TECHNICAL SCIENCES

NANOMODIFICATION OF WELD METAL DENDRITE STRUCTURE

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Abstract

The shape of dendrite grains in low-alloy steel submerged-arc weld deposits has been examined; it is found that the dendrite grain morphology can be modified because of dispersed refractory inclusions inoculation in the weld pool. Influences of inoculated inclusions on dendrites grain size are also discussed. An increase in the dendrite size has been found to increases content of toughness ferrite structure in weld metal.

Keywords: steels; weld metals; microstructure; transmission electron microscopy; dendrites size modification; dispersed inoculates.

1. Introduction

Rolled steel remains the main material in the manufacture of welded metal structures and will maintain its position in this area in the near future. The constantly growing requirements for the reliability and performance of structures, combined with the need to reduce the costs of their manufacture, have caused an intensive growth in the use of innovative solutions in steel rolling production. Modern low-alloy high-strength steels have a submicron or micron structure, which ensures their high service properties, however, practice has shown that the technology complication for the production of rolled products causes an increase in the number of problems arising during its welding.

The weld metal structure formation begins during the crystallization of the weld pool from the base metal partially melted grains boundaries, but in this process the principle of heredity is violated. So, for example, when welded metal with a grain size up to 10 microns, a weld metal is formed with the grain size up to 100 microns or more. This discrepancy is due to the fact that during the rolling process, the steel billet undergoes the most complex thermomechanical treatment with different reheating regimes and the cyclicity of applied forces in order to obtain a fine-grained structure. The weld metal is formed as a cast metal that does not undergo such processing, therefore, other technological methods are required to refine its structure. To refine the structure of the low-alloy steels weld metal, in addition to varying the parameters of the welding process, alloying, microalloying and modification technologies are traditionally used.

Appearing at the end of the of the last century 50s years, with the entry of high-strength low-alloy steels into the rolled metal market, these technologies developed and improved until recently, however, today they have significantly exhausted their capabilities. As practice has shown, an increase in the alloying level leads to a decrease in the plasticity and toughness of the metal, and an increase in the content of modifiers can lead to embrittlement of grain boundaries. Further development requires the use of new technologies for the formation of the weld metal fine-grained structure.

Traditionally, for these purposes, modification processes are used, which are well studied, described in detail (for example, in monograph [1]) and are widely used in practice. The development of the using equipment resolving possibility for metallographic research has contributed to the growth of publications in the of nanomaterials and nanotechnology field, including nanomodification [2-5].

Modification processes make it possible to change the size and shape of primary crystals, and studies carried out in recent years [6-10] have shown that the use of nanotechnology based on the physicochemical features and surface properties of powder materials can have a significant modifying effect due to the high specific nanomaterials surface area. nanoparticles high energy activity.

Based on the differences in the hydrodynamic conditions in the weld pool from the metal melt during steel smelting, the main possibilities of the weld metal dendritic structure formation are associated with the presence of high-speed convective flows at the crystallization front, thermocapillary motion in the interdendritic space and the value of interfacial tension at the boundary of the growing dendrite with the metal melt. While the first two factors can be influenced by changing the welding process parameters, the last largely depends on the surface-active refractory compounds presence in the molten metallayer ahead of the growing dendrite front.

To increase the effectiveness of this effect, the refractory particles size should correspond to the growing dendrite tip size. In the process of pool crystallization duringlow-alloy high-strength steels welding, dendrites with a 30–40 µm size are formed. Such dendrites surface are new growth initiation centers (branches of the second order) with a about 10 µm size appear [11]. The introducing efficiency refractory particles into the weld pool (inoculating) depends on their size, since too small particles, due to the high intensity of their dissociation in the melt, may not affect the crystallization of the metal, and too large can manifest themselves as large non-metallic inclusions [5]. To select the optimal size of inoculants, it is necessary to determine the possible lifetime of dispersed particles in the metal melt, i.e. the time during which they can influence the weld metal crystal structure formation.

2. Experimental details

To perform calculations, we will use the methodology proposed in [12]. When welding low-alloy steels, much attention is paid to the influence of non-metallic inclusions containing titanium or zirconium compounds on the structure and properties of the weld metal; therefore, we will consider the possibility of using some refractory titanium and zirconium compounds as dispersed inoculants. Physical-chemical characteristics of usinginiculants are given in Table 1.

To carry out thermodynamic calculations, a scheme was adopted, according to which a transition layer is formed around a refractory inclusion with radius r_0 located in a steel melt, containing [i] the elements of the inclusion. The time of complete the inclusion dissociation t is calculated from the expression

$$= \frac{{}_{0}^{2}}{2}$$

where A_i and A_B are the atomic masses of the element included in the inclusion and inclusion; $[i]_o$ and D_i are the content of the element in the metal melt and the coefficient of its diffusion in this melt; ρ_B - inclusion density.

Table 1

Parameters	Magnitude
Steel density, kg/м^3	$7{\cdot}10^3$
TiC density, kg/м^3	$5{,}4{\cdot}10^3$
TiN, density kg/м^3	$5{,}4{\cdot}10^3$
TiO_2, density kg/м^3	$4{,}25{\cdot}10^3$
Ti content in the weld metal, %	0,04
C content in the weld metal, %	0,07
N content in the weld metal, %	0,01
O content in the weld metal, %	0,06
Diffusion coefficient Ti in steel, м^2/s	$8{\cdot}10^{-9}$
Diffusion coefficient C in steel, м^2/s	$7{,}9{\cdot}10^{-9}$
Diffusion coefficient N in steel, м^2/s	$3{,}8{\cdot}10^{-9}$
Diffusion coefficient O in steel, м^2/s	$4{,}5{\cdot}10^{-9}$

According to the data given in the literature [13], the weld pool lifetime, depending on the welding mode parameters, can range from 2 to 15 seconds. Table 2 shows calculating results the time required for complete inoculants dissociation in the steel melt in the absence of stirring.

Table 2

Inoculant	Time required for complete dissociation(s) inclusions with size, mkm									
	1,0	2,0	5,0	10	20	40	80	120	160	200
TiC	0,05	0,21	1,34	5,35	21,40	85,61	342,46	770,53	1369,8	2140,4
TiN	0,01	0,06	0,35	1,40	5,60	22,40	89,61	201,62	358,4	560,1
TiO_2	0,03	0,13	0,83	3,33	13,32	53,29	213,15	479,59	852,6	1332,3

Intense flows of molten metal in the weld pool, with the speed magnitude higher than the welding speed [13], significantly increases the rate of particle dissociation. Estimated calculations performed according to the method [12] show that the dissociation processes activity in this case can increase by two orders of magnitude compared with stationary conditions.

Based on the result of the performed calculations, the following conclusions can be drawn: firstly, in order to preserve inoculants as active influence centers on the weld pool metal crystallization processes, it is advisable to introduce them in the form of refractory crystalline compounds with a size at least 0.2 mm (200 µm); secondly, the TiN compounds use for these purposes does not allow achieving the set goals, since inclusions up to 50 µm in size almost completely dissolve in the steel melt, and the presence of larger inclusions in the weld metal structure can cause a decrease in the level of their plasticity and toughness.

During the solid phase growth in the metal melt at the interface, a metal layer is formed with an increased content of liquidating elements, which determines the energy of interphase interaction at the “liquid - solid” interface, and, consequently, the supercooling amount and the crystallization rate, in accordance with the expression

$$\Delta \quad = \frac{- \ \cdot}{\cdot \ \ \cdot},$$

where $\sigma_{l\text{-}s}$ is the value of the interfacial tension at the “liquid - solid” interface, T_l is the liquidus temperature of the metal melt, r is the critical radius of the solid phase nucleus, ρ□and q_s are the density and specific heat of the metal crystallization. Upon contact of a refractory inclusion with the growing dendrite boundary the composition of the boundary layer changes due to enrichment in the inclusion dissociation products, which can be described by the expression

$$\Delta \quad = \frac{{}_{0}(1- \ )}{},$$

where m is the tangent of the alloy liquidus line slope, C_0 is the initial impurity content in the melt, k and D are the distribution and diffusion coefficients of the impurityin the melt. By changing the interfacial tension at the “liquid - solid” interface, inclusions can affect the growth rate and morphology of dendrites in the solidifying metal, and the closer the sizes of the dendrite growth initiation centers and non-metallic inclusions are, the more noticeable this effect will be.

In a fundamental review of the processes of forming the metal structure of weld seams [14], it was shown that the modifying effect of inoculants critically depends on the size of the modifier particles and the time of residence in the liquid metal of the welding bath. The importance of the energy of the catalyst/metal interface in controlling the effectiveness of materials as catalysts for crystal nucleation from the melt was shown, and it was also established that an effective catalyst must have a close structural connection with the metal.

Non-metallic inclusions cause significant damage (such as surface and internal defects) in steel products and can reduce the strength and toughness of welded joints, but the addition of certain elements has a modifying effect to suppress the columnar grain structure of cast steel.

Titanium is one of the most effective alloying elements that improves the mechanical properties of materials in steelmaking and welding metallurgy. It is known that Ti-containing phases, such as TiC, TiN, Ti(CN), TiOx, and MnTiOx, can inhibit grain growth due to the Zener pinning effect, leading to the formation of more dispersed metal grains, and can also act as nucleation centers for acicular ferrite morphology.

The work [15] shows the effectiveness of steel modification with titanium and TiC particles dispersed in the melt.

When choosing the type of inoculants for research, they proceeded from their surface activity when interacting with an iron-based melt. The size of the inoculants was chosen taking into account their subsequent dissolution in the molten metal of the welding bath. Based on the data on the physicochemical parameters of refractory compounds, given in the table. 2.34, TiC and ZrO_2 were chosen for further experiments as materials with the highest liquid iron wetting angle.

Physical and chemical characteristics of refractory inoculants [16]

Type of inoculant	Melting point, T_m, °C	Surface tension of the liquid phase σ_l, mJ/m^2	Marginal wetting angle θ, degree	Adhesion work Wa, mJ/м^2
TiC	3260	1780	125	760
TiN	2930	1780	132	590
SiC	2730	1780	82	2030
TiO_2	1843	1780	≈ 0	3560
Al_2O_3	2044	1785	40	3155
ZrO_2	2715	1785	102	1020

2.1. Weld preparation

For investigation possibility modification weld metal structure with nanosize inclusions, the weld metals were obtained by high-strength low-alloy steel arc welding with the refractory non-metallic inclusions introduction into the weld pool. Studies were carried out on deposited metal samplesobtained without introducing nanomodifiers (weld NM-0) and with introducing refractory compounds of titanium carbide (weld TiC) and zirconium oxide (weld ZrO_2). Zirconium oxide and titanium carbide particles up to 200 μm in size were introduced through a flux-cored wire, which was fed into the weld pool in the form of an additive. Chemical composition of welded metals are show in table 3.

Table3

Chemical composition of weld metals

Weld№	C	Si	Mn	S	P	Ni	Mo	Al	Ti	Zr
NM-0	0,050	0,290	1,32	0,024	0,014	2,19	0,27	0,039	0,019	н/о
ZrO_2	0,053	0,138	0,94	0,020	0,024	1,55	0,23	0,021	0,005	0,06
TiC	0,046	0,340	1,39	0,021	0,019	1,70	0,24	0,033	0,011	н/о

2.2. Quantitative metallography

In Fig. 1 shows the structure of weld metal samples. Metallographic studies using transmissio electron microscopy, performed by DSci Markashova L.I. on a JEM-200 CX device (JEOL company) at an accelerating voltage of 200 kV, showed that the introduced dispersed inclusions, firstly, do not dissociate completely in the liquid metal, and, secondly, they are located at the grain boundaries of the secondary structure.

When dispersed refractory compounds with a size of not more than 200 μm were introduced into the weld pool, corresponding compounds with sizes ranging from 30 to 100 nm were revealed at the grain boundaries of the secondary structure, which indicates afairly high resistance of these inclusions both in liquid and solid steel solutions.

To clarify the question of these inclusions possible influence on the dendritic structure, we investigated the weld metal primary structure on polished samples etched in a boiling saturated solution of sodium picrate in water. The microstructure of the last passin a multipass weld (cast structure) was investigated. The samples were cut in a direction perpendicular to the weld longitudinal axis, so that dendrites were visible on the surface section. The dendrites grew in greatest thermal gradient direction in the weld pool. The study of the primary structure according to the images obtained by the optical metallography method was arried out by Ph.D. Ermolenko D.Yu. using a NEOPHOT 30 optical microscope. The results of the columnar dendrites dimensions (dimensions λ) are show in Fig. 2.

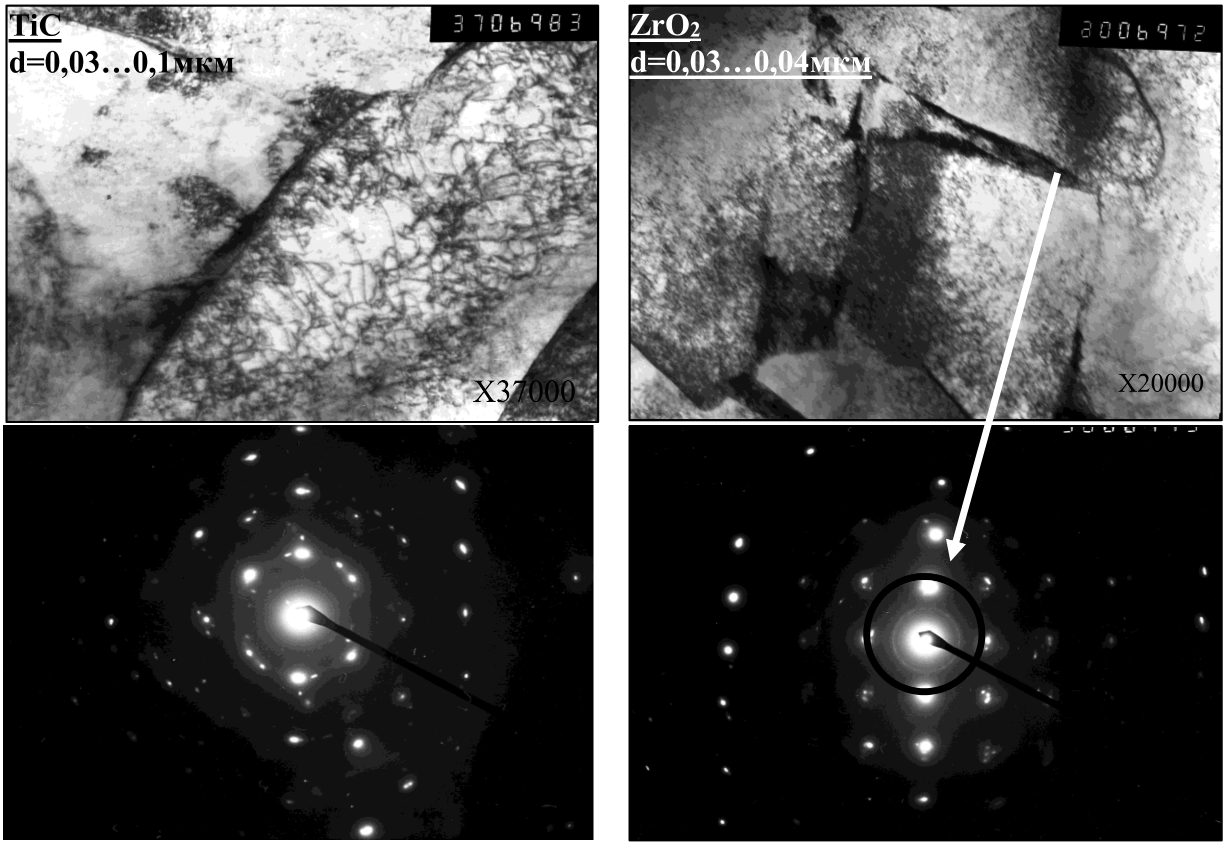
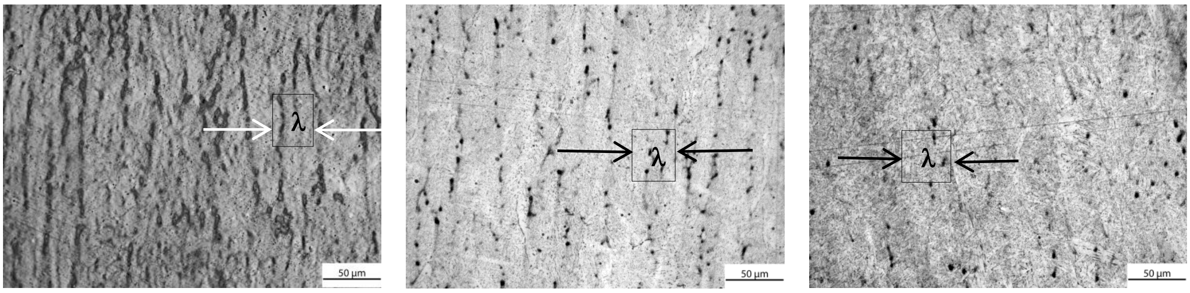


Fig. 1. Fine structure of weld metal

3. Results and discussion

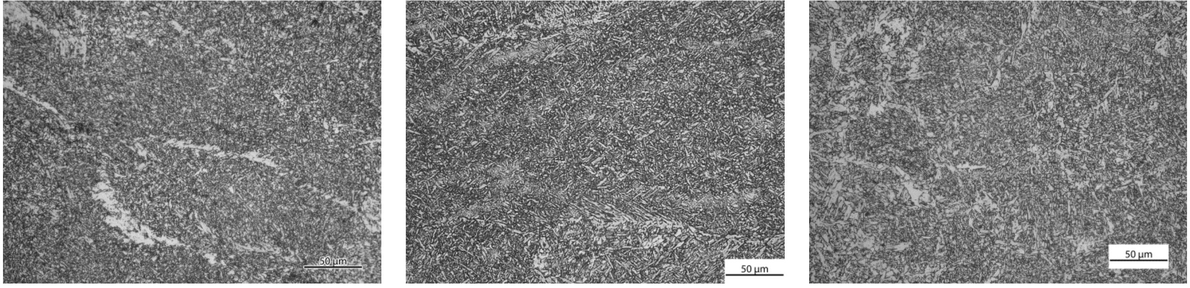
The results of the analysis showed that the presence of nanosized refractory compounds in the weld pool has a modifying effect on the dendrites size. If in themetal with nonmodification(welds NM-0) the average dendrites width was 25 μm, then, as a result of the introduction of nanosized compounds of titanium carbide (TiC weld) and zirconium oxide (ZrO_2 weld), the average dendrites width increased to 44 and 37 μm, respectively.



Weld metal NM-0 Weld metal TiC Weld metal ZrO_2

Fig. 2. Dendritic structure of weld metals

The change in the of dendrites morphology affected on the secondary structure formation (Fig. 3, Table 4) and the weld metal mechanical properties level (Table 5). From the data given in Tables 4-6, it can be seen that the introduction of nanomodifiers practically did not affect the chemical composition of the weld metal, while the composition of their structural components noticeably changed.



Weld metal NM-0 Weld metal TiC Weld metal ZrO_2

Fig. 3. Secondary structure of weld metal

An increase in the size of dendrites, noted as a result of titanium carbide and zirconium oxide compounds introduction into the weld pool, is accompanied by a change in the ratio between the content of upper (B_u) and lower (B_l) bainite while maintaining the proportion of martensite (M) and allotriomorphic ferrite (F). As a result, both the plasticity and the toughness of the weld metal increase (Table 5).

Table 4

Weld №	Content (%) in microstructure of weld metals			
	B_l	B_u	M	F
NM-0	25	60	10	5
ZrO_2	65	20	10	5
TiC	50	30	10	10

Table 5

Weld №	σ_B	$\sigma_{0,2}$	δ	ψ	KCV, J/cm^2 at T, ^{0}C			
	MPa		%		+ 20	0	– 20	– 40
NM-0	788	739	11,4	35	60	58	57	52
ZrO_2	645	556	21	60	116	96	98	82
TiC	728	665	19	61	82	72	63	52

This work did not consider problems related to the technology of modifiers inoculation into the weld pool, the choice of their type, size and content. These problems are related to the topics of forthcoming research. The purpose of this work was to demonstrate the possibilities of using refractory dispersed inclusins for nanomodification of weld metal.

Conclusions

Research has been carried out to determine the possibility the dendritic structure nano-modification of the low-alloy steels weld metals by inoculating dispersed refractory joints into the weld pool. As a result of the work performed, it was found that

1. Taking into account the thermodynamics and kinetics of non-metallic inclusions dissolution in the weld pool, the optimal size of inoculants is within 200 - 500 □m. Smaller inclusions have a high tendency to dissolve in the metal melt before the start of the crystallization process, while larger ones can serve as a source of weld metal brittle fracture.
2. It has been shown that inoculated inclusions are present in the weld metal structure in the form of interlayers with 30 to 100 nm thicknesses at grain boundaries, which indicates a sufficiently high resistance of these inclusions both in liquid and solid steel solutions.
3. It has been established that the inoculation of dispersed refractory inclusions into the weld pool can have a modifying effect on the dendrites formation.
4. Changes in the width of dendrites, wich grew during metal crystallization, affect the conditions for the secondary structure formation and the level of weld metal mechanical properties.

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