

POSSIBILITIES OF NANOMODIFICATION OF DENDRITE STRUCTURE OF WELD METAL

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Possibility of application of refractory disperse compounds for nanomodification of weld metal was shown. The results of calculation of the optimum size of modifier particles for weld pool conditions are given. Effect of the refractory particles on the parameters of weld metal primary structure was determined. Increase of dendrite size, noted as a result of addition into a weld pool of titanium carbide and zirconium oxide compounds, is accompanied by change of relationship between content of upper and lower bainite preserving fraction of martensite and xenomorphic ferrite. Indices of ductility as well as toughness of weld metal increase as a result. 14 Ref., 4 Tables, 3 Figures.

Keywords: *fusion welding; weld metal modification, nanodisperse particles, particle size, dendrite size, microstructure, mechanical properties*

Rolled steel continues to be the main material in manufacture of welded metal structures and in the closest time will keep its position in this sphere. Continuous growth of the requirements to safety and workability of structures in combination with the necessity to reduce costs on their manufacture have promoted intensive growth of application of innovative solutions in steel rolling production. Modern low-alloy high-strength steels have submicron or micron structure, that provides their high service properties, however, the practice showed that complication of rolled stock production technology promotes increase of amount of problems appearing in its welding.

Formation of weld metal structure starts in the process of solidification of the weld pool from the boundaries of partially fused grains of the base metal, but heredity principle is violated in this process. Thus, for example, welding of metal with grain size up to 10 μm forms the weld, in which grain size can reach 100 μm and more. Such nonconformity is related with the fact that a steel billet in process of rolling is subjected to complex thermomechanical treatment with different mode of reheating and cycle of applied forces for the purpose of production of fine structure. The weld is formed as cast metal, which is not subjected to such treatment, therefore, other technological means are necessary for refinement of its structure. Traditionally, technologies of alloying, microalloying and modification are used for refinement of weld metal structure in addition to variation of welding mode parameters. These technologies, which has appeared at the end of 1950th and entered to the market of rolling of high-strength low-alloy steels, have been de-

veloped and improved till the recent time, however, up to the moment they have exhausted their potential. The practice showed that increase of alloying level results in decrease of ductility and toughness indices of metal, and rise of content of modifiers can lead to grain boundary embrittlement. Further development requires application of new technologies of formation of weld metal fine structure.

Traditionally, the modification processes, which are well studied and described in details (for example in monograph [1]) and widely used in practice, are applied for these purposes. Improvement of resolution capability of the equipment used for metallographic investigations, promoted increase of number of publications in the field of nanomaterials and nanotechnologies, including nanomodification [2–5].

Modification processes allow changing size and shape of primary crystals and carried in the recent years investigations showed that [6–10] application of nanotechnologies, which is based on peculiarities of physical-chemical and surface properties of powder materials, can have significant modifying effect due to high specific surface of nanomaterials and high energy activity of the nanoparticles.

Proceeding from the differences of hydrodynamic situation in the weld pool from the metallic melt in steel casting, the main possibilities of effect on formation of dendrite structure of weld metal are related with presence of high-speed convective flows close to a solidification front, thermocapillary movement in interdendritic space and value of interphase tension at the boundary of growing dendrite with metallic melt. If the first two factors can be effect by variation of the parameters of welding modes, than the latter to signif-

Table 1. Time of dissociation of inclusions, s

Inoculant	Size of inclusions, μm									
	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

icant extent depends on presence of the surface-active refractory compounds in a layer of metallic melt before growing dendrite front. In order to increase the efficiency of such effect the size of refractory particles should correspond to the size of growing dendrite tip. Process of pool solidification in welding of low-alloy high-strength steels provokes formation of dendrites of 30–40 μm size, on surface of which appear new centers of growth initiation (branches of second order) of around 10 μm size [11]. Efficiency of addition into the weld pool (inoculation) of the refractory particles depends on their size, since too small particles, due to high intensity of their dissociation in the melt, can have no effect on metal solidification, but too big are able to behave themselves as coarse nonmetallic inclusions [5]. In order to choose the optimum inoculant size it is necessary to determine probable time of existence of the disperse particles in the metal melt, i.e. the time during which they can have effect on formation of weld solidification structure.

Let's use procedure proposed in work [12] for calculations. In welding of low-alloy steels significant attention should be paid on effect of nonmetallic inclusions containing titanium compounds on structure and properties of weld metal. In this connection, let's consider the possibility of application of some refractory compounds of titanium as disperse inoculants. Their physical-chemical characteristics presented below and they were used for thermodynamic calculations.

Physical-chemical characteristics

Density, $\cdot 10^3$, kg/m ³ :	
steel	7
TiC	5.4
TiN	5.4
TiO ₂	4.25
Content in weld metal, wt.% (kg/m ³):	
Ti	0.04 (2.8)
C	0.07 (4.9)
N	0.01 (0.7)
O	0.06 (4.2)
Coefficient of diffusion in steel, $\cdot 10^{-9}$ m ² /s:	
Ti	8
C	7.9
N	3.8
O	4.5
Equilibrium constant of dissociation reaction at 1873 K:	
TiC	-0.475
TiN	2.515
TiO ₂	-2.485

Coefficient of activity in weld metal:

Ti	8.70
C	0.29
N	0.11
O	1.0

Thermodynamic calculations were carried out following the scheme, in accordance with which a transition layer, containing $[i]_{\text{sur}}$ elements present in inclusion content, is formed around a refractory inclusion of radius r_0 located in steel melt.

Time of complete dissociation t is calculated from the expression

$$t = \frac{r_0^2 A_i \rho_B}{2A_B D_i ([i]_{\text{sur}} - [i]_0)},$$

where A_i and A_{inc} are the atomic weights of element present in the inclusion and the inclusion itself; $[i]_0$ and D_i are the content of element in metallic melt and coefficient of its diffusion in this melt; ρ_{inc} is the inclusion density.

Based on the data, provided in the literature [13], time of existence of the weld pool depending on parameters of welding mode can lie in the limits from 2 to 15 s. Table 1 shows the results of calculation of time necessary for complete dissociation of inoculants in steel melt without mixing.

Presence of the intensive flows of molten metal in the weld pool, rate of which can be an order higher than the welding rate [13], significantly increase rate of particles dissociation. The calculation estimations, carried on procedure [12], show that activity of dissociation processes in this case can rise by two orders in comparison with stationary conditions.

Proceeding from the received results of carried data calculations, it can be concluded that, first of all, to preserve the inoculants as active centers of effect on weld pool metal solidification processes it is reasonable to add them in form of disperse particles of refractory crystalline compounds of not less than 0.2 mm (200 μm) size; secondly, application of TiN for these purposes does not allow achievement of determined purposes since inclusions of up to 50 μm size are virtually completely dissolved in steel melt and presence of coarser inclusions in the weld metal structure can promote decrease of level of their ductility and toughness indices.

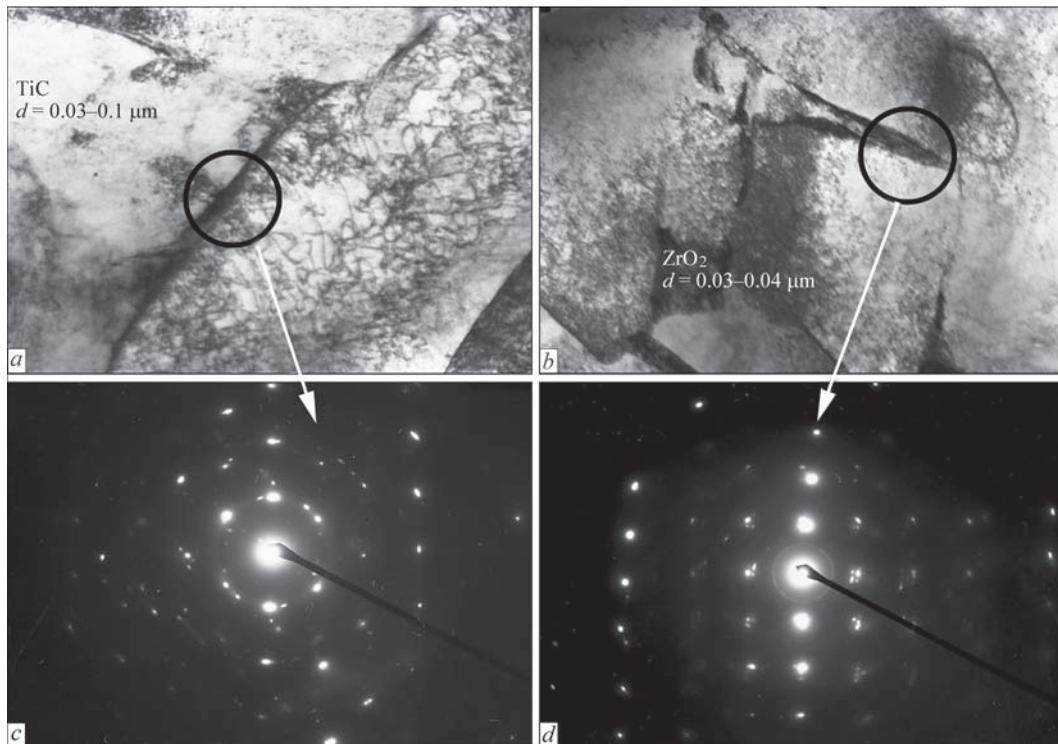


Figure 1. Fine structure of weld metal of 12GN2KhM type, containing inclusions of TiC (a, $\times 37000$), ZrO_2 (b, $\times 20000$); c, d — diffraction pattern of areas with inclusions

In the process of growth of solid phase at interphase boundary in the metallic melt there is a layer of metal with increased content of liquation elements, which determines energy of interphase interaction at «liquid–solid» boundary, and, thus, value of overcooling and solidification rate, in accordance with expression

$$\Delta T = \frac{\sigma_{l-s} T_l}{r \rho q_s},$$

where σ_{l-s} is the value of interphase tension at «liquid–solid» boundary; T_l is the liquidus temperature of metallic melt; r — is the critical radius of solid phase nucleus; ρ and q_s are the density and specific heat of metal solidification.

Contact of the refractory inclusion with the boundary of growing dendrite changes the composition of boundary layer due to saturation with the products of inclusion dissociation that can be described by expression

$$\Delta T = \frac{m C_0 (1-k)}{k D},$$

where m is the tangent of inclination angle of alloy liquidus line; C_0 is the initial content of impurity in the melt; k and D are the coefficients of distribution and diffusion of impurity in the melt.

Varying the value of interphase tension at «liquid–solid» boundary, the inclusions can effect the rate of growth and morphology of dendrites in the solidifying metal, and the closer the dimensions of centers

of dendrite and non-metallic inclusion initiation, the more noticeable this effect will be.

Figure 1 shows the samples of weld metal structure, received in arc welding of high-strength low-alloy steel with addition into the weld pool of refractory nonmetallic inclusions. The investigations were carried out with the samples of deposited metal received without addition of nanomodifiers (weld NM-0) as well as with addition of refractory compounds of titanium carbide (weld TiC) and zirconium oxide (weld ZrO_2). The particles of zirconium oxide and titanium carbide of 200 μm size were added through a flux-cored wire core, which were supplied into the weld pool in form of filler. Metallographic examinations using transmission electron microscopy*, made on JEM-200CX device (JEOL Company) at accelerating voltage of 200 kV showed that the added disperse inclusions do not have complete dissociation in the liquid metal and locate at the boundaries of secondary structure grains. When adding disperse refractory compounds of not more than 200 μm size in the weld pool corresponding compounds of 30–100 nm size were revealed at the boundaries of secondary structure grains. It indicates sufficiently high resistance of these inclusions in liquid as well as solid steel solutions.

To clear up the problem of possible effect of these inclusions on the dendrite structure, the primary struc-

*The examinations were carried out by Dr. L.I. Markashova.

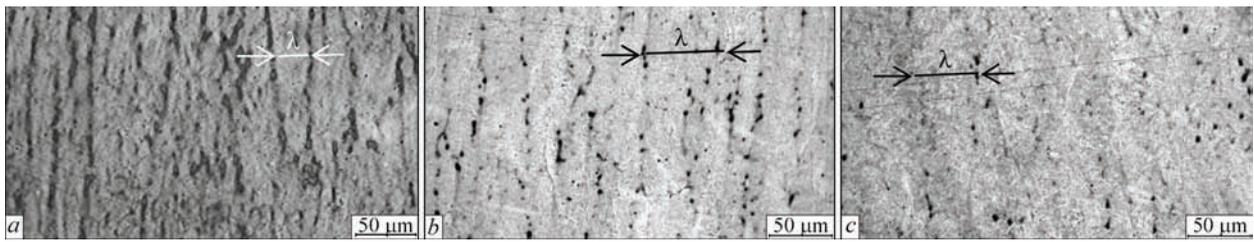


Figure 2. Dendrite structure of weld metal: *a* — NM-0; *b* — TiC; *c* — ZrO₂ (λ — size of columnar dendrites)

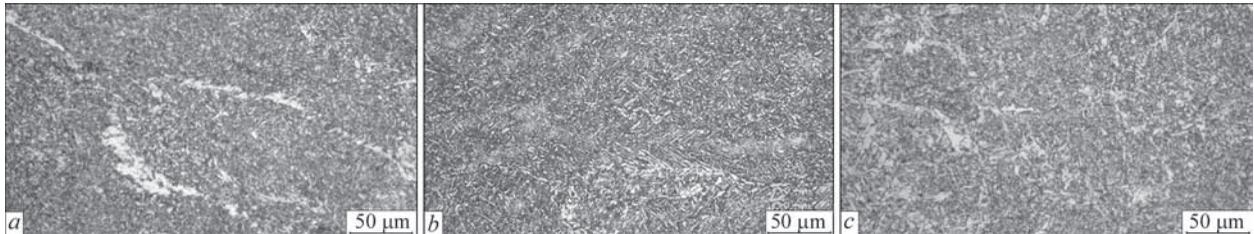


Figure 3. Secondary structure of weld metal: *a* — NM-0; *b* — ZrO₂

ture of weld metal was examined on polished samples, etched in boiling saturated sodium picrate solution (C₆H₂(NO₂)₃ONa) in water. A microstructure of the last pass of metal of multipass weld (cast structure) was examined. The samples were cut out in a direction normal to longitudinal weld axis, in such a way that dendrites, which grew in the direction of the highest thermal gradient in the weld pool, were observed on section surface. The dimensions of columnar dendrites (dimensions λ on Figure 2) were determined during examination of the primary structure on the images, received by method of optical metallography*, which were made on optical microscope NEOPHOT 30.

The analysis results showed that presence in the weld pool of nanosize refractory compounds have modifying effect on dendrite sizes. If in the initial metal (weld NM-0) the averaged width of dendrites made 25 μm , than as a result in addition of nanosize titanium carbide compounds (weld TiC) and zirconi-

um oxide (weld ZrO₂) this index rose to 44 and 37 μm level, respectively.

Change of dendrite morphology effected formation of secondary structure (Figure 3, Table 2) and level of mechanical properties of weld metal (Table 3). It can be seen from data presented in Tables 2–4 that addition of nanomodifiers has virtually no effect on chemical composition of the weld metal, but content of their structural constituents significantly changed at that.

Increase of dendrite size, noted as a result of addition of titanium carbide and zirconium oxide compounds into the weld pool is accompanied by change

Table 2. Content of main structural constituents of weld metal

Weld	Portion of constituents in weld microstructure, %			
	Bl	Bu	M	F
NM-0	25	60	10	5
ZrO ₂	65	20	10	5
TiC	50	30	10	10

Table 3. Mechanical properties of weld metal

Weld	σ_t	$\sigma_{0.2}$	δ	ψ	<i>KCV</i> , J/cm ² at <i>T</i> , °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

Table 4. Composition of weld metal

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	n/o
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	n/o

*The examinations were carried out by Cand. of Tech. Sci. D.Yu. Ermolenko.

of relationship between content of upper (B_u) and lower bainite (B_l) at preservation of portion of martensite (M) and xenomorphic ferrite (F). It results in rise of ductility as well as toughness indices of the weld metal (Table 3).

Present paper does not consider the problems related with technology of addition of the modifiers into the weld pool, selection of their type, size and composition. These problems are referred to further investigations. This paper reflects the possibilities of application of refractory disperse compounds for nanomodification of weld metal.

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