ISSN 0036-0295, Russian Metallurgy (Metally), Vol. 2015, No. 13, pp. 1041–1045. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © A.V. Logunov, Yu.N. Shmotin, D.V. Danilov, 2014, published in Tekhnologiya Metallov, 2014, No. 5, pp. 3–9.

PROCESSES OF MANUFACTURE OF FERROUS AND NONFERROUS METALS

Methodological Fundamentals of Computer-Assisted Designing of Nickel-Based Superalloys

A. V. Logunov, Yu. N. Shmotin, and D. V. Danilov
OAO NPO Saturn, Russia
e-mail: vladimir.pavlov@npo-saturn.ru
Received November 26, 2013

Abstract—More than 180 Russian and foreign nickel superalloys are analyzed to develop regression models to find a relation between chemical composition and a number of the most important thermodynamic, structural, and strength parameters, which directly influence the high-temperature strength of the alloys. The high accuracy of constructing the characteristics of distribution of alloying elements between the γ and γ' phases under scarce experimental data conditions is ensured by the application of bunch map analysis of random characteristics, which allowed the reliability of the calculated results to be significantly increased.

DOI: 10.1134/S0036029515130121

SIMULATION PROCESS

Based on an analysis of the results of studying more than 180 Russian and foreign nickel superalloys, we develop regression models to determine a relation between chemical composition and a number of important thermodynamic, structural, and strength parameters, which directly affect the high-temperature strength of the materials.

The high accuracy of constructing the most important characteristics of alloying element distribution between γ and γ' phases under scarce experimental data conditions is provided by the application of bunch map analysis to increase the reliability of results substantially.

SIMULATION OF THE DEPENDENCES OF THE THERMODYNAMIC, STRUCTURAL, AND STRENGTH PARAMETERS OF NICKEL SUPERALLOYS ON THE LEVEL AND CHARACTER OF ALLOYING

The gas-turbine propulsion engineering is being actively developed due to the creation of fifth-generation engines, which are characterized by a significant increase in the specific thrust (military gas turbine engines) and a decrease in the fuel rate (passenger operations) at a simultaneous substantial increase in the reliability and the service life.

Therefore, active investigations for creating new materials and technologies are performed abroad according to state programs [1–4].

Simultaneously, researches carry out studies to replace second- and third-generation nickel superalloys by new single-crystal superalloys [5, 6].

The works performed in this field are significantly complicated, since the regions of optimum multicomponent alloying approach the regions of formation of embrittling topologically close-packed compounds and other dangerous phases. The allowable ranges of alloying elements were also substantially narrowed because of the necessity of ensuring high service characteristics of alloys.

Since analytical estimates of the strength parameters of promising compositions imply the calculation of a number of thermodynamic and structural parameters of new alloys (which directly affect their operability), to create models that can be used to find a relation between alloying and these parameters is a challenging problem. The accuracy and reliability of these models determine the success of the computer-assisted systems that are developed to optimize the compositions of promising (and existing) superalloys.

The importance of this problem is also caused by the fact that the system of alloying of nickel superalloys, including new elements (rhenium, tantalum, ruthenium) is complex. The volume of analytical generalization of dependences of the parameters described above on alloying is insufficient.

The authors of [7, 8] were the first to find a relation between the level and character of alloying and the parameters that determine the structural and phase stability and the strength of alloys. As a result, Kishkin, Logunov, Glezer, and Morozov created a ZhS-32 alloy, which was widely used in fourth-generation AL31F and RD33 engines and their later modifications. Due to its properties, the Russian ZhS-32 alloy left behind foreign companies in creating alloys of the same level.

This alloy has a long-term strength σ_{100}^{1000} = 2245 MPa and was created in 1980. The foreign alloys having a higher high-temperature strength appeared in 1986–1987 (United States alloys CMSX-4 (σ_{100}^{1000} = 260 MPa) and PWA1484 (σ_{100}^{1000} = 259 MPa)) [5].

The first investigations carried out in this field obtained results. This approach was then effectively used to develop new nickel superalloys for gas turbine plants [9, 10] and promising gas turbine engines [11–13].

Note an important specific feature of those works trying to find a relation between alloying and various alloy parameters. These studies allow one to take into account the peculiarities of multicomponent alloying regions and to significantly decrease the time and cost consumed to design new alloys. As a rule, they make up commercial classified information and are not published (or party published) by manufacturers [14].

Thus, computer simulation of the relation between composition and the alloy parameters is a necessary stage to increase the efficiency of works performed to improve nickel superalloys.

Simulation Directions

In this work, we simulate the following relations:

$$T_{\text{f.d.}\gamma'\text{-phase}} = f_1\sum_{i=1}^{n} C_i, \quad (1)$$

$$T_{\text{o.d.}\gamma'\text{-phase}} = f_2\sum_{i=1}^{n} C_i, \quad (2)$$

$$T_S = f_3\sum_{i=1}^{n} C_i, \quad (3)$$

$$T_L = f_4\sum_{i=1}^{n} C_i, \quad (4)$$

$$T_{\text{eut}} = f_5\sum_{i=1}^{n} C_i, \quad (5)$$

$$V_{\gamma'\text{-phase}} = f_6\sum_{i=1}^{n} C_i, \quad (6)$$

$$\sigma_{100}^{1000} = f_7\sum_{i=1}^{n} C_i, \quad (7)$$

$$K_i = \frac{C_{i\gamma'\text{-phase}}}{C_{i\gamma'\text{-phase}}} = f_8\sum_{i=1}^{n} C_i, \quad (8)$$

where C_i is the concentration of the ith component in the alloy; $T_{\text{o.d.}\gamma'\text{-phase}}$, $T_{\text{f.d.}\gamma'\text{-phase}}$, T_S, T_L, T_{eut}, and $V_{\gamma'\text{-phase}}$ are the temperatures of the onset and full dissolution of the γ' phase, the solidus temperature, the liquidus temperature, the eutectic dissolution temperature, and the volume fraction of the γ' phase in the alloy, respectively; σ_{100}^{1000} is the long-term strength at 1000°C for 100 h; and K_i is the coefficient of the ith element distribution between the γ' and γ phases, respectively.

It is interesting to create such models, since they can be used to estimate the efficiency of hardening of a γ matrix by the γ' phase, which depends on the volume fraction of this phase in an alloy ($v_{\gamma'\text{-phase}}$), the thermodynamic stability ($T_{\text{o.d.}\gamma'\text{-phase}}$, $T_{\text{f.d.}\gamma'\text{-phase}}$, T_S, T_L, T_{eut}), the compositions of the γ and γ' phases (calculated using the dependence of $V_{\gamma'\text{-phase}}$, the alloy composition, K_i), and the subsequent estimation of the lattice misfit and $M(\bar{d})_\gamma$. The last critical parameter depends on the total concentration of valence electrons in the γ matrix, which determines the sensitivity of the alloy to the formation of embrittling hcp precipitates.

As a result, these parameters influence the level, (which is most important) the temperature dependence of the strength characteristics of the γ matrix and the strengthening γ' phase, the interphase hardening, and the strength of the alloy.

DISTRIBUTION OF ALLOYING ELEMENTS IN THE γ AND γ' PHASES OF MODERN NICKEL SUPERALLOYS

To find the relation between the character and level of alloying of modern nickel superalloys and the distribution of alloying elements in the main hardening phases plays an important role in analyzing the thermodynamic and structural parameters of this class of materials and the mechanism of their hardening and in developing computer methods of calculating the compositions of promising alloys.

The implementation of a number of the main points of the theory of alloying of modern nickel superalloys, mainly for gas turbine disks and blades, is substantially related to the accuracy of calculating the coefficient of distribution of alloying elements between the γ and γ' phases. Therefore, works in this field seem to be important.

Nevertheless, the studies dealing with this problem are insufficient. In particular, the authors of [15, 16] presented data on the distribution of alloying elements between phases (K_i, in at %) in alloys ZhS-36, ZhS-40, CMSX, ZhS-32, and ZhS32M.

The accuracy of computer estimation of the lattice parameters of the γ and γ' phases and parameter $M(\bar{d})_\gamma$ (New Phacomp method), which predicts the probability of formation of embrittling lamellae of topolog-

Table 1. Distribution coefficients of alloying elements in the γ and γ' phases in nickel superalloys $K_i = C_{i\gamma'}/C_{i\gamma}$ (at %), where C_i is the concentration of the ith element in the phase

Alloy no.	Alloy	K_i								
		Cr	Co	W	Mo	Ti	Al	Nb	Ta	Re
1	ZhS-6U	0.1	0.4	0.5	0.4	3.2	3.4	5.8	–	–
2	ZhS-6F	0.2	0.5	0.6	0.2	5.1	2.0	2.5	–	–
3	ZhS-32	0.2	0.4	0.9	0.3	–	2.7	1.1	1.7	0.08
4	ZhS-36	0.3	0.4	0.6	0.5	6.8	5.0	3.0	–	0.08
5	ZhS-40	0.12	–	0.68	0.28	–	8.24	–	4.9	–
6	PWA1480	0.06	0.28	0.41	–	3.6	2.8	–	2.94	–
7	CMSX-2	0.17	0.49	0.85	0.34	3.4	2.4	–	5.6	–
8	CMSX-4	0.15	0.38	0.58	0.4	–	8.1	–	4.2	0.04
9	A*	0.17	0.2	0.77	0.42	–	4.4	–	11.6	0.045
10	B*	0.16	0.195	0.66	0.58	–	5.04	–	11.4	0.07
11	ZhS32M	0.15	0.42	1.158	0.3	–	3.8	3.7	6.2	0.05
12	ZhS6K	0.15	0.4	0.7	0.2	3.8	2.4	–	–	–
13	VZhL12U	0.13	0.36	0.75	0.22	4.04	7.8	–	–	–
14	MARM200	0.23	0.5	1.09	–	2.75	2.28	–	–	–
15	B1900	0.17	0.37	–	0.43	–	3.41	–	–	–
...										
37	"									
38	"									
$K_{i(av)}$		0.150	0.40	0.72	0.31	3.64	4.85	2.75	5.07	0.06

ically close-packed (tcp) phases from a γ solid solution depends on the knowledge of K_i.

Therefore, we analytically considered the results of experimental studies of the compositions of the γ and γ' phases in 38 high-temperature alloys [18], which were presented in [15–17, 19]. Some of them are generalized in Table 1.

Table 1 gives the average values of K_i obtained from the generalization of all well-known 38 nickel superalloys.

The experimentally determined compositions of the phases were determined by physicochemical analysis of nickel superalloys, where the hardening γ' phase precipitates almost fully and the phases are in equilibrium with each other after standard heat-treatment conditions. It follows from these data that the values of K_i given in Table 1 are valid for the temperatures at which the dissolution of the γ' phase is absent, i.e., to $T_{\text{o.d.}\gamma'\text{-phase}}$ (temperature of the onset of γ' phase dissolution), since the volume contents of the phases and their elemental compositions above this temperature become different.

These results allow us to conclude that the average values of K_i insufficiently accurately characterize the element distribution between the phases: the scatter of the values of K_i is 36.4% for five of the nine elements; it is 67.0% for Ti, Nb, and Ta; and the root-mean-square deviation of the values of K_i for Al is 82%. Thus, the accuracy of predicting the coefficients of element distribution can only be increased by taking into account the mutual effect of each element in an alloy.

Using detailed analysis of the data for 38 alloys and statistical processing methods, we obtained mathematical relationships to accurately calculate the distribution coefficients of ten alloying elements (Cr, Co, W, Mo, Ti, Al, Nb, Ta, Hf, Re). Equations (9)–(11) represent examples of distribution coefficients for Cr, Co, and W, respectively:

$$K_{Cr} = 0.2702 - 0.0147C_{Cr} + 0.0023C_{Co} + 0.0008C_{W} - 0.0019C_{Mo} + 0.0005C_{Al} + 0.0246C_{Ti} + 0.0013C_{Ta} + 0.002C_{Re} + 0.0258C_{Nb} + 0.0004C_{Ru}, \quad (9)$$

$$K_{Co} = 0.0119 - 0.0093C_{Cr} + 0.0109C_{Co} + 0.0357C_{W} + 0.0345C_{Mo} - 0.0197C_{Al} + 0.0643C_{Ti} + 0.0109C_{Ta} + 0.0108C_{Re} + 0.0159C_{Nb}, \quad (10)$$

$$K_{W} = 1.152 - 0.0023C_{Cr} - 0.0123C_{Co} + 0.0436C_{W} + 0.0278C_{Mo} - 0.0983C_{Al} - 0.04C_{Ti} - 0.0273C_{Ta} + 0.047C_{Re} + 0.0984C_{Nb}. \quad (11)$$

Table 2. Allowed region of alloying using K_i relations

Elements	Mass fraction, %																				
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Co	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■						
Re	■	■	■	■	■	■	■	■	■	■	■	■	■	■							
W	■	■	■	■	■	■	■	■	■	■	■	■	■								
Ta	■	■	■	■	■	■	■	■	■	■	■	■									
Cr				■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Mo	■	■	■	■	■	■	■	■	■	■											
Al			■	■	■	■	■														
Ti	■	■	■	■	■																
Nb	■	■																			
V	■	■	■																		
Hf	■	■																			

Their root-mean-square deviations are 6.4, 8.1, and 6.7%, respectively.

These calculations are characterized by the fact that bunch map analysis of random characteristics was used to increase the accuracy of constructing the relationships [20].

Because of scarce experimental data, K_{Ru} was taken to be constant (0.799) and $K_{i\mathrm{Hf}}$ and $K_{i\mathrm{V}}$ were not determined due to their relatively low values in a certain number of alloys. Their values were taken to be constant and corresponding to the values given in [11], $K_{i\mathrm{Hf}} = 5.25$ and $K_{i\mathrm{V}} = 0.64$. The values of C_i are given in %.

The choice of these alloys from a standpoint of constructing reliable dependences of K_i on the level, character, and degree of alloying is caused by the following factors: they cover a wide range of alloying of alloys from the second to the fifth generation for the main elements (2.3–20.5% Cr, 0–14% Co, 0.1–12.5% W, 0–10% Mo, 0–4.5% Ti, 0.85–6.0% Al, 0–1.8% Nb, 0–12% Ta, 0–13% Re). They include the alloys where a number of elements is absent (as a result, we can estimate their influence on the redistribution of the remaining elements between phases more exactly): alloy B* has no titanium and chromium; alloys PWA1480 and MARM200 have no molybdenum; alloys ZhS-32 and ZhS-40 have no titanium; alloys PWA1480 and ZhS6K have no niobium; and alloys ZhS-6U, ZhS-6F, ZhS-36, and ZhS-40 have no tantalum and/or rhenium. The list of alloys includes the alloys that have a significant number of the elements that have a significant number of the elements that most strongly affect the high-temperature strength at high temperatures, namely, tungsten up to 12.5% (MARM200), rhenium up to 13% (alloy B*), and tantalum up to 12% (PWA1480).

Table 2 schematically presents the multicomponent region of alloying of nickel superalloys for which the obtained relationships, which are partly represented by Eqs. (9)–(11), are valid.

The estimation of the possibility of using the developed models for K_i, the calculation of the atomic composition of the γ' phase, and the subsequent estimation of criterion $M(\bar{d})_\gamma$ (New Phacomp method [21]) were carried out for an N-18 alloy. From [22], for this alloy we have $M(\bar{d})_\gamma = 0.942$ and the atomic fraction of the γ' phase is 56%.

The atomic composition of the γ' phase was determined by the formula

$$C^{\gamma}_{i(\mathrm{at})} = \frac{C^{\mathrm{al}}_{i(\mathrm{at})}}{K_{i(\mathrm{at})}V_{\gamma(\mathrm{at})} + (1 - V_{\gamma'(\mathrm{at})})}, \qquad (9)$$

where $C^{\gamma}_{i(\mathrm{at})}$ is the atomic concentration of the ith element in the γ' phase, $C^{\mathrm{al}}_{i(\mathrm{at})}$ is the atomic concentration of the ith element in the alloy, $K_{i(\mathrm{at})}$ is the coefficient of distribution of the ith element between the γ' and γ phases ($K_{i(\mathrm{at})} = C^{\gamma'}_i / C^{\gamma}_i$, where $C^{\gamma'}_i$ and C^{γ}_i are the concentrations of the ith element expressed in atomic percent in the γ' and γ phases, respectively), and $V_{\gamma'(\mathrm{at})}$ is the atomic fraction of the γ' phase in the alloy ($V_{\gamma'(\mathrm{at})} = P_{\gamma'(\mathrm{at})}/P_{\mathrm{al}'(\mathrm{at})}$ is the ratio of the atomic weight of the γ' phase to the atomic weight of the alloy). In our case, we have $V_{\gamma'(\mathrm{at})} = 0.56$ (N-18 alloy).

The value of $M(\bar{d})_\gamma$ determined by Eq. (10) presented in [12],

$$\begin{aligned} M(\bar{d})_\gamma = {} & 0.717C_{\mathrm{Ni}} + 1.9C_{\mathrm{Al}} + 1.142C_{\mathrm{Cr}} + 1.55C_{\mathrm{Mo}} \\ & + 1.655C_{\mathrm{W}} + 2.224C_{\mathrm{Ta}} + 0.777C_{\mathrm{Co}} + 2.117C_{\mathrm{Nb}} \\ & + 2.27C_{\mathrm{Ti}} + 1.267C_{\mathrm{Re}} + 1.006C_{\mathrm{Ru}} + 3.02C_{\mathrm{Hf}}, \end{aligned} \qquad (10)$$

is 0.939. This value of close to that given in [22], $M(\bar{d})_\gamma = 0.942$; here, C_{Ni}, C_{Al}, ..., and C_{Hf} are the con-

centrations of the corresponding elements in the γ phase (at %).

The atomic fraction of the γ' phase is calculated to be 55.4%; that is, the discrepancy between the calculated and experimental values of $v_{\gamma' at}$ is 1.0%.

CONCLUSIONS

We proposed a technique, which is based on the mathematical models of K_i that were obtained by regression analysis of the coefficients of distribution of elements between the γ' and γ phases in 38 nickel superalloys, to calculate the compositions of the main hardening phases in nickel-based superalloys, which are widely used in important parts in novel engineering.

This technique can be applied to a large number of nickel superalloys, the alloying element concentrations in which are in the limits presented in Table 2.

The preliminary results used to obtain sufficiently accurate parameters were the first stage in solving the problem of simulating composition–properties relations.

REFERENCES

1. V. A. Skibin, V. I. Solonin, and V. A. Palkin, *Works of the Leading Aviation Engine Making Companies on Creating Promising Aviation Engines* (TsIAM, Moscow, 2004).
2. A. A. Inozemtsev and V. L. Sandratskii, *Gas Turbine Engines. Part 1* (Aviadvigatel', Perm', 2006).
3. *Foreign Aviation Engines*, Ed. by G. V. Skvortsova (TsIAM, Moscow, 1984).
4. Yu. S. Eliseev, V. V. Krymov, S. A. Kolesnikov, and Yu. N. Vasil'ev, *Nonmetallic Composite Materials in Structural Members and the Production of Aviation Gas Turbine Engines* (MGTU, Moscow, 2007).
5. R. C. Reed, *The Superalloys. Fundamentals and Applications* (University Press, Cambridge, 2006).
6. B. E. Paton, S. T. Kishkin, S. Z. Bokshtein, A. V. Logunov, et al., *High-Temperature Strength of Cast Nickel Superalloys and Their Protection against Oxidation* (Naukova Dumka, Kiev, 1987).
7. A. V. Logunov, N. V. Petrushin, Yu. M. Dolzhanskii, et al., "Prediction of the change in the properties of nickel superalloys as a function of alloying with Cr, Co, Ti, and Al," in *Alloys of Rare and Refractory Metals with Specific Physical Properties* (Nauka, Moscow, 1979).
8. A. V. Logunov, N. V. Petrushin, E. A. Kuleshova, and Yu. M. Dolzhanskii, "Prediction of the effect of structural factors on the mechanical properties of high-temperature alloys," Metalloved. Term. Obrab. Met., No. 6, 16 (1981).
9. E. L. Kats, V. P. Lubenets, and M. L. Konter, "New corrosion-resistant nickel superalloys and the technological processes of casting gas turbine parts with directional, single-crystal, and equiaxed structures," in *Proceedings of VI Conference on Mechanical Properties of Materials* (Pergamon, Kioto, 1991), p. 111.
10. V. V. Rtishchev, "Calculation methods for predicting the phase composition, the structural characteristics, and the long-term strength from the chemical composition of a nickel-bases superalloy," in *Nickel-Based High-Temperature and Heat-Resistant Alloys*, Ed. by O. A. Bannykh (Nauka, Moscow, 1984).
11. E. N. Kablov and N. V. Petrushin, "Computer method of designing casting nickel superalloys," in *Casting Superalloys: Kishkin's Effect* (Nauka, Moscow, 2006), p. 56.
12. P. Caron, "High γ'-solvus new generation nickel-based superalloys far single turbine blade application," in *Superalloys* (Champion, Pennsylvania, 2000).
13. I. N. Egorov-Yegorov, and G. S. Dulikravich, "Inverse design of alloys for specified stress, temperature and time-to-rupture by using stochastic optimization," in *Proceedings of International Symposium on Inverse Problems, Design and Optimization*, Ed. by M. J. Colaco, G. S. Dulikravich, and H. R. B. Orlande (Rio de Janeiro, 2004).
14. A. V. Logunov, A. V. Logachev, A. I. Logacheva, et al., "Software package for an analysis and estimation of the phase composition, the lattice misfit of the γ and γ' phases, and the critical content of electron vacancies in nickel superalloys," in *Proceedings of 3rd International Engineering Conference Metalldeform 2009* (Samara, 2009), Vol. 1, pp. 100–109.
15. R. E. Shalin, I. L. Svetlov, E. B. Kachanov, et al., *Nickel Superalloy Single Crystals* (Mashinostroenie, Moscow, 1997).
16. E. N. Kablov, N. V. Petrushin, G. I. Morozova, et al., "Physicochemical factors of the high-temperature strength of rhenium-containing nickel superalloys," in *Casting Superalloys: Kishkin's Effect* (Nauka, Moscow, 2006), p. 116.
17. *Encyclopedia of Mechanical Engineering* (Mashinostroenie, Moscow, 2001), Vol. 2.
18. A. V. Logunov, Yu. N. Shmotin, and V. V. Rogozina, "Distribution of alloying elements in the γ and γ' phases in modern nickel superalloys," Vestnik MGOU. Ser. Tekhnika Tekhnologiya, No. 3, 5–9 (2011).
19. N. F. Lashko, L. V. Zaslavskaya, M. N. Kozlova, G. I. Morozova, et al., *Physicochemical Phase Analysis of Steels and Alloys* (Metallurgiya, Moscow, 1978).
20. A. V. Logunov, V. N. Shishkin, O. V. Vinogradova, and N. A. Zaitsev, "Information technology of confluent analysis of the service properties of nickel superalloys: A handbook," Inzh. Zh., No. 9(174), 51–56 (2011).
21. M. Morinaga, N. Yukawa, H. Adachi, and H. Ezaki, "New PHACOMP and its application to alloy design," in *Superalloys* (Champion, Pennsylvania, 1984), pp. 523–532.
22. L. Y. Guedou, I. Augustins-Lecallier, I. Naze, P. Caron, and D. Locg, "Development of a new fatigue and creep resistant PM nickel-base superalloys for disk applications," in *Superalloys* (TMS, Pennsylvania, 2008), pp. 21–30.

(To be Continued)

Translated by K. Shakhlevich