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# IMPROVEMENT OF TECHNOLOGY OF PRODUCING Ti–TiC MODIFIERS AND STUDYING THEIR IMPACT ON THE STRUCTURE OF DEPOSITED METAL OF TYPE 25Kh5FMS

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## ABSTRACT

The technology of producing Ti–TiC modifiers was improved, which allowed reducing the average diameter of its particles by more than 6 times. The use of the proposed treatment procedure made it possible to produce a Ti–TiC powder with at least 20 % of TiC in its composition. It was found that for the investigated modes, treatment in kerosene is more effective in terms of dispersion than treatment in ethanol. The use of the produced powder as a modifier at its content in a deposited metal 25Kh5FMS at a level of 0.01 %, leads to a significant change in the microstructure and its transformation from a columnar into a cellular one. In terms of the possibility to control the structure and properties of the deposited metal, the most promising is the use of modified Ti–TiC powders of N2 and N4 type, which were produced as a result of high-voltage treatment of the mixture of corresponding powders in a hydrocarbon liquid using a volumetrically-distributed multi-spark discharge mode. This provides a significant effect on the structure of the deposited metal of type 25Kh5FMS, but at the same time does not lead to the formation of microcracks in the deposited metal.

**KEYWORDS:** modification, technology of producing modifiers, high-voltage treatment, hydrocarbon liquid, arc surfacing, flux-cored wire, deposited metal, structure of deposited metal, nonmetallic inclusions

## INTRODUCTION

The introduction of different types of modifiers into the melt of metals is a fairly common method of refining their structure and enhancing mechanical and service properties. Modifiers and microalloying elements are also used to refine the structure and prevent crystalline growth orientation during solidification of the welding pool in surfacing and welding production [1–8]. Technical literature gives data on the use of modifiers containing boron or yttrium, to refine the structure and increase the service properties of the deposited metal [2, 3]. However, modifiers containing these elements are very expensive, which does not always justify their use from an economic point of view.

In [9], the example of using Ti–TiC modifier at casting shows that its introduction has made it possible to reduce the size of the grain and increase the mechanical characteristics of the heat-resistant SM88U alloy. This indicates the prospect of using Ti–TiC metal powders for modification and microalloying of deposited metal of different alloying systems.

The technology of producing Ti–TiC modifier was developed at the Institute of Pulse Processes and Technology of the NASU. According to this technology, to

produce Ti–TiC modifiers, the treatment of a mixture of corresponding powders with a high-voltage electric discharge (HED) in the hydrocarbon liquid is used.

HED in the liquid is a unique comprehensive method of influencing various dispersed systems in order to disperse them, which is accompanied by a change in the structure and phase composition of the latter. HED is characterized by instantaneous release of a large amount of energy (units, tens or hundreds of kJ) in the original small volume of the discharge channel within a few microseconds. A high concentration of energy in the plasma channel of discharge leads to generation of electromagnetic and thermal fields, intensive waves of pressure, hydraulic flows, volumetric microcavitation and electro-erosion processes in the volume of a discharge chamber, that promote dispersion and evolution in the structure of dispersed systems [10, 11].

The work investigates the possibility of using Ti–TiC modifier to refine the metal structure using PP-Np-25Kh5FMS flux-cored wire. Also the results of improving the technology of producing Ti–TiC modifier using different technological modes and hydrocarbon liquid media are presented.

Thus, the aim of the work is to improve the technology of producing Ti–TiC modifier with the use of

HED and investigation of its impact on the structure of the deposited metal of type 25Kh5FMS.

## PROCEDURES OF INVESTIGATIONS

Improvement of the technology of producing Ti–TiC modifier using HED was performed in an experimental bench, the circuit of which is shown in Figure 1, and the principle of operation is described in the article [11].

The study of HED in the dispersed system “liquid dielectric–metal powder” was performed at the voltage of capacitors charge  $U = 50$  kV, the inductance of the discharge circuit  $L = 0.7$   $\mu$ H and the discharge gap  $l_d$ , which was selected depending on the working liquid and amounted to  $\sim 17$  mm for kerosene and  $\sim 24$  mm for ethanol. The capacity of the capacitor  $C$  was  $0.8$   $\mu$ F, so the value of a stored single discharge energy  $W_1$  was 1 kJ. The specific treatment energy was 20 MJ/kg. According to the results given in [10, 11], namely such values of the parameters of HED-treatment allow reaching the balance between refining, the amount of synthesized titanium carbide powder and the number of free nanocarbon particles.

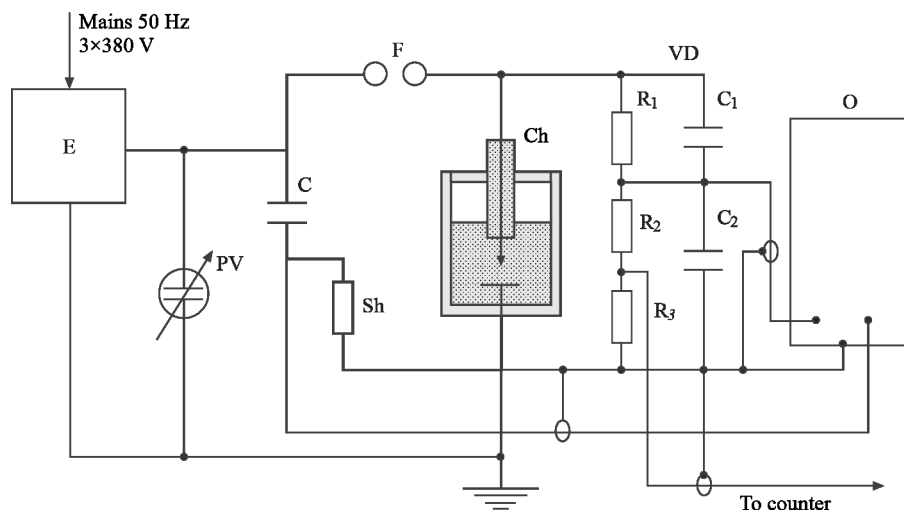
The use of kerosene as a working medium in the treatment of mixtures of powders allows synthesizing nanocarbon of different allotropic modifications as a result of pyrolysis of hydrocarbon chains by plasma of the discharge channel. Active nanocarbon is able to react with Ti powder, resulting in synthesis of titanium carbide [12]. Due to the change in the composition of the hydrocarbon liquid, it is possible to control the amount of a synthesized nanocarbon, so in the work as a working medium for the realization of HED, kerosene and ethanol were used. The ratio of the solid and liquid phase in the studies was 1:15 (the weight of the treated powder was 100 g, the volume of a working liquid was  $1.5$   $\text{dm}^3$ ).

During each treatment, the record of discharge current and voltage within every 100 discharges was performed by means of the oscillograms. The values of electrical and hydrodynamic characteristics for each of the treatments were averaged according to the results of the calculations for recorded oscillograms. For each of the following modes, no less than three experiments were performed.

HED-treatment of Ti powder with the use of single-edge and three-edge electrode systems (ES) in kerosene or ethanol medium was performed. When using the “one edge-plane” system, HED propagates according to the classical mechanism of the spark discharge (SD) in the dispersed system, while the use of ES of type “three edges-plane” allows realizing the mode of volumetrically-distributed multi-spark discharge (VMD). Modifiers produced as a result of treatment were marked respectively as N1 and N2 (kerosene medium) and N3 and N4 (ethanol medium) (Table 1).

To estimate the degree of HED exposure in the hydrocarbon medium on the morphology and the sizes of powders particles, an optical microscope BI-OLAM-I with a maximum magnification of  $\times 1350$ , a scanning electron microscope REM-MA-102 with a range of magnification from 10 to  $\times 250000$  and a digital camera Canon were used. The powder samples for optical microscopy were selected in accordance with GOST 23402–78.

The study of the phase composition of powders was performed by X-ray-phase analysis using a DRON-4-07 diffractometer at  $\text{CuK}\alpha$ -radiation. The phase identification on diffractograms was carried out according to the bases POW\_COD. The quantitative phase composition was determined according to the procedure of evaluating the intensity using the corundum number



**Figure 1.** Circuit of experimental bench for electric discharge treatment of powders: E — power part; PV — kilovolt meter; C — capacitive capacitor; Sh — coaxial shunt; K — working chamber; O — memorizing oscilloscope; F — air discharger; VD — voltage divider; R1, R2, R3, C1, C2 — elements of voltage divider

**Table 1.** Characteristics of metal, deposited using flux-cored wires PP-Np-25Kh5FMS containing Ti-TiC modifiers, which are produced by HED-treatment on different modes

Modifier description	Working medium	Discharge mode	Content of TiC in the powder after treatment, %	Size of crystallites $l_c$ , $\mu\text{m}/\text{type of structure}$	Hardness of deposited metal HV1, MPa
Without modifier	—	—	—	30–60/columnar	5920–6060
N1	Kerosene	SD	20	30–180/cellular	6410–6420
N2		VMD	23	20–80/cellular	5700–5800
N3	Ethanol	SD	20	35–170/cellular	6350–6600
N4		VMD	23	30–100/cellular	5250–5330

of RIR (Reference Intensity Ratio) using QualX and a full profile analysis using Maud program.

The specimens for microstructure examination were produced by arc surfacing with the flux-cored wires on plates of 40Kh steel. For surfacing, the flux-cored wire PP-Np-25Kh5FMS was used, in the charge of which powders modifiers were added with such a calculation as to obtain the content of a modifier in the deposited metal at a level of 0.01 %. As a reference, the specimens deposited by the flux-cored wire PP-Np-25Kh5FMS without modifiers were used. The diameter of all the developed wires is 1.8 mm, the filling factor is 25 %. In total, five experimental flux-cored wires were manufactured (see Table 1).

Surfacing of all the specimens was performed under the flux AN-26P on the same mode: current — 220–230 A, voltage — 36–37 V, deposition rate — 25 m/h. In order to avoid the impact of the base metal stirring, on each specimen the surfacing was performed in four layers. In order to avoid crystallization cracks, before surfacing, the specimens were heated to 200 °C and after surfacing, they were cooled with the furnace. After complete cooling, from the deposited specimens, transverse billets were cut out for preparation of appropriate microsections and conducting metallographic examinations.

The specimens for metallographic examinations were prepared by standard procedures. To reveal microstructure, the specimens were etched electrolytically in a 20 % solution of chromic acid at a voltage of 20 V.

Examinations of microstructure and nonmetallic inclusions of the deposited metal were carried out in NEOPHOT-32 microscope. The hardness measurements were carried out in M-400 LECO hardness meter at a load of 100 g and 1 kg. The photos of microstructures were obtained with OLYMPUS C-500 camera.

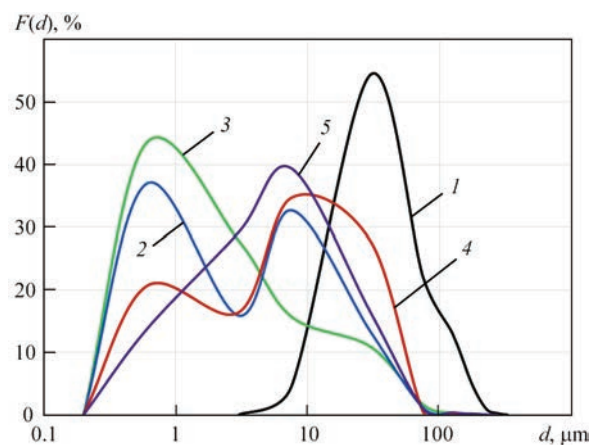
## RESEARCH RESULTS AND DISCUSSION

The results of studying the change in the dispersion of Ti powder after HED-treatment in different modes are shown in Figure 2. The original titanium powder had a monomodal distribution of particles by sizes, the peak

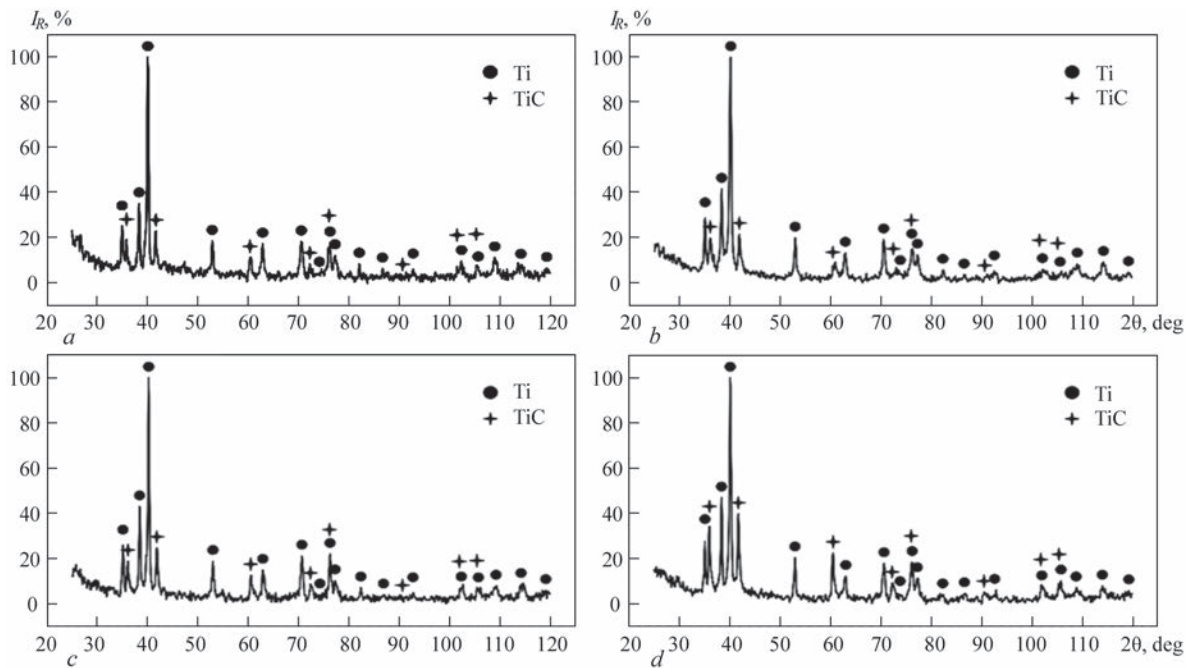
of which was at a point corresponding to the diameter of  $\sim 30 \mu\text{m}$  and 54 % of the powder particles had a size smaller than this value (see Figure 2, curve 1), and the average diameter of such powder was 60  $\mu\text{m}$ .

Analyzing the results presented in Figure 2, it should be noted that HED-treatment in all studied modes provided a significant reduction in the average diameter of the powder particles and changed the nature of its distribution by sizes. Thus, HED-treatment in kerosene in SD mode allowed producing a Ti-TiC system powder with an average diameter of 8.2  $\mu\text{m}$ . The distribution of such powder by sizes had a bimodal nature (curve 2) — one of the peaks was close to the initial range of sizes and amounted to 7.5  $\mu\text{m}$  (32 %) and the other was in the size range of less than 1  $\mu\text{m}$  (0.6  $\mu\text{m}$ , 37 %).

Changing the treatment mode on VMD with the preservation of kerosene as a working medium allowed increasing the efficiency of dispersion — the produced Ti-TiC system powder had an average diameter of 7.4  $\mu\text{m}$ . It was characterized by an almost monomodal distribution (curve 3), the main peak of which was at a point corresponding to a diameter of 0.7  $\mu\text{m}$  (44 %). Namely such a mode was the most effective in terms of dispersion of powder particles.



**Figure 2.** Distribution of powder particles of modifiers by sizes  $d$  before and after HED-treatment at different modes: 1 — initial Ti powder; 2 — modifier N1, treatment medium — kerosene, SD mode; 3 — modifier N2, treatment medium — kerosene, VMD mode; 4 — modifier N3, treatment medium — ethanol, SD mode; 5 — modifier N4, treatment medium — ethanol, VMD mode



**Figure 3.** Diffraction patterns of Ti–TiC powder mixture produced by HED-treatment of titanium powder: *a* — modifier N1, treatment medium — kerosene, SD mode; *b* — modifier N2, treatment medium — kerosene, VMD mode; *c* — modifier N3, treatment medium — ethanol, SD mode; *d* — modifier N4, treatment medium — ethanol, VMD mode

The change in a working medium from kerosene to ethanol during the realization of SD mode allowed producing a Ti–TiC powder with an average diameter of 12.1  $\mu\text{m}$ . The distribution of this powder by sizes had a bimodal nature (curve 4) — peaks were observed at the points of 10 (35 %) and 0.8  $\mu\text{m}$  (21 %).

The change in the discharge mode on VMD by replacement of the electrode system “one edge–plane” with the electrode system “three edges–plane” with the preservation of ethanol as a working medium of HED made it possible to increase the efficiency of dispersion in ethanol. The produced Ti–TiC powder was characterized by an average diameter of 10.2  $\mu\text{m}$ , and its distribution had a monomodal nature (curve 5) with a peak at a point that corresponds to a diameter of 7.5  $\mu\text{m}$  (40 %).

Thus, treatment of Ti powder in all the considered modes allowed reducing its average diameter by more than 6 times. VMD treatment allows obtaining an almost monomodal distribution of particles by sizes and is distinguished by a higher efficiency of dispersion. Treatment in kerosene for the investigated modes is more effective in terms of dispersion than treatment in ethanol.

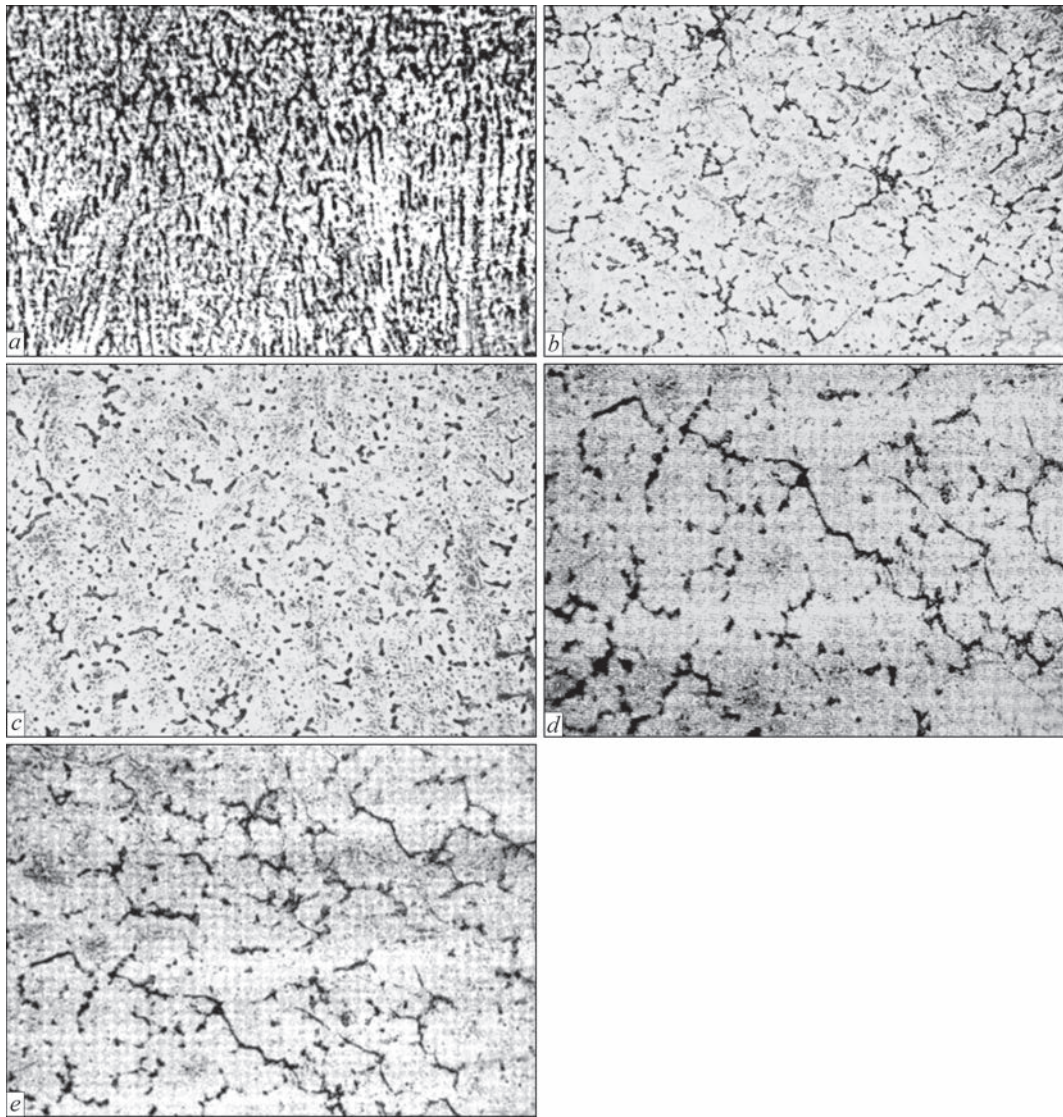
The studies of the diffraction patterns of samples of the treated powders obtained in the X-ray diffractometer DRON-4 are shown in Figure 3. On all the diffraction patterns in addition to the peaks characteristic of Ti, there are also peaks that indicate the synthesis of TiC in the process of HED-treatment of the initial titanium powder.

The results of quantitative analysis by the RIR method indicate that the amount of a synthesized titanium carbide for all studied modes differs within the error (Table 1). Somewhat better results in terms of carbidization efficiency were observed during treatment in ethanol in SD mode, but all the modes allowed producing no less than 20 % of TiC in the powder composition after its treatment. These results confirm the conclusion made in [8, 9], that Ti powder carbidization efficiency is most influenced by the specific energy of treatment, which was constant for all the studied modes and amounted to 20 MJ/kg.

The microstructure of the metal was studied, deposited with five experimental flux-cored wires (Figure 4, *a–e* and Figure 5, *a, b*).

The microstructure of the specimen metal, deposited by the wire PP-Np-25Kh5FMS without adding modifier (Table 1, line 1) consists of columnar crystallites (Figure 4, *a*), which grow in the direction of heat removal. The width of the crystallites is in the range of 30–60  $\mu\text{m}$ . In the body of crystallites, an acicular martensitic structure is observed, on the boundaries of cast crystallites, light precipitates are observed that correspond to residual austenite (Figure 4, *a*). The precipitates of a rounded shape, that can be complex carbides, are quite rarely observed. The hardness of the deposited metal is  $HV1 - 5920-6060$  MPa. The defects both in the deposited metal and near the fusion line are absent.

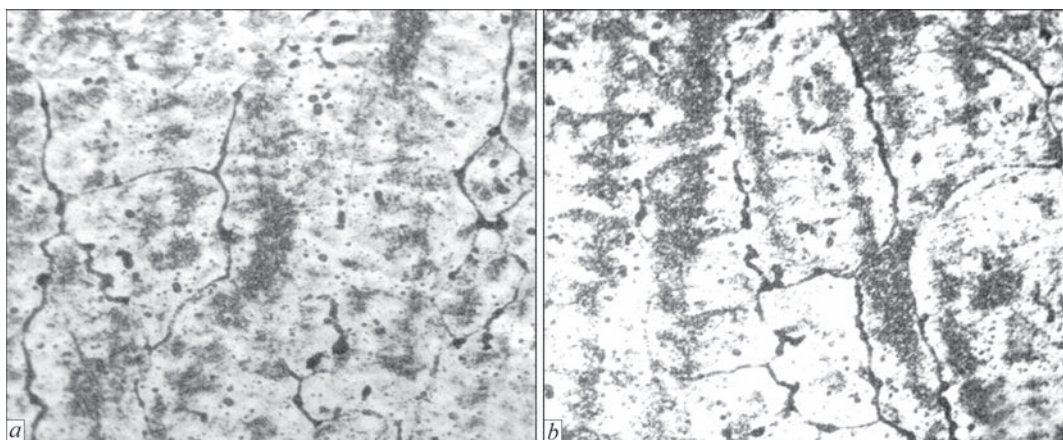
Microstructure of the metal of the specimen deposited by the PP-Np-25Kh5FMS wire with the content of the modifier N1 with the content of 80 % of



**Figure 4.** Microstructure ( $\times 200$ ) of metal, deposited with a flux-cored wire PP-Np-25Kh5FMS: *a* — without microalloying additives; *b* — using modifier N1; *c* — N2; *d* — N3; *e* — N4

Ti + 20 % TiC (Table 1, line 2), was refined (Figure 4, *b*). The structure of martensite was also refined. The size of the cells is within 30–180  $\mu\text{m}$ . On the boundaries of cells, a quite large number of dark-etched phase and rounded precipitates is observed that are

built into chains and probably may represent carbides. In addition, in the upper layer of the deposited metal microcracks are observed, which is undesirable (Figure 5, *a*). The hardness of the deposited metal is  $HV1 - 6410-6420$  MPa.



**Figure 5.** Microstructure ( $\times 600$ ) of metal, deposited with PP-Np-25Kh5FMS flux-cored wire, with microcracks: *a* — with the use of modifier N1; *b* — N3

Microstructure of the specimen metal, deposited by PP-Np-25Kh5FMS wire with the content of the modifier N2 with a composition of 77 % Ti + 23 % TiC (Table 1, line 3), represents a cast cellular structure (Figure 4, *c*). In the body of crystallites, a large acicular martensitic structure with the hardness  $HV_{0.1}$  — 4900–5450 MPa is observed. On the boundaries of cast crystallites, a light-etched austenitic structure with the hardness  $HV_{0.1}$  — 5100 MPa with a few precipitates of carbides and intermetallics is observed. The integrated hardness of this specimen is within  $HV1$  — 700–5800 MPa. The size of the cells is 20–80  $\mu\text{m}$ . Microcracks in this specimen were not detected.

The microstructure of the specimen, deposited by the wire PP-Np-25Kh5FMS with the content of the modifier N3 with a composition of 80 % Ti + 20 % TiC (Table 1, line 4; Figure 4, *d*) was investigated. It represents a matrix, consisting of slightly-etched dispersed needles of martensite with the precipitates of carbides or intermetallics, or both of them on the boundaries of cast crystallites in the form of separate or chain inclusions (Figure 4, *d*). The hardness of martensite matrix is  $HV_{0.1}$  — 5700–5750 MPa, and integral hardness is within  $HV1$  — 6350–6600 MPa. The size of the cells is 35–170  $\mu\text{m}$ . In this specimen, as well as in the specimen with the modifier N1, in the upper layers of deposited metal microcracks were found (Figure 5, *b*).

It should be noted that the modifiers N1 and N3 were produced using HED-treatment in SD mode. In contrast, the modifiers N2 and N4 were produced using HED-treatment in VMD mode. As was shown above, VMD treatment provides producing a larger amount of smaller titanium carbides. In our opinion, this is one of the reasons for the absence of microcracks in the deposited metal with the modifiers N2 and N4.

The microstructure of the specimen, deposited by PP-Np-25Kh5FMS wire with the content of the modifier N4 with a composition of 77 % Ti + 23 % TiC (Table 1, line 5), was also significantly refined (Figure 4, *e*). On the cell boundaries, dark-etched precipitates are observed, but a number of these precipitates is lower than in the similar area of the specimen with the modifier N1. In addition, they do not merge into long chains. Microcracks in this area are also not noted. The hardness of the deposited metal is  $HV1$  — 5250–5330 MPa.

Also, according to the procedure of GOST 1778–70, on the polished non-etched microsections, the level of the deposited metal contamination with nonmetallic inclusions was determined. From the presented specimens, the biggest contamination of the

deposited metal with nonmetallic inclusions, mainly oxides, is observed in the specimen without modifiers. It corresponds to the grain size No. 3a according to the Table 1 “Spot oxides” GOST 1778–70. The specimens with the modifiers N1, N2, N3 are significantly cleaner from nonmetallic inclusions than the specimen without modifiers and their contamination corresponds to the size No. 1a of the same Table 1. In the specimen with the modifier N4, contamination of the deposited metal with nonmetallic inclusions is the least and amounts to less than the size No. 1 a of the Table 1 “Spot oxides”.

## CONCLUSIONS

1. The method of HED-treatment of Ti–TiC powder on different modes in the hydrocarbon liquid allowed reducing the average diameter of its particles by more than 6 times. As a result, a powder with an almost monomodal distribution of particles by sizes was produced.

2. The use of the produced Ti–TiC powder as a modifier with its content in the deposited metal of type 25Kh5FMS at a level of 0.01 % leads to a significant change in the microstructure and its transformation from a columnar into a cellular one.

3. The use of modifiers of type N2 and N4 for Ti–TiC powders seems to be the most promising in terms of the ability to control the structure and properties of the deposited metal, which can significantly affect the structure of the deposited metal of type 25Kh5FMS, but at the same time do not lead to the formation of microcracks on the deposited metal due to the presence of a larger amount of smaller titanium carbides in the composition of these modifiers.

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#### CONFLICT OF INTEREST

The Authors declare no conflict of interest

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