

**DEVELOPMENT OF A NEW HEAT-RESISTANT NICKEL-BASE ALLOY FOR GAS
TURBINE UNITS USED ON OFFSHORE SHELF UNDER CONDITIONS OF ACTIVE SEA
SALT CORROSION**

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Abstract

Currently in Russia, a transition is underway to a new stage of development of oil and gas fields located offshore Russia, as well as to the creation, construction and operation of advanced thermal power plants where simultaneous joint action of gas and steam turbines is performed. Energy utilization ratio reaches 0.55—0.58 in such plants instead of the traditional 0.28—0.36.

Key words: heat-resistant, development, advanced thermal power plants

One of the main problems whose solution will provide access to the forefront in this knowledge-intensive and innovative area is to develop the scientific base and thus create a new generation of cast nickel-base single crystal heat-resistant alloys for cooled rotor blades and nozzle blades for advanced gas turbine engines and units intended to work under the active influence of sea salt medium.

A characteristic feature of the modern period in the development of materials and technologies is a significant complication of both alloy compositions and processes of production of parts with special properties using these alloys (including single crystal rotor and nozzle cooled blades with perfect structure, with no harmful phase formations, with no porosity and microporosity, with reliable coating that effectively protects them from high temperature corrosion effects during the service life of their parts).

The main problem is that the achieved complexity of alloying (especially heat-resistant cast nickel-base alloys) has led to the point where their further development and optimization of promising compositions is directly related to simultaneous consideration of a significant number of factors that directly affect their performance, such as:

- $v_{\gamma'}$ phase (volume fraction of γ' phase precipitates);
 - γ' phase Tcons. (γ' phase consolute temperature);
 - $M(\bar{d}_{\gamma})$ (a parameter characterizing the level of concentration of valence electrons of γ phase, which determines the possibility of embrittling topologically close-packed (TPU) compounds formation);
 - $\frac{\Delta a}{a}$ (relative difference between the lattice parameters of γ and γ' phases);
 - σ_t^T (life of the alloy at temperature and load t);
 - γ (specific weight of the alloy);
- and others.

Naturally, the optimal solution of the problem of creating new generations of alloys at present is possible by active development of the approaches based on modeling of interrelation processes of the nature and the level of alloying with thermodynamic, structural and strength parameters of the studied high-temperature metal materials.

The difficulty of the problem lies in the fact that it is necessary to find an optimal solution satisfying the two major conflicting requirements at the same time, namely:

- an alloy should have increased sulfidation resistance, and therefore, it should have a sufficient chromium content (in Fig. 1 [1] it can be seen that nickel-base alloys have a satisfactory sulfidation resistance if their chromium content is 12 wt.% and more);

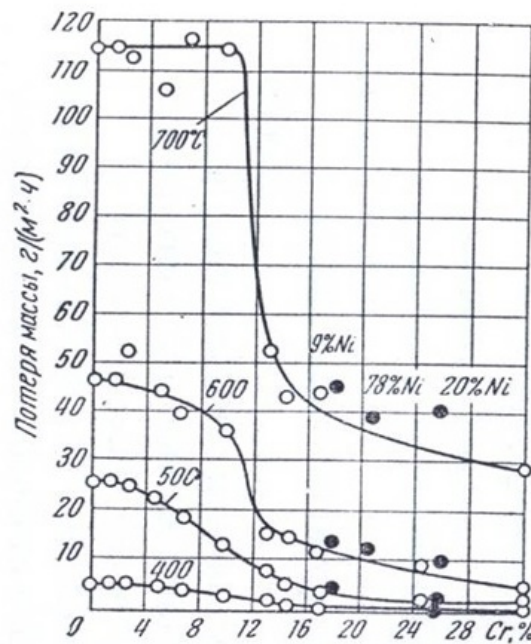


Fig. 1. Chromium influence on gas corrosion resistance in hydrogen sulfide atmosphere.

потеря массы	mass loss
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- an alloy should be highly heat resistant. This is related to its increased alloying with elements which are effective in high temperatures, such as tungsten, molybdenum, and rhenium.

However, an alloy with a high chromium content starts to form embrittling sheet-like topologically close-packed (TPU) phases with these elements.

Besides, titanium actively increases heat resistance and sulfidation resistance. However, in this case, increasing titanium concentration beyond a certain limit results in a situation when $\text{Ni}_3(\text{Al}, \text{Ti}) \gamma'$ cubic precipitates (which are the main strengthening agents for nickel-base alloys at high temperatures) form Ni_3Ti -type sheet-like η phase formations, which also soften the alloy dramatically.

Thus, a successful solution of the problem of optimizing the composition of a new alloy having an improved sulfidation resistance and high heat resistance at the same time, is only possible by building appropriate "composition-properties" models and developing a computer method of alloying optimization for the new generation of alloys based on these models.

For this purpose, on the basis of experimental data on more than 200 Russian and foreign nickel-base alloys, models have been created and software has been developed for the analytical estimation of composition relation to structural, thermodynamic, physical-chemical and strength parameters of nickel-base heat-resistant alloys.

The software developed on the basis of an embedded Microsoft Windows Excel program includes:

- calculation of the volume content of γ' phase in the alloy of a given composition ($V_{\gamma'}$);
- calculation of consolute temperature of the strengthening γ' phase ($T_{\text{cons. } \gamma'}$);
- calculation of γ and γ' phase lattice parameters (a_{γ} and $a_{\gamma'}$):
- calculation of the probability factor of TPU - phase formation in alloys γ matrix ($M\bar{d}$) in accordance with the NEW PHACOMP method;
- calculation of the alloys stress-rupture value at 1000 °C ($\sigma_{100}^{1000^\circ\text{C}}$), etc.
- The analysis of the factors determining the high-temperature performance of heat-resistant nickel-base alloys.

These factors include:

1. Thermodynamic parameters.

It is well known that the level of high temperature performance is primarily determined by the structural stability which is dependent on the thermodynamic criteria such as solidus and liquidus temperatures (T_S и T_L), local eutectic melting temperature ($T_{loc.}$) as well as the strengthening γ' phase sweating temperature and consolute temperature ($T_{sw.\gamma'}$ and $T_{cons.\gamma'}$). These parameters simultaneously determine the level of thermodynamic stability of the structure, the nature of high temperature softening and hence the heat resistance level at high temperatures.

The solidus temperature value determines the maximum possible operating temperature of alloys because:

- The higher T_S , the higher the temperature the alloy can be used at.
- An increase in T_S in nickel superalloys is primarily affected by high-melting refractory elements — W, Re, Ta. Due to having the lowest diffusion mobility of all the alloying elements, they dramatically slow down diffusion processes at high temperatures that are associated with coagulation of fine precipitates of the strengthening γ' phase at high temperatures, and hence with structure degradation and softening of alloys.
- Temperature difference ($T_L - T_S$) determines the level of dendritic segregation: the smaller it is, the lower the segregation is and thus the more uniform (by composition) the alloy is, and the smaller the alloy's tendency is to form supersaturated local volumes and hence carboboride eutectic phases, in which upon alloy cooling microporosity can be seen, which reduces its strength characteristics.
- Local melting temperature of carboboride eutectic phases is also an important alloys parameter because:
- it is necessary to have a large temperature "window" for heat treatment, which is located between $T_{cons.\gamma'}$ and $T_{loc.}$. A number of studies indicate that $T_{loc.}$ can reach or even be lower than $T_{cons.\gamma'}$. In this case, the ordinary homogenization may lead to local melting of the alloy microvolumes and hence to alloy softening.

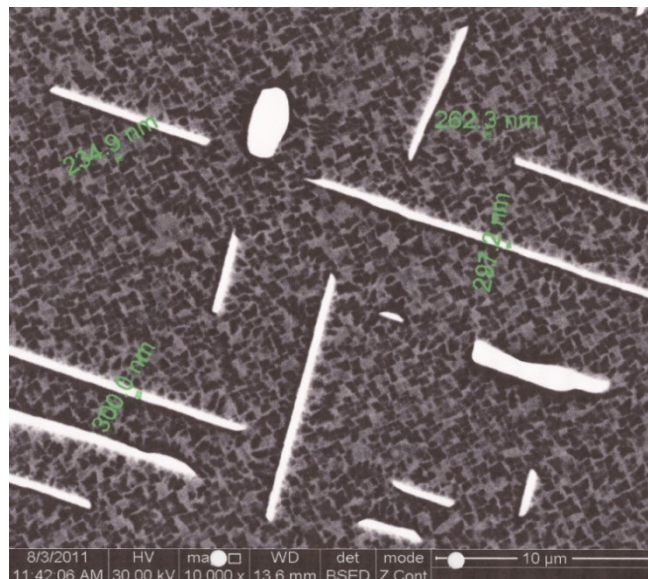


Fig. 2. TPU phases in a cast heat resistant nickel-base alloy.

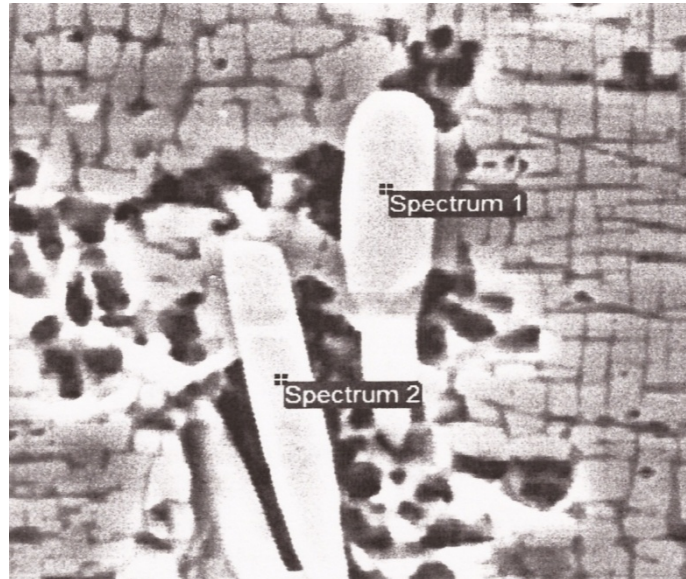


Fig. 3. α -tungsten phases in a nickel-base alloy.

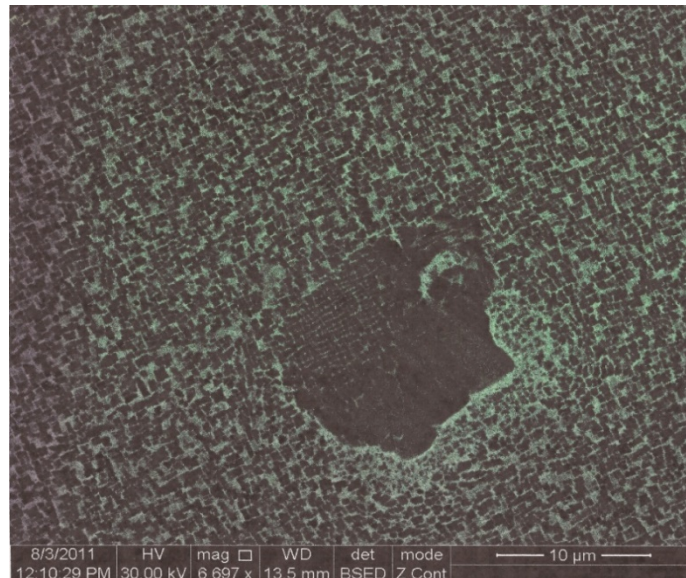


Fig. 4. γ' phase

Fig. 5 shows the microstructure of a heat resistant nickel-base alloy (x 10000). It is evident that it represents a γ matrix which is strengthened by cubic precipitates of finest γ' phase particles (0.3—0.6 μm).

2. Structural factors, which include:

volume content of the main strengthening γ' phase ($v_{\gamma'}$);

(a_{γ}) and ($a_{\gamma'}$) phase lattice periods and the value of their dimensional mismatch

$$\frac{\Delta a(\gamma - \gamma')}{a} = 2 \cdot \frac{a_{\gamma} - a_{\gamma'}}{a_{\gamma} + a_{\gamma'}} \cdot 100(\%)$$

Alloy heat resistance directly depends on the content of the strengthening γ' phase and the magnitude and sign of the dimensional mismatch of the γ - and γ' phase crystal lattice parameters. Optimum values of heat resistance are at $\sim (0.15—0.35) \%$ level.

The structural factors determining the performance of alloys, are sheet-like topologically close-packed (TPU) phases which dramatically soften the alloy (Fig. 2) as well as α phases (namely, α -Cr, α -W etc.), that take important elements from the alloy (including W). As a result, their concentration in the alloy and hence their reinforcing effect is significantly reduced. Fig. 3 shows α -W phase formations. Fig. 4 shows eutectic precipitates of γ' phase, which was formed during alloy crystallization from liquid and the strengthening effect which is quite small. At the same time, W, Ta, Al, Ti, etc. are also present in the composition. Besides, all of these elements are somewhat withdrawn from the material, hence their strengthening effect on the alloy has become much lower.

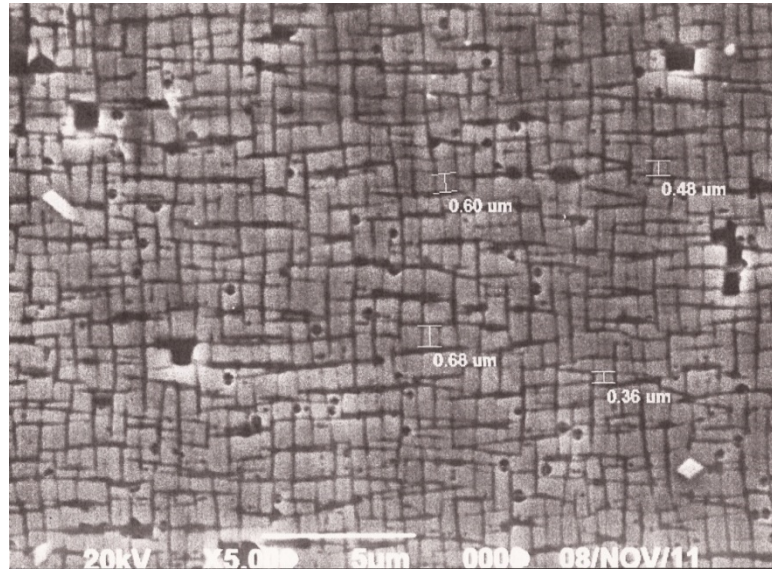


Fig. 5. Heat resistant nickel-base alloy γ - γ' structure.

3. Another group of factors that determine the performance of heat resistant nickel-base alloys are strength parameters, first of all:

E - elastic modulus,

as well as strength characteristics:

Short-term strength

$$\sigma_B^{20^\circ C}, \delta_{20^\circ C}, \psi_{20^\circ C}$$

Stress-rupture strength

Fatigue strength

$$\sigma_{-1(N_{\text{цикл}})}^{t^\circ C}$$

Impact viscosity

KCV

4. Another group of parameters that help to avoid the formation sheet-like embrittling phases in the alloy are "concentration" characteristics.

This term means providing such a ratio of a number of elements in the alloy, that there will be no precipitation of harmful sheet-like compounds.

In particular:

At

$$\frac{Al}{Ti} < 0,7 \frac{at\%}{at\%}$$

a sheet-like η phase is formed (Ni_3Ti).

At

$$\frac{Al}{(Nb + Ta)} < 5,9 \frac{at\%}{at\%}$$

the following sheet-like phases begin to appear

$$\delta - phase[Ni_3(Nb, Ta)]$$

At

$$\frac{Al}{(Ti + Nb + Ta)} < 1 \frac{at\%}{at\%}$$

Sheet-like η and δ phases appear.

5. Finally, there is a group of factors that determine the sulfidation resistance of nickel-base alloys. In particular, since it is Cr and Ti that provide a stable alloy operation under the action of marine corrosion products, the following criteria have been designed:

Sulfidation and oxidation resistance

$$\frac{Ti}{Al} \approx 1 \frac{mac.\%}{mac.\%};$$

$$\frac{Al}{Ti \cdot Cr^{1/2}} \leq 0,2 \frac{mac.\%}{mac.\%}$$

$$\frac{Ti \cdot Cr^{1/2}}{Al(Mo + 0,7W)} \geq 0,6 \frac{mac.\%}{mac.\%}$$

Transition temperature from slow "low-temperature" corrosion to catastrophic "high-temperature" corrosion.

$$\dot{O}_{critical} = 651,95 + 4,9C_{Cr} + 8,19C_{Ti} - 0,49C_{Al} - 1,52C_{Mo} - 0,3C_{W}$$

Alloy	TsNK7	ZhS6K	ZhS6U
$T_{cr.}$	850	725	700

Thus, the development of the alloy resistant to sulfidation and oxidation, can only be successfully performed by creating models for all 5 groups of criteria. Moreover, the new alloys must simultaneously satisfy all the criteria presented. This in turn is possible in the process of computerization and through the development of appropriate programs.

The computer method being developed for optimizing heat-resistant nickel-base alloy compositions (KMO ZhS) created new heat resistant cast nickel-base alloys having highly resistant to sulfidation.

The new alloy being developed, called SLZhS-5, has a level of heat resistance, comparable to the best alloys for aircraft VI generation GTE. Furthermore, it is characterized by high resistance to sea salt corrosion, comparable to that of In-792 and ChS-70 alloys.

Fig. 6 shows that the SLZhS-5 alloy exceeds all national and foreign counterparts for GTU in terms of stress-rupture value $\sigma_{100}^{1000^{\circ}\text{C}}$.

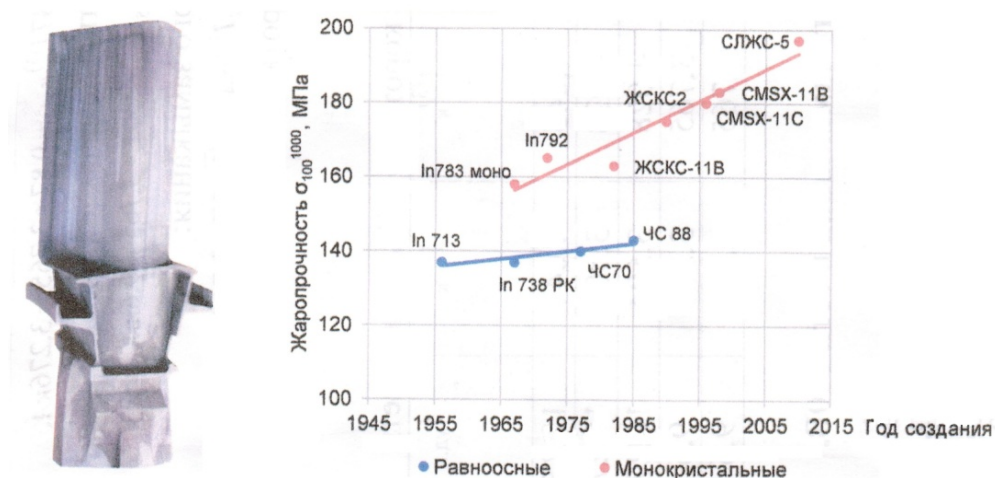


Fig. 6. Stress-rupture (, МПа) of heat resistant nickel-base alloys for GTU.

жаропрочность	heat resistance
равноосные	equiaxial
монокристалльные	single crystal
год создания	year of manufacture

Comparative studies of corrosion resistance of SLZhS-5 alloy (various modifications), as well as ChS-70 and ChS-88 alloys widely used for national GTU are shown in Fig. 7.

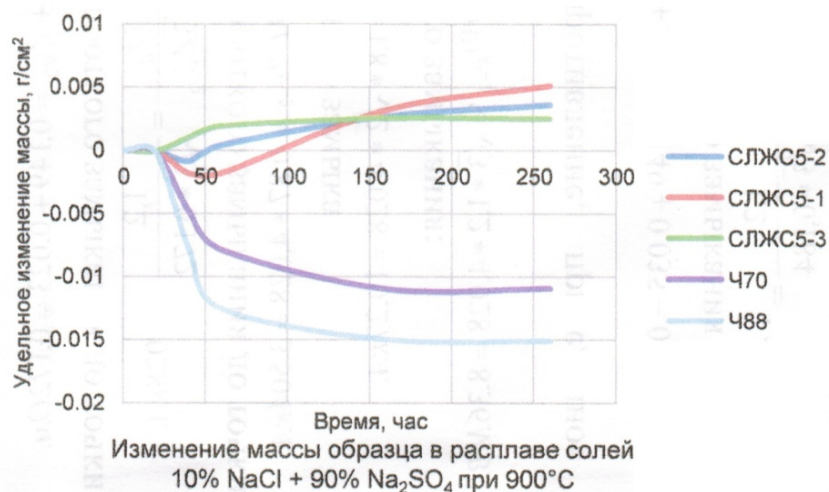


Fig. 7. Results of corrosion resistance comparative tests of heat resistant nickel-base alloys for GTU.

удельное изменение массы	specific mass change
время, час	time, hr
изменение массы образца в расплаве солей	specimen mass change in molten salt

It is obvious, when tested in saline medium at 900 °C (molten salt, 10 % NaCl + 90 % Na₂SO₄) for 250 hours, the new alloy has certain advantages over ChS-70 and ChS-88 alloys in terms of the absolute value of specific mass change.

The alloy has no tendency to form embrittling TPU phases. It has good casting properties, which offers an opportunity to manufacture large-size cast single crystal turbine blades.

REFERENCES

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