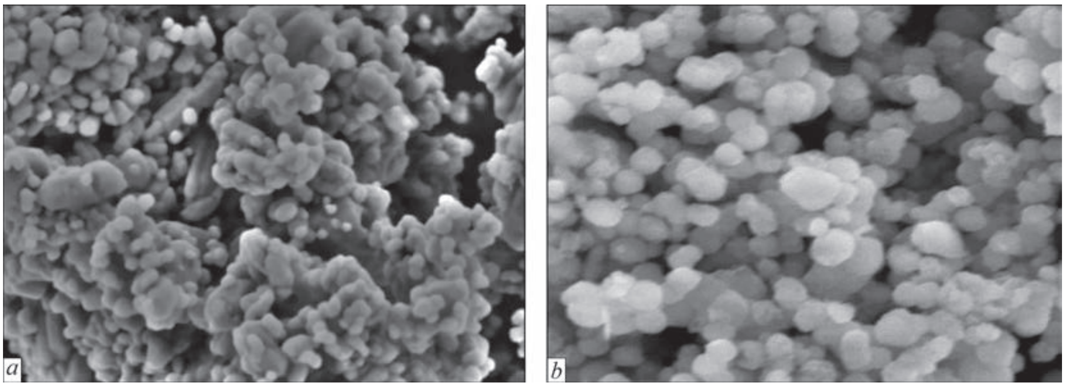


Figure 7. General appearance of nanopowders: *a* — Al_2O_3; *b* — TiO_2 (×100000)

ure 7) [31, 32]. They most often coalesce, forming conglomerates or clusters of nanoparticles, or precipitate at the bottom of the weld pool. Moreover, in welding processes the temperature in the zone of heat source impact is higher than the melting temperature of many refractory nanodispersed compounds causing their dissociation and further dissolution of the products in the weld pool melt [33].

In work [15] the influence of titanium-containing nanoparticles on crystallization of acicular ferrite and mechanical properties of metals for multipass arc welding was studied. In the study particle dispersion was conducted, using ultrasonic treatment. However, achievement of a uniform distribution of nanoparticles in liquid glass for further coating of the electrodes requires treatment for 6 hours that is not practical in serial production. The authors also determined that the percentage of acicular ferrite in the weld metal becomes higher with increase of the amount of nanoparticles of TiO_2 titanium oxide in the electrode coating.

In work [34] the influence of TiO, SiO_2, Al_2O_3 and Mn_2O_3 nanoparticles on the features of destruction of Charpy impact V-notch specimens produced by submerged-arc welding was studied. Increase of strength and impact toughness of the welds as a result of greater surface density of acicular ferrite at decrease of the lath thickness as a result of modification by TiO_2, SiO_2, Al_2O_3 or Mn_2O_3 nanoparticles was found.

In work [35] SiC and TiO_2 nanoparticles were used at friction stir welding of AA7075 and AA2024 aluminium alloys. It was established that the nanoparticles are dispersed in the welding one, forming a refined microstructure and preventing formation of harmful defects. This distribution improves the load-carrying capacity, effectively increasing the tensile strength of the joint. The nanoparticles promote a more uniform stress distribution and slow down crack initiation and propagation.

Work [36] is a study of the influence of SiO_2 nanoparticles, graphene nanoplatelets (Gnps) and biocoal, added to the weld pool at FSW of AISI-SAE 1010 steel and CDA 101 copper. It was found that additions of a considerable quantity of nanoparticles resulted in undesirable values of the strength intensity factor. At the same time, the microstructure of the weld with application of nanoparticles was quite favourable. The grains in the HAZ and TMAZ were considerably refined, due to application of nanoparticles. The result showed that biocoal nanoparticles obtained naturally have a potential to replace expensive nanofillers in metal welding.

Cracking during weld pool solidification was a serious problem in fusion welding of high-strength and high alloys for many years. It has been established recently that application of TiC nanoparticles as filler materials is an effective method of preventing cracks at solidification during TIG welding of sheet aluminium alloy AA7075. Experimental results showed that filler metal with TiC nanoparticles effectively prevents cracks at crystallization. Evaluation of microstructure reveals an equiaxed morphology of the grains in the fusion zones [37].

Thus, application of nanomodification in welding offers a number of advantages. First, this is structure improvement: nanomodifiers allow producing a more dispersed structure in the weld metal, and under appropriate conditions reaching a more homogeneous structure, reducing its defectiveness, lowering the level of residual hydrogen, improving the brittle fracture resistance, and reducing porosity. Secondly, this is increase of mechanical characteristics: during primary crystallization the nanoparticles will slow down the growth of crystallites, concentrating predominantly on their boundaries, and this will lead to refinement of the secondary microstructure, which will promote an increase of hardness, strength, and, most importantly, impact toughness at negative test temperatures. Thirdly, this is improvement of the weld metal resistance to the influence of the environment: nanoparticles can improve the weld metal resistance to oxidation, corrosion and other aggressive factors, acting under extreme conditions.

CONCLUSIONS

1. Performed analysis of literature sources showed that modification and microalloying of the metal of welds by feeding flux-cored wire with dispersed particles of oxide compounds is a promising technological measure of controlling the structure and improving the mechanical properties of weld metal of HSLA steels, which can be used under production conditions.

2. In modern modification technologies, application of refractory chemical compounds of various elements is designed for active regulation of primary crystallization processes, change of the degree of the solidifying phase dispersity and formation of a fine secondary structure.

3. Nanomodification of weld metal of HSLA steels and other alloys can be used with success for different welding methods (TIG, MIG/MAG, FSW) which allows significantly influencing the weld metal structure, refining both the primary and secondary structure, reducing the grain size, lowering liquation and improving their functional characteristics of strength, ductility, toughness and wear resistance.

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CONFLICT OF INTEREST
The Authors declare no conflict of interest

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