

EFFECT OF AL-TI-C SYSTEM MASTER ALLOY HIGH ENERGY SYNTHESIS ON EFFICIENCY OF NI BASED SUPERALLOY INOCULATION

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Abstract: *The possibility of high energy synthesis of Ti–Al–C system powder grain refiner by using high voltage electric discharges for treatment of powder mixtures of 75 % Ti + 25 % Al and 85 % Ti + 15 % Al composition in kerosene with subsequent briquetting by spark plasma sintering is shown in present work. It is found out that high voltage electric discharge treatment of powders leads to the increase of dispersity as well as to synthesis of new carbon containing phases during chemical interaction between system components and products of working hydrocarbon liquid destruction. The possibility of controlling this process by changing initial composition of powders, specific treatment energy and spatial distribution of plasma formations by changing electrode system type is shown. It is also shown that changing master alloy synthesis parameters allows controlling inoculation efficiency. Thereby it is possible to achieve surface or volumetric inoculation, so selective increasing of plastic or strength properties of Ni-based cast superalloys becomes possible. Introduction of 0.01 % of synthesized grain refiner during the casting of SM88U (CM88Y) superalloy allows decreasing mean grain size from 1...2 mm to 0.2...0.5 mm. Tensile strength of inoculated superalloy at the temperature of 900 °C was 68 MPa while their stress rupture strength increased by 20 % in average. Composition and properties of inoculated alloys comply with standard technical documentation, which allows their usage for the production of gas turbines blades.*

KEYWORDS: high voltage electric discharge, powder, synthesis, grinding, inoculation, superalloy, grain refinement, melt, master alloy

1. Introduction

Superalloys, based, in particular, on Nickel, are widely used in the production of gas turbines and in aerospace industry. This is due to their excellent mechanical properties and structural stability at the increased temperatures [1–3]. However, the use of conventional production methods has significant fundamental flaws which lead to limitation of obtained superalloys working range and efficiency [4].

In the work [3] it is stressed, that the process of melt crystallization is the most significant for materials properties formation. Modification of alloys during their casting is an efficient method of impacting crystallization process, which has wide practical application and well-developed technology. Modification in essence is an addition of modifiers (in quantities that in most cases are not more than tenths of a percent) into the molten metals (alloys). These modifiers cause almost no impact on chemical composition, but they impact the structure of cast metals, which leads to increase of their mechanical and other properties. By impacting crystallization process, modification promotes the decrease of metals primary structure size, change of forms, sizes and distribution of inclusions. There are two types of modifiers – inoculants, that create additional crystallization centers in the metal (alloy) and thus impact the crystallization process, and inhibitors, that prevent grain growth. Grain refinement by inoculation includes addition of particles, that can act as substrates for heterogeneous nucleus formation. Inoculants must also decrease content of elements that promote alloys liquation, namely Oxygen, Carbon, Sulfur, Phosphorus. In most cases, components that content Titanium, Aluminum, Boron and Carbon are used as inoculants.

The size of separate refractory particles, its chemical purity and cost are the main quality characteristics of inoculant. Inoculation of melt by refractory nanostructured compositions leads to an increase of metals mechanical properties due to the formation of fine structure. Most inoculants are produced using powder metallurgy methods. Mechanical methods are most commonly used for preparation of particles by their grinding. In order to increase the destruction energy conversion efficiency and specific performance, most commonly existing technologies and technological processes are improved instead of developing new ones [4-7]. For example, improvement of existing grinding and milling machines and creation of new ones with increased productivity is often performed [6, 7]. However, such approach leads to increase of energy and raw materials (metals) consumption and demands the use of expensive high quality steels and alloys while increase of technical and economical characteristics of such machines is relatively low.

At the same time, search for fundamentally new methods of grinding, including electrophysical ones, is going on [8-11]. It is known, that high voltage electric discharge (HVED) in metal

powders – kerosene disperse system can lead not only to dispersion of metal particles, but also to the initiation of chemical reaction. HVED treatment of Al and Ti powders and their mixtures in kerosene can lead to synthesis of such refractory compounds as TiC, intermetallic compounds of AlTi₃, AlTi, Al₂Ti an Al₃Ti composition as well as Ti₃AlC₂ and Ti₃AlC MAX-phases [9, 11].

The goal of present work is to study the impact of Ti–Al–C system, inoculants after their HVED synthesis and briquetting by spar plasma sintering on the changes of structure and properties of cast Ni based superalloy.

2. Materials and Methods

Studies were performed by casting Ni based SM88U (CM88Y) superalloy (density of 8100 kg/m³, Young modulus of 1.79·10⁶ MPa and Poisson's ratio of 0.3), which is used for turbine blades production. Powder master alloys of Ti–Al–C system, obtained after HVED treatment of powders of 75 % Ti + 25 % Al (№ 1) and 85 % Ti + 15 % Al (№ 2) initial composition in kerosene were used as an inoculant.

Schematics and overview of discharge chamber and stand for HVED impact on treated powders are described in detail in work [9]. Selection of impact parameters is justified in work [11].

Inoculant № 1 was obtained by treatment of initial Ti : Al powder mixture with mass relation of 75 : 25 in kerosene with specific energy of MJ/kg using “point – plane” (P – P) electrode system. In order to synthesize inoculant № 2, initial Ti : Al powder mixture with mass relation of 85 : 15 was used, and specific treatment energy was increased to 15 MJ/kg (due to higher Ti content). “Multipoint anode – plane” electrode system with 15 points was used in this case in order to change the distribution of plasma formations in “kerosene – powder” disperse system.

The impact of HVED treatment on the dispersity of powder composition was studied using metallographic analysis of photographs, obtained with BIOLAM I (БИОЛАМ И) optic microscope. Functions of density of distribution of particles by their size were obtained by numerical differentiation of integral particles distribution by their size curve. Obtained functions can be well described by lognormal dependences.

Studies of phase composition of powders were performed using methods of X-ray diffraction analysis. Recording of X-ray diffraction patterns was performed with DRON-4-07 (ДРОН-4-07) X-ray diffraction meter at CuK α radiation. Identification of phases on X-ray diffraction patterns was performed according to JCPDS ICDD PDF2 and POWCOD databases. Quantitative phase composition was evaluated using RIR (Reference Intensity Ratio) method of intensity evaluation with the use of corundum reference.

Obtained powder composition (master alloy) was briquetted as a tablets with mass of 7.5 g using GEFEST-10 (ГЕФЕСТ-10) [8] universal experimental spark plasma sintering (SPS) complex by passage of superposition of direct and alternating currents with amplitude of 1.1 kA and frequency of alternating component of 10 kHz through powder load in vacuum (~ 100 Pa) at the following conditions: pressure ~ 25 MPa, temperature on matrix in range from 300 to 400 °C (which means that temperature of the specimen was ~ 580 °C), sintering time of 300 s.

Inoculation was performed in the following way. Iwo inoculant tablets were placed on the bottom of ceramic casting mold. This mold was then heated up to 900 °C and moved to the working chamber of VIM-25 vertical ceramic induction vacuum furnace, where melting of superalloy and its pouring into the mold with the following slow cooling.

Obtained blocks of cast finger-like specimens were cut (see Fig. 1) at the distance of ~ 10 mm from the edge of finger-like specimen and in longitudinal section. Etching of the macrostructure until clear revelation of grains was performed for the head part of specimens and for the specimens-plates, that were cast-on to the blocks.

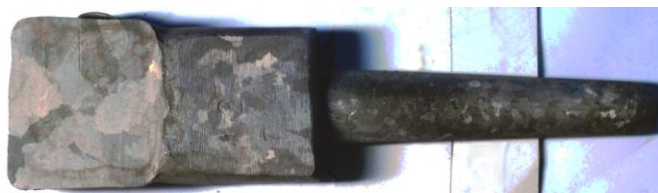


Fig. 1. Appearance of finger-like specimen

Mechanical testing of finger-like cast specimens for short-term (at the temperatures of 600 and 900 °C) and long-term (900 °C, stress of 280 MPa) ultimate tensile strength was performed. Obtained results were checked for compliance to the standards of I ZhAKI.105.015-89 („И ЖАКИ“) “Quality system. Vacuum pouring cast superalloys. Technical requirements. Rules for inspection and methods of control” of State Enterprise Scientific and Production Complex of Gas Turbine Production “Zorya-Mashproekt” (Mykolaiv, Ukraine).

Chemical composition of obtained castings was controlled using chemically-spectral and X-ray diffraction methods.

3. Results and discussion

Density of the distributions of particles quantity by their size for initial powder mixtures is well described by logarithmical normal law (see Fig. 2, curves 1 and 2), as it was noted earlier. Distributions are characterized by such values as mean arithmetical diameter of particles d_a , median diameter d_{50} and peak value (mode) d_m . For initial powder of 25 % Al + 75 % Ti composition these values are $d_a = 34.2$ μm , $d_{50} = 25.6$ μm and $d_m = 14.3$ μm . For initial powder of 15 % Al + 85 % Ti composition their values are slightly higher: $d_a = 39.7$ μm , $d_{50} = 29.7$ μm , $d_m = 16.6$ μm , which is due to different sizes of Ti and Al particles (Ti particles have higher size).

Size of powder mixture particles decreases as a result of cyclic HVED impact, while logarithmically normal type of dependence of their size distribution remains (see Fig. 2, curves 3 and 4). Numeric values of distribution of powder of 25 % Al + 75 % Ti initial composition after HVED treatment are as follows: $d_a = 10.3$ μm , $d_{50} = 7.1$ μm , $d_m = 3.3$ μm . For powder mixture of 15 % Al + 85 % Ti initial composition their values are $d_a = 16.7$ μm , $d_{50} = 10.0$ μm , $d_m = 3.5$ μm . Thus, despite higher specific treatment energy, powder with higher Ti content has larger diameter after HVED treatment. First of all, this is due to the use of different types of electrode system (ES) and not because of different initial particle sizes. Use of single-point ES leads to increase of efficiency of hydrodynamic factors impact (compression wave and hydro flows), while the use of multi-point ES leads to increase of efficiency of thermal factors impact (low-temperature plasma) [11]. In total, HVED treatment ensures changes of powders dispersity by

at least one order of magnitude and ~ 3 times decrease of numeric characteristics of distribution. Even while the use of “multipoint anode – plane” ES with 15 points doesn’t leads to such intensive grinding as in case of using “point – plane” ES (wider size range, higher d_a value (see Fig. 2, curves 3 and 4), but due to the impact of microplasma channels and ablation effect it promotes appearance of large quantity of ultrafine particles (left part of the distribution, see Fig. 2, curve 3), while peak value (mode) for both distribution is almost equal (~ 3.5 μm).

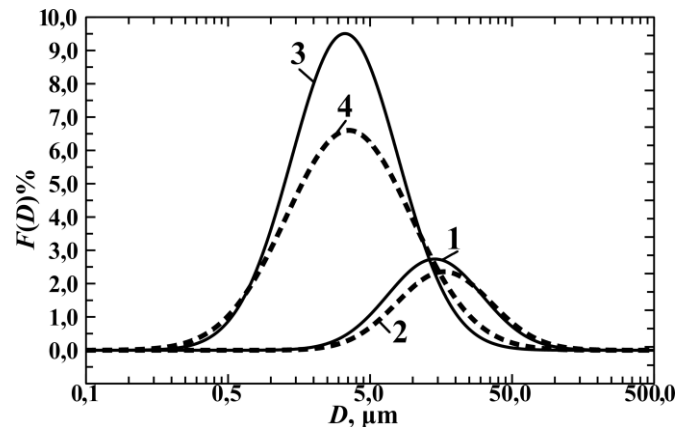


Fig. 2. Curves of density of distribution of particles by their size before (1, 2) and after HVED treatment (3, 4) of powders of 75 % Ti + 25 % Al (1, 3) and 85 % Ti + 15 % Al (2, 4) initial composition (logarithmic scale)

According to results of X-ray diffraction analysis, phase composition of initial powders is (Ti: Al for inoculant № 1 is 75:25 and 85:15 for inoculant №2), they consist only from particles of titanium and aluminum (see Fig. 3, a, b).

As a result of HVED treatment of powder of 25 % Al + 75 % Ti initial composition, titanium carbide is synthesized (see Fig. 3, c), quantity of which is in range from 6.6 to 9.5 % according to evaluation by different methods. Appearance of ultrafine particles (and even nanosized) is indirectly confirmed by broadening of X-ray diffraction pattern peaks.

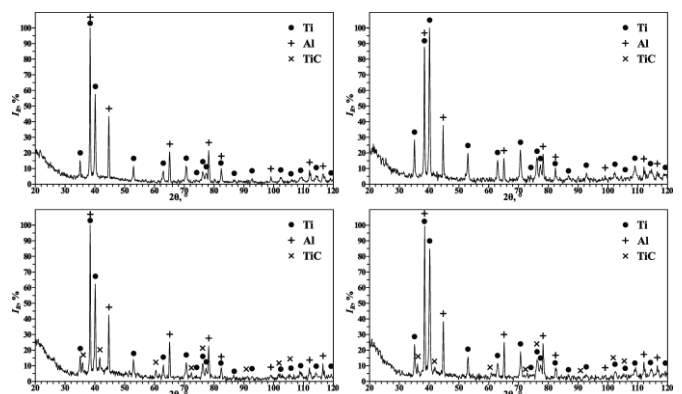


Fig. 3. X-ray diffraction patterns of powders before (a, b) and after HVED treatment (c, d) for powders of 75 % Ti + 25 % Al (a, c) and 85 % Ti + 15 % Al (b, d) initial composition

Similar changes occur as a result of HVED treatment of powders of 15 % Al + 85 % Ti initial composition. However, despite larger value of specific treatment energy, quantity of synthesized titanium carbide is ~ 5 % (which is not very different from results, observed in case of HVED treatment of powder of 25 % Al + 75 % Ti initial composition).

It should be noted, that in works [8, 10] much higher titanium carbide content was observed as a result of HVED treatment of Ti and Fe–Ti powders. Moreover, in works [9, 11] there is an evidence of the synthesis of complex Aluminum, Titanium and Carbon compounds, including MAX-phases. At the same time, in the work

[12] it is stressed that MAX-phases must be synthesized using two-stage process.

During the briquetting of the inoculant in the present work, it was important to preserve structure dispersity in maximal possible way, ensure that briquette has enough strength (so it can be easily added to the melt) and that it can easily decompose during inoculation process (to ensure homogeneous distribution of inoculant particles in the casting volume) due to its porosity. Thus, relatively low temperature (~ 580°C), sintering time (300 s) and pressure (~ 25 MPa) were used if compared to sintering regimes that were used during the studies of metal-matrix composites obtainment [10].

Analysis of chemical composition of cast specimens of SM88U (CM88Y) have shown that all of studied specimens, including modified ones, comply to the demands of I ZhAKI.105.015-89 („И ЖАКИ“) standard. All specimens contain from 57.38 to 58.01 % Ni (base); from 15.47 to 15.87 % Cu; from 10.98 to 11.13 % Co; from 4.65 to 4.92 % Ti; from 4.73 to 4.88 % W; from 3.12 to 3.21 % Al; from 1.76 to 1.87 % Mo; from 0.32 to 0.34 % Hf; 0.19 % Nb; from 0.08 to 0.09 % Fe; from 0.08 to 0.09 % B; from 0.05 to 0.08 % Si; from 0.06 to 0.09 % C; from 0.03 to 0.03 % Mn; 0.004 % P; from 0.002 to 0.008 % Si. These results confirm that during studies melt undergoes inoculation, not alloying.

Analysis of the structure of obtained specimens have shown that specimens of unmodified alloy have relatively coarse grain with mean diameter of 1...2 mm (see Fig. 4, a). Grains of unmodified specimens are homogeneously distributed by casting volume.

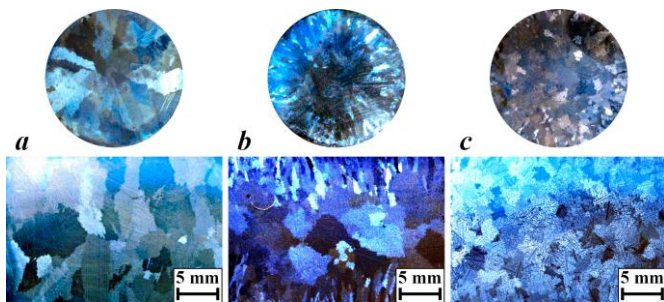


Fig. 4. Structure of SM88U (CM88Y) alloy specimens without inoculation (a) and after inoculation with inoculant obtained by HVED treatment of 85 % Ti + 15 % Al powder at $W_{sp} = 15$ MJ/kg (№ 2) (b) and 75 % Ti + 25 % Al at $W_{sp} = 10$ MJ/kg (№ 1) (c)

Addition of inoculant № 1 (25 % Al + 75 % Ti, treated with $W_{sp} = 10$ MJ/kg, “multipoint anode -plane” electrode system) leads to significant refinement of specimens structure and the mean size of crystallites is 0,3...0,5 μ m. Grain sizes are changing both on the boundaries of the casting and in its central area and their volumetric distribution is relatively homogeneous (see Fig. 4, c). Thus spatial inoculation takes place in this case.

Inoculation leads to significant decrease of grain size. Addition of inoculant № 2 (15 % Al + 85 % Ti, treated with $W_{sp} = 15$ MJ/kg, “point-plane” electrode system) leads to formation of grains with inhomogeneous size (see Fig. 4, b) – in the central area of the casting relatively coarse grains remain, while on the boundaries of the casting grains are significantly refined. Thus, only surface inoculation takes place in this case. Mean size of crystallites in this case is 0,2...0,3 μ m.

Studies of short-term and long-term ultimate tensile strength allows comparison of the indicators of strength and plasticity of obtained specimens – namely ultimate tensile strength σ , percentage elongation after fracture δ , reduction of area after fracture ψ and rupture life time τ , values of which are given in table 1. Characteristics of unmodified and modified specimens were compared between each other and with the demands of I ZhAKI.105.015-89 („И ЖАКИ“) standard.

Table 1. Results of the mechanical tests

| No | Specimen type | Stress test at the temperature | | | | | | Stress rupture test (900 °C, stress 280 MPa) | | |
|----|---------------|--------------------------------|--------------|------------|----------------|--------------|------------|--|--------------|------------|
| | | 600 °C | | | 900 °C | | | | | |
| | | σ , MPa | δ , % | ψ , % | σ , MPa | δ , % | ψ , % | τ , h | δ , % | ψ , % |
| 1 | I ZhAKI | 90 | 3.0 | 6.0 | 65 | 8.0 | 16.0 | – | – | – |
| 2 | Unmodified | 105 | 4.8 | 10.0 | 63 | 14.0 | 36.0 | 131.5 | 8.3 | 23.0 |
| 3 | Inoculant № 1 | 103 | 8.0 | 10.0 | 66 | 15.0 | 35.0 | 183.2 | 10.5 | 22.5 |
| 4 | Inoculant № 2 | 107 | 4.8 | 8.1 | 68 | 24.0 | 33.0 | 182.7 | 9.5 | 19.3 |

Generally, there is an increase of mechanical properties of alloys as a result of inoculation. Application of inoculants leads to an increase of the values of allots ultimate tensile strength so they begin to comply with normative documentation demands. It should be noted that the use of inoculant № 1 (25 % Al + 75 % Ti, treated with $W_{sp} = 10$ MJ/kg, “multipoint anode-plane” electrode system) leads to higher increase of plasticity while applying inoculant № 2 (15 % Al + 85 % Ti, treated with $W_{sp} = 15$ MJ/kg, “point-plane” electrode system) leads to higher increase of strength characteristics due to different structures of obtained alloys.

5. Conclusions

1. The possibility of obtainment of inoculant of Ti – Al – C system for SM88U (CM88Y) cast alloy by HVED treatment of powders of 75 % Ti + 25 % Al and 85 % Ti + 15 % Al initial composition in kerosene with subsequent briquetting using SPS method.
2. HVED treatment of studied powder mixtures leads to decrease of their size by one order of magnitude while quantitative indicators of their distribution by size is decreased ~ 3 times.
3. HVED treatment leads to change of powders phase composition. Titanium carbide is synthesized in quantity from 6.6 to 9.5 % according to results of evaluation with different methods. Appearance of peaks widening on X-ray diffraction patterns indicates formation of ultrafine components.
4. It is shown, that addition of inoculant of Ti – Al – C system in quantity of 0.01 mass %, which was synthesized by HVED treatment of Ti – Al system powder mixture in kerosene and then briquetted by SPS, leads to decreasing grain size from 1-2 mm to 0.2-0/6 mm in all studied inoculated specimens of SM88U (CM88Y) superalloy while their ultimate tensile strength at the temperature of 900 °C was ~68 MPa and long-time strength have in increased by 20 % in average.

6. References

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Acknowledgements

Authors would like to express gratitude to deputy head of metallurgy department of State Enterprise Scientific and Production Complex of Gas Turbine Production "Zorya-Mashproekt" G. Ph. Myalnitsa for his contribution to experimental studies.