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PULSED-DISHARGE TREATMENT OF THE Al–Ti–C SYSTEM MODIFIER

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The results of studying the influence of the modifier of the Al–Ti–C system, obtained by high-voltage electric discharge treatment in a hydrocarbon liquid, on the structure and properties of the cast $AK7_{pch}$ (A357) alloy are presented. The prospects for the use of a modifier produced by the method of a high-voltage electric discharge treatment of metal powders to improve the structure of cast alloys and weld metal are shown. 25 Ref., 1 Table, 4 Figures.

Keywords: welded joint, weld metal, high-voltage electric discharge, modifier of the structure of cast alloys, metallurgy, dispersion, carbidization

The introduction of modifiers into the melt is one of the traditional methods of producing fine-grained metal structures, as far as the more nuclei are in the unit volume of a melt, the more crystals are formed and the smaller they are, and therefore, the better mechanical properties of the metal in foundry and welding. Modern tasks of materials science and engineering practice are the study of the efficiency of nanomodification in welding and surfacing technologies by introducing nanoparticles of refractory chemical compounds into the welding pool [1]. During surfacing with heat-resistant alloys based on iron, nickel and chromium and carbon steels, which are modified by nanoparticles, the stability of the deposited tool is increased. Nanoparticles also eliminate transcrystallization zones in the deposited metal or a weld, the sizes of dendrites are sharply reduced, the morphology and topography of the strengthening phases is improved. This increases the heat resistance, structural stability and life of welded joints [2, 3]. The efficiency of modification of cast metal with nanostructured powders is confirmed, for example, in the conditions of production of gas turbines at modification of heat-resistant SM88U alloy [4]. Taking into account the peculiarities of foundry production and fusion welding in terms of modification of liquid metal, the conceptual approaches to the creation of modifiers for the mentioned technologies are quite close. Thus, the positive results of using liquid metal modifiers in the process of casting are the basis for creation of technologies for modifying the liquid metal of the welding pool under fusion welding conditions. Based on the abovementioned, in the future the modern method of manufacturing modifiers for foundry production can also be used in welding production.

Most modifiers are manufactured by powder metallurgy. Moreover, ultradispersion nanostructured powder mixtures are the most promising for use. Now the main directions of development of methods of obtaining such mixtures are as follows [5–8]:

improvement of existing equipment and technological processes based on widespread mechanical methods of grinding materials; search for fundamentally new ways of grinding, research and development of effective types of equipment and technology on their basis.

The first direction is aimed at increasing the efficiency of destruction and specific efficiency and improving the existing and creating the new machines (crushers and mills) of increased efficiency [7, 8] and is accom-

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panied by an increased power consumption, metal consumption of structures, using of expensive high quality steels and alloys along with a disproportionately small growth in technical and economic indices.

The second direction is aimed at finding fundamentally new methods of grinding, in particular, electrophysical [9–11]. Thus, one of the efficient electrophysical methods is a pulsed discharge preparation of powders by using high-voltage electric discharge (HED) in the disperse system «liquid–powder». This is a cyclic process, which is characterized by the release of power in the discharge channel during microseconds and is accompanied by the action of compression waves (which under the certain conditions is transformed into a shock one), powerful hydraulic flows, cavitation, electromagnetic and thermal fields [9–11].

At the cyclic action of HED the possibility of fine grinding by pressure waves is created due to the presence of a large number of defects in the powder, which reduces the power of destruction of crystals and the formation of a large number of active centers and facilitates the chemical interaction between the system elements under a dynamic load.

The use of a hydrocarbon liquid as a working medium in HED-treatment of mixtures of powders allows not only eliminating their oxidation, but also creating thermodynamic conditions for pyrolysis of kerosene with the formation of solid carbon, which is able to enter the carbidization reaction with powder particles, forming nanostructured strengthening phases [12].

In [13], an example of using a modifier in casting showed that the introduction of 0.01 wt.% of the Ti–TiC modifier, synthesized by a high-voltage electrodischarge treatment of Ti powder in kerosene and briquetted by spark plasma sintering, allowed reducing the grain size from 1–2 to 0.2–0.6 mm in all modified specimens of heat-resistant SM88U alloy. In this case, the tensile strength at a temperature of 900 °C was 65–69 MPa, and the long-term strength increased by an average of 20 %. This indicates the prospects of using metal powders after HED-treatment to modify the structure of cast alloys.

However, the possibility of using metal powders after HED-treatment to modify the cast metal structure of welds has not yet been sufficiently studied. To establish the prospects of using metal powders after HED-treatment to modify the structure of welds, it is advisable to analyze the effect of a modifier of the Ti–Al–C system after HED-synthesis to grind the structure and improve the properties of cast $AK7_{pch}$ (A357) alloy.

The aim of the work consists in the fact that to establish the prospects of application of metal powders after HED-treatment in fusion welding to modify the structure of welds, it is advisable to investigate the effect of a modifier of Ti–Al–C system after HED to grind the structure and improve the properties of cast $AK7_{pch}$ (A357) alloy.

Procedure of studies. Modification of aluminium alloys was considered on the example of silumins and involved the obtainment of a fine-grained eutectic silicon in a cast structure. Such a structure of eutectic silicon increases the mechanical properties of the casting, including relative elongation, as well as, in many cases, casting properties of the aluminium melt. As a rule, modification of silumin is carried out by adding small amounts of sodium or strontium [14–17].

In silumins with a silicon content of more than 7 %, eutectic silicon occupies most of the area of the metallographic specimen. With a silicon content from 7 to 13 %, the type of eutectic structure (e.g., granular or modified) significantly affects the mechanical properties of the material, in particular, ductility, which is defined as a relative elongation δ. Therefore, when during the tests of the specimen it is necessary to increase the value δ, aluminium alloys with a silicon content from 7 to 13 % are modified by adding approximately 0.0040–0.0100 % of sodium [18, 19].

In silumins with a silicon content of about 11 %, especially for low pressure casting, as a long-term modifier, strontium is used. The difference between strontium and sodium as a modifier consists in the fact that it burns out much less from the melt, which is especially important in fusion welding. Strontium is added in an amount of 0.014–0.040 %.

Since sodium burns out from the melt relatively quickly, further modification of silumins with sodium should be carried out at certain intervals, which complicates its use in welding, where the process of introducing a modifier should be continuous. In addition, high cost and complexity of the technology of applying sodium and strontium creates the need in finding cheaper and no less effective weld modifiers on the basis of those studied in the works [20–22].

To study the effect of modifier on crystallization of the cast aluminium $AK7_{pch}$ (A357) alloy, a modifier obtained by HED treatment of a mixture of powders of 15 % Al + 85 % Ti with an average diameter d_{av} = = 40 μm in illuminating kerosene was used. The study was performed in an experimental bench, described in detail in [9, 10, 23].

To evaluate the degree of influence of HED in kerosene on the morphology and size of powder particles, as well as to study the structure of cast alloy specimens, the following equipment was used: BIOLAM-I optical microscope with the maximum magnification ×1350, JEOL JEM-2100F scanning electron microscope with a magnification range from 50 to 1500000 and Canon digital camera.

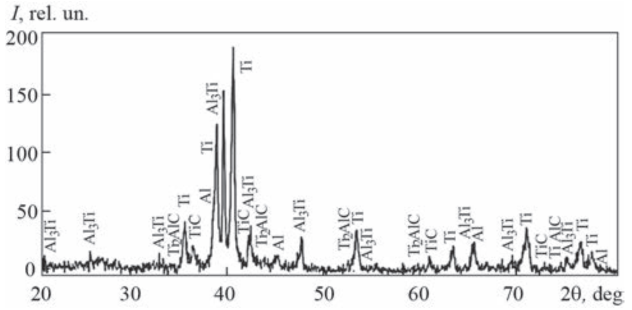

Figure 1. Diffractograms of powder mixture of the initial composition 85 % Ti + 15 % Al after HED-treatment in kerosene using an electrode system of type «3V-P» with a specific energy of 20 MJ/kg

X-ray diffraction and X-ray phase analysis were performed in a general-purpose Bruker D8 Discover diffractometer (CuKα radiation), and Raman spectroscopy was carried out using Renishaw InVia Micro Raman.

To study the effect of the selected modifier on the mechanical characteristics of the $AK7_{pch}$ alloy in a shaft furnace using metal crucibles, three specimens were melted: a reference specimen (mass of 650 g) and two modified specimens: a modified 0.7 wt.% AlTiB (mass of 170 g), which is traditionally used to modify the structure of silumins [3, 14, 16–18] and with a content of 0.2 wt.% of a modifier obtained by HED-treatment of a mixture of powders of 15 % Al + 85 % Ti (mass of 630 g).

In the reference specimen at a temperature of T_m = 760 °C, the slag was removed, and the melt was mixed with a mixer for 10 s. After isothermal holding for 10 min, the melt was poured into a metal mold heated to a temperature of T_k = 280 °C. The cooling time until surface solidification was 30 s.

The modified specimen was made according to the same scheme, and a modifier was introduced before mixing in the form of a «bell» (powder wrapped in aluminium foil).

After cooling, the specimens were cut in half, ground and the microstructure was revealed using a 5 % HF solution in a distilled water. A 15 % NaOH solution in a distilled water was used to reveal the macrostructure of individual specimens.

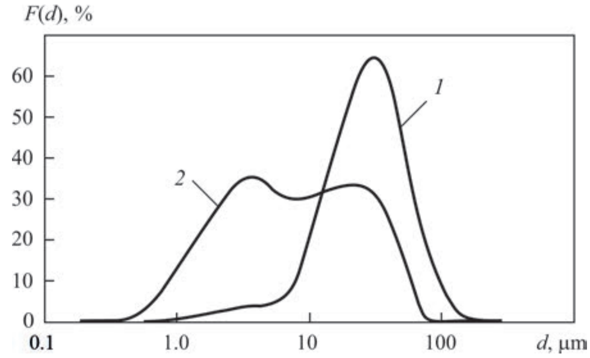

Figure 2. Distribution of particles of the used modifier of the Ti–Al system by the size: *1* — before HED-treatment; *2* — after HED-treatment

Research results and their discussion. All acting factors in HED can be divided into two groups: mechanical, which include a compression wave, hydrocurrents in the pulsation of the vapor-gas cavity and cavitation, and thermal, which include a low-temperature plasma in the discharge channel and microplasma formations between particles, as well as the discharge current flowing through the particles of the processed metal and leading to electroerosion destruction of powder particles [24]. At HED the conditions are created (pressure in the discharge channel reaches 1 GPa and the temperature in the discharge channel can reach 50000 K) for kerosene pyrolysis with the formation of a solid-phase nanocarbon. The synthesized carbon nanoparticles of different allotropic modifications, in particular, C_{60} and C_{70}, are able to chemically interact with titanium particles, forming nanostructured reinforcing carbide phases [9–13, 23, 24]. Therefore, HED-treatment of powders of the Al–Ti system in kerosene, in addition to grinding, provides a synthesis of titanium carbide and Ti_3AlC and Ti_2AlC phases without the additional graphite.

After HED-treatment in the mode with a single discharge energy W_1 = 1 kJ and a specific energy W_{sp} = 20 MJ/kg using an electrode system of the type «three-tip anode–plane» the charge contains Al, Ti, TiC, $Ti_3AlC + Ti_2AlC$ (Figure 1).

The powder mixture of the initial composition of 85 % Ti + 15 % Al after treatment has an average particle size of about 10 μm, with a peak value of the amount of particles with a 5 μm diameter of about 37 % (Figure 2). The particle size distribution has a bimodal appearance, approximately 30 % of the mixture particles maintain sizes close to the original.

Figure 3 shows the macrostructures of a reference specimen of $AK7_{pch}$ alloy and the specimens of the alloy modified by 0.7 wt.% of AlTiB and 0.2 wt.% of HED-treated Ti–Al mixture.

The reference specimen has a shrinkage cavity depth of 4 mm. The area of columnar grains is about 10 mm, their width is 2–6 mm. In the center of the casting, grains of 2–8 mm in size predominate (Figure 4, *a*). The specimen modified by 0.2 wt.% of AlTiB has a shrinkage depth of 3 mm. The area of columnar grains is about 1.5 mm, their width is up to 1 mm. The macrostructure is quite uniform, the grain size is from 1 mm to 2.5 mm (see Figure 4, *b*). The melt modified by 0.2 wt.% of HED-treated mixture, has a shrinkage cavity, which reaches 3 mm, the looseness under shrinkage is almost absent, the area of columnar crystals is up to 5 mm, the grain width is

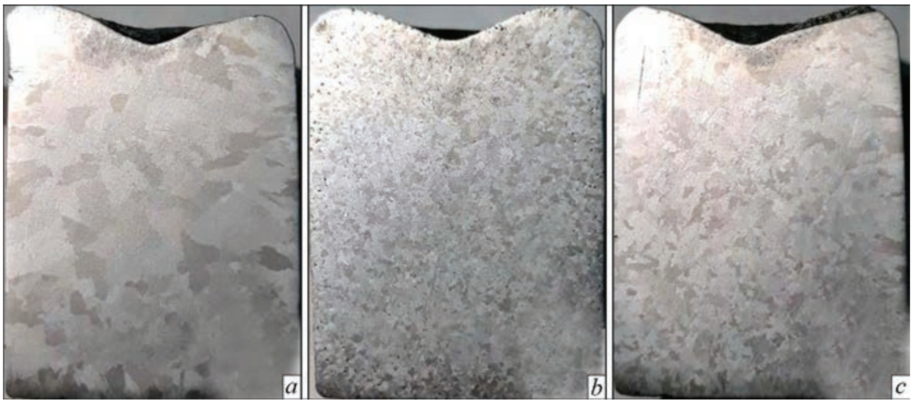

Figure 3. Macrostructure of $AK7_{pch}$ (A357) alloy: *a* — reference specimen; *b* — specimen modified by 0.7 wt.% of AlTiB; *c* — specimen modified by 0.2 wt.% of the Ti–Al–C mixture produced by HED-treatment

from 1.5 to 2.0 mm, the structure is uniform, grains have a size of 1.5–3.5 mm.

Figure 4 shows the microstructure of reference (*a*, *b*, *c*, *d*), modified 0.7 wt.% of AlTiB (*e, f, g, h*) and modified 0.2 wt.% HED-treated mixture (*i*, *j*, *k*, *l*) of $AK7_{pch}$ alloy.

Metallographic analysis of the reference specimen revealed dendrites of α-solid solution, the size of which exceeds 1500 μm and a significant amount of eutectic silicon, which has a rounded shape.

Melt modification of 0.2 wt.% of AlTiB leads to insignificant dispersion of dendrites of α-solid solution, but at the same time the growth of separate α grains is observed. This modifier had a negative effect on eutectic silicon, which received a needle shape with the size of individual needles of up to 80 μm,

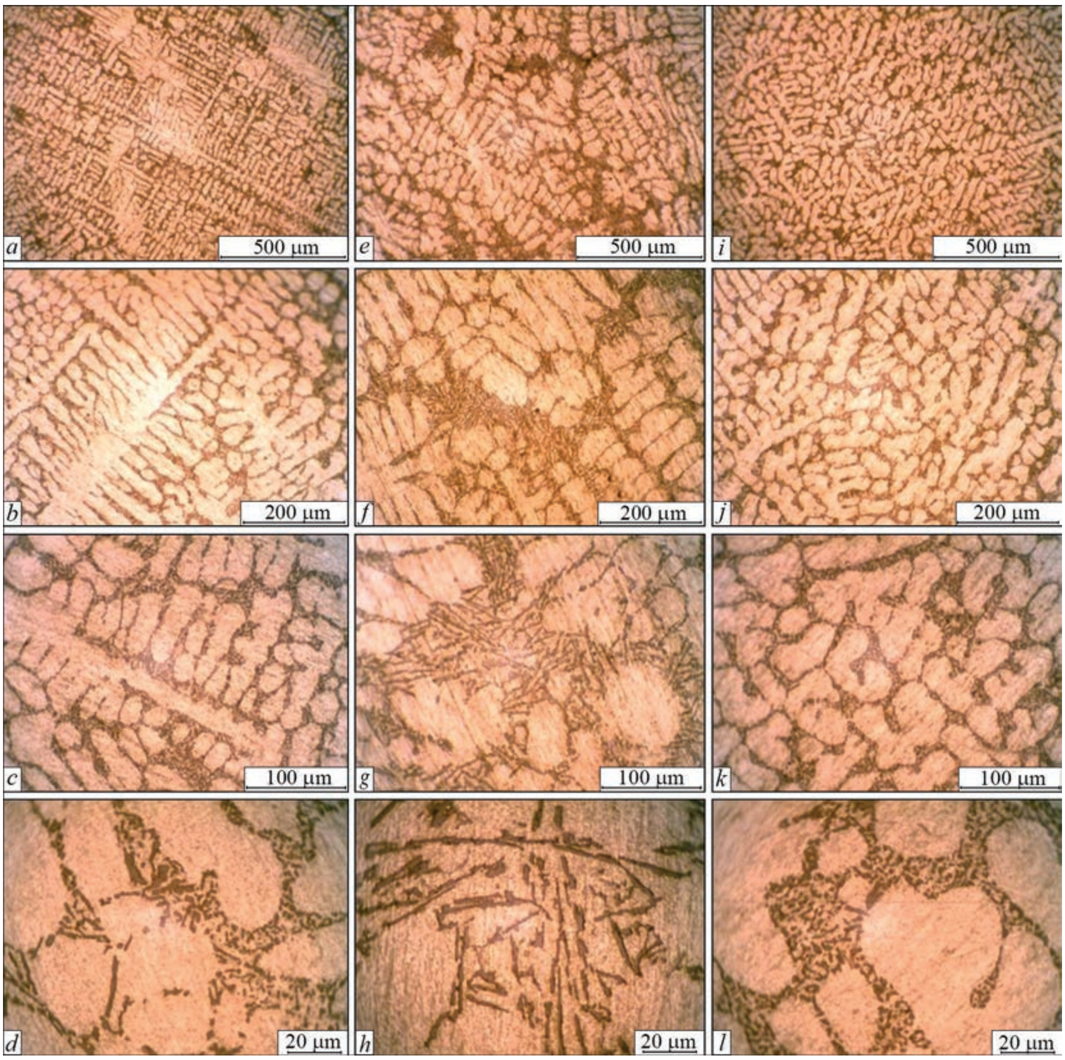

Figure 4. Microstructures of $AK7_{pch}$ alloy: *a, b, c, d* — reference specimen; *e, f, g, h* — specimen modified by 0.7 wt.% of AlTiB; *i, j, k, l* — specimen modified by 0.2 wt.% of the Ti–Al–C mixture produced by HED-treatment

Properties of $AK7_{pch}$ alloy specimens

Specimen	σ_t, MPa	$\sigma_{0.2}$, MPa	*HB*
Reference specimen	148	62	48
	143	65	
Specimen modified by 0.7 wt.% of AlTiB	133	62	36
	131	61	
Specimen modified by 0.2 wt.% of mixture of Al–Ti–C-system after HED-treatment	135	66	48
	140	65	

which negatively affects the fatigue strength of the modified metal.

Modification of the specimen of alloy 0.2 wt.% by HED-treated mixture of powders 15 % A1 + 85 % Ti led to a significant reduction in the size of the dendrites of α-solid solution from 1500 to 300 μm, the grains obtained a round shape, also a significant modification of eutectic silicon (Figure 5, *i, j, k, l*) is observed. The obtained grain shape has a positive effect on the fatigue strength of the metal modified by HED-treated mixture. Such results are associated with the presence of carbon nanoparticles and nanostructured particles of refractory TiC, Ti_3A1C + Ti_2A1C compounds in the powder mixture, which act as additional crystallization centers.

The hardness of the reference specimen was *HB* 48, and for those modified by AlTiB and HED-treated mixture, it was *HB* 36 and *HB* 48, respectively (Table).

Studies of the change in the ultimate strength σ_t and yield strength $\sigma_{0.2}$ of modified specimens (see Table) show that in contrast to the modification of 0.7 wt.% of AlTiB, adding 0.2 wt.% of the mixture of Al–Ti–C system after HED-treatment does not lead to a decrease in these characteristics as compared to the reference specimen.

The obtained results in combination with the results presented in [13] indicate that the use of HED-treated powders of the Al–Ti–C system in a hydrocarbon liquid as a modifier leads to a significant reduction in the structural elements of a crystallized alloy. In turn, the refinement of the structure of welds allows increasing heat resistance, structural stability and fatigue strength and long life of welded joints. This allows predicting the possibility of using HED-treated particles of metal powders metal in a hydrocarbon liquid to modify the structure of welds with the prupose of improving the service characteristics of parts and structures produced by different methods of fusion welding.

Conclusions

1. The possibility of using HED-treated particles of metal powders in a hydrocarbon liquid to modify the structure of welds is shown.

2. It is shown that introduction of the mixture of powders of the initial composition 15 % Al + 85 % Ti obtained by HED-treatment in kerosene as a modifier by the «bell» method allows influencing the structure and properties of the cast aluminium $AK7_{pch}$ alloy (A357).

3. Adding of 0.2 wt.% HED-treated mixture of powders 15 % Al + 85 % Ti to $AK7_{pch}$ (A357) alloy led to a significant change in the size of the dendrites of the α-solid solution from 1500 to 300 μm. The hardness of the modified specimens is *HB* 48, and the yield strength is at the level of 66 MPa.

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