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INFLUENCE OF MODIFICATION AND MICROALLOYING ON DEPOSITED METAL STRUCTURE AND PROPERTIES (Review)

A.A. Babinets and **I.O. Ryabtsev**

E.O. Paton Electric Welding Institute of the NASU
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine

ABSTRACT

Proceeding from published data, the influence of modification and microalloying by boron, titanium, tungsten, zirconium, yttrium, etc., on the deposited metal structure, mechanical and service properties is shown. It is demonstrated that addition of these elements or their compounds with carbon and nitrogen in the quantity of up to 0.2 %, allows producing a fine-grained, homogeneous structure of metal, a more uniform distribution of alloying elements, that makes a positive effect on the values of strength, ductility, wear and heat resistance. It was determined that introducing small additives of boron or its compounds (in the quantity of up to 0.2 %), cerium or yttrium (in the quantity of up to 0.015 % of each), or application of complex master alloys, which can have the above-mentioned elements in their composition, as well as such modifiers, as zirconium, titanium carbides and borides or tungsten carbides, looks promising in terms of increase of wear and heat resistance of the deposited metal. Proceeding from the performed analysis, it was also shown that addition of titanium and zirconium diborides to the composition of flux-cored wire charge, promotes activation of the processes of formation of molten metal drops at the electrode wire tip, resulting in improvement of the quality of metal transfer in the welding arc that leads to greater values of the coefficients of alloying element transition into the deposited metal and improves deposited bead formation.

KEY WORDS: arc surfacing, deposited metal, tool steel, modification, microalloying, metal structure, wear resistance, heat resistance

It is widely known that mechanical and service properties of steels and alloys are determined by their chemical composition and structure. Thus, influencing the metal structure allows changing its properties within a certain range. In work [1] the main methods of deposited metal modification and microalloying were analyzed, and it was shown that the simplest and most rational of the considered methods is introducing small additives (up to 0.2 %) of chemical elements or their compounds directly through the charge of flux-cored electrode wires.

The objective of this work is analysis of published data on the influence of small additives (up to 0.2 %) of chemical elements or their compounds on the deposited metal structure, and its service properties, as well as on indices of stability of electric arc surfacing process.

It should be noted that in the majority of works, analyzed in this paper, studied was the influence of individual chemical elements or their compounds of exactly the modifying particles, that is those, the action of which consists in regulation of primary crystallization and/or change of the degree of dispersity of the crystallizing phases. As to microalloying, this term is mostly applied to such an element as boron and its compounds with other elements, the role of which is manifested predominantly as a result of an impact on the solid state of the metal (formation of interstitial or substitutional solid solution, etc.) [1].

Influence of elements-modifiers and their compounds on the deposited metal structure, its mechanical and service properties. In the general case it can be noted that application of modifiers leads to refinement of the deposited metal grain, and producing a more uniform structure that has a positive effect on its ductile characteristics, and influences the technological and other properties of the metal [2–6, etc.].

As the grain size depends on the ratio of the rates of crystal nucleation and growth, its modification is essentially aimed at the change of these parameters in the required direction. Usually, a large number of crystallization centers form in the liquid metal at modification. Their further growth depends on the nature of the influence of modifying additives or physical impacts on the situation in the crystal–melt near-boundary zone [1]. In the majority of the cases, the soluble or insoluble additives demonstrate an inhibitory effect on crystal growth. Here, the specific braking mechanism depends on the modifying additive nature and mechanism of its action. Two types of the influence of modifier content on the metal structure were found [2]: monotonic refinement of the grain at gradual increase of modifier content and nonmonotonic grain refinement with the area of optimum concentration of modifiers in the range of 0.01–0.10 %, going above which again leads to coarsening of the grain.

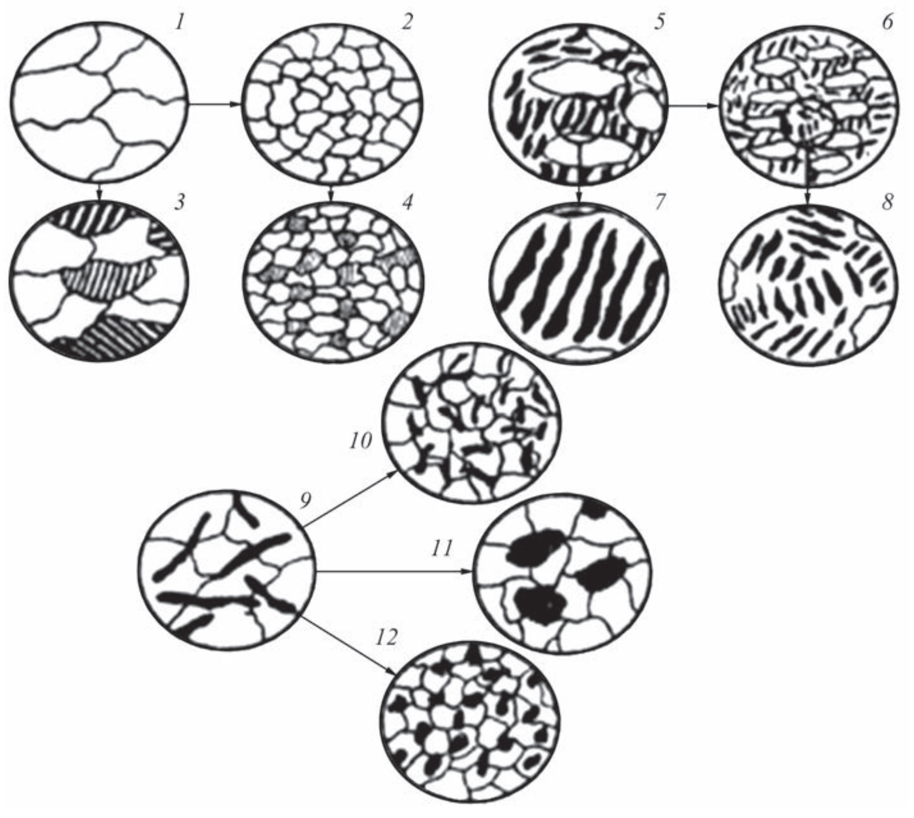

Figure 1. Influence of modifiers on the alloy structural components [2]

The variant of monotonic refinement of the grain with increase of modifier concentration is characteristic for insoluble catalyst additives (for instance, titanium in aluminium), while the variant of nonmonotonic grain refinement is characteristic for surface-active soluble additives (for instance, magnesium in zinc) [2]. Influence of modifiers on individual structural components of steel (alloy) is schematically shown in Figure 1 and in the Table 1.

Let us consider the influence of modification and microalloying on the structure and properties of steels and alloys in greater detail, grouping the data available in technical literature by the name of the respective chemical elements.

Boron. It is widely known that boron microadditives are used to improve a set of mechanical properties of steels, subjected to quenching and tempering. Here, the influence of boron is associated with increase of hardening and refinement of austenite grain [3–6].

In addition to refinement of the grain size, boron microalloying influences the deposited metal hardness and microhardness of solid solution grains, while the carbide phase microhardness remains practically unchanged. Increase of the deposited metal hardness at a slight lowering of hardness of austenite decomposition products, in the opinion of the authors of [7], is related to greater density and branching of intergranular boundaries, strengthened by boron.

In work [5] it was established that application of flux-cored wire with microadditives of boron nitride is promising for restoration by surfacing of the rollers of machines for continuous casting of billets (MCCB). It results in formation on the surface of MCCB rollers of a wear-resistant layer of the deposited metal of 30Kh5M2V2GF type with the hardness of up to

Table 1. Results of the influence of modifiers on the structure of steels and alloys [2]

Alloy type	Result	Structure (see Figure 1)
Alloys — solid solutions (carbon steels with ferrite-pearlite structure)	Initial grain refinement	1, 2
	Phase recrystallization	1, 3
	Secondary grain refinement after phase recrystallization	1, 2, 4
Alloys with primary precipitates and eutectics (grey and high-strength cast iron)	Refinement of both the structural components	5, 6
	Coarse-crystalline eutectics	7
	Thin-plate eutectics with very short plates	8
	Refinement of individual coarse structural components	9, 10
	Coagulation and spheroidization of structural components	11, 12

HRC 57, high heat-resistance and low coefficient of friction, compared to a layer deposited by unmodified material.

On the other hand, the data on the influence of boron microadditives on the ductility properties of steels are quite ambiguous. In work [8] it is shown that at boron content in the metal on the level of 0.0015–0.0025 % it is possible to effectively control the ductility properties of low-alloyed steels of K40 strength class. Microalloying of low-alloyed steels of 08G2S, 10G2S type, etc., by boron (0.002–0.004 %) promotes an improvement of their metallurgical purity, resulting in increase of the level of steel impact toughness [9], but a decrease of its ductility [10]. Lowering of ductility and impact toughness of structural steel 35 is reported in work [11] at microalloying with boron in the same amounts (up to 0.005 %).

Such an unambiguous influence of boron on the steel properties is associated with the fact that it is a more active deoxidizer, compared to silicon and manganese, and has high surface activity. Due to that boron is predominantly located along the grain boundaries, which leads to impurity redistribution also on the grain boundaries, and the concentration of sulphur, manganese, nitrogen and titanium decreases markedly. More over, boron can form an interstitial solid solution in combination with the ability to drive the impurities from the boundaries into the grain volume [10].

Titanium. Titanium in the form of its compounds with carbon, nitrogen and boron is rather widely used at steel modification, primarily due to the high melting temperature of these compounds (> 3000 K). Titanium carbonitrides are most often used as modifiers. By the data of works [12, 13], microalloying of high-alloyed steels of 10Kh15N4AM3 type by titanium carbonitride leads to marked refinement of the macrograin, elimination of grain columnarity and different grain size. Carbides take a compact equiaxed shape and are uniformly distributed in the grain volume: in an unmodified alloy, carbides have an elongated shape, and reach the size of 50 μm, while in the modified alloy carbides take a compact shape of 4–8 μm size. Such a change of the microstructure is favourable for the long-term strength, wear and heat resistance of the samples, raising it up to 2–3 times.

We can assume that the particles of titanium carbonitride, which have a high thermodynamic stability, only slightly dissolving in the metal melt, migrate from the flux-cored wire charge into the weld pool, influencing the kinetics of molten metal crystallization [12]. By the data of [13], carbonitride particles have the role of effective inoculants, promoting refinement of primary grain of the alloy matrix. Increase of the quantity of modifier in the wire above 0.4 wt.% does not lead to further refinement of the grains.

The influence of steel modification by titanium nitride is less unambiguous. In keeping with the data of [14], the average width of primary crystallites in low-alloyed structural steel becomes smaller, but the scatter of width values becomes greater. There is also information that addition of titanium nitride particles leads to formation of pores in the weld metal. Opposite results are reported in [4], where it is shown that addition of up to 0.4 wt.% of titanium nitride particles in the composition of filler flux-cored wire to high-carbon chromium steel of 320Kh12M2NR type does not lead to formation of pores and promotes increase of the deposited metal hardness from *HRC* 55 to *HRC* 57, while increasing the abrasive wear resistance of high-alloyed chromium-molybdenum deposited metal by 20 %. Such an ambiguous influence of titanium nitride is attributable to different class of materials used in the above studies.

In work [6] it was shown that modification of structural steel 45 by titanium diborides lowers the dendritic heterogeneity, fragmentation of columnar den-

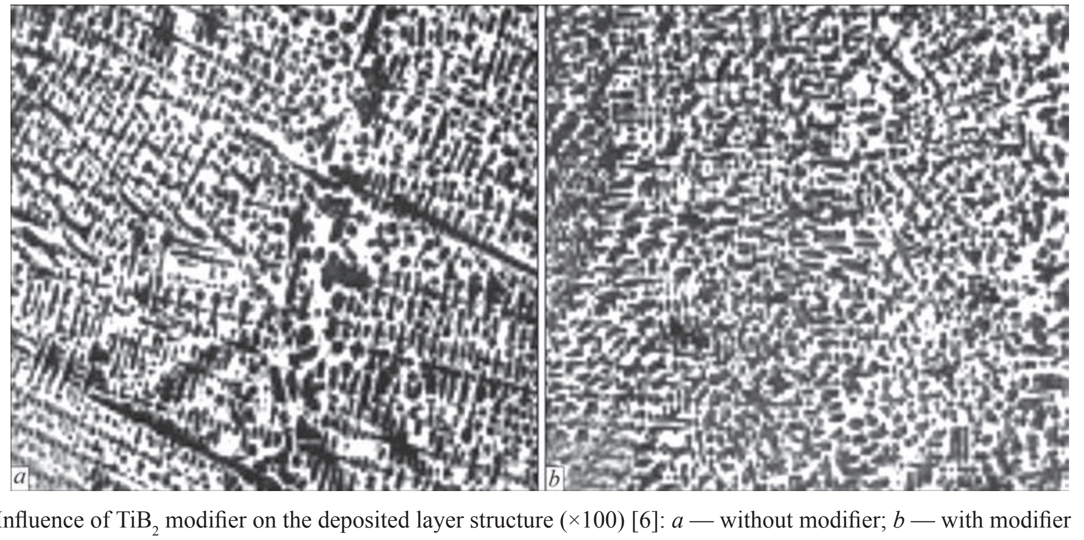

Figure 2. Influence of TiB_2 modifier on the deposited layer structure (×100) [6]: *a* — without modifier; *b* — with modifier

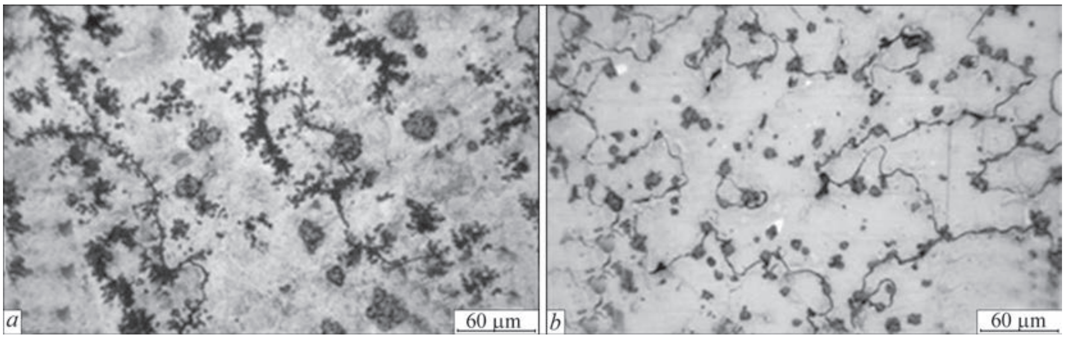

Figure 3. Initial structure of metal deposited by ESS with flux-cored wire (*a*), and with the same wire, but with the charge containing tungsten nanocrabides (*b*) (×200) [16]

drites, structure refinement, and elimination of coarse primary precipitates of the carbide phase (Figure 2). Here, the structural changes, that have taken place, did not influence the metal hardness, while increasing its wear resistance [6]. By the data of works [12, 15] addition of titanium dioxide to the filler material in welding raises the yield limit and ultimate strength of welds in medium- and high-alloyed steels.

Tungsten. Refinement of the structure of low-carbon low-alloyed [14, 16], as well as medium- and high-alloyed metal of chromium steel type [16] was found at their modification by powders of tungsten carbide at their content in the metal of up to 0.04 %. It was noted that in the modified metal of the type of low-alloyed steel the structure becomes more homogeneous, demonstrating the positive influence on the ductility characteristics [14].

A similar influence of tungsten carbide additives was noted in work [16], where it was shown that the structure of the deposited metal of the type of high-carbon chromium steel in the initial state is a ferrite-pearlite mixture (Figure 3, *a*). Addition of tungsten nanocarbides leads to transformation of the metal structure into a modified subdispersed solid solution based on α-Fe with residual austenite, located on the grain boundaries (Figure 3, *b*). The quantity of nonmetallic inclusions, which at some time had rather arbitrary contours and were nonuniformly distributed in the metal, decreased by 15–20 %. The remaining inclusions are more uniformly distributed and are of a globular shape. Such a structure of the metal, in the opinion of the authors of the work, should promote an increase of its ductility properties under cyclic loading.

Zirconium. Use of zirconium is due to its ability to inhibit grain growth, and actively interact with carbon and nitrogen (more actively than titanium does), leading to formation of dispersed carbides and nitrides [3, 17]. Their influence on the joint properties is manifested in the form of grain refinement, improvement of mechanical properties, lowering of cold brittleness threshold and sensitivity to stress raisers of both steels and alloys, including those from light metals [11, 18]. For instance, aluminium alloy modification by adding potassium fluorozirconate (K_2ZrF_6) to the composition of the flux-cored wire charge [18] leads to refinement of weld pool metal and increase of the total number of crystallization centers, resulting in the deposited metal having a fine-grained structure with uniform distribution of alloying elements that causes 1.2 times increase in wear resistance. By the data of work [11], zirconium nitrides and carbides exceed similar compounds of titanium, vanadium and molybdenum by their strength and resistance. This leads to an essential increase of strength and ductility values of structural steels (Figure 4).

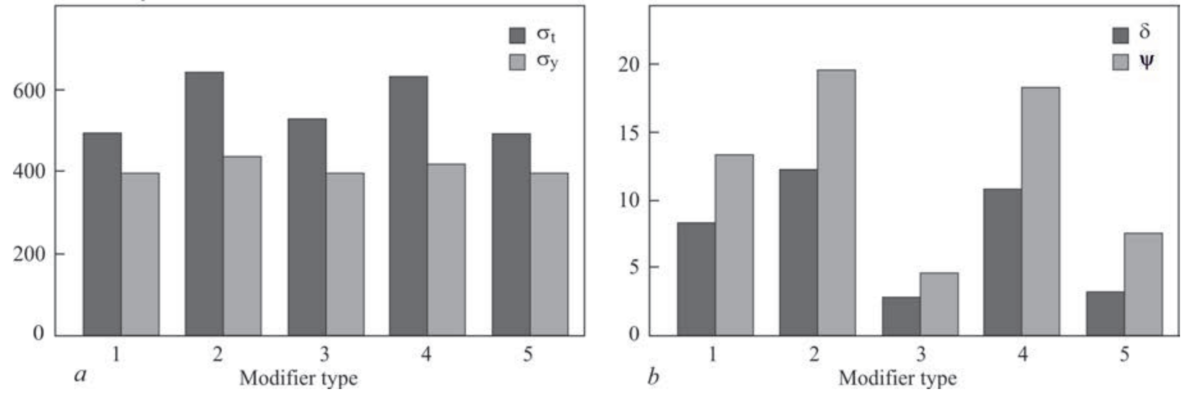

Figure 4. Influence of different elements on the values of strength (*a*) and ductility (*b*) of structural steel, unmodified (1) and modified by vanadium (2), molybdenum (3), zirconium (4) and boron (5) [11]

Cerium. Cerium is known due to its ability to neutralize the influence of surface-active sulphur during deposited metal solidification and at long-term high-temperature heating [19]. Modification of steels of 30KhGSA, Kh5MF, Kh12MF type by cerium in the quantities of up to 0.009 %, leads to increase of the technological strength, impact toughness and resistance to thermal fatigue failure of the deposited metal [19, 20]. This effect is achieved through sulphur binding into refractory finely-dispersed compounds, lowering of microchemical heterogeneity and refinement of austenite grain. Here, weld metal contamination by nonmetallic inclusions is also reduced [21].

Yttrium. Yttrium has an exceptionally high affinity to oxygen, nitrogen, sulphur and other elements, forming thermodynamically stable compounds with them. Among the rare-earth elements (REM) the affinity of yttrium to oxygen at weld pool temperatures is the highest. According to the data of [17], investigations of yttrium-modified deposited metal of 15Kh8N2M2F type showed that it has certain technological advantages, compared to cerium: at its addition to liquid metal the pyroeffect is absent, it is assimilated by liquid steel in a more stable manner and, in addition, 3–4 times smaller amount of it is required, in order to obtain optimum steel properties, than that of cerium. Optimum yttrium content in the deposited metal is in the range of 0.013–0.015 % [17].

So, deposited metal microalloying by yttrium leads to an increase of mechanical and service properties, namely wear resistance and heat resistance by 20–30 % (Figure 5), which is, apparently, attributable to metal structure refinement, change of the shape, size and nature of distribution of nonmetallic inclusions, cleaning of grain boundaries from sulphur and other harmful impurities [17, 22].

Calcium. In the general case, addition of calcium to steel increases its fluidity, modifies the oxide and sulphide inclusions, improves the ductility properties, etc. Calcium features low solubility in the metal and low melting and boiling temperatures, so that it is practically completely removed from the metal. Therefore, in order to preserve the modification effect, it is necessary to add a lot of other elements to the master alloy composition, which promote prolongation of calcium effect [3].

Strontium. By its physico-chemical properties strontium takes up an intermediate position between calcium and barium, and it also has a limited use to improve the effectiveness of metal modification [3].

Barium. Barium is often used in combination with calcium to improve its absorption and enhance the positive impact of the latter, although the effectiveness of using just barium (without calcium) is noted in a number of cases [3].

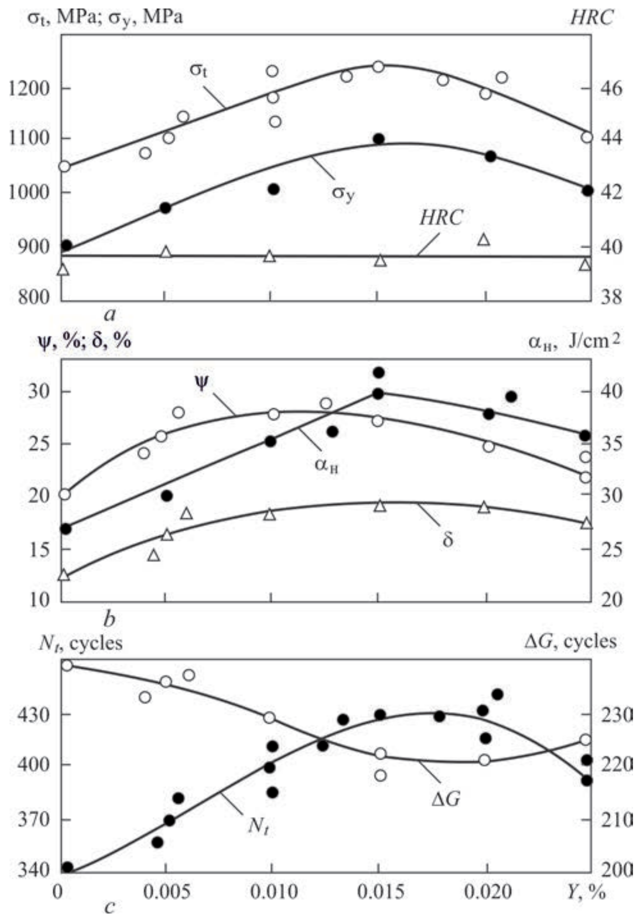

Figure 5. Influence of yttrium on mechanical properties (*a*, *b*), wear resistance ΔG and heat resistance *Nt* (*c*) of deposited metal of 15Kh8N2M2F type [17]

Influence of complex modifiers on the deposited metal structure, its mechanical and service properties. Proceeding from the fact that some additives-modifiers refine the structure and block the impurity elements on the intergranular and interphase boundaries, while others inhibit the recrystallization processes and intragranular decomposition, the idea of steel modifying by complex additives looks promising. In combination they can promote formation of a homogeneous structural-phase state, enhancement of the effects from each other, etc.

So, for instance, microalloying of low-alloyed steels of 08G2S, 10G2S type by titanium and zirconium, led to a significant improvement of metal strength and ductility [23]. In works [19, 24] the joint effect of fine powder of titanium and zirconium diborides, and well as cerium dioxide was studied. It was shown [24], that weld microalloying by titanium and boron at multiarc welding using neutral or slightly acidic fluxes improves the structure of metal of the type of low-alloyed steel 10G2FB, resulting in 1.5–2.5 times increase of the steel impact toughness. The optimum content of titanium and boron in the weld metal is equal to 0.022–0.038 and 0.0025–0.0065 wt.%, respectively.

In work [11], introducing microadditives (up to 0.2 %) of highly active elements (V, Mo, Zr, B) to the composition of structural steel St. 35 allowed improving the material structure and service properties.

Similarly, by applying an optimum combination of surface-active modifying additives of Ti, Al, B, Ce, Ca and V, at simultaneous alloying of the welds (wire material was 10KhGNM steel, base metal was 33KhSN2MA steel), in work [25] it was possible to achieve a stable crack resistance of welded joints, while ensuring rather high strength of the weld metal. Due to reaching a certain balance between Ti, B, Ni and Mo, in work [26] an increase of the homogeneity of chemical composition of welds and, consequently, improvement of impact toughness of welded joints on low-alloyed steel 08G2S, was achieved.

In work [27] the influence of addition to the charge of flux-cored wire, used as filler wire at plasma surfacing, of a complex master alloy, containing fluorine, alumocalcium, ferrocerium and copper-beryllium alloy, was studied. Beryllium was added to strengthen the steel, and improve its high-temperature mechanical properties. Alumocalcium and ferrocerium were added to remove oxygen, sulphur and phosphorus. Presence of fluorine in the arc, which has a high ionization potential, leads to improvement of the arc self-regulation and increase of the surfacing process stability. As a result, deposited metal of 2Kh13N12GD2Yu type with higher mechanical and service properties was produced, in particular with high resistance to thermocyclic loading.

Influence of modification and microalloying on welding-technological properties of surfacing materials. It is known that one of the ways to improve the stability of melting and transfer of electrode metal in the arc, is application of a process with superposition of additional current pulses of a certain frequency [19]. However, in the case of application of flux-cored wires, controlling the frequency of detachment of electrode metal drop requires ensuring the synchronism of melting of the sheath and the core (filler) that at practical application of pulsed-arc processes is quite successfully applied only when small diameter wires are used.

Another method of influencing the process of electrode wire melting is addition to its charge of modifying microadditives of various elements, the action of which is based on the change of electrophysical characteristics of the welding arc, and of the conditions of heat transfer in the arc gap, respectively. At the same time, technical literature contains practically no data on the influence of modifying additives on such welding-technological properties of surfacing materials as arcing stability, coefficient of alloying element transfer, quality of deposited bead formation and their geometrical dimensions. There are just a few works, devoted to these subjects.

By the data of [18], use of potassium fluorozirconate in the composition of the flux-cored wire charge not only refines the deposited metal structure, but also improves the arc process stability and deposited metal formation. This effect is achieved at the action of surface-active elements, which lower the surface tension force, holding the drop at the electrode tip. In addition, the alkaline element potassium with a low ionization potential enhances the arc burning stability due to lowering the effective ionization potential of the arc gap.

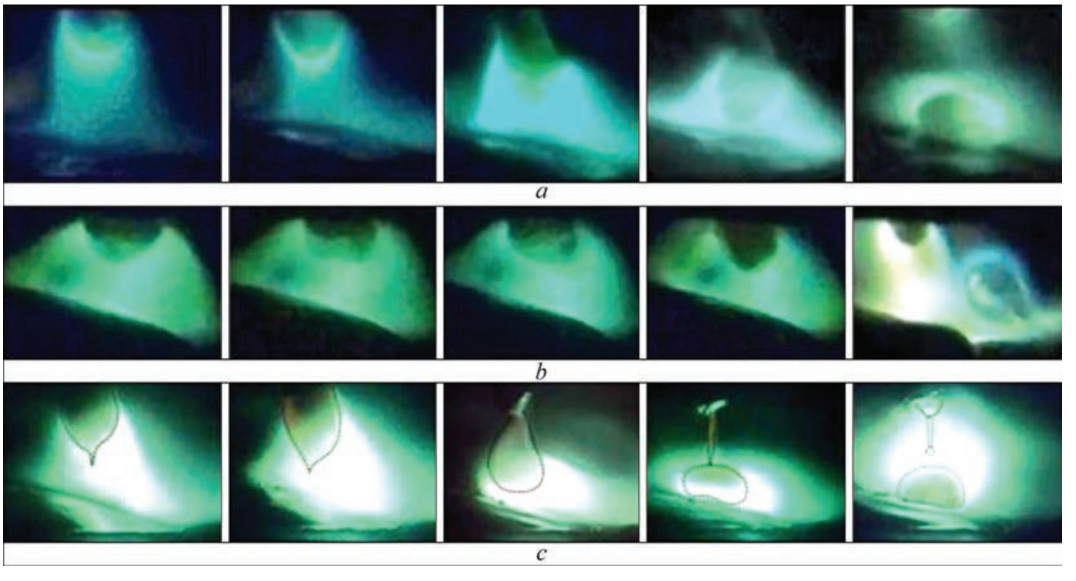

Figure 6. Nature of formation of electrode metal drop at deposition by flux-cored wire, using particles of TiB_2 (*a*), CeO_2 (*b*) and without them (*c*) [19]

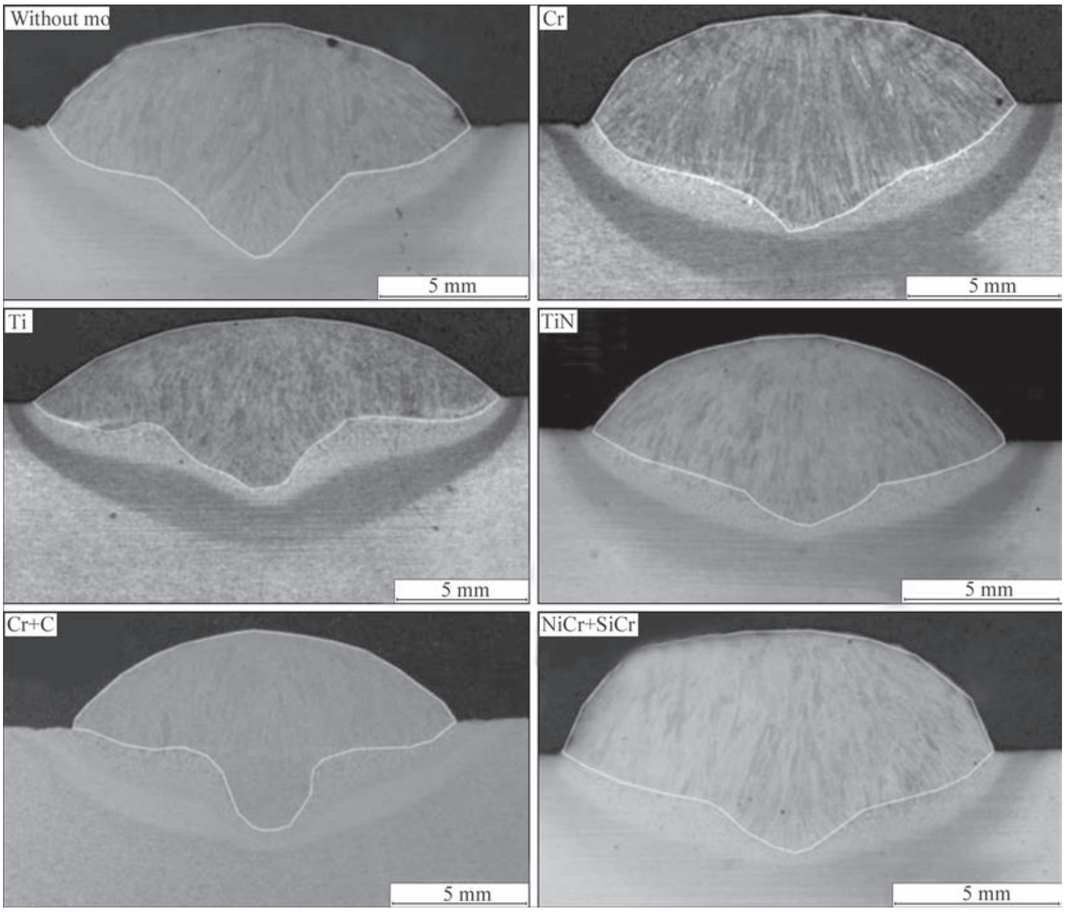

Figure 7. Influence of modifier type on penetration shape and depth at gas-shielded welding with solid wire with a modified coating [28]

In work [19] it was established that introducing into electrode material composition microadditives of titanium and zirconium diborides promotes creation of the conditions, at which the sheath and components of flux-cored wire core, dissimilar by their thermophysical properties, more actively melt and form into a metal drop (Figure 6). It results in reduction of the drop size and increase of their detachment frequency that is accompanied by increase of the periodicity with which the arc anode spot moves between the refractory core end face and metal drop surface. The result of such an influence is improvement of the quality of metal transfer in the welding arc, leading to greater values of the coefficients of alloying element transfer into the deposited metal. It is also noted that at > 0.05 % boron content in the deposited metal, liquation areas with chemical heterogeneity and metal embrittlement were detected.

By the data of [28], the impact on the arc and drop transfer can be applied through thin coatings, deposited on electrode wire surface, which also affects the geometrical dimensions of the deposited beads. The influence of some coatings is shown in Figure 7, from which one can see that the smallest penetration depth was reported for the case of deposition of a pure titanium coating. In this case, a considerable increase of weld metal resistance at cyclic loading was also noted.

CONCLUSIONS

1. As one can see from the results of analyzed studies, modification or microalloying of steels, leading to their grain refinement, redistribution of nonmetallic inclusions, cleaning of grains boundaries, etc., on the whole has a positive effect on the deposited metal mechanical and service properties, in particular, increase of wear- and heat resistance take place.

2. Various compounds of titanium, tungsten, zirconium and boron are the most often used for modification and microalloying of steels and alloys. Here, complex modification by such elements can demonstrate a more significant influence on the steel properties, than use of such elements as monoadditives.

3. From the view point of ensuring a high stability of arc burning, lowering of spattering and improvement of the quality of deposited metal formation, application of zirconium and titanium as modifiers in combination with such elements as potassium, calcium, fluorine, etc., looks promising.

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ORCID

A.A. Babinets: 0000-0003-4432-8879,
I.O. Ryabtsev: 0000-0001-7180-7782

CONFLICT OF INTEREST

The Authors declare no conflict of interest

CORRESPONDING AUTHOR

I.O. Ryabtsev
E.O. Paton Electric Welding Institute of the NASU
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine
E-mail: ryabtsev39@gmail.com

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