EFFECT OF MODIFICATION OF WELD METAL OF HIGH-STRENGTH LOW-ALLOY STEELS ON THEIR STRUCTURE AND PROPERTIES

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The work studies the influence of modification of different compounds by dispersed particles on the structure, nonmetallic inclusions, their size and distribution, change of phase transformation temperatures and mechanical properties of weld metal joints of high-strength low-alloy steels. It is shown that the use of the temperature of maximum intensity of phase transformations allowed separating the influence of oxide, carbide and titanium-containing compounds on the structure and mechanical properties of weld metal of high-strength low-alloy steels. The use of powders of TiO₂, ZrO_2 and MgO oxides promotes formation of a dispersed structure of acicular ferrite (from 30 to 90 %), which allows obtaining a favourable combination of high strength and impact toughness, especially at low extremely test temperatures (-40– -60 °C) in the weld metal. 11 Ref., 5 Tables, 9 Figures.

K e y w o r d s : high-strength low-alloy steels, austenite decomposition diagram, phase transformations, critical transformation temperatures, automatic welding, weld metal, modification, microstructure, mechanical properties

High-strength low-alloy (HSLA) steels with a level of strength of 350–700 MPa and a high complex of toughness and ductility properties are now extensively used in construction, transport engineering, and ship-building in fabrication and repair of engineering welded structures of hoisting and transportation mechanisms, large-sized engineering constructions and frame structures [1–3].

Ever increasing requirements for improving the reliability and safety of welded structures, the level of operational loads, their fatigue life and cost-effectiveness make it necessary to use new HSLA steels. At present there is a problem of lowering the toughness values of weld metal in the welded joints at increase of strength values, in connection with development and application in industry of new HSLA steels with the strength level of 600–700 and even 800 MPa [4].

This problem can be solved by switching to the use of new HSLA steels with ferritic-bainitic or bainitic-martnesitic structures in welded structures. This, on the one hand, requires application of new welding consumables, namely wires and fluxes, and on the other hand, more profound understanding of the processes of structure formation, influence of phase transformation kinetics and features of disperse phase formation on the structure and properties of HSLA steel welded joints.

Traditionally, the problem of improvement of weld metal strength to the level of 90–95 % of base metal

strength was solved by using higher alloyed welding wires, flux-cored wires of complex chemical composition or changing the welding mode [5].

At the same time, traditional approaches to increase of welded joint performance cannot always be applied, because of lowering of ductility, impact toughness, brittle fracture resistance and increase of cold cracking susceptibility of weld metal and HAZ [6]. This is related to the fact that the features of structure formation, kinetics of phase transformation development, mechanisms of the influence of dispersed exogenous phases on the structure and properties of welded joints of HSLA steels are not yet fully understood.

Determination of phase transformation temperatures in HSLA steels and their welded joints is a quite complex task that directly affects selection of welding, heat treatment modes and, consequently also the microstructure and mechanical properties of the weld metal.

In view of the above, the objective of the work consisted in studying the influence of different composition of modifier powders on structure formation processes, phase transformation temperatures, their distribution in the weld metal and establishing the influence of these parameters on the mechanical properties of weld metal of HSLA steels.

Investigation materials. The work presents the results of investigations of structural transformations in metal of welded joints on HSLA 14KhGNDTs

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Figure 1. Scheme of filling the butt (a) and appearance of modifier powders (b): 1 - TiC; 2 - TiN; 2 - TiN; $3 - \text{TiO}_2$; $4 - \text{ZrO}_2$

steel, where modifier powders of different compounds, namely nitrides, carbides and oxides of different metals (TiC, TiN, SiC, VC, NbC, TiO₂, Al₂O₃, MgO, ZrO₂) were added. Liquid metal modification was performed by welding, using flux-cored welding wires, which included particles of the required composition. Welds Nos 1–9 were not modified, whereas welds Nos 10–18 were produced using modified fluxcored welding wires (Figure 1).

A feature of application of the proposed welding scheme for modifying the liquid metal is the need to protect the added powders from direct influence of the welding arc, in order to prevent their complete melting or evaporation. In this connection, we used the technology of adding flux-cored welding wires to the relatively «cold» part of the weld pool with pool temperature close to 1600–1800 °C, which was lower than the melting temperature of most of the particles.

Butt welded joints of 14KhGNDTs steel plates 20 mm thick were produced at reverse polarity direct current. Welding was performed in Ar + 18 % CO_2 shielding gas atmosphere, using Sv-08 flux-

cored wire of 1.6 mm diameter, filling factor being 18 %. Total content of TiC, TiN, SiC, VC, NbC, TiO₂, Al₂O₃, MgO, ZrO₂ modifiers was 0.09 %. Welding was performed at reverse polarity direct current I = 240-250 A, voltage U = 31-32 V, welding speed of 10–12 m/h, heat input of 26–28 J/cm. Chemical composition and mechanical properties of test welds are shown in Table 1 and Table 2.

The nature of structural transformations in the metal of welds modified by powders was studied by the method of simulation of thermodeformational cycles of welding, using Gleeble 380 complex (DSI, USA), which was fitted with a high-speed dilatometer [7]. Samples were heated in a vacuum chamber up to the temperature of 1170 °C, and then were cooled by a thermal cycle characteristic for automatic sub-merged-arc welding at the speeds of 5; 10; 17; 30; 45 °C/s in the temperature range of 600–500 °C.

Weld microstructure was studied by light (NEO-PHOT 32), scanning (JSM 840 (Jeol, Japan), transmission (JEM 200CX, Japan) and Auger-microprobe (JAMP 9500F, Japan) electron microscopy.

 Table 1. Chemical composition of metal of the produced welded joints, wt.%

Туре	C	Si	Mn	S	Р	Cr	Ni	Mo	V	Cu	Al	Ti	Nb	Zr
Without mod.	0.042	0.34	1.19	0.021	0.02	0.106	2.13	0.282	_	0.72	0.028	0.029	0.004	_
FeTi	0.049	0.298	1.39	0.023	0.015	0.15	2.26	0.25	< 0.02	0.44	0.039	0.008	0.006	-
TiN	0.035	0.317	1.4	0.019	0.009	0.14	2.29	0.26	< 0.02	0.56	0.036	0.011	< 0.002	-
SiC	0.053	0.321	1.2	0.02	0.025	0.22	2.42	0.26	< 0.02	0.45	0.025	0.004	0.003	0.002
TiC	0.046	0.34	1.39	0.021	0.019	0.13	1.7	0.24	< 0.02	0.54	0.033	0.011	0.007	-
VC	0.052	0.227	1.21	0.022	0.021	0.14	2.03	0.25	0.07	0.51	0.027	0.004	0.004	-
NbC	0.049	0.253	1.19	0.021	0.02	0.13	2.25	0.27	< 0.02	0.55	0.029	0.003	0.075	-
ZrO ₂	0.041	0.288	1.32	0.021	0.024	0.12	1.36	0.25	< 0.02	0.37	0.029	0.004	0.004	0.06
TiO ₂	0.035	0.405	1.24	0.016	0.021	0.11	1.97	0.27	0.009	0.68	0.031	0.017	0.002	-
Al ₂ O ₃	0.023	0.424	1.4	0.017	0.023	0.11	2.15	0.29	0.007	0.77	0.032	0.015	0.002	_
MgO	0.031	0.227	1.11	0.025	0.024	0.14	1.85	0.29	_	0.6	0.023	0.03	-	-

					KOU 1/22+ T OC						
Modifier	σ_t	σ _{0.2}	δ	ο ψ		KCV, J/cm ² at 1, °C					
	М	Pa	ģ	%	+20	0	-20	-40			
Without modi- fying	693	605	14.5	48.4	97	87	75	53			
FeTi	747	690	19	60	74	69	63	61			
TiN	712	580	5.3	14.7	55	47	40				
SiC	775	729	18	60	55	49	44	36			
TiC	728	665	19	61	82	72	63	52			
VC	780	706	14	56	57	55	52	_			
NbC	594	594	3	5.75	44	35	24	_			
ZrO ₂	645	556	21	60	116	96	98	82			
TiO ₂	709	636	19	57	85	72	60	50			
Al ₂ O ₃	728	621	18	54	82	58	50	36			
MgO	644	586	19	60	103	_	69	60			

Table 2. Mechanical properties of modified weld metal

Investigation results. The process of the influence of liquid weld metal modification on improvement of its mechanical properties is guite complicated and ambiguous. Modifiers added to the liquid metal pool, can react with additives in the metal to form nonmetallic inclusions. Modification can also lead to decomposition of the existing nonmetallic inclusions and formation of new ones. Atoms of modifier compounds can also join the existing nonmetallic inclusions, forming more complex nonmetallic inclusions. Modifier particles can also dissolve, and, as a result, change the solid solution composition [8]. At liquid metal solidification modifiers can affect the primary dendrite structure of weld metal, parameters and nature of the dendrite structure of the weld [9]. At the same time, however, the nonmetallic inclusions formed as

a result of modification can influence the processes of secondary crystallization and structure formation during overcooled austenite transformation [10].

Change of the weld metal chemical composition and particles of refractory compounds will also have an impact on the kinetics of solid-state transformations, transformation temperature and forming microstructure. The microstructure will be also influenced by the composition, distribution and size of the modifying and secondary phases [10, 11].

Addition of powderlike material to the liquid metal pool (Figure 2) may have the following result: weld metal can contain the initial modifier particles; particles can dissolve, changing the solid solution composition; particles can precipitate in the form of dispersed nonmetallic inclusions; coagulation and sticking to-



Figure 2. Influence of weld metal modifying on the nature of dispersed particle transformations

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Figure 3. Mutual influence of chemical composition, austenite transformation temperature, structural-phase composition on mechanical properties of weld metal

gether of modifier particles with further formation of extended phase precipitates can take place. Dissolved particles can also change the morphology and composition of the already existing nonmetallic inclusions.

That is, the chemical composition and parameters of the particles will influence the austenite transformation temperature and the structural-phase composition, as well as mechanical properties of the metal. This mutual influence is conditionally presented in Figure 3.

Nonmetallic inclusions and phase precipitates can have a strong influence on formation of the metal structural-phase composition, they can be the centers of crystallization and recrystallization that may facilitate in terms of energy formation of a particular structural component, changing not only the temperature range of transformation, but also the kinetics of structural-phase transformation, structural-phase composition and mechanical properties of the metal.

Change of austenite transformation kinetics as a result of modifying cannot change the temperature of the start or end of transformation, but it will influence the nature of metal deformation, associated with crys-



Figure 4. Influence of modifying on the change of phase transformation kinetics: a — dilatogram; b — first derivative of dilatation with respect to temperature



Figure 5. Microstructure (×1000) of the metal of welds modified by powders: a - TiC; b - TiN; $c - \text{TiO}_2$; $d - \text{ZrO}_2$

Modifier type	AF	GBF	IGF	WF	B _u	B ₁	MAC	Ferrite	Bainite
-	27	18	8	9	14	24	-	35	65
FeTi	55	18	13	11	-	-	3	42	55
TiN	52	16	18	8	_	-	6	42	52
TiC	30	16	3	6	20	25	-	25	75
SiC	17	15	3	4	11	43	7	22	71
VC	11	9	-	18	47	12	3	27	70
NbC	9	7	-	11	43	9	21	18	61
ZrO ₂	31	16	9	7	11	26	_	32	68
Al ₂ O ₃	3	3	_	32	50	12	_	35	65
MgO	32	12	10	7	16	23	_	29	71
TiO ₂	60	12	20	-	-	8	-	32	68

Table 3. Structural composition of modified weld metal, %

talline lattice restructuring during transformation, i.e. with the transformation «speed» (Figure 4).

In connection with the above, the influence of modifying on weld metal microstructure, nonmetallic inclusion composition and distribution and phase transformation temperature was studied.

The results of studying the influence of modifying by dispersed particles the metal of HSLA steel weld on formation of the secondary crystalline structure are shown in Figure 5.

It was found that formation of different structural components is observed for all the studied samples of welded joint weld metal, such as upper bainite (B_u) , lower bainite (B_l) , Widmanstatten ferrite (WF), acicular ferrite (AF), grain-boundary ferrite (GBF), intragranular ferrite (IGF), and martensite-austenite-carbide (MAC) precipitates. Quantitative metallography methods were used to determine the volume fraction of structural components, forming in modified welds (Table 3).

Electron transmission microscopy methods were used to conduct «transmission» analysis of the fine structure forming in the weld metal: substructure, lath parameters, distribution, dimensions and composition of phase precipitates, change of dislocation density of metal in modified welded joints, as well as for comparison with weld metal without modifying (Figure 6, Table 4).

It is found that nonmetallic inclusions based on titanium compounds form inside weld metal grains with dislocation density $\rho = 10^{10} - 10^{11}$ cm⁻² around the inclusions, and increase the values of metal strength



Figure 6. Phase precipitates in the metal of welds modified by: a - SiC; $b - \text{ZrO}_2$; c - TiN; d - TiC

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Modifier type	$h_{ m lath},\mu{ m m}$	$d_{ m fr}$, µm	D _p , μm	λ _p , μm	ρ, cm ⁻²				
Without modifier	0.5–1.7	0.4–1.5	0.01-0.05*	0.05-0.17*	(4-6) 1010				
FeTi	0.7–2.3	0.4–1.6	0.03-0.05* 0.01-0.02**	0.06-0.15* 0.02-0.03*	$\begin{array}{c} (4-6) \ 10_{1} \\ (1-2) 10 \\ \end{array}^{10^{*}}$				
TiN	0.4–1.2	0.3–1.0	0.02–0.08* 0.03–0.05**	0.08–0.15* 0.03–0.1**	$\begin{array}{c} (4-6) \ 10^{10*} \\ (2-3) \ 10^{11**} \end{array}$				
SiC	0.7-1.5	0.4–0.8	0.03–0.1* 0.02–0.07**	0.03-0.15	(4-8) 1010				
ZrO ₂	0.4–1.4	0.2–1.0	0.017-0.08	0.05-0.13	(6-8) 1010				
TiC	0.5–1.5	0.2–1.2	0.013-0.07	0.04-0.1	(4-8) 1010				
<i>Note.</i> * — in the grain volume; ** — on grain boundaries; h_{lath} — lath width; d_{fr} — fragment size, D_{p} — size of phase precipitate particles and distances between them (λ), ρ — dislocation density.									

Table 4. Parameters of fine structure of modified weld metal

and lower the crack resistance, while oxide nonmetallic inclusions form near the grain boundaries with dislocation density $\rho = 10^8 - 10^9$ cm⁻².

Analysis of the influence of modifying on nonmetallic inclusion size distribution in the weld metal is shown in Figure 7, a.

It is found that modifying leads to coarsening of nonmetallic inclusions in the weld metal. The number of up to 0.3 μ m particles becomes smaller, due to increase of the fraction of particles of more than 0.5 μ m size. This is indicative of the fact that after dissolution the modifier particles, in addition to the possibility of formation of individual phase precipitates, similar in their composition to that of the modifiers, can coagulate with dispersed nonmetallic inclusions (of oxide type) present in the weld metal.

Determination of nonmetallic inclusion composition was conducted on microsections and fractures of samples after testing (Figure 7, *b*). Identification of the composition of nonmetallic inclusions by the method of X-ray spectrum microanalysis (RSMA), using Auger-microprobe JAMP-9500F showed that practically all the analyzed inclusions are a composition of manganese, silicon, aluminium, titanium and sulphur oxides with different ratio of the components.

Analysis of the influence of modifying on temperature parameters of transformation of HSLA steel weld metal is given in Figure 8. Thermokinetic diagrams (TKD) of overcooled austenite decomposition were plotted, critical temperatures A_{c1} and A_{c3} , temperatures of the start and end of austenite decomposition, as well as the temperature of maximum transformation intensity T_v were determined (Table 5).

It is found that modifying by ZrO_2 and MgO particles leads to a certain increase of the temperatures of transformation start for cooling rates below 17 °C/s. Modifying by TiC, SiC, NbC, TiO₂, Al₂O₃ and TiN particles leads to lowering of critical transformation temperatures (see Table 5). Modifying by carbide modifiers and TiN leads to occurrence of a pronounced martensite phase at dilatometric and metallographic studies. The highest content of martensite and the highest values of metal microhardness were obtained for samples modified by TiN particles.







Figure 8. TKD of weld metal: a — without modification; b — modification by ZrO₂

Dependence of transformation temperature on the cooling rate demonstrates a lowering of transformation temperature for all the studied samples. It should be noted that modifying by ZrO₂ and MgO particles leads to increase of transformation temperature by 50–75 °C, and, on the whole, the values of transformation temperatures for MgO, ZrO₂, TiO₂, Al₂O₃ oxide modifiers are located higher than those for SiC, VC, NbC carbide particles. The lowest values of transformation temperature are observed for a sample modified by TiN titanium nitride.

Analyzing the modifier influence on the structure and mechanical properties of HSLA steel weld metal it was established that application of titanium nitride TiN powders leads to increase of the fraction of intragranular and polygonal ferrite (up to 50 %) that has a negative effect on the value of impact toughness of the weld metal already at relatively high test temperature: KCV_{-20} 40 J/cm².

Application of TiO₂, ZrO₂, MgO oxide powders promotes formation of a dispersed structure of acicular ferrite (from 30 to 90 %), which, as is known, allows obtaining a more favourable combination of high strength and impact toughness in the weld metal, particularly at extremely low test temperatures -40--60 °C (Figure 9).

Analysis of the obtained results shows that the strength values decrease with increase of transformation temperature (Figure 9, a), while impact toughness values (Figure 9, b) and ductility of metal in the

modified welds increase. Samples modified by niobium carbide NbC and titanium nitride TiN are an exception. Both the samples are characterized by lowering of the values of strength and ductility at relatively low value of the temperature of maximum intensity of austenite transformation.

It is found that for metal of modified welds the ratio of the structural components is almost linearly related to the temperature of maximum transformation intensity T_{v} .

Influence of structural composition on mechanical properties of modified weld metal showed that at increase of the ratio of ferrite phase quantity to that of bainite one, a lowering of strength characteristics and increase of ductility characteristics of weld metal is observed. Differences from the general dependence are demonstrated by samples of the metal of welds, modified by TiN and NbC that is attributable to formation of martensite phase, as a result of dissolution of carbide forming modifier elements.

Thus, it was found that the temperature of maximum transformation intensity T_v is the most significant value among the parameters, having the greatest influence on the mechanical properties of modified weld metal (chemical composition, nonmetallic and phase inclusions, transformation temperature, structural-phase composition, etc.). It is established that there is a clear dependence correlating the above-mentioned parameters for samples modified by oxide and carbide particles.

Table 5. Characteristic temperatures of modified weld transformation

T %C		Modifier particle type											
<i>I</i> , C	Base	FeTi	TiN	ZrO ₂	TiO ₂	Al ₂ O ₃	MgO	SiC	TiC	VC	NbC		
B	677	654	600	678	652	651	684	647	653	645	647		
B _f	470	472	422	492	478	466	486	440	476	460	458		
	576	573	505	579	575	564	587	535	573	559	545		



Figure 9. Influence of temperature of maximum transformation intensity T_v on structural-phase composition and mechanical properties of modified weld metal: a — ultimate strength; b — impact toughness KCV

Dissolving in the metal of welds, carbide modifiers change the solid solution composition and thus affect the nature of structure formation. For welds modified by oxide and titanium compounds containing modifiers, a certain deviation of the values of kinetic transformation parameters is observed that confirms an essential influence of exogenous nonmetallic inclusions and phase precipitates and of the morphology of endogenous nonmetallic inclusions on the conditions of secondary structure formation and mechanical properties of HSLA steel welds.

Conclusions

1. It is found that the composition of nonmetallic inclusions (oxide or based on titanium compounds), nature of their location relative to the grain boundaries (near the boundary or inside the grain) and the value of dislocation density gradient near the inclusion influence the kinetics of phase transformation and mechanical properties of HSLA steel welds.

2. Nonmetallic inclusions based on titanium carbide compounds form inside the metal grain with dislocation density of 10^{10} – 10^{11} cm⁻² around the inclusions, increase the values of metal strength and lower the crack resistance, while oxide nonmetallic inclusions form near the metal grain boundaries with dislocation density of 10^8 – 10^9 cm⁻².

Application of powders of titanium nitride TiN leads to increase of the fraction of intragrnular and polygonal ferrite (up to 50 %) that adversely affects the value of impact toughness of weld metal already at relatively high testing temperature KCV_{-20} 40 J/cm².

Use of powders of TiO_2 , ZrO_2 , MgO oxides promotes formation of a dispersed structure of acicular ferrite (from 30 to 90 %) that allows obtaining in the weld metal a favourable combination of high strength and impact toughness, particularly at extremely low testing temperature (-40 - -60 °C).

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