

RESULTS OF DEVELOPMENT AND TESTS OF ECONOMICALLY DOPED SINGLE CRYSTAL SUPERALLOY FOR ROTOR BLADES OF GAS TURBINES

Logunov A.V., Leshchenko I. A., Danilov D. V., Khryashchev I. I.

JSC NPO "SATURN", Rybinsk, Russia

Abstract

New alloy SLGS32BR was developed, having no Rhenium and Ruthenium in its composition. The alloy provides high-temperature rupture strength 238 MPa (100 hours at 1000 degrees Centigrade), and has density 8.83 grams per cubic centimeter. These performances are equivalent to that of widely used in Russia alloy GS32VI, which contains about 4% of Rhenium. Thus, the price of new material is 2.4 times less as compared with existing alloy GS32VI.

The composition of new alloy was obtained using novel computer technology, based on mathematical model of alloy and numerical optimization.

Key words: *nickel, superalloy, doping elements, composition, rhenium, strength, heat-resistance*

1. INTRODUCTION

Application of rhenium and ruthenium for doping nickel heat-resistant alloys has allowed the raise of their high-temperature rupture strength 1.5 times. Owing to introduction of these elements it was possible to make a leap forward in the field of aviation materials progress, connected with creation of 4-th and 5-th generations of superalloys.

At the same time, rhenium and ruthenium differ in the highest cost. With their total weight amount in alloys of the forth generation about 10...13 %, the useful effect from doping with these elements can appear unjustified from the economic point of view. This fact could be confirmed by limited application of the forth generation alloys, and also by large enough demand concerning inexpensive alloys of previous generations.

Now in Russia the alloy of the 2nd generation GS32VI is widely applied. Created in the seventies of the last century, this alloy possessed in due time the ultimate value of high-temperature rupture strength (100 hours at 1000 degrees Centigrade) $\sigma_{100}^{1000} = 240 - 245 \text{ MPa}$. It was reached at the expense of doping it with rhenium in amount of 4 ... 4.5% by weight, thus the cost of its blend is rather high (about USD 300 per kilogram). Considering a demand for the material with the specified properties, the task of creating a similar in properties alloy, being economically doped with expensive rhenium, or absolutely not containing it, is becoming more urgent.

Work in this direction is conducted for a long time. So, the alloy SLGS-1 [Logunov, A.V. et al] at the moment of its creation possessed the highest rupture strength among non-rhenium alloys; however its high density of 9.03 g/cm³ has not allowed to use it for manufacturing rotor blades of turbines, despite the level of $\sigma_{100}^{1000} = 255 \text{ MPa}$. At the 12th international symposium "SUPERALLOYS-2012" Cannon-Muskegon Corporation has presented new non-rhenium alloy CMSX-7 [Wahl J.B. et al], which provides $\sigma_{100}^{1000} = 237 \text{ MPa}$ and density about 8.8/cm³.

In the present work there are presented the results of research, aimed at creation of a new material, known as SLGS32BR, which provides the similar level of parameters as GS32VI, but is not doped with rhenium.

2. CRITERIA OF ASSESSMENT OF ALLOY QUALITY

The considerable complication of both alloy compositions and processes of producing details of these materials, which provide special characteristics, is characteristic of up-to-date development period of heat resisting materials and technologies. When producing single-crystal cooled rotor and stator blades, it is necessary to consider a large number of the factors, connected with providing perfect structure of the material, which must have no harmful phase inclusions, porosities and friability, as well as with the need of covering the blades with effective coating, which must protect reliably the engine details from high-temperature corrosive attack during all term of their operation.

One more factor, significantly complicating work in the direction of creation new superalloys with utmost high-temperature strength, is connected with the fact that the areas of an optimum multicomponent doping came very close to the areas of presence of brittle topologically close packed (TCP) compositions. Therefore, admissible intervals of alloying components percentage are considerably narrower owing to need of ensuring the guaranteed absence of harmful phases in alloys structure, and also highest values of alloys quality indexes.

When carrying out the search for optimum doping compositions for heat resisting alloys, there were taken into account the following groups of parameters, presenting operability of the alloys:

1. Strength parameters

- σ_{τ}^t - long term high temperature strength of the alloy (before specimen destruction), at temperature t , °C, during τ hours.

2. Thermodynamic parameters

- T_{Solvus} - temperature of complete dissolution of γ' - phase;
- T_{BD} - temperature of beginning of γ' - phase dissolution;
- T_S - temperature solidus;
- T_L - temperature liquidus;
- etc.

3. Structural factors

- «Misfit» - a relative difference of parameters of crystal lattices in γ and γ' phases

$$\left(\frac{\Delta a_{\gamma-\gamma'}}{a_{\gamma}} = \frac{a_{\gamma} - a_{\gamma'}}{0,5 \cdot (a_{\gamma} + a_{\gamma'})} \cdot 100\% \right), \quad (1)$$

where a_{γ} and $a_{\gamma'}$ - parameters of crystal lattices in γ and γ' phases respectively;

- $V_{\gamma'}$ - a volume fraction of γ' phases;

- $M(\bar{d})_{\gamma}$ - the parameter characterizing the level of concentration of valence electrons of γ - phase; it presents the probability of forming the brittle TCP compounds (according to method New PHACOMP [Morinaga M. et al]); if $M(\bar{d})_{\gamma} > 0.93$, TCP compounds are highly probable according to this method;

4. Concentration parameters, characterizing the probability of laminated compounds formation, based on Ni_3Ti , Ni_3Nb , Ni_3Ta , etc, inside the γ' phases:

$$- \frac{m_{Al}}{m_{Ti}}, \frac{m_{Al}}{m_{Nb} + m_{Ta}}, \frac{m_{Al}}{m_{Ti} + m_{Nb} + m_{Ta}};$$

Thus, during search for optimum composition of new alloy, multifactor analysis must be carried out, considering all abovementioned indices of heat resistant alloy efficiency.

3. ALLOY DEVELOPMENT

The search of efficient composition of new material was carried out on the basis of computer modeling of heat-resistant nickel alloys properties, in a combination with procedure of numerical optimization.

To obtain the composition of highly effective and economically doped alloy, development of special methods is required. On the one hand, there is necessary to do the quick, inexpensive and reliable assessment and analysis of considerable number of thermodynamic, structural, strength, concentration, kinetic, physical, chemical and other parameters. Special computer models must provide information on these parameters. On the other hand, availability of adequate model is not enough for solving such task, because it is required to coordinate optimally about a dozen of independent parameters – mass fractions of the doping elements. From the mathematical point of view it is a difficult task.

Therefore, the problem of search of efficient doping of alloys can be solved successfully only on the basis of a combination of computer modeling of heat resisting nickel alloys with a procedure of numerical optimization of their composition. In the present work there was used the technology, based on mathematical modeling and numerical optimization, aimed at obtaining the alloy composition, providing the defined set of material properties [Shmotin Y. et al].

The mathematical model of single-crystal superalloy is based on response surface techniques, which fit the dependences of alloy properties on its composition. IOSO multiobjective optimizer [5], being used for search of optimum composition, repeatedly started the model for calculation of alloy efficiency indexes for different concentrations of doping elements. As a result of such search, the final set of the solutions was found, which were Pareto-optimum and provided various degrees of optimum compromise between inconsistent objectives. [Egorov I.N. et al]

As a prototype the alloy composition was chosen, which according to the model estimations provided the level of rupture strength $\sigma_{100}^{1000} = 250 \text{ MPa}$ and had the density $d = 8.83 \text{ g/cm}^3$. The composition of the investigated alloy is presented in table 1. Its distinctive feature from alloys similar in composition or properties is the content of molybdenum of 3 % by weight.

	Cr	Co	W	Mo	Al	Ti	Ta	Re	Nb	Hf	C	Ni
GS32	4.9	9	8.5	1	5.9	-	4	4	1.6	-	<0.15	Bal
SLGS-1	5	10	11.5	0.01	5	0.01	9	-	0.01	0.01	<0.01	Bal
CMSX-7	6	10	9	0.6	5.7	0.8	9	-	-	0.2	-	Bal
SLGS32BR	6	9	8	3	5.6	-	8.2	-	-	0.4	<0.02	Bal

Table 1. Compositions of the alloys

4. MICROSTRUCTURE STUDIES AND HEAT-TREATMENT

Presence of molybdenum in rather considerable quantity has led to a certain problem: phases sated with refractory elements were found in a cast condition of the alloy. Figures 1 and 2 show casting microstructure with no heat-treatment (crystallographic orientation is [001]). Studying of microstructure revealed significant amount (nearly 1 % by volume) of abovementioned phases (light at figure 1, it is allocated mainly along the border of eutectic inclusions), and also $\gamma'_{\text{eutectic}}$ phases (about 6 % by volume). However, topologically close packed (TCP) phases were not observed.

γ' particles have an appropriate shape, close to cubic (Figure 2). The size and morphology of precipitates in dendrite axes and interdendritic space are different, which is a direct consequence of nonequilibrium processes, having place during solidification, causing microliquation of doping elements in dendritic cells.

To provide the composition homogenization and to dissolve the harmful phases as much as possible, the cyclogram of heat-treatment has been developed and applied. The procedure is carried out in vacuum or in inert gas environment (argon). The rate of heating does not exceed 20 °C/minute. The following heat-treatment cycle was used:

1. Heating to $t=1180\pm5$ °C, holding 8 hours;
2. Heating to $t=1285\pm5$ °C, holding 4 hours and the subsequent cooling to $t=800$ °C with average speed of 80-100 °C/minute;
3. Heating to $t=1030\pm10$ °C, holding 4 hours, cooling to $t<800$ °C with average speed of 80-100 °C/minute;
4. Heating to $t=870\pm5$ °C, holding 28 hours and the subsequent cooling in the furnace.

The microstructure of the alloy after heat-treatment is shown in Figure 3.

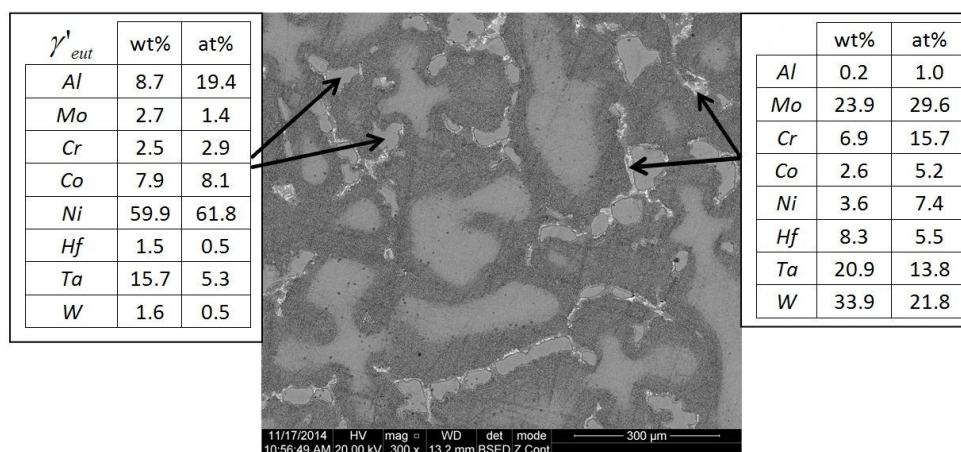


Figure 1. Casting microstructure before heat-treatment.

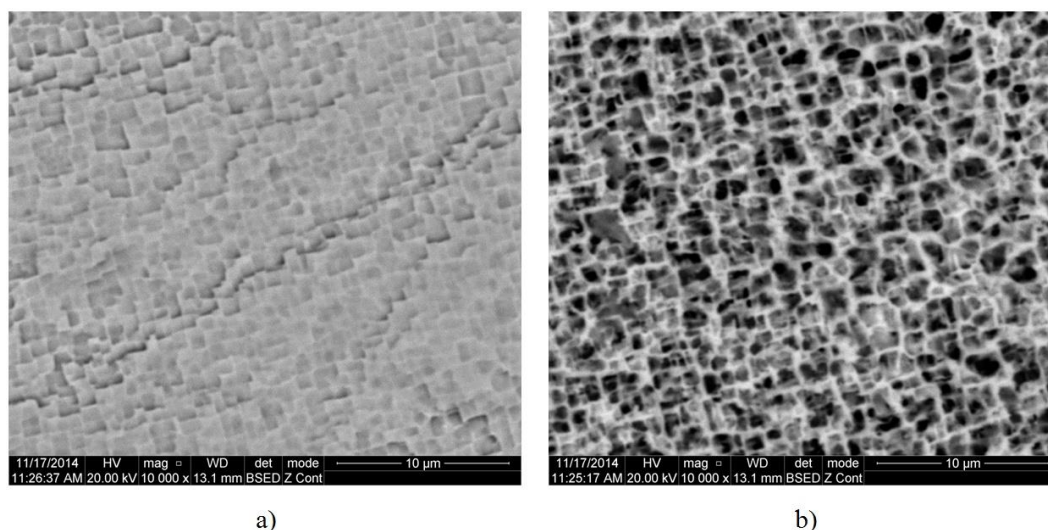


Figure 2. Casting microstructure before heat-treatment:

a) – dendrite axis, b) – interdendritic space

In the structure of the alloy after complete cycle of heat treatment the quantity of eutectic precipitations, emitted from γ' phase, does not exceed 1.85 %. On the one hand, this fact confirms the efficiency of the chosen mode of heat treatment. On the other hand, it demonstrates extremely full use of the strengthening effect achieved by doping with tungsten and tantalum. In heat-treated sample γ' phase particles have cubic shape, their sizes are about 850 nanometers. Presence of TCP phases and other harmful phases it is not observed.

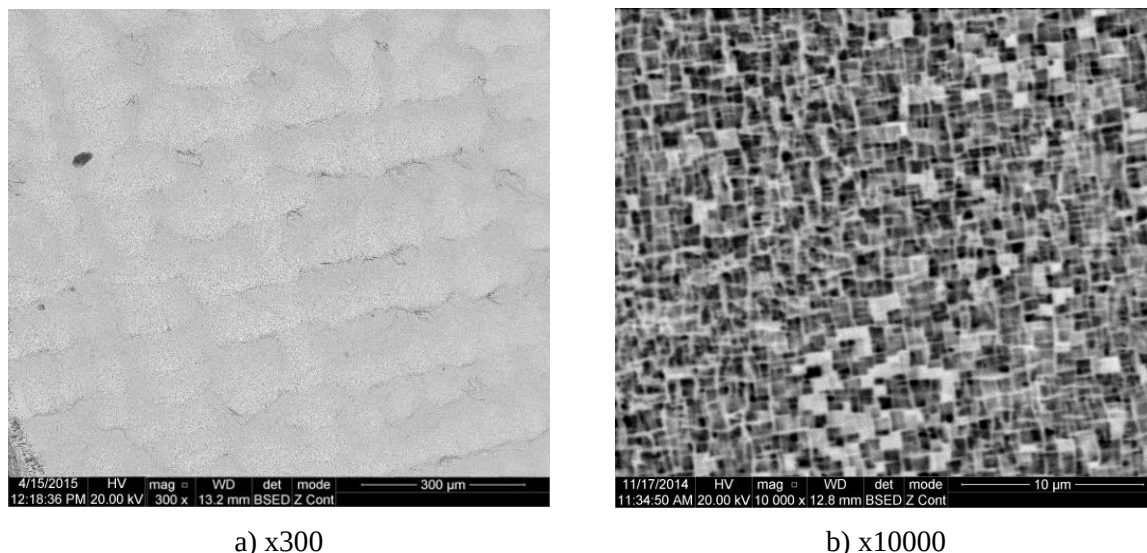


Figure 3. Cast microstructure after heat-treatment.

5. RESEARCHES OF MECHANICAL PROPERTIES

For research of mechanical properties the samples were manufactured according to industrial standards AM-TU 293-62 and GOST 9651-84 (Figure 4). Results of tests are typed in the Table 2.



Figure 4. Test sample after high temperature creep-rupture test

The results of tests discovered that ultimate strength σ_b of experimental composition coincides with the same indicator of GS32VI alloy indicators, while the creep strength $\sigma_{0.2}$ considerably (by 17%) exceeds the corresponding parameter of GS32VI. Relative elongation δ and narrowing ψ of new alloy SLGS32BR sample are slightly less than that of GS32VI, but these parameters have high enough level for service conditions. Thus, at low temperatures conditions SLGS32BR alloy completely corresponds to indicators of serial alloy GS32VI.

SLGS32BR experiment points	σ_B , MPa	$\sigma_{0.2}$, MPa	δ , %	ψ , %
	1039.50	963.01	-	13.0
	990.47	943.39	8.19	14.7
	990.47	944.38	8.36	14.6
SLGS32BR Average	1006.81	950.26	8.28	14.1
GS32VI	1045	809	20	26

Table 2. Results of mechanical properties tests at 20°C

Results of material microstructure research after sample rupture are presented at Figure 5. It is visible that cracks appear firstly in the eutectic phase areas, and they initiate the destruction of the sample. The microcracks do connection of eutectic phase areas into a chain (Figure 5a). At the same time material quite well resists the growth of cracks. High plasticity of material is observed (the $\gamma'_{\text{Eutectic}}$ phase is strongly stretched along the axis of a mechanical loading).

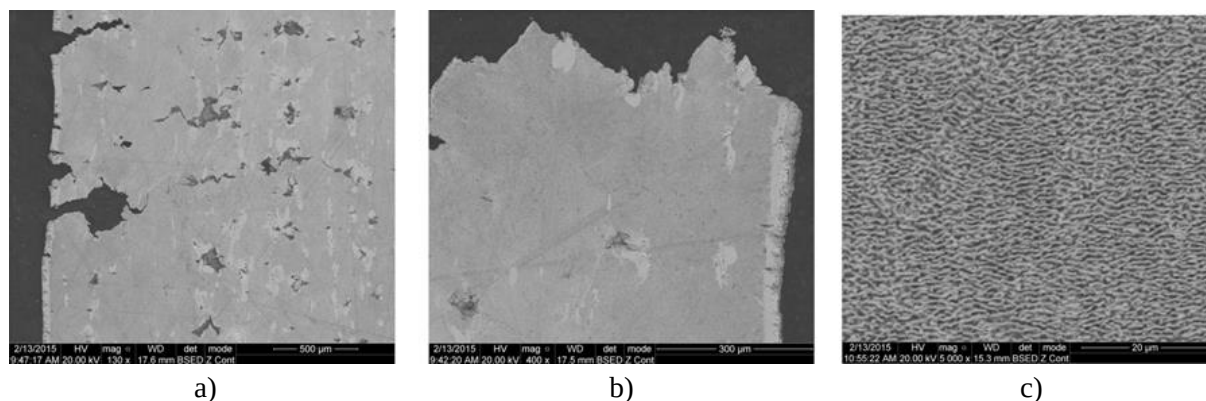


Figure 5. Microstructure of the sample after creep rupture tests at 1000 °C and $\sigma = 245$ MPa.

a) magnification 130x; б) magnification 400x; в) magnification 5000x

During the process of high-temperature creep the alloy undergoes the evolution of structural and phase state. On all samples which passed tests, it is observed so-called “raft-structure”, characteristic for heat resistant nickel alloys, which had been exposed to long-time stress at high temperatures. Initial cubic particles of γ' - phase (figure 3b) coagulate into alternating plates perpendicular to a loading axis (figure 5c). After tests at 1000°C in the samples of the alloy there was not revealed an existence of lamellar TCP phases, thus high phase stability is confirmed.

For the purposes of comparison of long-time high-temperature strength the Larson-Miller's criterion is widely applied, which considers the working temperature and time of loading action in the complex:

$$P(L.M.) = T \times [20 + \log(\tau)] / 10^3 \quad (2)$$

where T – temperature of test, Kelvin; τ – time before rupture, hours.

The results of creep-rupture tests for SLGS32BR alloy were processed using Larson-Miller parameter coordinates, which allow doing the reasonable forecasting of service life of the material depending on time of loading and temperature.

In the Table 3 there are presented the results of analytical calculation of creep strength of SLGS32BR alloy for various loadings at 1000°C, and also the experimental data, obtained at this temperature.

Computation results			Experimental results		
σ , MPa	τ , hours	$P(L.M.)$	σ , MPa	τ , hours	$P(L.M.)$
238	100	28.006	245	84	27.9
214	200	28.38	226	112	28.1
198	300	28.61	206	264	28.5
187	400	28.77			
180	500	28.9			

Table 3. Analytical and experimental values of creep strength of SLGS32BR alloy at 1000°C.

Averaged experimental creep-rupture strength values of SLGS32BR alloy in comparison with that of serial alloy GS32VI are presented in the Table 4. One can see that according to the level of long-time high-temperature strength SLGS32BR alloy is on the same level with GS32VI alloy.

Alloy	Creep-rupture strength at 1000°C , MPa		
	100 hours	200 hours	300 hours
SLGS32BR	238	214	198
GS32VI	240	216	200

Table 4. Comparison of SLGS32BR and GS32VI alloys.

The long time high temperature strength of SLGS32BR alloy, calculated by approximation of Larson-Miller curve, in comparison with 2nd generation alloys and up-to-date material CMSX-7, is presented at Figure 6. One can see that the experimental material SLGS32BR doesn't concede to neither modern alloy CMSX-7, nor 2nd generation single-crystal alloy GS32VI, which contains 4% of rhenium.

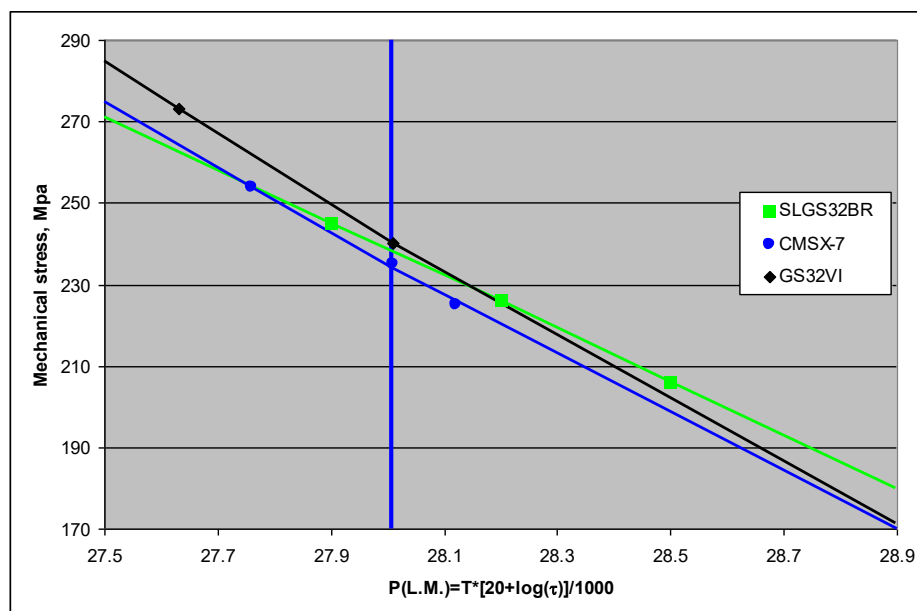


Figure 6. Comparing creep-rupture strength

The cost of SLGS32BR alloy is about 126 US \$/kg, while the price of furnace charge of GS32VI alloy, possessing the same level of working capacity, is 299 US \$/kg, i.e. is 2.4 times as higher. The given results show the potential of gaining considerable economic and technological effect, if wide

application of new alloy is implemented in practice. Main operation indicators and the cost of new and comparable alloys are presented in the Table 5.

Alloy	σ_{100}^{1000} , MPa	σ_{500}^{1000} , MPa	d, $\frac{g}{cm^3}$	Cost, US \$/kg
GS32	240	175	8.87	298.9
SLGS-1	255	191	9.01	67.2
CMSX-7	235	175	8.8	134.3
SLGS32BR	238	180	8.83	125.9

Table 5. High temperature rupture strength, density and cost of alloys

SUMMARY

New economically doped single-crystal alloy was developed, investigated and successfully experimentally tested. According to high temperature creep rupture strength it corresponds to 2nd generation serial alloy GS32VI, but differs from it more than twice by lower cost of furnace blend.

Researches of new alloy microstructure showed that it is close to optimum, thus practically there are no undesirable phases, the desirable morphology and the necessary size of the strengthening γ' -phase particles are provided. Well enough phase stability is provided when the material works in the conditions of high temperature under high mechanical loading.

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