STUDY OF NANOMODIFICATION OF NICKEL ALLOY GS3 WITH TITANIUM CARBIDE

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The work deals with the fundamentals of nanomodification of the GS3 heat-resisting multicomponent nickel alloy, out of which blades for gas turbine engines are made. The selection of the modifier for the experimental alloy was justified; the technology of acquiring the nanomodifier, using the plasma-chemical synthesis method, was developed; and the calculations of the specific surface of the TiC particles were performed. The required quantity of nanomodifier introduced to the liquid alloy to acquire the set structure was determined experimentally. Through electronic microprobe analysis, introduction to the metal matric of nanoparticles of titanium carbide is approved. Nanomodification allows achieving refinement of the GS3 nickel alloy structure, which is going to provide an opportunity to increase the effective life of gas turbine engine blades.

INTRODUCTION

In modern aviation gas turbine engines (GTE) the fraction of heat-resisting alloys is up to 40% of the engine mass; according to the forecasts, this proportion is going to remain like that in the nearest future. Besides, cast alloys are on the leading positions among heat-resisting alloys, because all the characteristics of aviation engines are determined by operating characteristics of turbine blades.

Higher temperature strength of cast alloys compared to deformable ones, higher materials utilization rate (0.6…0.8 instead of 0.1…0.2) and three- or fourfold saving of labour during the manufacturing of cooled blades – this all ensures wide use of casting of heat-resisting nickel alloys in modern aviation gas turbine engines [1, 2].

The conditions of work of blades in the new-generation GTEs are becoming tenser due to higher temperature of turbine inlet gases, flight velocity increment, engine lifetime and cycling engine work. These extreme conditions require using functional materials with completely new structure and properties different from those of usual materials.

PROBLEM STATEMENT

During the crystallization process, the multicomponent structure of nickel alloy is formed; the after-heat treatment allows optimizing the structure of the second phases only. During casting of heat-resisting nickel alloys that contain around 50% of strengthening phases, the influence of heat treatment on the structure is inefficient. In this case, the primary structure first of all determines the properties of multicomponent alloys.

Achievements in the area of technology of casting blades with equiaxial structure allow stabilizing thermophysical crystallization properties, get the stable structure of casts and regulate the cast structure. The quantitative parameters of the primary structure are the number of crystallization nuclei and their growth speed.

During casting of blades with equiaxial structure controlling the growth speed of dendritic crystals is hard due to high crystallization speeds. Therefore, the development of technological processes ensuring the formation of additional crystallization nuclei in the liquid alloy is required. Particles and compounds of high-melting point metals (carbides, nitrides and borides), both intentionally introduced to the liquid alloy and synthesized in it, may be such nuclei. Modification of the liquid alloy is an efficient way of influencing the structure and properties of cast materials. There are classic works dealing with modification of nickel alloys [3–5], but they do not deal with the modification technology and the criteria of modifier selection applied to various alloys are not generalized in them.

During the modification of nickel alloys with high-melting point metals, additional crystallization nuclei supporting the refinement of the cast structure are formed in the liquid alloy [4]. But the accumulation of non-metallic impurities leading to flaws of blades is a weak point of this way.

MATERIALS AND METHODS OF THE STUDY

One of efficient ways of influencing liquid alloys is the modification with nanosized disperse particles [6]. Such technological operation allows changing the material structure for obtaining the required properties along with other operations [7, 8]. Disperse systems have special features of their surface conditions, because the fraction of surface atoms prevails in those particles. Disperse high-melting point nanomodifiers are the crystallization nuclei and implement the heredity of the alloy structure, which is formed in the cast metal and remains during further treatment.

In this work, the method of volumetric modification of heat-resisting nickel alloys with nanodisperse titanium-based compositions, the size of which is up to

200 nm. The nanomodifier selection was based in the P.D. Dankov's principle of size and structural correspondence of the injected metal-based particles. Namely the hard-melting point titanium carbide particles, which have the face-centered cubic lattice with the parameters closes to the FCC lattice of nickel, are the most efficient modifiers. An additional moment is that titanium carbide particles do not form their own clusters, but are located between the liquid alloy clusters [9, 10].

Multicomponent nickel alloys, the chemical composition of which is provided in Table 1, were studied.

Table 1

Chemical composition of studied nickel alloys

Alloy grade	Element content, %wt				
	Al	Ti	Cr	Mo	W
GS6U-V1	5.1-6.0	2.0-2.9	8.0-9.5	1.2-2.4	9.5-11.0
GS6K	5.0-6.0	2.5-3.2	9.5-12.0	3.5-4.8	4.5-5.5
GS3	4.0-4.8	2.5-3.2	11.0-12.5	3.8-4.5	3.8-4.5
Alloy grade	Element content, %wt				
	Co	C	Fe	Mn, Si	Ni
GS6U-V1	9.0-10.5	0.13-0.2	1.0	0.4	Basis
GS6K	4.0-5.5	0.13-0.2	2.0	0.4	
GS3	8.0-10.0	0.09-0.12	≤ 2.0	≤ 0.4	

The nanodisperse titanium carbide (TiC) with the particle size from 50 to 100 nm was selected as a modifier of nickel alloys. The modifier is obtained by plasma-chemical synthesis [11, 120]. This method may be used for obtaining multicomponent sub-microcrystalline powders that are the mixtures of carbides and nitrides, nitrides and borides and nitrides of various elements. The initial raw material was the microcrystalline titanium powders. The process took place under nitrogen of electric arc plasma at the temperature around 5,000 °C [11].

The final products were the TiC powders with the particles sized from 50 to 200 nm. The powders were sodded for protection from oxidation and aggregation.

RESULTS AND DISCUSSION

In order to calculate the specific surface of the studied material, the model where all the particles are of the same shape and size was used. Considering that the m mass of a particle with the ρ density and the R radius is $(4\pi/3)R^3{\cdot}\rho$, and the S surface area is correspondingly $4\pi R^2$, the surface area may be determined using the following proportion (1):

$$S_{ud} = S/m = 3/\rho{\cdot}R. \quad (1)$$

The particle size calculated according to the (1) proportion was from 50 to 200 nm, and the specific surface was within the limits from 2.5 to 12.5 m²/g [14]. The synthesized titanium carbide contained from 15 through 20% of mass, from 80 to 87% of titanium and from 0.5 to 1.0 of C_{free}. Literature sources [4, 5] approve that the fine structure of the cast metal can be acquired in case if the crystallization nuclei size is up to 40 nm, and their concentration is $10^8...10^9$ cm⁻². At the same time, the distance between the particles should be at least $\sim 10^3$ nm upon condition of 0.01% of introduced nanodisperse titanium carbide.

It should be noted that the stability of the nanoparticle solvent depends on the following parameters: particle size, interphase surface energy and tension.

The granulated nanomodifier of the following composition was used during the work for the purpose of studies: Ti(C) powder; T powder (20 μm); aluminum powder of 40 μm dispersion degree; powdered GS3 nickel alloy and aluminum dust. Upon condition of 50% absorption of the nanomodifier by the liquid metal, the modifier content was changing within the framework from 0.01 to 0.1% of the liquid alloy mass.

The modification process was performed according to the following technological operations:

1. Mixing of the powdered Ni alloy and the Ti(C) powders.

2. Bricketing and introduction of premeasured amount of the modifier into the liquid alloy.

3. Mechanical mixing of the modifier for the purpose of its uniform distribution. The modifier was introduced to the already molten mixture at 1,580 °C, holding time being 90…120 s.

The analysis of the GS3 alloy structure demonstrated good absorption of the titanium modifier within 3.4%. It should be noted that the titanium absorption in the initial alloy was 3.2%.

The mechanism of action of the nanomodifier in the liquid alloy is as follows: primary particles of the austenitic γ-phase appear on the surface of the Ti(C) particles. The nanomodifier disperses the dendrites of the primary austenite in the GS3 alloy. The microstructural analysis of the initial alloy showed that cross-sectionally it has non-uniform structure: large dendrites with coarse slip lines were discovered on the surface. From the opposite side of the studied surface, the dendrites are more spread in terms of volume and have a relatively large grade of branching (fractality) and location ordering. Before the nanomodification, the samples had non-uniform coarse-grained structure, the grain size being from 5 to 8 mm. After the nanomodification, the samples had uniform fine structure, the grain dispersion degree being up to 1 mm. Eventually, during the nanomodification, the grain size reduced up to eight times, which is shown on Fig. 1.
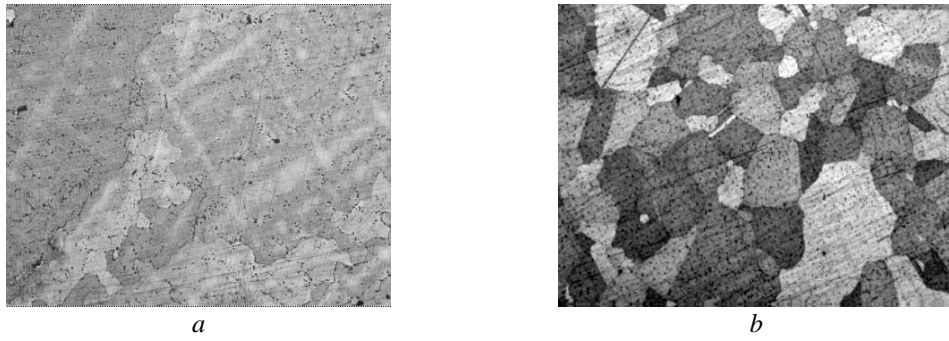
Fig. 1. Macrostructure of the GS3 nickel alloy, x100:
a – before the modification; b – after the modification

The grain boundaries in the non-modified GS3 alloy often do not match the boundaries of the contacting dendrites. Along those boundaries, which break the initial dendritic structure into granulated, the dealloying of the hard nickel alloy with formation of intermetallic phases on its basis takes place. But the intragranular formation of those phases prevails. The comparative assessment of the macrostructure of the dendritic structure after the process of chemical etching showed their prevailing formation in the interdendritic areas due to the difference of colors of the axial and peripheral zones and location of solid solution precipitation of intermetallic phases.

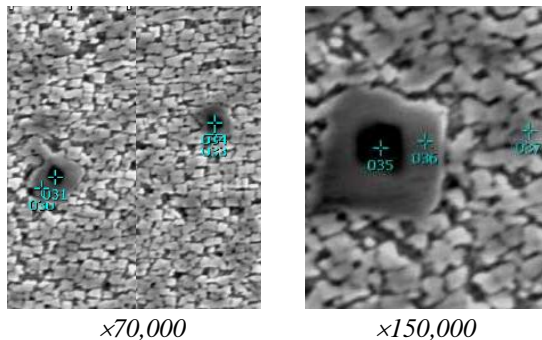The appearance of the nanomodifier (titanium carbide) particles is shown on Fig. 2.

×70,000   ×150,000

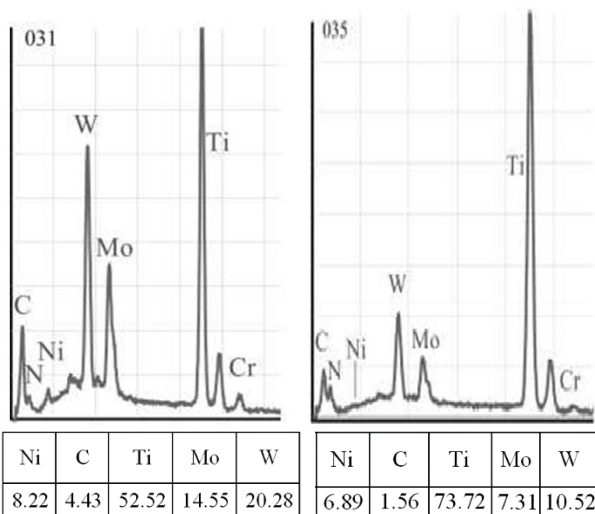*Fig. 2. Structure of the modified GS3 alloy*

Fig. 3. Content of doping elements in the studied fixed points of the modified GS3 alloy

In order to approve the efficiency of influence of TiC as a nanomodifier, the electronic microprobe analysis of the GS3 alloy samples before and after the modification was performed. The distribution of the content of doping and modifying elements in the structural components of the GS3 alloy was determined using the JSM-6360LA versatile scanning microscope equipped with the JED2200 roentgenospectral energy-dispersive microanalysis (Fig. 3).The analysis of the results of data provided on Fig. 3 and in Table 2 approved the existence of rapid increase of intensity of the Ti and C elements in the modified sample, which approves the modifying influence of titanium carbide.

Table 2

Chemical composition of the studied zones of the GS3 alloy before the modification

Point No.	Ni	C	Ti	Mo	W
006	22.74	5.81	37.16	16.85	17.44
007	23.03	6.51	34.02	17.2	19.24

The results of the electronic microprobe analysis approve the efficiency of nanomodification of the GS3 nickel alloy with TiC.

CONCLUSIONS

1. Titanium carbide, which was selected as a nanomodifier for the GS3 high-melting point nickel alloy was acquired, using the method of plasma-chemical synthesis. The nanomodifier particle size was from 50 to 20 nm, and their specific surface was varying from 2.5 to 12.5 m^2/g.

2. Technological operations for the GS3, including mixing, bricketing and mechanical mixing, were developed. The suboptimal amount of the modifier introduced to the liquid alloy was from 0.01 to 0.1%.

3. Uniform and highly refined alloy structure was acquired as a result of modification. The grain size refinement increased from five up to eight times.

4. The absorption of the nanomodifier by the nickel liquid alloy was approved with electronic microprobe analysis.

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ДОСЛІДЖЕННЯ НАНОМОДИФІКУВАННЯ НІКЕЛЕВОГО СПЛАВУ ЖС3 КАРБІДОМ ТИТАНУ

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Розглянуто основи наномодифікування жароміцного багатокомпонентного нікелевого сплаву ЖС3, з якого виготовляються лопатки для газотурбінних двигунів. Обґрунтовано вибір модифікатора для експериментального сплаву; розроблено технологію отримання наномодифікатора за допомогою методу плазмохімічного синтезу; проведено розрахунки питомої поверхні частинок TiC. Експериментальним шляхом встановлено необхідну кількість наномодифікатора, що вводиться в розплав для отримання заданої структури. За допомогою мікрорентгеноспектрального аналізу підтверджується впровадження у металеву матрицю наночастинок карбіду титану. Наномодифікація дозволяє досягти подрібнення структури нікелевого сплаву ЖС3, що дасть можливість збільшити термін експлуатації лопаток газотурбінних двигунів.