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AIRCRAFT PRODUCTION TECHNOLOGY

# Alloys for Blades of Industrial and Marine Gas Turbine Plants: the Operation Peculiarities and Development Directions

**A. V. Logunov[a], D. V. Danilov[b], M. N. Burov[b, *], and S. A. Zavodov[b]**

[a]*PAO United Engine Corporation Saturn, ul. Lenina 163, Rybinsk, 152903 Russia*

[b]*PAO United Engine Corporation, prospekt Budennogo 16, Moscow, 105118 Russia*

**e-mail: maxim.burov@uec-saturn.ru*

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**Abstract**—The paper considers peculiarities of operation conditions of blades of industrial and marine gas turbine plants and prospects of their development. The new nickel single-crystal high-temperature alloy is proposed for gas turbine cooled blades, which is distinguished by high structure stability and resistance to marine salt corrosion.

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*Keywords*: gas turbine plants, marine salt corrosion, nickel single-crystal high-temperature alloy.

## INTRODUCTION

Due to recent increase in the cost of extraction and the increasing scarcity of all types of carbon fuel, improving the efficiency of gas turbines is of crucial importance. Practically, the single approach to solving this problem is to increase the fuel combustion temperature and, accordingly, the parameters of the gas flow entering the turbine. The development of power plants with improved efficiency requires the application of new materials for parts and assemblies of the hot path, which, first of all, include single-crystal nickel alloys. However, alloys created for aircraft gas turbine plants (GTPs) are not quite suitable for power and transport turbines due to insufficient resistance to highly aggressive combustion products of industrial fuels.

At present, the mature economies of the world sharply intensify work associated with a significant increase in the share of electricity in the nations' total gross domestic product (GDP), which generally corresponds to a significant increase in GDP, lowering the costs per unit of GDP produced, significant increase of production efficiency (both in industry, construction and agriculture).

Russia has been considerably lagging behind the mature economies by such important indicator as a share of electric power in gross product, being behind not only the USA, England, France, Germany, but also China, India, Brazil.

We should point out that in almost all countries a very serious attention has been paid to the solution of this problem. Presidential or governmental programs have been developed and approved that involved creation, acquisition, and commissioning of new generations of GTPs of different power categories, designed to work in combination with combined heat and power plants and thermal units, which use gaseous or liquid fuel to heat the working body. As is well known, modern combined units and thermal units are able to produce additional heat and electric energy with an efficiency of 55–60% (instead of 30–32% for conventional cogeneration plants and 20–25% for boilers) without increasing gas and oil production.

This innovative technology in a very short time (10–15 years) has drastically changed the energy industry in the Western countries, primarily.

A dramatic growth of power and heat capacities generated by GTPs caused an active development of works on creation of a new generation of these units, distinguished by high utilization rate and increased (up to 120–160 thousand hours) service life, considerably higher efficiency (up to 38% instead of 30–31%), very high maximum power output. Now, *Siemens* and *General Electric* have successfully completed tests of new GTPs with a unit capacity of about 300 and 500 MW, accordingly, while in Russia, the largest power engine is GTE-110 rated at 110 MW.

We should point out that the above-mentioned works have been performed in Russia since 1990s. In particular, today the GTPs created at UEC-Saturn successfully operate at two thermal power plants (TPPs) in Ivanovo, three TPPs in Moscow and a number of other cities. However, these works are singular and their volume, level and rates do not obviously correspond to indicators typical for the mature economies of the world.

Currently, in accordance with the program of the United States Department of Energy, the creation of GTPs with turbine inlet temperature greater than 1700 K, has been completed, and in 2015 this value reached 1800 K. For comparison, the turbine inlet temperature in domestic GTE-110 unit is about 1480 K.

Today in the United States the volume of orders for power generation GTPs is 200 packages (60 customers) for a total output of 40 million kW.

In 1992, the United States adopted the Advanced Turbine Systems (ATS) program, funded by the government. The goals of the ATS program are the development of reliable and low-cost GTP designs for industrial power and heat generation with an efficiency of 60% and more, recruiting the most promising developers and manufacturers of power GTPs, ensuring the leading position of the USA in the sphere of energy generating equipment manufacture.

The USA is currently prioritizing gas turbines in its economic and ecological struggles.

The active extraction of minerals from the sea shelf, which begins in Russia, as well as the development of shipbuilding, make it necessary to develop and implement new materials for the power plants of floating drilling platforms, fishing, passenger and other ships. In conditions of proximity to the sea surface, the air is saturated with salts, and elements of the hot part of the engine are exposed to aggressive effect of high-temperature salt corrosion. Protective coatings do not fully solve the problem of corrosion protection, so it is necessary that the blade construction material itself is resistant to the high-temperature effects of the sea salt. Alloys ChS-70 and ChS-88, which are widely used in Russia, were developed more than 30 years ago, so there is an urgent need for new alloys for marine applications with higher values of operating temperature and heat resistance.

The purpose of the work is to create a new high-temperature super-alloy for GTP blades, which would be resistant to marine salt corrosion and noninferior to the best foreign counterparts in terms of performance characteristics.

## STATE-OF-THE-ART

Gas corrosion in a broad sense of the word should be understood not only as oxidation at high temperatures in a gas environment, but also sulfurizing from compounds containing sulfur, nitriding from gas components containing nitrogen, carbon saturation from gas components containing carbon, interaction with compounds containing chlorine and other substances of the gas flow [1].

During incomplete combustion of fuel, carbon in the form of soot is formed in certain quantities. It was shown [2] that carburizing has a negative effect on corrosion resistance in the sulfurous atmosphere.

The natural gas used as fuel in gas turbines, may contain sulfur in the form of hydrogen sulfide in rather large quantities [3]. For example, the volumetric hydrogen sulfide content in natural gas of the Orenburg field is (1.5–4.5 %). Natural gas can also be polluted by gas condensate, which includes compounds of sulfur and alkali metals [4], in particular, $H_2S$, $CO_2$, $C_mH_n$, $H_2$, etc. [4].

Most of these compounds are characterized by the low (at a level of 380–630 °C) melting point. Therefore, being present in the working gas environment having a temperature of 1000–1400 °C and more, they get on the surface of blades and nozzle vanes in the form of liquid drops and, being highly aggressive, actively interact with heat-resistant nickel alloys. In particular, the boiling point of such sulfur and sodium compounds ($Na_2SO_4$, NaCl, NaCl+$MgCl_2$, $CaSO_4$, etc.) are 384; 742; 450; 630 °C, respectively [3].

Let us consider the results of research of influence of the alloying elements on the resistance of nickel heat-resistant alloys to sulfide-oxide corrosion.

According to [3, 5], chromium has an active positive effect on their corrosion resistance.

The influence of aluminum may not be so unambiguous. According to [3], with increasing of aluminum concentration in the alloys from 2.0 to 4.5 wt. %, the degree of corrosion increases and only with its content above 4.5 wt. %, the degree of corrosion increases inconsiderably.

Titanium improves the corrosion resistance of alloys, in which case this characteristic is improved not only as a result of increasing the titanium concentration in the alloy, but also under the conditions of increasing the ratio of titanium to aluminum concentration.

Molybdenum with concentration of up to 3–4 wt. % decreases the corrosion. However, with further increase of its concentration, the transition to catastrophic corrosion is observed.

Tungsten alloying has a negative effect on the corrosion resistance of alloys.

Niobium at a concentration of more than 1–3 wt. % increases the sulfide-oxide corrosion resistance of alloys, and vanadium similarly to tungsten accelerates the corrosion. The introduction of tantalum and silicon into the compositions of nickel alloys has a positive effect on their corrosion resistance. However, the results of work [6] should be taken into account, which shows that if silicon contains in alloys in greater amount than 0.25 wt. %, it begins to adversely affect their heat resistance. Manganese also increases the alloy resistance to sulfide-oxide corrosion.

According to [1], the tantalum content of up to 3% in alloys drastically improves resistance to high-temperature oxidation at 1000–1100 °C, and rhenium, at concentration of up to 10 wt. %, has almost no effect on the heat resistance of alloys in the range of 1000–1200 °C.

Hafnium, present in alloys in an amount of 1–2 wt. %, has a positive effect on the kinetics of cyclic oxidation and slows down corrosion damage.

Cobalt effectively increases corrosion resistance in air, but it significantly reduces corrosion resistance under sulfide-oxide conditions.

The elements of platinum group—platinum, ruthenium, rhodium have a significant positive effect on corrosion resistance.

Zirconium and calcium in small amounts (up to 0.3 wt. %) improve the heat resistance of nickel alloys, and alloying them with lanthanum, yttrium and cerium in amounts up to 1 wt. % causes a significant decrease in the corrosion rate. At the same time, microalloying additives also cause a more noticeable reduction in sulfide-oxide corrosion. According to [3], the maximum effect in improving the resistance to sulfide-oxide corrosion is provided by the total alloying of alloys (La+Y+Ce+Zr+Hf+Si) at the level of 0.65 wt. %. With further increase of the total concentration of these elements in alloys, their positive effect begins to decrease sharply.

In [3], the following criteria based on the ratio of the concentrations of alloying elements in the alloy and their boundary values at different operating temperatures, are proposed (Table 1).

**Table 1**

| $T$, °C | Ti/Al | Cr/Al | $Cr^{0.5}\times Ti/Al$ | $Cr^{0.5}\times Ti/Al(Mo+0.7W)$ | $Cr^{0.5}\times Ti\times 10^2/Al\times Ni\times(Mo+0.7W)$ |
|---|---|---|---|---|---|
| 750 | | 6 | 3 | 0.5 | - |
| 800 | 1 | 6 | 4 | 0.5 | 1 |
| 850 | | 8 | 5 | 0.6 | - |

Figure 1 shows the relation of alloy resistance (expressed in terms of mass loss $\Delta m$ as a result of high-temperature oxidation) to the content of chromium $C_{Cr}$ under various temperatures.

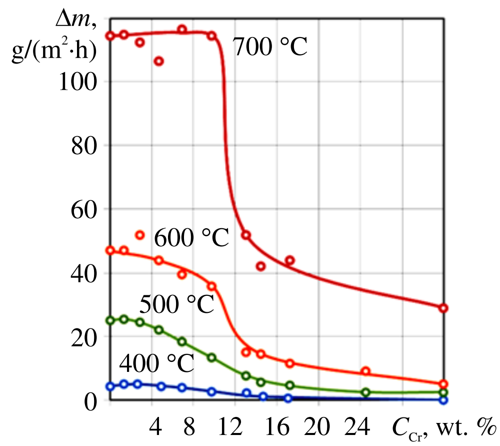


**Fig. 1.**

It can be seen from Fig. 1 that only when chromium concentration in the alloys is greater than 12 wt. %, the necessary anti-corrosive properties are ensured. However, the high content of this alloying element leads to such problematic phenomena as increased material brittleness due to the presence of chromium-based circumferential intermetalide phases and refractory elements (topologically close-packed phases, TCP phases), and reduced heat resistance of the material. There are also technological difficulties in obtaining an alloy from the charge with high chromium content associated with its high liquation activity and volatility. Therefore, the area of existence of alloying components compositions for such alloys is very limited, and the search for this area is a challenging technological problem calling for the use of special methods for its solution.

## NEW ALLOYS IN THE GLOBAL ENERGY SECTOR

By the mid-1990s, *Cannon-Muskegon Corp*. developed a series of materials CMSX-11 belonging to the first generation of single-crystal alloys and specially designed for casting blades of ground-based and marine gas turbines. These alloys were developed under the Collaborative Advanced Gas Turbine Program (CAGT), which included 17 participants from both sides and was extended by the ATS and COST projects [6].

The composition of the new CMSX-11B and CMSX-11C alloys is given in Table 2 [7].

**Table 2**

| Alloy | Chemical composition | | | | | | | | | | ρ, g/cm³ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Co | Mo | W | Ta | Nb | Al | Ti | Hf | Ni | |
| CMSX-11C | 14.4–14.5 | 2.5–3 | 0.35–0.55 | 4.4–4.6 | 4.95–5.1 | 0.08–0.02 | 3.4 | 4.15–4.2 | 0.03–0.04 | Base | 8.36 |
| CMSX-11B | 12.5 | 6 | 0.55 | 5 | 5.15 | 0.2 | 3.6 | 4.2 | 0.04 | Base | 8.44 |

The new alloys combined a high resistance to salt corrosion similar to IN7Z8 LC and an oxidation resistance comparable to CM186 LC. In addition, the alloys have shown very good processability when used for casting parts of any size.

In the 1990s, *Cannon-Muskegon Corp*. also developed the CMSX-10 alloy, which belongs to the third generation of single-crystal alloys. Initially, the alloy was intended for aircraft gas turbine engines (GTEs), but its characteristics, first of all, its long-term strength at 850–950 °C, attracted the attention of GTP developers and manufacturers. In addition, the alloy demonstrated a very good combination of tensile strength and impact strength, as well as fairly easy heat treatability and resistance to harsh environments [8].

In Europe, projects for developing single-crystal nickel alloys for industrial turbines started in the 1980s under the COST501-2 ONERA program (Office National d'Etudes et de Researches/Aerospatiales), whose main goal was to develop nickel superalloys of directional solidification (DS) with a single crystal or columnar structure and high creep resistance.

As part of the program, the SC16 single-crystal alloy [8] as well as the SCA and SCB series alloys containing 16 and 12 wt. % Cr, respectively, was developed for these purposes [9].

Mechanical testing of SCA425 single-crystal samples has demonstrated that the new SCA series alloys are comparable in strength to the known alloys IN6203 (DS) and equiaxial MarM247NIR, being slightly inferior to the target parameters of IN792 alloy and of relatively recently developed CM186LC (DS).

The compositions and heat treatment technologies of the alloys are patented in 2000 as SCA425, SCB444 brand grade.

Currently, Siemens has developed the SCA425+ alloy with improved oxidation resistance and intends to use it in their SGT-800 gas turbine.

In Japan, the creation of high-temperature nickel super-alloys for promising gas turbine plants within the framework of Project 21 is carried out mainly on the basis of the well-known Japanese low-chromium alloys TMS-82 and TMS-75 of the second–third generations, despite their high cost and other disadvantages associated with the use of rhenium as the $\gamma$-matrix hardening element.

The target of the project was to provide creep resistance for 1000 hours at 1100 °C and 137 MPa.

NIMS (National Institute for Metals Research) worked with Toshiba Company developed the TMS-82+ alloy with reduced content of rhenium compared to the third and even second generation alloys for use in aircraft engines and land-based turbines. In the development, the well-known NRIM-ADP program was used that based on an empirical equation that takes into account the mechanical characteristics of a single-crystal alloy, the volume content of $\gamma'$-phase, the $\gamma$ and $\gamma'$ lattice misfit and the concentration of elements—solid solution reinforcing agents (this program is used to create all NIMS alloys) [10].

The optimal composition of the new alloy TMS-82+, due to the effective use of negative misfit, provides high creep resistance, in particular, at 1100 °C and 137 MPa the durability is 200 h (for CMSX-4 is 100 h). In addition, the TMS-82+ alloy owing to the reduced rhenium content has a long-term phase stability. The alloy density is 8.9 g/cm$^3$, the process window is over 60 °C.

The presented data show that the creep resistance of TMS-82+ exceeds these indices for the second generation CMSX-4 and Rene N5 alloys in the whole range of temperatures and stresses. At 137 MPa, the temperature potential of TMS-82+ is by 50–60 °C higher than that of Rene N5's. At higher temperatures and lower stresses, TMS-82+ has a higher strength than the third generation TMS-75 and Rene N6 alloys [11].

The study of the specimen microstructure after creep fracture has demonstrated the complete absence of TCP phases in the TMS-82+ alloy and the presence of longer $\gamma'$-rafting formations, which are perpendicular to the axis of stress and ensure a more effective barrier against dislocation migration, than that of the TMS-75's.

In order to reduce production cost of cast gas turbine blades, by the beginning of 2000s, NIMS in cooperation with *Kawasaki Company* developed the TMD-103 directional solidification alloy (TMD-103DS) based on the single-crystal TMS-75 alloy, which is now considered the third generation of DS alloys in the world.

The new DS alloy differs from the prototype by the presence of additives: 0.07 wt. % of carbon and 0.015 wt. % boron [12]. In computer simulation of the alloy composition, the presence of MC and $M_6C$ carbides was predicted, with tantalum predomination in MC, and tungsten and molybdenum—in $M_6C$. The behavior of rhenium in such a ligature could not be modeled due to the lack of experimental data.

## DEVELOPMENT OF A NEW CORROSION-RESISTANT ALLOY

The authors have developed a special technique aimed at automated search for optimized alloy compositions that ensure extremely high heat resistance with maximum chromium content [13–16]. The technique is based on the two constituents:

—the mathematical model including the dependences of the alloy characteristics from the chemical composition, which are built using the methods of statistical processing of experimental data relating to existing high-temperature alloys;

—software package of multicriteria optimization.

The absolute advantage of this system is the ability to quickly calculate the number of Pareto-optimal solutions that best meet the specified requirements for many parameters at once.

As a result of solving a series of optimization problems and analysis of the data obtained, the alloying area of a new class of high-temperature corrosion-resistant alloys was determined. This alloying area should meet the corrosion resistance requirements, which imply the presence of chromium in the composition in an amount of at least 12 wt.%. This boundary conditionally separates marine heat-resistant alloys from aviation alloys (Fig. 2).

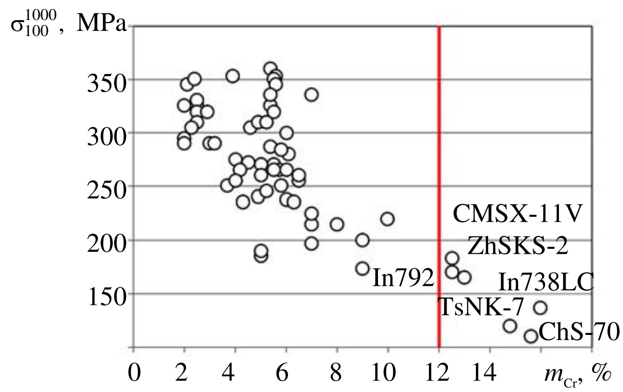


**Fig. 2.**

Today we are working with basic compositions containing rhenium in amount from 1 to 4 wt. %. Ranges of alloying elements of SLZhS5 alloy are given in Table 3.

**Table 3**

| Alloy | Chemical composition, wt. % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | Cr | Co | W+Mo+Nb+Ta | Ti | Al | Re | La | Y | Ce |
| 1 | Less than 0.05 | 12.1 | 11.5 | 10.1 | 3.6 | 3.2 | 1.0 | 0.02 | 0.02 | 0.02 |
| 2 | | 12.1 | 13.3 | 9.8 | 3.5 | 2.9 | 2.4 | 0.02 | 0.02 | 0.02 |
| 3 | | 12.7 | 10.1 | 10.6 | 3.5 | 3 | 3.9 | 0.02 | 0.02 | 0.02 |
| 4 | | 12.8 | 7.4 | 11.1 | 4.0 | 3.8 | 3.8 | 0.02 | 0.02 | 0.02 |

## THE NEW ALLOY EXAMINATION RESULTS

Preliminary corrosion tests in molten salt mixture (10% NaCl + 90% $Na_2SO_4$) at 900 °C have demonstrated high corrosion resistance.

Figure 3 shows changes of the specific weight of single-crystal samples of experimental compositions versus the serial ChS70 and ChS88 alloys under long-term heating at 900 °C in a salt solution (10% NaCl + 90% $Na_2SO_4$).

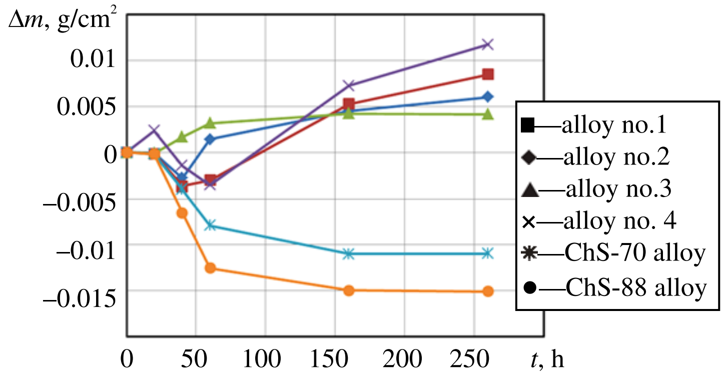


**Fig. 3.**

We compare the post-salt tests appearance of the samples of alloy no. 1 (Fig. 4a), alloy no. 2 (Fig. 4b), alloy no. 3 (Fig. 4c), alloy no. 4 (Fig. 4d) with the ChS-70 (Fig. 4e) and ChS88 (Fig. 4f) alloys after tests at 900 °C in molten salts.


**Fig. 4.**

Preliminary studies of long-term strength have shown the possibility of achieving a value of $\sigma_{100}^{1000}$ equaling to 200 MPa and greater.

Figure 5 shows the experimental points obtained on the single-crystal samples of the SLZhS5 alloy [16], which was a further development of the experimental compositions, as a dependence of the strength on the Larson–Miller parameter defined as $\mathrm{LMP} = T\left(\log(\tau) + 20\right)10^{-3}$.

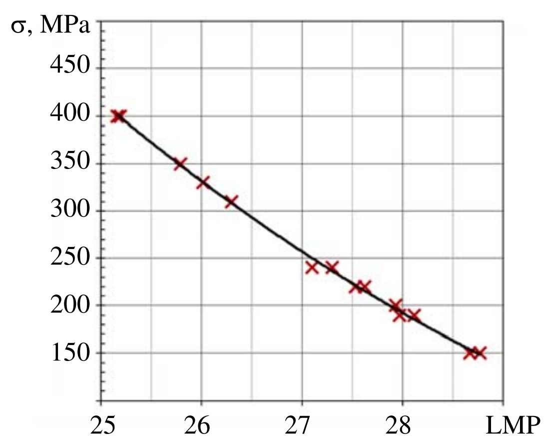


**Fig. 5.**

Comparison of the design characteristics of the SLZhS5 alloy with the existing alloys shown in Table 4 enables us to conclude that in terms of structural stability and corrosion resistance criteria, the SLZhS5 alloy meets the materials that have proven in practice their efficiency in aggressive environments, while at the same time it provides increased heat resistance.

**Table 4**

| Alloy grade | $\sigma_{100}^{1000}$, MPa | $V_{\gamma'}$,% | Misfit, % | $M(\bar{d})_\gamma$ | $\frac{m_{Al}}{m_{Ti}\sqrt{m_{Cr}}} < 0.24$ | $d, \frac{g}{cm^3}$ | $\sigma_{100}^{1000}/d$, $cm \times 10^{-6}$ | Notes |
|---|---|---|---|---|---|---|---|---|
| ChS-70 | 126 | 47 | 0.183 | 0.934 | 0.17 | 8.2 | 15.37 | Formation of TCP phases is possible |
| ChS-88 | 137 | 47 | 0.023 | 0.938 | 0.17 | 8.22 | 16.67 | |
| TsNK-7 | 135 | 53 | 0.142 | 0.929 | 0.25 | 8.19 | 16.48 | - |
| ln 792 | 168 | 53 | –0.295 | 0.913 | 0.25 | 8.38 | 20.05 | Increased rate of softening |
| ln738LC | 118 | 47 | 0.05 | 0.926 | 0.25 | 8.15 | 14.48 | - |
| CMSX-11C | 180 | 56 | –0.293 | 0.922 | 0.21 | 8.45 | 21.45 | Increased rate of softening |
| CMSX-11B | 188 | 60 | –0.211 | 0.916 | 0.24 | 8.39 | 22.37 | |
| NKM-1 | 208 | 56 | –0.132 | 0.89 | 0.41 | 8.6 | 24.2 | Alloy for land-based gas turbines, 9 wt.%Cr; insufficient resistance to salt corrosion; increased rate of softening |
| ZhSKS-1 | 154 | 53 | 0.323 | 0.944 | 0.27 | 8.23 | 18.71 | Formation of TCP phases is possible |
| ZhSKS-2 | 170 | 60 | 0.217 | 0.937 | 0.23 | 8.24 | 20.63 | |
| SLZhS-5 | 206 | 54 | 0.15 | 0.906 | 0.24 | 8.6 | 23.95 | Recommended for all types of gas turbines |
| ZhS6U | 160 | 61 | 0.247 | 0.922 | 0.76 | 8.36 | 19.14 | Aircraft-grade alloy with low corrosion resistance |
| ZhS-32 | 243 | 68 | 0.236 | 0.893 | – | 8.82 | 27.55 | |

It has been found that the microstructure of the new material does not contain TCP-phases and other undesirable inclusions; according to the calculation under the *NewPhacomp* method, the parameter $M(\bar{d})_\gamma$ characterizing the probability of lamellar topologically close packed phases formation from γ-solid solution is 0.906, with the maximum permissible limit of 0.93. The shape of γ′-precipitates is close to cubic, which is provided by the optimal value of the parameter of crystalline lattice misfit of the hardening γ′-phase and the alloy matrix. The volume content of γ′-phase $V_{\gamma'}$ is about 55%, which is optimal for alloys with such a high mass fraction of chromium.

The alloying complex for corrosion resistance is typical for heat-resistant alloys of marine application $\frac{m_{Al}}{m_{Ti}\sqrt{m_{Cr}}} = 0.24$. In terms of heat resistance, it is comparable to aircraft grade alloys, while significantly exceeding them in corrosion resistance. The alloy is characterized by the highest level of specific heat resistance in its class (the long-term strength limit to density ratio, $\sigma_{100}^{1000}/d$ ).

Introduction of the above alloy into the structure of marine GTEs will allow one, at the existing level of efficiency of turbine blade cooling, to increase the gas temperature in the cycle by 70...100 K, which will result in development of the augmented modifications of Russian marine GTEs and will also lay the groundwork for the development of a new generation family of marine GTEs and aggregates.

## CONCLUSIONS

A new heat resistant nickel alloy SLZhS5 with high resistance to marine salt corrosion has been developed.

The SLZhS5 alloy corresponds (or even exceeds) the indicators of russian and world's counterparts in terms of performance characteristics.

The alloy is recommended for use in domestic marine and land-based power and pumping gas turbines.

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