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Effect of Nanoparticles on the Structure and Properties of Welds Made of High Strength Low-Alloy Steels

Abstract: The article presents test results concerning the structure of welds made of high strength low-alloy steel 14HGNDC which, in the molten state, was provided with nanoparticles of various refractory compounds including oxides, carbides and nitrides (TiC, TiN, SiC, VC, NbC, TiO_2, Al_2O_3, MgO and ZrO_2). The performed tests revealed the effective use of the nano-oxides of titanium (TiO_2) and zirconium (ZrO_2) enabling the obtainment of high mechanical properties of the weld metal (R_m –708 MPa and 621 MPa, KCV_{-20} – 60 J/cm² and 72,9 J/cm², a – 21 and 19%). The use of a Gleeble 3800 welding cycle simulator made it possible to determine the dependence between temperature ranges of transformations, amount of structural constituents and types of modifying nanoparticles.

Keywords: arc welding, ingot, weld deposit, nanopowder modifiers, diagram of przemian austenite transformations, microstructure

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Topicality

The issue of increasing the reliability and load-carrying capacity of various building structures is primarily related to the reliability of their welded structures. The popularity of high-strength low-alloy steels in pipeline/gas pipeline-based transport, building engineering and mechanical engineering results from relatively low production-related investments and costs without compromising high mechanical properties of end-products. An increase in the strength of the above-named steels to 700...800...900 MPa (steel X80, X90 and X100) could significantly widen their application potential in welded structures. The problem of reducing the properties of welded joints made of high-strength low-alloy steels (HSLA) can be solved by the controlled effect on the crystallisation of liquid metal, phase transformations as well as on the parameters of grain structure, non-metallic inclusions and phases.

One of promising methods enabling the control of liquid metal crystallisation processes during welding and casting is the use of refractory particles from the nanodimensional range (≤100 nm) [1-3].

The use of large particles (>10 µm) in the metallurgy of the production of steels and alloys is known adequately well [4], whereas the use of nanodispersive particles aimed to control the structure of metal during arc welding poses numerous difficulties including the necessity to ensure the uniform arrangement of particles in the volume of liquid metal, to prevent

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the removal of particles from the bath through flowing out or interacting with fluxes, to ensure the appropriate wettability of molten metal as well as to prevent against coagulation, dissolution and oxidation during welding.

Previous research [5] revealed that automatic arc welding can be applied as a physical model enabling the examination of crystallisation processes and the development of phase transformations in metals subjected to welding. The results of such research could be used in conventional metallurgy during the production of steel.

The research work aimed to investigate the effect of nanodispersive particles of refractory metals on the crystallisation of the weld pool liquid metal and the kinetics of austenite transformation in the weld metal of high strength steels.

Test Materials and Methodology

The article presents test results concerning the structure of welds made of high strength low-alloy steel 14HGNDC which, in the molten state, was provided with nanopowder particle modifiers of various refractory compounds including oxides, carbides and nitrides of various metals (TiC, TiN, SiC, VC, NbC, TiO_2, Al_2O_3, MgO and ZrO_2). The modifier particles were provided to the liquid metal using arc welding and flux-cored wires containing the flux mixture including particles of required composition. The use of welding technology for the modification of the molten metal composition required the protection of fluxes against the direct effect of welding arc which could trigger their entire melting or evaporation. For this reason, the flux-cored wires were entered into the relatively "cool" part of the weld pool having a temperature restricted within the range of 1600 to 1800°C, i.e. lower than the melting points of most compounds.

The determination of the effect of nanodispersive particles on the formation of the structure and mechanical properties of the weld metal required the making of welded joints in 20 mm thick steel 14HGNDC. The process involved straight polarity DC submerged arc welding performed using the Al_2O_3–MgO–SiO_2–CaF_2 slag system activating ceramic flux and a Sv-09G flux-cored wire filled with refractory compounds of TiC, TiN, SiC, VC, NbC, TiO_2, Al_2O_3, MgO, ZrO_2 nano and microparticles as filler metals.

The test nanopowders were obtained using various methods (mechanical refinement, reduction synthesis and self-developing high-temperature synthesis (SHS)). As a result, the particles obtained were characterised by appropriate composition, size and uniform distribution. The main view of modifier particles is presented in Figure 1.

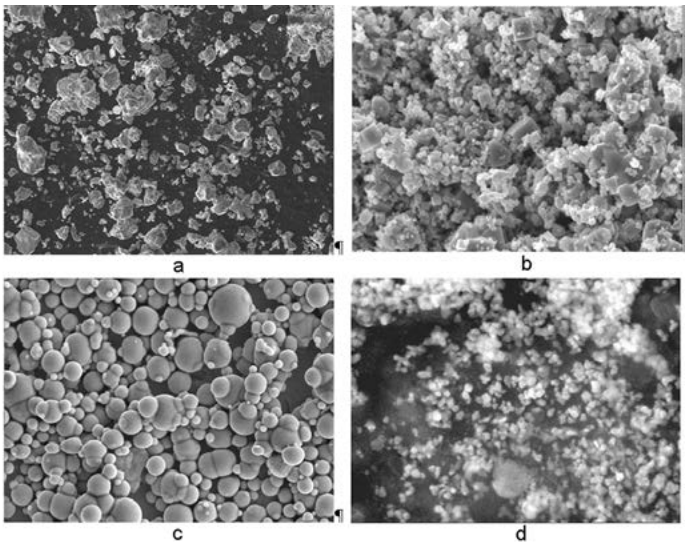

Fig. 1. Initial powder nanomaterials: a) TiC, b) TiN, c) TiO_2, d) ZrO_2; mag. x30000

The character of structural transformations in the weld metal containing alloying nanoparticles was tested using the simulation of welding thermal-strain cycles and a Gleeble 3800 simulator (DSI, USA) provided with a quick dilatometer [6]. In accordance with a methodology developed at E.O. Paton Electric Welding Institute, specimens were heated in a vacuum chamber to a temperature of 1170°C and cooled in accordance with a thermal cycle characteristic of automatic welding under flux performed at a welding rate of 5; 10; 17; 30 and 45°C/s within the temperature range of 800°C to 500°C. When testing the kinetics of austenite decomposition, the temperatures of transformation start and end as well as the amounts of transformation products were identified using the methodology described in publication [7].

The microstructure of the weld metal containing carbide, nitride and oxide modifier particles are presented in Figure 2.

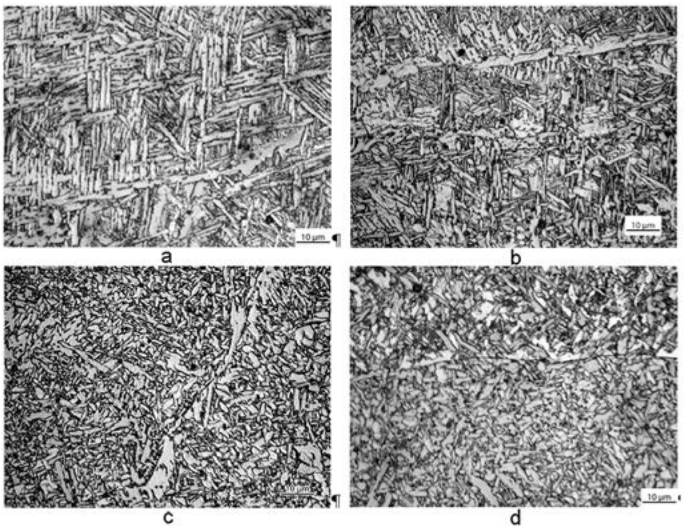

Fig. 2. Microstructure of the weld metal containing the following modifiers: a) TiC; b) NbC; c) TiO_2; d) ZrO_2; mag. x500

The analysis of the weld metal structure revealed that the use of modifiers containing VC, NbC and SiC led to the formation of primarily upper bainite (Fig. 2a) (between 40% and 70%), which significantly reduced the toughness of the welds at sub-zero temperatures (Table 1).

The use of titanium nitride (TiN) nanoparticles led to an increase in the content of intra-grain and polygonal ferrite (Fig. 2b) to 50%, which also extremely negatively affected the toughness of the weld metal at the relatively high temperature of the tests, i.e. KCV_{-20} = 40 J/cm².

The use of TiO_2, ZrO_2 and MgO nanoparticles (Fig. 2c and d) favoured the formation of dispersive acicular ferrite (between 30% and 90%) enabling the obtainment of the more favourable combination of high strength and toughness, particularly at very low temperatures (-40°C and -60°C).

The clarification of the positive effect of TiO_2, ZrO_2 and MgO nanoparticles on the structure and mechanical properties of the weld metal (in comparison with the effect of carbide and nitride particles) required the performance of tests concerning the kinetics of austenite decomposition. The test results enabled the development of diagrams concerning austenite decomposition in the weld metal (Fig. 3).

The analysis of results revealed that austenite decomposition in the weld metal modified using TiO_2, ZrO_2, Al_2O_3, and MgO nanoparticles occurred at significantly higher temperatures (by 100÷150°C) than those at which austenite decomposition in the weld metal modified using carbide or nitride nanoparticles took place.

During the modification of weld metal performed using the particles of nano-oxides, the initiation of bainitic transformation occurs at 670÷700°C and at a cooling rate of 5°C/s, which

Table 1. Mechanical properties the weld metal subjected to the tests

Type of nanoparticles	R_m	$R_{0,2}$	a	Z	KCV, J/cm² at T, °C			
	MPa		%		+ 20	0	– 20	– 40
–	693	605	14.5	48.4	97	87	75	53
TiC	716	644	19	63	–	–	85	73
TiN	712	580	5.3	14.7	55	47	40	–
SiC	726	650	21	62	85	72	65	61
VC	780	706	14	56	57	55	52	–
NbC	544	594	3.0	5.75	44	35	24	–
TiO_2	708.7	636.4	19.3	56.7	84.6	71.7	60.0	50.0
Al_2O_3	728.2	621.4	17.5	54.4	82.1	58.3	50.4	35.8
MgO	644.5	586	18.6	59.9	102.9	–	69.2	60.0
ZrO_2	621.6	532.2	19.5	65	119.6	–	72.9	64.6

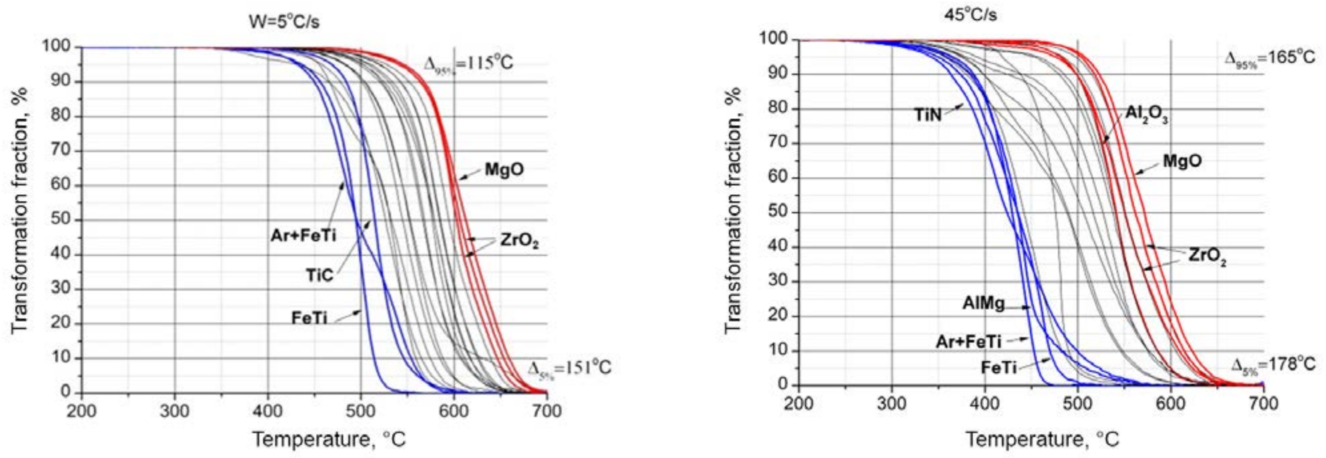

Fig. 3. Kinetic diagrams of the decomposition of austenite in the metal of the welds subjected to tests performed using various types of modifiers and the following welding rates: a) 5°C/s, b) 45°C/s (range of temperature changes: Δ5% – start of transformation, Δ95% – end of transformation)

corresponds to the technological conditions of arc welding performed at 630÷670°C and at a high cooling rate of 45°C/s, which, in turn, corresponds to the technological conditions of laser or hybrid welding.

During the modification of weld metal using carbide and nitride nanoparticles, the transformation of austenite in welds begins at significantly lower temperatures (at a cooling rate of 5°C/s – 550÷600°C, whereas at a cooling rate of 45°C/s – 450÷470°C). The temperature accompanying the termination of bainitic transformation and the initiation of martensitic transformation nearly never depends on the types of provided nanoparticles and amounts to 420÷450°C.

The results obtained in the tests revealed that, in the weld metal of low-alloy high strength steels, the decomposition of austenite occurred in the high-temperature area of bainitic transformation. In contrast to weld metal structures obtained using conventional methods of providing alloying elements leading to the formation of Widmanstätten polygonal ferrite and upper bainite, the modification of weld metal using oxide nanoparticles leads to the formation of acicular ferrite. Such an effect of nanoparticles results from the fact that nano-oxides in the weld metal of high strength low-alloy steels constitute additional crystallisation nuclei during the formation of acicular ferrite.

The increased resistance of supercooled austenite to transformation when modifying the weld metal using the nanoparticles of carbides and nitrides was probably connected with the difference of surface energy on the phase-particle boundary (*γ*-phase/carbide and *γ*-phase/oxide). For this reason, the surface energy on the *γ*-phase/oxide boundary favours the early initiation of transformation development.

The second probable reason for the higher stability of austenite was the size of micro-stresses generated on the *γ*-phase/nanoparticle boundary. At low temperatures, the formation of ferritic phases around nanoparticles (through diffusion) is significantly impeded. The reduction of transformation temperature generates additional micro-stresses around nanoparticles favouring the development of the $\gamma \rightarrow \alpha$ transformation in accordance with mobility kinetics. Micro-stresses generated around globular VC, NbC and SiC nanoparticles are probably significantly higher than those generated around regularly shaped nanoparticles (affecting the character of transformation). The hypothesis was verified using micro-diffraction images of areas located on the inclusion/nanoparticle boundary (Fig. 4). The tests revealed that the angle of mutual orientation on the particle/ferrite boundary amounted to 15° in cases of nano-oxide and to 5÷10° in cases of nano-carbide particles.

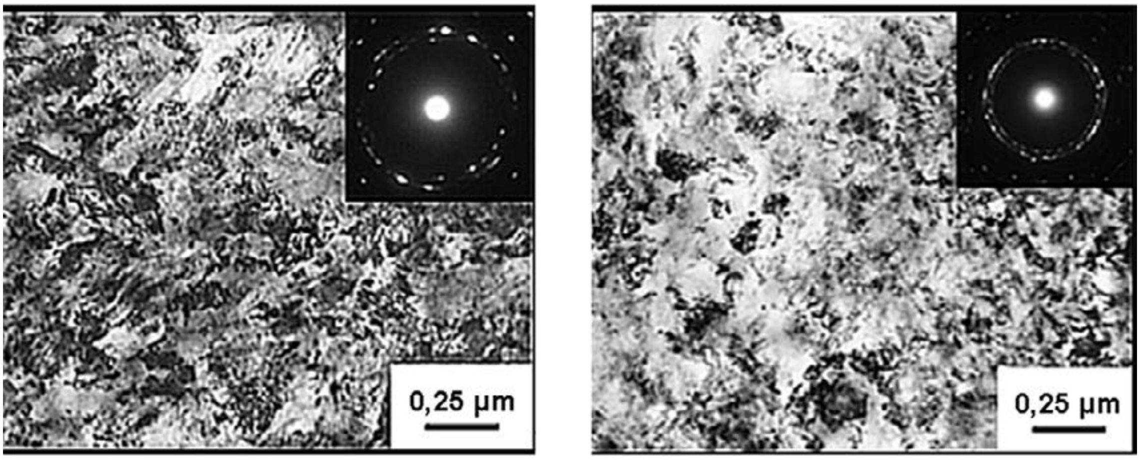

Fig. 4. Electron diffraction of weld metal with various types of modifiers: a) TiC, b) TiO_2

This results corresponds well with data presented in publication [8] stating that the difference between the size of crystal lattice and the of phase crystallisation lattice should not exceed 10÷15%.

Summary

The effectiveness of modifier particles provided to the metal of the welds in high strength steel 14HGNDC proved the higher, the lower their solubility and the higher their thermodynamic stability as well as the greater the difference between the melting points of the particles and that of the liquid metal bath were [9]. The nanoparticles changed the kinetics of austenite transformation favouring the formation of the appropriate weld metal structure (ferritic, bainitic or martensitic) providing required mechanical properties.

The modification of the weld metal using the nanoparticles of titanium and zirconium oxides (TiO_2 and ZrO_2 respectively) led to the development of transformation in the high-temperature area of the formation of bainite and acicular ferrite characterised by the favourable complex of mechanical and plastic properties. TiC and SiC carbides as well as TiN and NbN nitrides, reducing the initiation temperature of a bainitic transformation, led to the formation of bainitic-martensitic structures (lower bainite, micro-phases, MAC-phase) characterised by lower plastic properties. The VN, VC and ZrC compounds are readily soluble in the liquid metal of the weld pool and, because of that, of little use as effective modifiers of weld metal structures.

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