Structure and mechanical properties of 09Mn2Si steel surfaced layers and welds modified by adding titanium carbonitride nanoparticles

N K Galchenko¹, V P Samartsev¹, K A Kolesnikova¹, I V Vlasov¹, S V Panin¹², A V Yakovlev²
¹Institute of Strength Physics and Materials Science SB RAS, 2/4, pr. Akademicheskii, Tomsk, 634055, Russia
²National Research Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia
E-mail: viv@ispms.tsc.ru

Abstract. The study on structure and mechanical properties of surfaced coatings and welded joints of 09Mn2Si steel formed with the use of a standard electrode as well as one modified by adding titanium carbonitride nanoparticles was carried out. Optical and scanning electron microscopy, microhardness measurement were employed to investigate the structure at welding with a standard electrode, as well as to illustrate changes resulting from the electrode modification through adding titanium carbonitride nanoparticles. Evaluation of mechanical properties was performed by conducting tests on static, cyclic and impact loading. It is shown that welding with the use of the modified electrode gives rise to decreasing the size of ferrite grains and increasing impact toughness and fatigue life.

1. Introduction
Welding is one of the most efficient and widespread technologies for producing permanent joints [1]. Parts connected in this way are characterized by high strength, while the welding process itself is not costly. However, the weld itself represents a pronounced macroheterogeneity at the scale of entire structure (component) [2] comprising of a zone of increased brittleness (weld material) and a heat-affected zone (HAZ) located next to the weld and characterized by lower strength [3, 4]. The reduction of the mechanical properties of the weld as compared with the bulk material is observed under impact loading [5] and testing under negative temperatures [6]. To strengthen the welded joint some alloying elements are added into the electrodes which substantially modify the weld material [7]. In this concern the most relevant are nickel and molybdenum which contribute to both austenite stabilizing (in the first case) and the formation of molybdenum carbides during the secondary crystallization of the melt which can concentrate at \( \gamma \rightarrow \alpha \)-transformation boundary. The latter contributes to the refinement of ferrite grains.

However, increasing of strength and toughness may also be achieved due to synergistic effect of several structure–dependent factors. So, another promising way to improve properties of a welded joint might be adding of titanium carbonitride nanoparticles to the melting bath. This should reduce the size of the primary austenite grains and shift the transformation region into a zone of lower temperatures. In so doing, the reason of the latter is appearance of additional crystallization centers or supercooling zones.
Thus, the aim of the paper is studying structure and mechanical properties of surfaced coatings and welded joints formed with the use of electrodes modified through adding of nickel, molybdenum as well as titanium carbonitride nanoparticles. It is expected that this modification will increase mechanical properties of welded joints and protective coatings of low-carbon ductile steel operated at low temperature conditions as well. The low--alloyed structural steel 09Mn2Si used for manufacturing hot-rolled pipes and welded joints was the object of the studies.

2. Fabrication of experimental electrodes
Electrodes for manual arc welding/surfacing were made of a wire grade SV-08 with the diameter of 3 mm (for a root weld) and 4 mm (for coating surfacing) with the covering obtained on the basis of the charge from “OZS-12” electrodes (GOST-2246-60) as well as “MP-3” (GOST 9466-75, GOST 9467-75) whose chemical composition is presented in Table 1.

Self-propagating High-temperature Synthesis (SHS) composite powder of Fe-TiC<sub>0.5</sub>N<sub>0.5</sub> system was loaded into the electrode covering at the production stage as an additional component with the content of 0.15 wt% TiC<sub>0.5</sub>N<sub>0.5</sub> (for the electrode “MP-3”) and 0.25 wt% TiC<sub>0.5</sub>N<sub>0.5</sub> (for the electrode “OZS-12”). The content of TiC<sub>0.5</sub>N<sub>0.5</sub> was selected on the basis of preliminary tests on impact toughness. Welding and surfacing of sheet samples were performed by manual arc method.

| Grade          | C    | Si  | Mn  | S    | P    |
|----------------|------|-----|-----|------|------|
| “OZS-12”       | 0.09 | 0.15| 0.6 | 0.017| 0.026|
| “MP-3”         | 0.1  | 0.2 | 0.5–0.8 | 0.04 | 0.045|

Composite powders (TiC<sub>0.5</sub>N<sub>0.5</sub>–Fe) with the component ratio of 1/1 were prepared by the method of self-propagating high-temperature synthesis (SHS) in a flow reactor. The initial particle size of the composite mixture was less than 2 mm. Grinding was carried out in a continuous mode in a vibromill in argon atmosphere. The size of complex-content particles of TiC<sub>0.5</sub>N<sub>0.5</sub>–Fe composite after milling was 250–500 nm; the particle size of titanium carbonitride (TiC<sub>0.5</sub>N<sub>0.5</sub>) in the fused iron matrix was 80–120 nm. The phase composition of the SHS powder is presented in Table 2. The adding of nickel and molybdenum to the electrode covering was made in the following ratio: Ni (3 wt%), Mo (0.6 wt%).

| Phases     | TiC<sub>0.5</sub>N<sub>0.5</sub> | Ti<sub>2</sub>CN | Fe<sub>3</sub>C | α-Fe |
|------------|-------------------------------|----------------|---------------|------|
| Content (vol.%) | 71                           | 9.25          | 5.72         | 13.46|
| Lattice parameter (nm) | a = 0.4277                   | a = 0.30367, | a = 0.50525, | a = 0.28696|
|              | c = 1.49905                   |               | c = 0.45429  |      |

Table 2. Phase composition of the synthesized composite powder TiC<sub>0.5</sub>N<sub>0.5</sub>–Fe

For fabricating welded samples some plates with the size of 65×300 mm and the thickness of 16 mm with X and V - shaped groove edges were used. The angle between cutting edges was 35°, the blunting of edges made 1.8 ± 0.8 mm. Welding was conducted at the current – 200-220 A of a constant reverse polarity.

The strength properties of welded joints and surfaced coatings were evaluated under static stretching with the help of electromechanical testing machine “Instron 8801”. Macro- and microstructure were analyzed with the use of optical microscope AXIOVERT-200MAT (Zeiss, Germany), microhardness tester PMT-3 (according to the RF State standard referred to as GOST 9450-76) with the load of 100 g. Optical microscope Neophot-21 (Zeiss, Germany) was used for metallographic analysis.
The fatigue tests were carried out with the specimens of 09Mn2Si steel cut out from surfaced layers with the thickness of 6 mm produced by “MP-3” and “OZS-12” electrodes. These layers were then subjected to symmetrical cyclic bending loading at the frequency of 20 Hz at a constant load of 490 MPa with the help of Biss Nano servo-hydraulic testing machine. Impact toughness tests were performed with the use of instrumented pendulum Amsler RKP450 (according to GOST 10708-82) and a cryogenic chamber (produced by Lauda). Specimens for impact bending tests were fabricated in accordance with GOST 6996-66. The specimen design is shown in Figure 1.

![Figure 1](image1)

**Figure 1.** Schematic of specimens for fatigue (a) and impact bending tests with a surfaced coating (b)

3. Testing results

3.1. Coating surfacing

3.1.1. Structural studies. Metallographic analysis of all surfaced coatings deposited by the electrodes with the basic composition I) MP-3 and II) OZS-12 as well as experimental ones (with additives of titanium carbonitride nanoparticles) possess a ferrite-pearlite structure (Fig. 2). In contrast with the structures modified by adding titanium carbonitrides the basic composition is characterized by formation of numerous regions of Widmanstatten ferrite (Fig. 2a) as well as colonies oriented towards the direction of heat sink where dendrite structures represents axes of the first and second orders.

![Figure 2](image2)

**Figure 2.** Optical images of the ferrite-pearlite coating structure obtained by surfacing with a standard electrode (MP-3) (a), (OZS-12) (c) and experimental ones: “MP-3 + 0.15 wt% TiCN” (b) and “OZS-12 + 0.25 wt% TiCN” (d)

The presence of Widmanstatten ferrite at the grain boundaries indicates on the overheating of the fusion zone during electric arc surfacing with the use of standard “MP-3” and “OZS-12” electrodes. Grain size of the coatings surfaced by the standard electrode “MP-3” makes \( d \sim 100-200 \) μm (Fig. 2c). Surfacing with the electrode “MP-3 + 0.15 wt% TiCN” gave rise to refinement of the ferrite-pearlite structure down to a grain size of \( d \sim 20-100 \) μm (Fig. 2d). The average grain size also decreased almost twice at coating surfacing with the modified electrodes “OZS-12 + titanium carbonitrides”: from \( d \sim 5-25 \) μm down to \( d \sim 3-10 \) μm. In both cases, along with the refinement of the macrograins the columnar pattern of the grains as well as variation of grain size in the surfaced coating were also eliminated.

3.1.2. Mechanical properties. The microhardness of the surfaced coatings was evaluated for the use of the “MP-3” electrodes. It is shown that adding of the nanoparticles did not give rise to significant
change of their values. The mechanical properties of the deposited coatings were estimated over the testing results on impact bending, static tension (Table 3) and cyclic bending (Table 4). The tests were carried out at room temperature. The structural changes occurred in the coatings modified with nanosized particles of titanium carbonitride did not give rise to any significant increase of their basic strength properties; however, the impact toughness (\( KCV \)) has increased by \( \sim 2.5 \) times (Table 3).

**Table 3.** Mechanical properties of surfaced coating specimens applied by the electrodes “MP-3” and “MP-3 + 0.15 wt% TiCN” at \( T = 20^\circ \text{C} \).

| Electrode composition | \( KCV \) (J/cm\(^2\)) | \( \sigma_\text{x} \) (MPa) | \( \sigma_{0.2} \) (MPa) | \( \delta \) (%) |
|------------------------|--------------------------|---------------------------|------------------------|-----------------|
| “MP-3”                | 42                       | 679                       | 375                    | 11              |
| “MP-3 + 0.15 wt% TiCN”| 104                      | 710                       | 425                    | 13              |

**Table 4.** Fatigue life of 09Mn2Si steel welds

| \( N_e \) | Type of welding electrode | Load / frequency (MPa/Hz) | Cycles |
|-----------|---------------------------|---------------------------|--------|
| 1         | “OZS-12”                  | 490/20                    | 76445  |
| 2         | “OZS + 0.25 wt% TiCN”     | 490/20                    | 106994 |
| 3         | “MP-3”                    | 490/20                    | 186917 |
| 4         | “MP-3 + 0.15 wt% TiCN”    | 490/20                    | 519564 |

More than twofold increase of the impact toughness for the coated specimens formed with the use of “MP-3 + titanium carbonitride nanoparticles” electrode can be explained by I) structure refinement, II) significant decrease in the number and size of non-metallic inclusions and III) increase of the ductile structural component in the coatings by 70 % of. In addition, the increase of the impact toughness was stimulated by more dense and uniform grain structure of the crystallized metal.

The fatigue test results have shown that coating structure modification by nanosized titanium carbonitride particles introduced through covering of MP-3 and OZS-12 electrodes helps to slow down the accumulation of fatigue damage and increase cyclic durability: by 40% for specimens formed with the help of “OZS-12 + 0.25 wt% TiCN” electrode; by 278 % for the specimens formed with the use of “MP-3 + 0.15 wt% TiCN” one.

3.2. Weld

3.2.1. Structural studies. Additional alloying of the welding pool through the “OZS-12” electrode covering by nickel (3 wt%) and molybdenum (0.6 wt%) contributed to the enlargement of ferritic grains in comparison with the structure shown in Figure 3a.

**Figure 3.** Microstructure of welds produced by “OZS-12 + (3 wt% Ni + 0.6 wt% Mo)” (a) and “OZS-12 + (3 wt% Ni + 0.6 wt% Mo) + 0.25 wt% TiCN” (b) electrodes; microhardness values of welds depending on the electrode composition (c); loading diagrams of welded joints at various testing temperatures (d)
The adding of nano-dispersed refractory titanium carbonitrides into the weld metal made it possible to significantly reduce the size of the primary austenitic grain from 30 µm down to 1 µm (Fig. 3b). Also, the transformation region was shifted towards low temperature zone that contributes to the formation of needle-shaped ferrite (up to 30%).

The complex alloying of the weld with nickel, molybdenum and TiCN nanoparticles (Fig. 3b) proved to be the most effective from the standpoint of enhancement dispersion of structural components. Obviously, this is due to additional formation of crystallization centers in the molten bath as well as initiation of needle-shaped ferrites on them.

Thus, the analysis of the microstructures formed in the surfaced coating metal and weld metal has shown that depending on the alloying and modifying system with refractory nanosized particles the morphology and dimensions of the structural elements change. Also, additional amount of the large number of fine particles is stimulated which contributes to the formation of needle-shaped Ferrite and bainite component improving the performance of the welded joint.

3.2.2. Mechanical properties. Comparative studies of the microhardness of welded joints were carried out for specimens prepared with the use of welding electrodes of 4 compositions (Fig. 3c):

1. Standard electrode “OZS-12”;
2. Experimental – “OZS-12 + 0.25 wt% TiCN”;
3. Experimental – “OZS-12 + Ni (3 wt%) and Mo (0.6 wt%)”.
4. Experimental – “OZS-12 + (3 wt% Ni + 0.6 wt% Mo) + TiCN nanoparticles (0.25 wt%)”.

The results obtained have shown at the use of “OZS-12 + titanium carbonitrides” electrodes regardless of the alloying system employed the weld structures with higher microhardness is formed. Welded joints were tested at static tension for specimens formed with the use of experimental electrodes “OZS-12 + Ni and Mo”. Figure 3d presents their loading diagrams for testing under various temperatures. It is seen that with decreasing the temperature the values of the ultimate strength \( \sigma_U \) increases with a slight decrease of the relative elongation at failure. The values of the ultimate strength corresponding to the test temperatures of welds are following:

1. OZS -12 \( (\sigma_U) \) max (at \( T =-55 ^\circ C \)) = 675 MPa, \( \delta = 16 % \)
2. OZS -12 \( (\sigma_U) \) max (at \( T =-76 ^\circ C \)) = 800 MPa, \( \delta = 18 % \)
3. “OZS -12 + (3 wt% Ni + 0.6 wt% Mo)” (at \( T =-27 ^\circ C \)) \( (\sigma_U) \) max = 575 MPa, \( \delta = 22 % \)
4. “OZS -12 + (3 wt% Ni + 0.6 wt% Mo)” (at \( T =-46 ^\circ C \)) \( (\sigma_U) \) max = 600 MPa \( \delta = 17 % \)
5. “OZS -12 + (3 wt% Ni + 0.6 wt% Mo)” (at \( T =-82 ^\circ C \)) \( (\sigma_U) \) max = 650 MPa \( \delta = 18 % \)

The condition for a brittle crack initiation is running of the preceding microplastic deformation process that gives rise to a local stress concentration and further cracking. The ability of a metal to develop microdeformation predetermines running of local stress relaxation processes and, therefore, the possibility of preventing brittle fracture.

One of the important features of the materials for structural applications including formation of welded joints is ability to operate at low temperatures. In so doing, crack propagation resistance under dynamic bending conditions is of key relevance.

Table 5. Toughness of welded joints produced by electrodes the “OZS -12 + (Mo+Ni)” and “OZS -12 + (Mo+Ni) + 0.25 wt% TiCN”

| Electrode composition | T       | Impact toughness (J/cm²) |
|-----------------------|---------|-------------------------|
| “OZS-12 + (Mo+Ni)”    | +20 °C  | 82                      |
| “OZS -12 + (Mo+Ni) + 0.25 wt% TiCN” | +20 °C  | 92                      |
| “OZS-12 + (Mo+Ni)”    | -20 °C  | 51                      |
| “OZS -12 + (Mo+Ni) + 0.25 wt% TiCN” | -20 °C  | 53                      |
| “OZS-12 + (Mo+Ni)”    | -40 °C  | 23                      |
| “OZS -12 + (Mo+Ni) + 0.25 wt% TiCN” | -40 °C  | 32                      |
| “OZS-12 + (Mo+Ni)”    | -60 °C  | 9                       |
| “OZS -12 + (Mo+Ni) + 0.25 wt% TiCN” | -60 °C  | 17                      |
The obtained results have shown that adding of the titanium carbonitride nanoparticles is manifested only when specimens were tested at lowest temperatures (-40 and -70 °C). Thus, the fracture resistance under dynamic loading of the weld metal with titanium carbonitrides exceeded by 24 % ones of the welds formed by a standard “OZS-12” electrode (at testing under similar conditions).

4. Conclusion
Adding of 0.25 wt% titanium carbonitride in the welding pool for the “OZS-12” electrode surfaced coating results in decreasing average grain size and increasing impact toughness by 24 % at T=-40 °C and -70 °C. Increased impact toughness is primarily associated with more effective arresting of the main crack development at low temperatures.

Complex alloying with nickel (3 wt%), molybdenum (0.6 wt%) and titanium carbonitride nanoparticles (0.25 wt%) turned out to be the most efficient for enhancement dispersion of structural components and microhardness of the welds.

The surfaced coatings deposited with “MP-3 + 0.15 wt% TiC₃Nₓ” electrode undergoes certain changes which are expressed through increasing uniformity, significant structure refinement and substantial increasing impact toughness from 42 J/cm² to 104.5 J/ cm². In doing so, during the crystallization process of the coating deposited by the experimental electrode “MP-3 + 0.15 wt% TiCN” the more uniform structures with a smooth transition zone were formed that possesses more dense arrangement throughout the entire cross section of the coating.

The titanium carbonitride nanoparticles presented in the composition of the electrode covering exert a noticeable effect on the crystallization processes in the molten bath. They primarily act as additional crystallization centers and contribute to the accelerated and more uniform solidification of the surfaced coating.

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