*Vadim Ol'shanetskii, Alexander Glotka**

OPTIMISATION OF THE COMPOSITION AND MORPHOLOGY OF CARBIDES IN SINGLE-CRYSTAL NICKEL-BASED SUPERALLOYS

OPTIMIZACIJA SASTAVA I MORFOLOGIJA KARBIDA KOD MONOKRISTALA SUPERLEGURE NA BAZI NIKLA

Originalni naučni rad / Original scientific paper
UDK /UDC:
Rad primljen / Paper received: 31.01.2022

Adresa autora / Author's address:
Zaporizhzhia Polytechnic National University,
Zaporizhzhia, Ukraine *email: Glotka-alexander@ukr.net

Keywords
- nickel-based superalloy
- morphology
- composition of carbides
- precipitation (dissolution) temperatures of carbides

Ključne reči
- superlegura na bazi nikla
- morfologija
- sastav karbida
- temperature taloženja (rastvaranja) karbida

Abstract

In this work, modelling of thermodynamic processes of excess phase separation is carried out using the CALPHAD method as well as the study of the morphology and distribution of chemical elements in carbides depending on the alloying on a scanning electron microscope REM-106I. It has been established that in carbides of the Ni-11.5Cr-5Co-3.6Al-4.5Ti-7W-0.8Mo-0.06C system, there is a tendency to recrystallize depending on the level of alloying elements. Mathematical dependences are established of the alloying influence on the temperature of precipitation (dissolution) of carbides, and the influence of change in alloy chemical composition on the composition of carbides. The obtained dependences are confirmed experimentally using X-ray spectroscopy on nickel-based superalloys. It is recommended to use the obtained mathematical models not only in the design of new nickel-based superalloys but also in the improvement of known compositions within the stated concentrations.

Izvod

U ovom radu izvedeno je modeliranje termodinamičkih procesa taloženja viška sadržaja faze korišćenjem postupka CALPHAD, kao i proučavanje morfologije i raspodele hemijskih elemenata u karbidima, u zavisnosti od stepena legiranja primenom skenirajućeg elektronskog mikroskopa REM-1061. Utvrđeno je da u karbidima sistema Ni-11.5Cr-5Co-3.6Al-4.5Ti-7W-0.8Mo-0.06C postoji tendencija rekristalizacije u zavisnosti od nivoa legirajućih elemenata. Određene su matematičke zavisnosti uticaja legirajućih elemenata na temperaturu taloženja (rastvaranja) karbida, kao i uticaj promene u hemijskom sastavu legure na sastav karbida. Ove zavisnosti su eksperimentalno potvrđene korišćenjem rendgenske spektroskopije superlegura na bazi nikla. Preporučuje se primena dobijenih matematičkih modela ne samo u projektovanju novih superlegura na bazi nikla, već i za poboljšanje poznatih sastava unutar spomenutih koncentracija.

INTRODUCTION

With the improvement of the alloying system of nickel-based superalloys, their microstructure becomes more complicated and the phase composition changes. The convenience of the presence of carbides in the structure of nickel-based superalloys (NBS) has been discussed for decades, but an attempt to replace carbides with other compounds leads to a decrease in the performance of the alloys due to a decrease in the thermodynamic stability of the phases. The elimination of carbides became possible only in single-crystal carbon-free alloys which gave an increase in heat resistance due to the elimination of the boundaries of the phase distribution. Recently however, single-crystal alloys alloyed with carbon have become widespread, where the mechanical properties are at the level of carbon-free compositions. Therefore, the influence of MC carbides, especially within the temperature range of $0.8T_L$, has a high value when strengthening the material, /1-8/.

At present, a fairly large number of works have been published on the theory of alloying of multicomponent nickel systems, /9–17/, but the issues of the effect of individual alloying elements on the temperatures of precipitation or dissolution, as well as the topology, morphology, and chemical composition of different types of carbides in such systems, are insufficiently covered. The conditions for the separation of these phases during crystallization, the specifics of their formation, morphology, and quantity, as well as the dependence of their composition on the composition of the alloy, have not been adequately studied. To a greater extent, attention is paid to carbide phases in steels for which these phases are strengthening, however, for NBS, carbides are also fundamental in increasing the heat resistance, /17-24/.

The purpose of this work is to determine the possibility of optimising the composition and shape of MC carbides in nickel-based superalloys by changing the chemical composition of the alloy which will increase the service characteristics of industrial alloys.

METHODS OF RESEARCH

Modelling the processes of precipitation of MC carbides using the CALPHAD method makes it possible to carry out the computational prediction and a comparative assessment of the effect of alloying elements in carbides. Calculations were carried out for each studied composition individually with a step-by-step change of a specific alloying element into a fixed composition of a multi-component system.

In the multicomponent alloying system (Ni-11.5Cr-5Co-3.6Al-4.5Ti-7W-0.8Mo-0.06C) the range of element variation was chosen from considerations of the maximum and minimum amount of the element introduced into the NBS. Thus, carbide-forming elements were chosen for the study in the following alloying ranges: carbon 0.02-0.2 %; hafnium 0.1-2.5 %; titanium 1-6 %; tantalum 0.5-12 % by weight.

The modelling 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 crystallization.

Calculations were carried out on the initial chemical composition of the alloy with the determination of the most probable precipitation of the amount and type of carbides in the structure, as well as their chemical composition after modelling the crystallization process.

The experimental alloy was obtained on a high-gradient UVNK-8P single-crystal unit in special ceramic blocks, starting with crystals pre-installed inside, according to serial technology. The required cooling rate was provided by immersing the cast molds into a liquid metal mold (aluminium melt) at a rate of 10 mm/min. To obtain a given crystallographic orientation, starting crystals were used (seeds from an alloy of the Ni-W binary system) which deviated from the main crystallographic direction [001] by an angle of no more than $\alpha \leq 5°$. The growth of a single crystal in the sample was ensured by melting the outer surface of the seed with the metal that was poured. Before pouring, the melt was held in a crucible at a metal superheating temperature of 1620 °C for 8 to 10 minutes. Filling of samples was carried out at the following parameters: pouring temperature 1580 °C; lower heater temperature 1610 °C; temperature of upper heater 1580 °C. An alloy of the following composition Ni-11.5Cr-5Co-3.6Al-4.5Ti-7W-0.8Mo-0.06C was taken as a basis in which the value of tantalum was changed from 0 to 5 %.

The composition of carbides was experimentally determined using a REM-106I scanning electron microscope with an energy-dispersive X-ray spectral microanalysis system. This method was used to study morphology and chemical composition of precipitated carbides in the alloy structure. The conversion of qualitative values into quantitative analysis was carried out automatically according to the programme of the instrument. The relative error of the method is ±0.1 % (mass). The results of calculations of the type of carbides and their chemical composition were compared with experimental data obtained using electron microscopy.

RESULTS AND DISCUSSION

One of the disadvantages of MC-type carbides is their high brittleness, and as a result the formation of cracks on them. Also, there is no way to influence their shape and size with the help of heat treatment, since their dissolution temperatures are close to the solidus and liquidus temperatures of the alloys. Therefore, the main method of influencing the composition, shape, and size of MC carbides is to change the composition of high-temperature nickel alloys. The main elements that are included in their composition are titanium, tantalum, hafnium, and niobium, in connection with this, in the future a study of the distribution of these elements is carried out.

It has been established that the dependences of the dissolution (precipitation) of MC carbides and the amount of MC carbides on the carbon content are complex and are optimally described by the dependencies (Table 1), which are shown in Fig. 1.

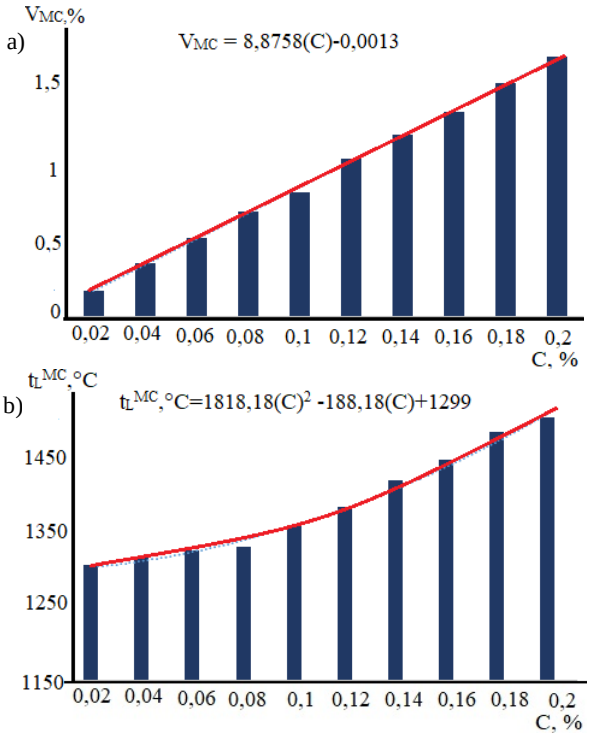

Figure 1. Temperature dependences of dissolution (precipitation) of carbides: a) on the amount of carbides MC; b) on the carbon content in the alloy.

Table 1. Dependences of the content of alloying elements in MC carbides on the content of alloying elements in the alloy.

Alloy. elem.	Content of elements in carbide (C), wt.%
Ta	$C_{Ta} = -0.7427(C_{Ta} \text{ in alloy})^2 + 15.668(C_{Ta} \text{ in alloy}) + 0.189$; $C_{Ti} = 57.135e^{-0.182(CTa \text{ in alloy})}$; $C_W = 32.103e^{-0.35(CTa \text{ in alloy})}$.
Ti	$C_{Ta} = 1.3478(C_{Ti} \text{ in alloy})^2 - 14.527(C_{Ti} \text{ in alloy}) + 89.293$; $C_{Ti} = -0.6788(C_{Ti} \text{ in alloy})^2 + 8.8497(C_{Ti} \text{ in alloy}) + 2.6473$; $C_W = -0.4277(C_{Ti} \text{ in alloy})^2 + 3.4424(C_{Ti} \text{ in alloy}) + 1.7964$
Hf	$C_{Hf} = 24.526 \ln(C_{Hf} \text{ in alloy}) + 68.343$; $C_{Ta} = -14.96 \ln(C_{Hf} \text{ in alloy}) + 19.696$; $C_{Ti} = 1.8744 (C_{Hf} \text{ in alloy})^{-1.111}$

The dependence of the carbide liquidus temperature (Fig. 2a) shows an extremum at 5 % Ti in the alloy, this is due to the precipitation of the σ-phase in the alloy, which reduces the operational properties. An increase in the titanium content in the alloy leads to an increase in its concentration in the MC carbide to 31 % (Fig. 2b) (Table 1). At the same time, the content of tantalum in the carbide is reduced to the level of 50 %. Ti-carbide precipitates in interdendritic spaces and have a font ‘Chinese characters’ shape which adversely affects the properties of the alloy, so it is necessary to limit alloying and prevent their precipitation.

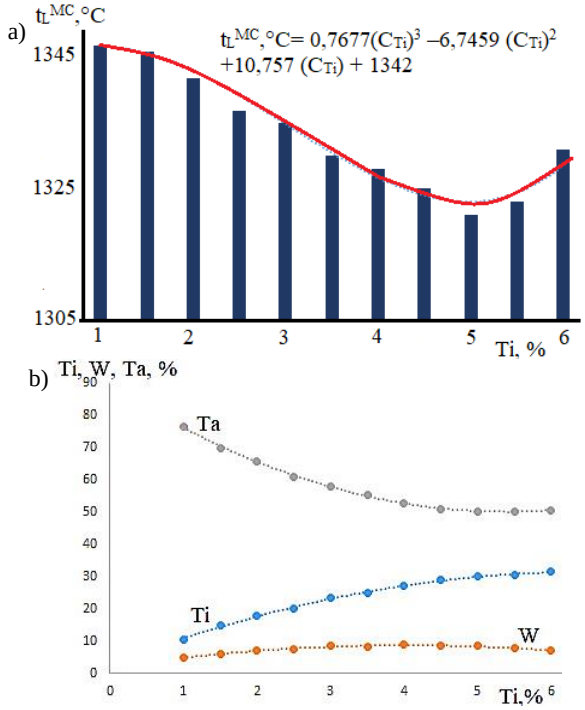

Figure 2. Temperature dependence of the dissolution of carbides of the MC type (a); the amount of tantalum, titanium, and tungsten in the MC carbide (b) versus the titanium content in the alloy.

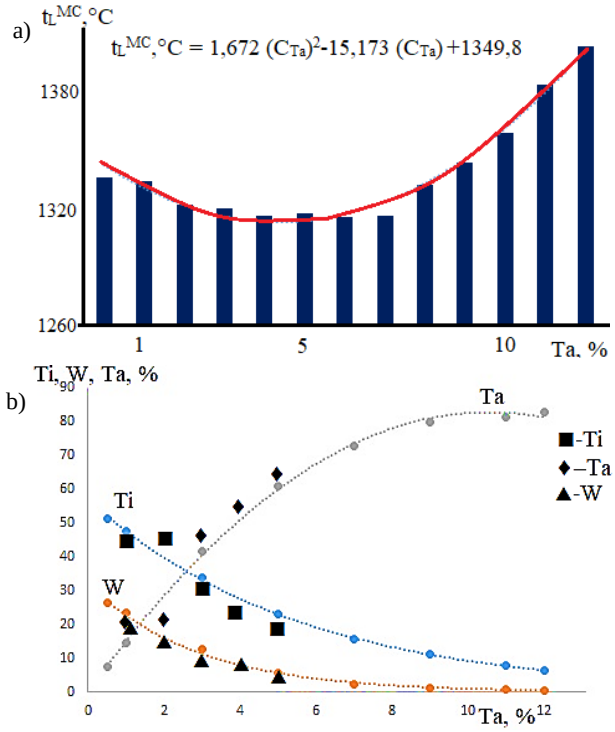

Figure 3. Temperature dependence of the dissolution of MC type carbides (a) and the amount of tantalum, titanium, and tungsten in MC carbide (b) on the tantalum content in the alloy (■, ▲, ♦ points obtained experimentally, Table 2).

An increase in the content of tantalum in the alloy leads to the appearance of an extremum of carbide liquidus temperatures at a content of 7% Ta in the alloy, which is associated with the formation of the σ-phase in the alloy (Fig. 3a). When tantalum is introduced into the alloy, a change in the base of MC carbides to tantalum is observed (Fig. 3b). The transition of MC carbide to tantalum-based carbide leads to an increase in interatomic bonds, which contributes to an increase in the dissolution (precipitation) temperature of the carbide (Fig. 3a). The introduction of tantalum changes the MC carbide morphology to a faceted irregular shape, which is caused by an increase in the carbide dissolution temperature. A decrease in the content of titanium and tungsten is also observed.

It has been established that hafnium reduces the temperature of dissolution (precipitation) of primary carbides (Fig. 4a), which is described by a linear dependence (Table 1).

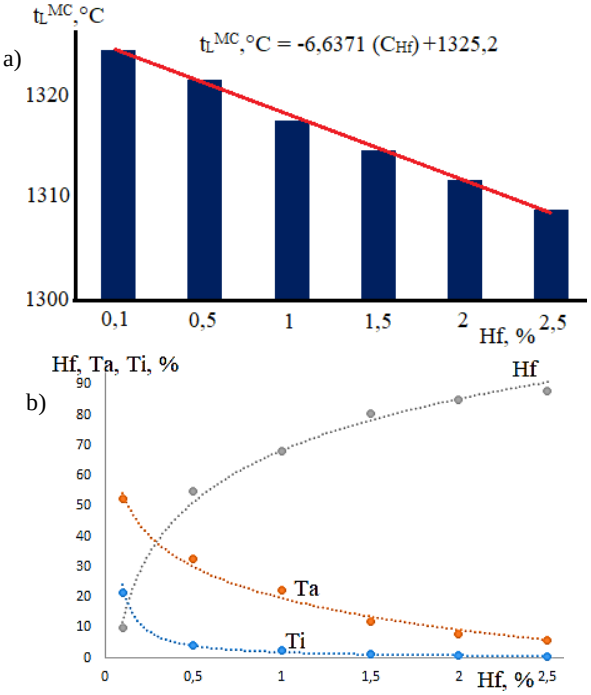

Figure 4. Temperature dependence of the dissolution of MC carbides (a); and the amount of tantalum, titanium, and hafnium in MC carbide (b), on the content of hafnium in alloy composition.

When the content of hafnium is more than 0.1 %, the carbide morphology changes. The titanium-based carbide is converted to hafnium-based carbide in which the hafnium content reaches 54.8 % and its concentration increases to 87 % at 2.5 % Hf. Accordingly, titanium and tantalum reduce the concentration in the primary carbide from 21 to 0.5 % and from 52 to 5.7 %, respectively. Hafnium has a positive effect on the morphology of MC carbides which simultaneously increases the strength and ductility of the alloy.

The carbides take on a spherical shape due to the segregation of hafnium along the distribution boundary between the carbide and the matrix, as well as the formation of an interlayer of the γ'-phase around the carbides.

Results of calculating the phase composition obtained according to the dependencies in Table 2 were further compared with experimental data obtained using electron microscopy in the microprobe mode on a scanning electron microscope, REM-106I.

Figure 5 shows a typical carbide morphology depending on the amount of tantalum in the alloy. It was found that carbides precipitate with different morphology typical for

primary precipitates in the form of rough cubic (block) and hieroglyphs (scripts). The size of primary carbides is practically independent of the amount of tantalum in the alloy (Fig. 5).

The chemical composition of carbides was determined experimentally by X-ray spectral microanalysis with which the intensity of X-ray radiation was recorded depending on the energy (keV). It has been experimentally established that titanium, tantalum, tungsten, molybdenum, cobalt, and chromium are included in the composition of carbides in the following ratios with calculated values (Table 2). The error in the determination of elements by this method did not exceed ±1 % by weight.

Table 2 shows that calculated and experimental data are in good agreement with each other for almost all elements. It has been established that at a content of 4 % Ta in the alloy, a change in the base of the carbide from titanium to tantalum is observed (the concentration of tantalum in the carbide exceeds 50 %). There is a decrease in the amount of tungsten in carbide (less than 10 %) and an increase in chromium and molybdenum (up to 1 %) which is explained as the interchangeability of these elements in crystal lattices. Increasing tantalum to 5 % in the alloy increases its concentration in the carbide to over 60 % and reduces titanium below 20 %. Such a distribution of elements in carbides can be associated with material properties, in particular, in the work /25/ it is indicated that the alloy receives optimal properties with the introduction of 4 % Ta. This is explained not only by a change in the composition of the carbide but also by the occurrence of other structural transformations in the alloy.

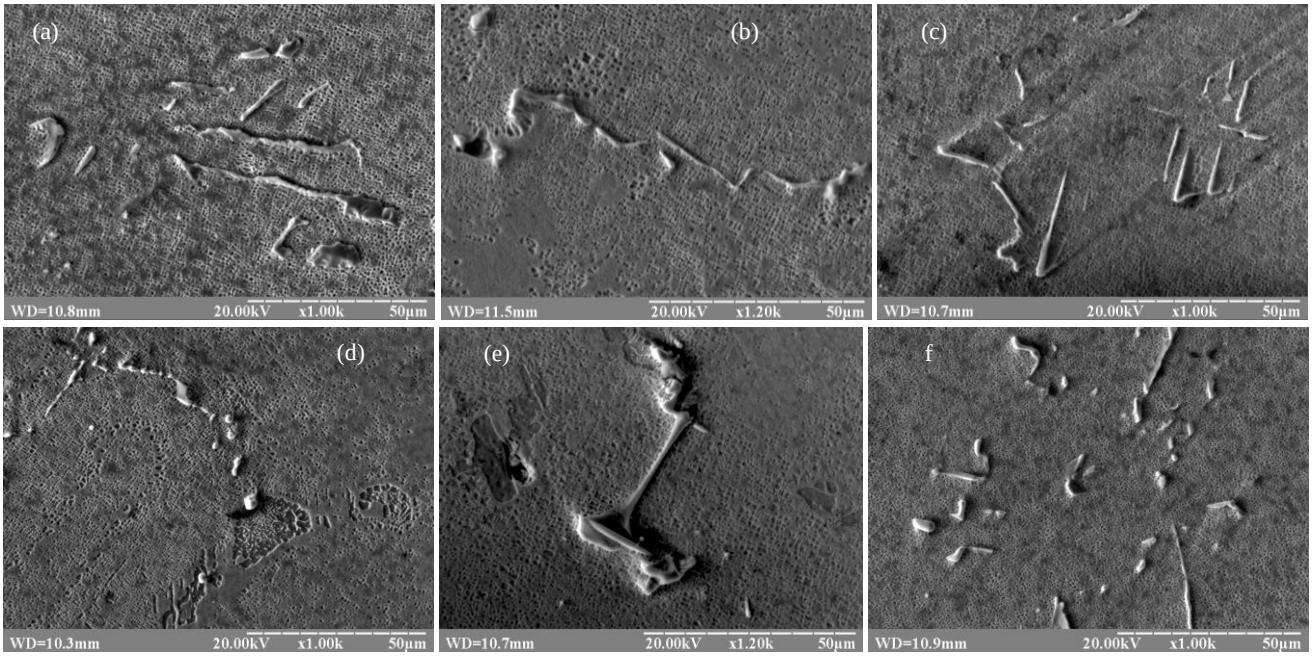

Figure 5. Morphology of carbides in the alloy structure of the system Ni-11.5Cr-5Co-3.6Al-4.5Ti-7W-0.8Mo-0.06C: a) 0 % Ta; b) 1 % Ta; c) 2 % Ta; d) 3 % Ta; e) 4 % Ta; f) 5 % Ta.

Table 2. Changes in compositions of primary carbides depending on Ta content in the system Ni-11.5Cr-5Co-3.6Al-4.5Ti-7W-0.8Mo-0.06C.

Method of obtaining results	% Ta	Element content, % weight						
		Ti	Ta	Cr	Co	Mo	W	C
Calculated	0 % Ta	55.66	-	0.6	-	0.14	28.69	14.92
Experimental		57.7	-	0.28	0.3	3.5	23.3	14.92
Calculated	1 % Ta	48.85	13.49	0.54	-	0.12	23.16	13.83
Experimental		45.01	21.46	0.23	0.25	0.95	18.3	13.8
Calculated	2 % Ta	42.02	27.09	0.45	-	0.13	17.63	12.68
Experimental		46.59	21.42	0.27	0.15	0.75	17.2	13.62
Calculated	3 % Ta	35.8	39.14	0.36	-	0.1	12.89	11.68
Experimental		33.91	45.05	0.34	0.16	0.6	8.26	11.68
Calculated	4 % Ta	28.6	51.5	0.27	-	0.08	8.99	10.53
Experimental		23.61	54.28	1.15	0.36	1.08	8.99	10.53
Calculated	5 % Ta	23.83	60.22	0.2	-	0.07	5.84	9.75
Experimental		19.01	63.68	1.05	0.25	0.4	5.86	9.75

Thus, the obtained mathematical dependences make it possible to determine the chemical composition of MC carbides, which makes it possible to determine the possibility of the formation of various types of carbides and thereby predict the properties of heat-resistant nickel alloys.

CONCLUSIONS

Based on an integrated approach for the multicomponent system Ni-11.5Cr-5Co-3.6Al-4.5Ti-7W-4Ta-0.8Mo-0.06C, mathematical models are obtained that allow determining the chemical composition of carbides by chemical composition of the alloy and thereby predicting alloy properties.

The dependences of the influence of alloying elements on dissolution (precipitation) temperatures of carbides have been established. It is shown that temperature dependences correlate with thermodynamic processes occurring in the system, that is, the curves show extremums accompanying a change in the stoichiometry of carbides or the precipitation of new phases.

It has been established that with an increase in the concentration of titanium over 5 % and tantalum over 7 %, a σ-phase is formed in the alloy which reduces the mechanical properties. The hafnium content of more than 0.1 % leads to a change in the base of the carbide from titanium to hafnium which reduces the temperature of formation (dissolution) of the carbide.

Satisfactory results of a comparative evaluation of the calculated and experimental data are shown. It is recommended to use the obtained mathematical dependences in the production of nickel-based superalloys.

The optimal content of tantalum in the system has been established, which should be from 4 to 7 %. Entering Ta in an amount of less than 4 % is impractical because the basis of carbides does not change (remains based on Ti), and more than 7 % due to the formation of the σ-phase and a decrease in the properties of the alloy.

REFERENCES

1. Horst, O.M., Schmitz, D., Schreuer, J. et al. (2021), *Thermo-elastic properties and γ'-solvus temperatures of single-crystal Ni-base superalloys*, J Mater. Sci. 56: 7637-7658. doi: 10.1007/s10853-020-05628-w
2. Chen, B., Wu, W.P., Chen, M.X. (2021), *Orientation-dependent morphology and evolution of interfacial dislocation networks in Ni-based single-crystal superalloys: A molecular dynamics simulation*, Acta Mech. Solida Sin. 34: 79-90. doi: 10.1007/s10338-020-00172-1
3. Saleh, A.A. (2021), *Investigating the microstructure and mechanical properties of brazed joint of Inconel 738 LC alloys bonded by 5Ni5Ti90Al filler alloy*, Struct. Integ. Life, 19(1): 13-17.
4. Song, W., Wang, X.G., Li, J.G., et al. (2020), *Role of Ru on the microstructural evolution during long-term aging of Ni-based single crystal superalloys*, Acta Metall. Sin. (Engl. Lett.) 33: 1689-1698. doi: 10.1007/s40195-020-01110-3
5. Borouni, A., Kermanpur, A. (2020), *Effect of Ta/W ratio on microstructural features and segregation patterns of the single crystal PWA1483 Ni-based superalloy*, J Mater. Eng. Perform. 29: 7567-7586. doi: 10.1007/s11665-020-05189-8
6. Kvasnytska, Y.H., Ivaskevych, L.M., Balytskyi, O.I. (2020), *High-temperature salt corrosion of a heat-resistant nickel alloy*, Mater. Sci. 56: 432-440. doi: 10.1007/s11003-020-00447-5
7. Yang, S., Yun, J., Seok, C.S. (2020), *Rejuvenation of IN738LC gas-turbine blades using hot isostatic pressing and a series of heat treatments*, J Mech. Sci. Technol. 34: 4605-4611. doi: 10.1007/s12206-020-1018-2
8. Jeremić, L., Đorđević, B., Sedmak, S., et al. (2018), *Effect of plasma hardfacing and carbides presence on the occurrence of cracks and microcracks*, Struct. Integ. Life, 18(2): 99-103.
9. Pandey, A., Hemker, K.J. (2015), *Temperature dependence of the anisotropy and creep in a single-crystal nickel superalloy*, JOM, 67: 1617-1623. doi: 10.1007/s11837-015-1414-8
10. Chai, L., Huang, J., Hou, J. (2015), *Effect of holding time on microstructure and properties of transient liquid-phase-bonded joints of a single crystal alloy*, J Mater. Eng. Perform. 24: 2287-2293. doi: 10.1007/s11665-015-1504-3
11. Glotka, A., Ol'shanetskii, V. (2021), *Prediction thermo-physical characteristics heat-resistant nickel alloys directional crystallization*, Acta Metall. Slovaca, 27(2): 68-71. doi: 10.36547/ams.27.2.813
12. Petronić, S., Burzić, M., Milovanović, D., et al. (2015), *Surface modification of laser welded Nimonic 263 sheets*, Struct. Integ. Life, 15(3): 153-156.
13. Oh, S.A., Lim, R.E., Aroh, J.W., et al. (2021), *Microscale observation via high-speed X-ray diffraction of alloy 718 during in situ laser melting*, JOM, 73: 212-222. doi: 10.1007/s11837-020-04481-1
14. Balitskii, A.I., Kvasnitska, Y.H., Ivaskevich, L.M., Mialnitsa, H.P. (2018), *Hydrogen and corrosion resistance of Ni-Co superalloys for gas turbine engines blades*, Arch. Mater. Sci. Eng. 91(1): 5-14. doi: 10.5604/01.3001.0012.1380
15. Kong, Y.H., Chen, Q.Z., Knowles, D.M. (2004), *Effects of minor additions on microstructure and creep performance of RR2086 SX superalloys*, J Mater. Sci. 39: 6993-7001. doi: 10.1023/B:JMSC.0000047543.64750.83
16. Tin, S., Pollock, T.M., Murphy, W. (2001), *Stabilization of thermosolutal convective instabilities in Ni-based single-crystal superalloys: Carbon additions and freckle formation*, Metall. Mater. Trans. A, 32: 1743-1753. doi: 10.1007/s11661-001-0151-5
17. Petrushin, N.V., Visik, E.M., Gorbovets, M.A., Nazarkin, R.M. (2016), *Structure-phase characteristics and the mechanical properties of single-crystal nickel-based rhenium-containing superalloys with carbide-intermetallic hardening*, Russ. Metall. 4: 630-641. doi: 10.1134/S0036029516070119
18. Petronić, S. (2014), *Transparent layer influence on microstructural changes of nimonic 263 in laser shock peening processing*, Struct. Integ. Life, 14(3): 155-160.
19. Pigrova, G.D., Rybnikov, A.I. (2013), *Carbide phases in a multicomponent superalloy Ni-Co-W-Cr-Ta-Re*, Phys. Metals Metallogr. 114: 593-595. doi: 10.1134/S0031918X13070089
20. Glotka, A.A., Gaiduk, S.V. (2020), *Distribution of alloying elements in the structure of heat-resistant nickel alloys in secondary carbides*, J Appl. Spectrosc. 87: 812-819. doi: 10.1007/s10812-020-01075-2
21. Saunders, N., Guo, U.K.Z., Li, X., et al. (2003), *Using JMatPro to model materials properties and behavior*, JOM, 55: 60-65. doi: 10.1007/s11837-003-0013-2
22. Tin, S., Pollock, T.M. (2003), *Stabilization of thermosolutal convective instabilities in Ni-based single-crystal superalloys: Carbide precipitation and Rayleigh numbers*, Metall. Mater. Trans. A, 34: 1953-1967. doi: 10.1007/s11661-003-0160-7
23. Buchanan, K.G., Kral, M.V., Bishop, C.M. (2014), *Crystallography and morphology of MC carbides in niobium-titanium modified as-cast HP alloys*, Metall. Mater. Trans. A, 45: 3373-3385. doi: 10.1007/s11661-014-2285-2
24. Balitskii, A. (2019), *Hydrogen assisted crack initiation and propagation in nickel-cobalt heat resistant superalloys*, Procedia Struct. Integ. 16: 134-140. doi: 10.1016/j.prostr.2019.07.032
25. Glotka, O.A. (2020), *Modelling the composition of carbides in nickel-based superalloys of directional crystallization*, J Achiev. Mater. Manuf. Eng. 102(1): 5-15. doi: 10.5604/01.3001.0014.6324