DOI: https://doi.org/10.24425/amm.2025.153473

V.L. GRESHTA<sup>©1</sup>, O.A. GLOTKA<sup>©1\*</sup>, K.V. OBNOSOV<sup>©1</sup>, D.E. SOTNIKOV<sup>©1</sup>

## EFFECT OF ALLOYING ON THE PHASE COMPOSITION OF NICKEL-BASED SUPERALLOYS

Theoretical modeling of thermodynamic processes of phase separation was carried out, as well as a practical study of the structure and distribution of chemical elements. Based on an integrated approach for the single-crystal system Ni-Al-Re-Ru-Cr-Co-W-Ta, new regression models were obtained that make it possible to predict the chemical composition of phases based on the chemical composition of the alloy. A comparative assessment of the calculation results obtained using regression models and experimental data obtained by X-ray spectroscopy was carried out. The experimental results obtained are as close as possible to the calculated data.

Keywords: Single-crystal nickel-based superalloys; alloying elements; mismatch; heat resistance

#### 1. Introduction

In gas turbine engines and gas turbine engines, there are guide vanes that serve to create directed flows of working gases. The use of single-crystal nickel-based superalloys for the manufacture of high-pressure turbine blades has made it possible to increase their strength and service life [1-12]. Improvement of existing compositions leads to an increase in operating temperature by an average of 25 degrees every year. To stabilize the phase composition and reduce precipitation of TCP- phases, single-crystal alloys are alloyed with rhenium and ruthenium [11-23]. However, the irrational introduction of these elements will lead not only to an increase in the cost of the product, but also to the release of unfavorable phases.

The purpose of the work is to establish the relationship between the chemical and phase composition in the single-crystal system Ni-Al-Re-Ru-Cr-Co-W-Ta. Determine the dependence of heat resistance on the content of alloying elements in the alloy.

# 2. Material and research technique

Modeling of thermodynamic processes of phase formation was carried out for the Ni-Al-Re-Ru-Cr-Co-W-Ta system in which the  $\gamma'$ -forming elements were changed step by step, within the limits given in TABLE 1. In the multicomponent al-

loying system, the range of varying elements was selected based on considerations of the maximum and minimum amount of element introduced into the nickel-based superalloys. Changes in the phase composition during crystallization (cooling) in the structure of the alloys were carried out by thermodynamic modeling using the CALPHAD method.

TABLE 1 Range of variation in the content of  $\gamma'$ -forming elements in the Ni-Al-Re-Ru-Cr-Co-W-Ta system

Element content, wt.%						
Re	Ta	Ru	Al			
1-9	1-9	1-6	1-5			

Process modeling allows for computational prediction and comparative assessment of the influence of alloying elements on the composition of the  $\gamma$ - and  $\gamma'$ -phases, on their distribution and phase composition in the compositions under study.

The modeling of the alloy crystallization process was carried out from the temperature of the liquid state (1600°C) to room temperature (20°C) with a temperature step of 10°C over the entire range, which made it possible to determine the temperature sequence of phase separation during the crystallization process.

Predictive calculations were carried out based on the initial chemical composition of the alloy with the determination of the most probable phases, as well as their chemical composition after

<sup>\*</sup> Corresponding author: glotka-alexander@ukr.net



 $<sup>^{1}\ \</sup> ZAPORIZHZHIA\ POLYTECHNIC\ NATIONAL\ UNIVERSITY, ZAPORIZHZHIA,\ ST.\ ZHUKOVSKOGO,\ 64,\ 69063,\ UKRAINE$ 

modeling the crystallization process. The obtained dependencies have fairly high coefficients of determination  $R^2 \ge 0.9$  and can be used for predictive calculations.

The composition of the phases was determined experimentally using a REM-106I scanning electron microscope with an energy-dispersive X-ray microanalysis system. This method was used to study the morphology and chemical composition of the precipitated phases in the alloy structure. To test the theoretical dependencies, the industrial alloy VZhM-4 (TABLE 2) was selected, which belongs to the system under study.

Chemical composition of the VZhM-4 alloy

TABLE 2

Element content, wt.%							
Re	Cr	Co	Al	Ru	Ta	W	
6.0	2.5	6.0	6.0	4.0	4.5	4.0	

The alloy is thermally treated according to the following regime: homogenization 1285-1320°C, holding for 26 hours, two-stage aging 1130°C and 870°C for 32 hours holding. This treatment significantly reduces the amount of  $(\gamma + \gamma')$  eutectic and increases the amount of the strengthening phase.

The conversion of qualitative values into quantitative analysis was carried out automatically using the device program. The relative error of the method is  $\pm 0.1\%$  (wt.%).

## 3. Research results and discussion

In the Ni-Al-Re-Ru-Cr-Co-W-Ta system, depending on the content of alloying elements, the formation of many phases is possible, but the main phases for this system remain the following:  $\gamma$  – solid solution; eutectic  $\gamma + \gamma'$ ; type  $\gamma'$  intermetallic compound based on (Ni<sub>3</sub>Al). The main elements that form the strengthening  $\gamma'$ -phase are aluminum and tantalum; sometimes they can be replaced by rhenium and ruthenium, but basically these elements are in the  $\gamma$ -solid solution. In the future, we will consider the influence of the chemical composition of the system on the chemical composition of the  $\gamma$ - and  $\gamma'$ -phases, the amount of the g¢-phase and the influence of the phase property on the properties.

When aluminum is introduced up to 3% into the system under study, it leads to its dissolution in the  $\gamma$ -solid solution and does not lead to the formation of the  $\gamma'$ -phase. Only when the aluminum content in the alloy exceeds 3%, a strengthening phase is formed in an amount of 21% and increases directly proportionally to 60% at an aluminum content of 6%. The dissolution temperature of the  $\gamma'$ -phase also increases linearly from 863°C to 1235°C, respectively. Comparing changes in alloying elements in the phases, it can be argued that an increase in aluminum in the system leads to an increase in it in both phases (Fig. 1). Other elements practically do not change their content: cobalt – 9±1%; ruthenium – 6±1%; tungsten – 3±1%; rhenium – 5±1; chromium – 4±1%, except tantalum. The amount of Ta simultaneously decreases both in the solid solution and

in the strengthening phase, which may be associated with an increase in the amount of the  $\gamma'$ -phase.

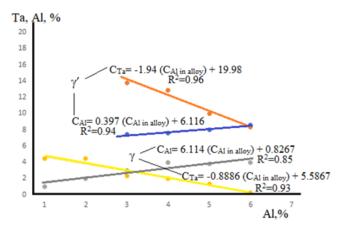
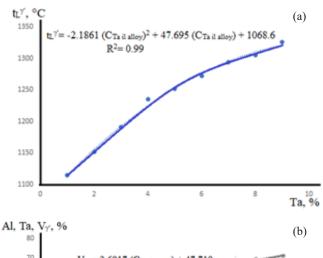


Fig. 1. Distribution of tantalum and aluminum between the  $\gamma$ - and  $\gamma'$ -phases when aluminum is introduced into the system

An increase in the amount of tantalum in the system leads to an increase in the dissolution temperature of the strengthening phase (Fig. 2(a)), which is associated with an increase in the strength of interatomic bonds. Also, the amount of  $\gamma'$ -phase increases with an increase in this element (Fig. 2(b)) and its predominance in the strengthening phase increases when it exceeds 5%. Thus, the  $\gamma'$ -phase basically increases the amount of tantalum. Other alloying elements practically do not change their presence both in the  $\gamma'$ -phase and in the  $\gamma$ -solid solution.



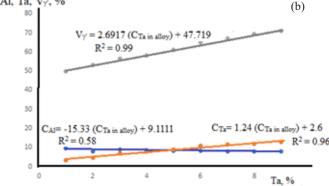


Fig. 2. Effect of tantalum on the dissolution temperature (a) and on the amount and chemical composition (b) of the  $\gamma'$ -phase

Rhenium and ruthenium have virtually no effect on the composition of other elements in the  $\gamma'$ -phase or  $\gamma$ -solid solution, but contribute to the release of TCP-phases. Thus, with an increase in the composition of the rhenium system, its amount in the  $\gamma'$ -phase increases from 0.14 to 0.91%, and the volume of the  $\gamma'$ -phase from 57 to 62% (Fig. 3).

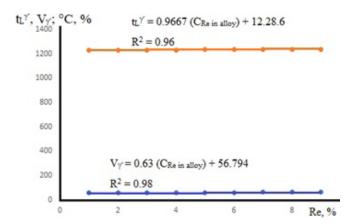
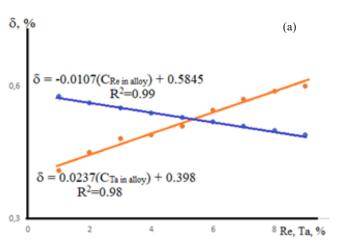


Fig. 3. Effect of rhenium on the amount and temperature of dissolution of the strengthening phase

Despite the increase in the dissolution temperature of the  $\gamma'$ -phase, TCP phases are formed in the system at 3% rhenium (HCP\_A3: 47.7 Ru, 40.9 Re, 5.0 Co, 2.58Mo) and at 6% rhenium (P phase: 55 Re, 4 Ru, 30 W, 5.8 Ni, 2.4 Co, 1.99 Cr) which significantly reduce the strength of the alloy. In this case, an increase in the amount of ruthenium in the system leads to an increase in the amount of  $\gamma'$ -phase by only 3% and practically does not affect the temperature of its dissolution, however, its amount increases from 0.59 to 3.5% in the  $\gamma'$ -phase and from 1.25 to 8.2% in the solid solution. The addition of ruthenium to the alloy does not lead to the formation of TCP phases.

The influence of rhenium and tantalum on the ratio of crystal lattice parameters of the  $\gamma'$ - and  $\gamma$ -phases (mismatch) at a temperature of 20°C is shown in Fig. 4(a). This behavior is explained by the fact that tantalum is present in the  $\gamma'$ -phase, which increases mismatch, and rhenium is present in a large amount in the solid solution, which reduces mismatch. Between 5 and 6% rhenium and tantalum in the alloy there is a mismatch equilibrium.

With an increase in the amount of rhenium and tantalum in the alloy, the heat resistance increases (Fig. 4(b)). However, with an increase in rhenium, TCP phases can form in the alloy,



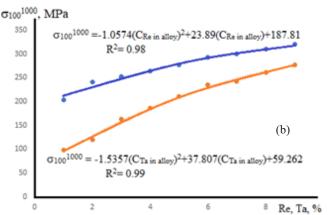


Fig. 4. Effect of rhenium and tantalum on mismatch (a) and heat resistance (b)

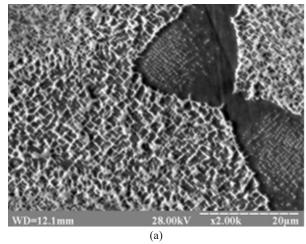
which increase the brittleness of the material and reduce the performance of parts. Thus, saturating an alloy with strengthening elements does not always lead to the desired effect.

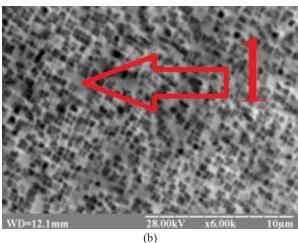
The dependences obtained above were tested on the industrial single-crystal superalloy VZhM-4. Using energy dispersive analysis on a scanning electron microscope REM-106I, microstructure studies were carried out (Fig. 5) and the chemical compositions of the phases were determined. It was established that the result obtained by the calculation method has good comparability with experimental data (TABLE 3).

TABLE 3 shows that the calculated and experimental data are in good agreement with each other for almost all elements. An increased content of tungsten, cobalt, rhenium and ruthenium in the solid solution and nickel, aluminum, tantalum in the  $\gamma'$ -phase are observed. Thus, the calculated data for determin-

TABLE 3 Chemical composition of  $\gamma'$ - and  $\gamma$ -phases calculated from the obtained dependencies and obtained experimentally by energy dispersive analysis at 20°C

Method for obtaining results		Element content, wt.%							
		Al	Ta	W	Co	Ru	Re	Cr	
Calculated composition of γ'-phase	70.09	8.69	7.76	4.85	2.78	2.6	0.5	0.9	
Calculated composition of γ-phase	63.12	3.25	0.7	3.12	10.36	7.45	7.16	4.56	
Experimental composition of the $\gamma'$ -phase (Fig. 5, point 1)	71.78	9.37	8.01	3.98	2.51	1.84	0.31	0.42	
Experimental composition of the γ-phase (Fig. 5, point 2)	60.25	2.47	0.53	3.53	11.46	8.44	8.59	4.7	





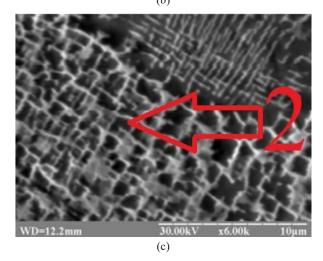


Fig. 5. Microstructure of the VZhM-4 alloy with designation of places for energy dispersive analysis

ing the type and chemical composition of phases showed good convergence and agreement with experimental data obtained by electron microscopy.

## 4. Conclusions

 Based on an integrated approach for the Ni-Al-Re-Ru-Cr-Co-W-Ta system, new regression models were obtained

- that make it possible to adequately predict the chemical composition of phases based on the chemical composition of the alloy. It is shown that the obtained dependences vary with the content of the element and closely correlate with the thermodynamic processes occurring in the system, accompanying changes in the composition of the phases.
- 2. It has been established that with increasing tantalum concentration, the amount of γ'-phase and the temperature of its complete dissolution increase. An increase in the rhenium content to 3% leads to the formation of the TCP phase (HCP\_A3), and at 6% rhenium (P phase), which significantly reduces the strength of the alloy. Between 5 and 6% rhenium and tantalum in the alloy there is a mismatch equilibrium.
- 3. A comparative assessment of the calculated results obtained from regression models and experimental data obtained by X-ray spectroscopy was carried out. Analysis of the results yielded good convergence, which makes it possible to recommend them for use in predicting structural components both in industrial alloys and in the development of new materials.

# REFERENCES

- [1] A.I. Balitskii, Y.H. Kvasnitska, L.M. Ivaskevich, H.P. Mialnitsa, Hydrogen and corrosion resistance of Ni-Co superalloys for gas turbine engines blades. Arch. Mater. Sci. Eng. 91, 1-5 (2018). DOI: https://doi.org/10.5604/01.3001.0012.1380
- [2] E.I. Galindo-nava, L.D. Connor, C.M.F. Rae, Prediction of the Yield Stress of Unimodal and Multimodal c Nickel-base Superalloys. Acta Mater. Mater. 98, 377-390 (2015). DOI: https://doi.org/10.1016/j.actamat.2015.07.048
- [3] A.I. Balyts'kyi, Y.H. Kvasnyts'ka, L.M. Ivas'kevich, H.P. Myal'nitsa, Corrosion- and Hydrogen-Resistance of Heat-Resistant Blade Nickel-Cobalt Alloys. Mater. Sci. 54, 230 (2018). DOI: https://doi.org/10.1007/s11003-018-0178-z
- [4] D.P. Moyye, S.S. Satheesh Kumar, D. Nagarajan, et al., Microstructural Evolution and Mechanical Behavior during Isothermal Multiaxial Forging of Nickel-Based Superalloy SUPERNI 718. J. of Materi Eng and Perform (2024). DOI:https://doi.org/10.1007/s11665-024-09249-1
- [5] H. Zhang, K. Zhang, S. Jiang, H. Zhou, C. Zhao, X. Yang, Dynamic Recrystallization Behavior of a γ'-hardened Nickel-based Superalloy during Hot Deformation. J. Alloys Compd. 623, 374-385 (2015). DOI: https://doi.org/10.1016/j.jallcom.2014.11.056
- [6] H. Wang, J. Zhang, H. Shang, A. Sha, Y. Cheng, H. Duan, Experiment and Modelling of the Pre-Strain Effect on the Creep Behaviour of P/M Ni-Based Superalloy FGH96. Materials 16, 3874 (2023). DOI: https://doi.org/10.3390/ma16103874
- [7] S. Bond, J. Martin, Surface Recrystallization in a Single Crystal Nickel-Based Superalloy. J. Mater. Sci. 19, 3867-3872 (1984).
   DOI: https://doi.org/10.1007/BF00980749
- [8] C. Zambaldi, F. Roters, D. Raabe et al., Modeling and Experiments on the Indentation Deformation and Recrystallization of a

- Single-Crystal Nickel- Base Superalloy. Mater. Sci. Eng. A **454**, 433-440 (2007). DOI: https://doi.org/10.1016/j.msea.2006.11.068
- [9] A.A. Glotka, V.Y. Ol'shanetskii, Mathematical Prediction of the Properties of Heat-Resistant Nickel Alloys After Directional Crystallization. Materials Science 58 (5), 679-685 (2023). DOI: https://doi.org/10.1007/s11003-023-00716-z
- [10] X. Dong, Z. Tang, G. Zhang, et al., Research on Finite Element Simulation and Recrystallization of Laser Shock Peened Nickel-Based Single-Crystal Superalloy. J. of Mater. Eng. and Perform. (2023). DOI: https://doi.org/10.1007/s11665-023-08823-3
- [11] V. Mishchenko, A. Kripak, D. Tonkonoh, Developing the optimal chemical composition of heat-resistant Cr-Ni steel for aerospace equipment. Eastern-European Journal of Enterprise Technologies 6 (126), 16-21 (2023). DOI: https://doi.org/10.15587/1729-4061.2023.288224
- [12] T. Steiner, M. Akhlaghi, S.R. Meka, E.J. Mittemeijer, Diffractionline shifts and broadenings in continuously and discontinuously coarsening precipitate-matrix systems: coarsening of initially coherent nitride precipitates in a ferrite matrix. Journal of Materials
  - DOI: https://doi.org/10.1007/s10853-015-9262-z

Science 50 (21), 7075-7086, 16 (2015).

- [13] M. Akhlaghi, T. Steiner, S.R. Meka, A. Leineweber, E.J. Mittemeijer, Lattice-parameter change induced by accommodation of precipitate/matrix misfit; misfitting nitrides in ferrite. Acta Materialia 98, 254-262 (2915).
  - DOI: https://doi.org/10.1016/j.actamat.2015.07.017
- [14] L. Zhang, L. Zhao, R. Jiang, C. Bullough, Crystal plasticity finiteelement modelling of cyclic deformation and crack initiation in a nickel-based single-crystal superalloy under low-cycle fatigue. Fatigue Fract. Eng. Mater. Struct. 43, 1769-1783 (2020). DOI: https://doi.org/10.1111/ffe.13228
- [15] A. Glotka, V. Ol'shanetskii, Prediction thermo-physical characteristics heat-resistant nickel alloys directional crystallization. Acta Metallurgica Slovaca 27 (2), 68-71 (2021).
  DOI: https://doi.org/10.36547/ams.27.2.813
- [16] Y.S. Jeong, K.M. Kim, H. Lee, S.M. Seo, E.J. Chun, Effect of Single Crystal Growth and Solidification Grain Boundaries on

- Weld Solidification Cracking Behavior of CMSX-4 Superalloy. Korean J. Met. Mater. **59**, 445 (2021). DOI: https://doi.org/10.3365/KJMM.2024.62.1.22
- [17] S.S. Babu, S.A. David, J.W. Park, J.M. Vitek, Joining of nickel base superalloy single crystals. Sci. Technol. Weld. Joining 9 (1), 1-12. (2004).
  - DOI: https://doi.org/10.1179/136217104225017080
- [18] M. Ramsperger, R.F. Singer, C. Körner, Microstructure of the nickel-base superalloy CMSX-4 fabricated by selective electron beam melting. Metallurgical and Materials Transactions A 47 (3), 1469-1480 (2016).
  - DOI: https://doi.org/10.1007/s11661-015-3300-y
- [19] O.A. Glotka, Distribution of Alloying Elements in Carbides of Refractory Nickel Alloys under the Conditions of Equiaxial Crystallization. Materials Science 56 (5), 714-721 (2021). DOI: https://doi.org/10.1007/s11003-021-00487-5
- [20] D. Bürger, A.B. Parsa, M. Ramsperger, C. Körner, G. Eggeler, Creep properties of single crystal Ni-base superalloys (SX): a comparison between conventionally cast and additive manufactured CMSX-4 materials. Materials Science and Engineering: A 762, 138098 (2019).
  - DOI: https://doi.org/10.1016/j.msea.2019.138098
- [21] V.G. Mishchenko, S.P. Sheyko, Structural changes of multiphase low-carbon steel in deformation and heat treatment. Steel in Translation 44 (12), 928-930 (2014).
  DOI: https://doi.org/10.3103/S0967091214120122
- [22] O.I. Balitskii, Y.H. Kvasnytska, L.M. Ivaskevych, H.P. Mialnitsa, K.H. Kvasnytska, Fatigue Fracture of the Blades of Gas-Turbine Engines Made of a New Refractory Nickel Alloy. Materials Science 57 (4), 475-483 (2022). DOI: https://doi.org/10.1007/s11003-022-00568-z
- [23] A.I. Balitskii, Y.H. Kvasnytska, L.M. Ivaskevych, K.H. Kvasnytska, O.A. Balitskii, I.A. Shalevska, O.Y. Shynskii, J.M. Jaworski, J.M. Dowejko, Hydrogen and Corrosion Resistance of Nickel Superalloys for Gas Turbines. Engines Cooled Blades Energies 16 (3), 1154 (2023).
  - DOI: https://doi.org/10.3390/en16031154