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PROCESSES OF MANUFACTURE OF FERROUS AND NONFERROUS METALS

Methodological Fundamentals of Computer-Assisted Designing of Nickel-Based Superalloys[1]

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Abstract—The criteria that determine the operating ability of nickel superalloys are described. The binary Ni–W, W–Re, and Re–Ni phase diagrams are analyzed to find concentration characteristics and the probability of formation of β, α, and other undesirable phases based on refractory elements from a γ solid solution. The NewPhacomp method is corrected for single-crystal nickel superalloys. Additional criteria are introduced to estimate the probability of decomposition of the hardening γ' phase and the precipitation of embrittling lamellar η and δ compounds from this phase.

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ANALYSIS AND ESTIMATION OF THE CRITERIA THAT DETERMINE THE OPERATING ABILITY OF NICKEL SUPERALLOYS

Criteria and Operating Ability of Nickel Superalloys

The creation of a new nickel superalloy implies searching for an optimum combination of the parameters that determine the operating ability of nickel superalloys. In this case, it is difficult to improve all properties of a material simultaneously. Some properties are often increased due to a decrease in other ones. On the whole, all characteristics can be divided into the following five groups:

1. Thermodynamic parameters. The high-temperature operating ability is mainly determined by structural stability, which depends on thermodynamic criteria, such as solidus and liquidus temperatures T_S and T_L, respectively; local eutectic melting temperature $T_{\text{loc.m}}$; and the temperatures of the onset and full dissolution of the hardening γ' phase ($T_{\text{o.d.}\gamma'}$ and $T_{\text{f.d.}\gamma'}$, respectively). These parameters determine the thermodynamic stability of a structure, the high-temperature softening, and (hence) the high-temperature strength at operating temperatures, which reach the temperature range of the dissolution of the main hardening γ' phase.

The solidus temperature points to the maximum possible operating temperature of alloys according to the following factors. The higher T_S, the higher the operating temperature of the alloy. Refractory elements with a high melting temperature (W, Mo, Re, Ta) mainly increase T_S in nickel superalloys. Simultaneously, these elements increase the temperatures of the onset and full dissolution of the γ' phase. Moreover, having the lowest diffusion mobility among all alloying elements, they significantly retard diffusion processes at high temperatures, which are related to the coalescence of fine hardening γ'-phase precipitates and dissolution of this phase at high temperatures (i.e., to structure degradation and alloy softening). The temperature difference $T_L - T_S$ determines the level of dendritic segregation: the smaller this difference, the smaller the segregation, the more homogeneous composition of the alloy, and the smaller the sensitivity of the alloy to the formation of supersaturated local volumes (and correspondingly eutectic carboboride phases, where microporosity appear upon cooling of an alloy and decreases its strength characteristics).

The solidification temperature of a carboboride eutectic phase is also an important characteristic of an alloy, since the temperature "window" between $T_{\text{f.d.}\gamma'}$ and T_{eut} should be sufficiently large. Some authors note that T_{eut} can reach $T_{\text{f.d.}\gamma'}$ or even be lower than $T_{\text{f.d.}\gamma'}$. In this case, standard homogenization can result in local melting of alloy microvolumes and, correspondingly, alloy softening. Therefore, researchers often use slow heating to $T_{\text{f.d.}\gamma'}$ or preliminary heating at a lower temperature before reaching $T_{\text{f.d.}\gamma'}$.

2. Structural parameters. The parameters that characterize the structure and the perfection of single-crystal nickel superalloys are as follows: the basic hardening γ' phase based on the $Ni_3(Al, Ti)$ intermetallic compound, its size, its morphology, its stability at high temperatures (under complex static, fatigue, and thermal loads), the volume fraction of the basic γ'

[1] Continuation.

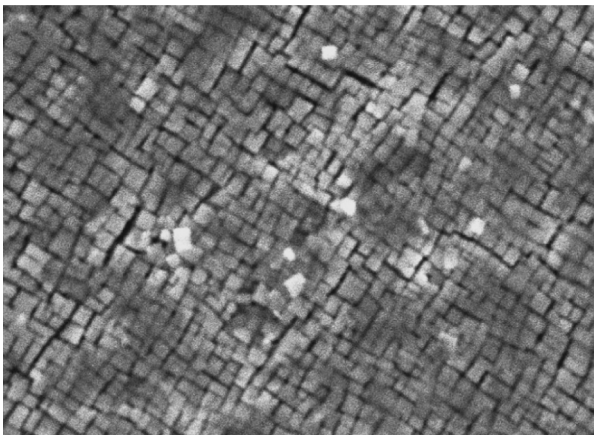

Fig. 1. γ–γ' structure of a nickel superalloy (×20000).

phase $V_{\gamma'}$, lattice parameters a_γ and $a_{\gamma'}$, and the lattice misfit.

An analysis of the relations between the composition and the lattice parameters of the γ and γ' phases (a_γ, $a_{\gamma'}$) that are given in [1, 2] shows that the models in [1] are preferable, since they take into account the effect of the maximum number of alloying elements on these parameters. In the formulas presented in [2], the estimation of parameter a_γ did not take into account the contribution of Hf, which is important for new alloys, and the estimation of parameter $a_{\gamma'}$ had no Hf, Co, and V.

Thus, the following relations from [1] were used in the developed technique:

to calculate lattice parameter $[a_\gamma(X_i)]$ of a multicomponent γ' solid solution, we used the relation

$$\begin{aligned} a_\gamma(X_i) \times 10^{10} &= 3.5219 + 0.00221X_{\mathrm{Al}} \\ &+ 0.00122X_{\mathrm{Cr}} + 0.00412X_{\mathrm{Mo}} + 0.00435X_{\mathrm{W}} \\ &+ 0.00693X_{\mathrm{Ta}} + 0.00059X_{\mathrm{Co}} + 0.00142X_{\mathrm{Ti}} \\ &+ 0.00142X_{(\mathrm{V})} + 0.00382X_{\mathrm{Re}} + 0.00303X_{\mathrm{Ru}} \\ &+ 0.01599X_{\mathrm{Hf}}; \end{aligned} \quad (1)$$

to calculate lattice parameter $a_{\gamma'}(Y_i)$ of a nickel superalloy, we used the relation

$$\begin{aligned} a_{(\gamma')}(Y_i) \times 10^{10} &= 3.5691 + 0.00014\,Y_{\mathrm{Cr}} \\ &+ 0.00097\,Y_{(\mathrm{Mo})} + 0.00151\,Y_{\mathrm{W}} + 0.00398\,Y_{\mathrm{Ta}} \\ &+ 0.00002\,Y_{\mathrm{Co}} + 0.00275\,Y_{\mathrm{Nb}} + 0.00149\,Y_{\mathrm{Ti}} \\ &+ 0.00189\,Y_{\mathrm{V}} + 0.00504\,Y_{\mathrm{Re}} + 0.00083\,Y_{\mathrm{Ru}} \\ &+ 0.01339\,Y_{\mathrm{Hf}}, \end{aligned} \quad (2)$$

where X_i and Y_i are the contents (at %) of the ith element in the γ and γ' phases, respectively.

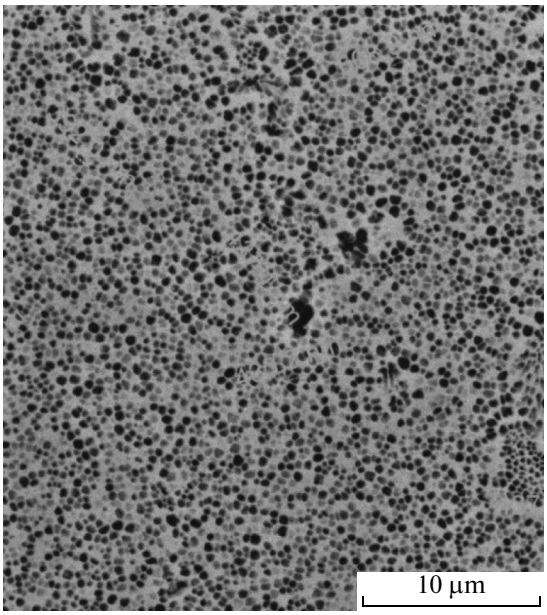

Fig. 2. Structure of a nickel superalloy at $a_{\gamma'} > a_\gamma$, ×10000.

Formulas (1) and (2) were used to calculate the lattice misfit, i.e., the relative difference between the lattice parameters of the γ and γ' phases ($a_{\gamma'}$ and a_γ),

$$\frac{\Delta a(\gamma - \gamma')}{a} = 2\frac{a_\gamma - a_{\gamma'}}{a_\gamma + a_{\gamma'}} \times 100(\%)_{\gamma'}. \quad (3)$$

The high-temperature strength of the alloy depends on the volume fraction of the hardening γ' phase and the value and the sign of the lattice misfit between the γ and γ' phases, and its optimum is 0.15–0.35%. In this case, the hardening γ' phase has a pronounced cubic shape and exhibits the maximum hardening effect (Fig. 1) [3]. If the lattice parameter of the hardening phase is larger than the lattice parameter of the γ solid solution or they are equal to each other, the γ' phase acquires a spherical shape and its hardening efficiency becomes significantly lower (Fig. 2).

The structural factors that determine the operating ability of alloys include topologically close-packed (tcp) lamellar phases, which strongly soften an alloy and break a lamellar structure (Fig. 3), and α phases (α-Cr, α-W, etc.) to which important elements (including tungsten) pass from an alloy. As a result, their concentrations in an alloy and the corresponding hardening effect decrease substantially. Figure 4 shows α-W particles, and Fig. 5 depicts eutectic γ'-phase precipitates, which form during the solidification of an alloy and exhibit a high hardening effect. The γ' phase contains W, Ta, Al, and Ti; these elements having passed from the base material; and, correspondingly, their hardening effect on the alloy is significantly weakened.

The NewPhacomp method [4] is most widely used to estimate the sensitivity of a nickel superalloy to the

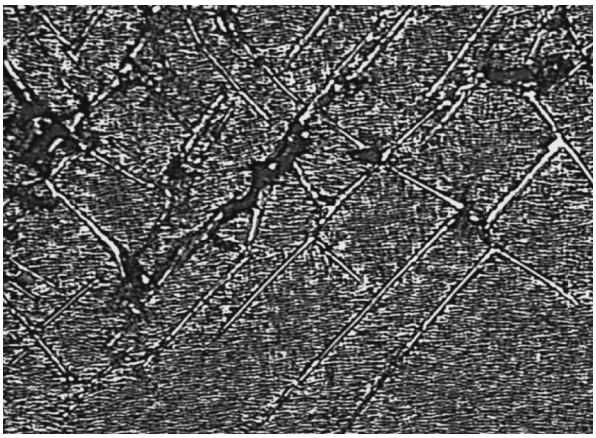

Fig. 3. Zone of fracture along the aggregation of tcp phases in an as-cast nickel superalloy. ×5000.

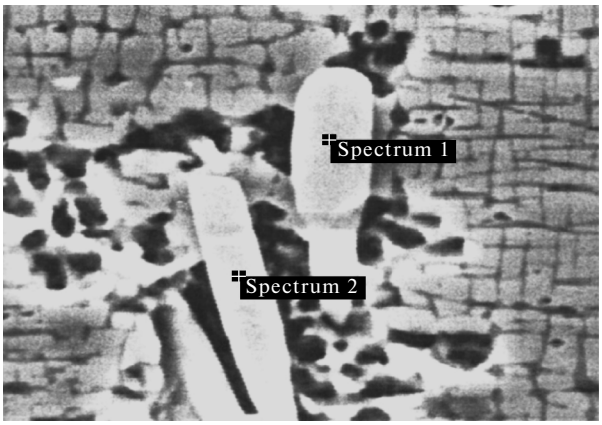

Fig. 4. α-W phases in a nickel superalloy. ×20000.

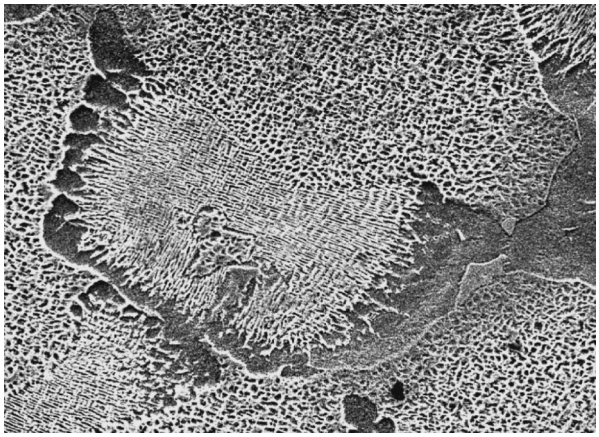

Fig. 5. γ'_{eut} phase. ×5000.

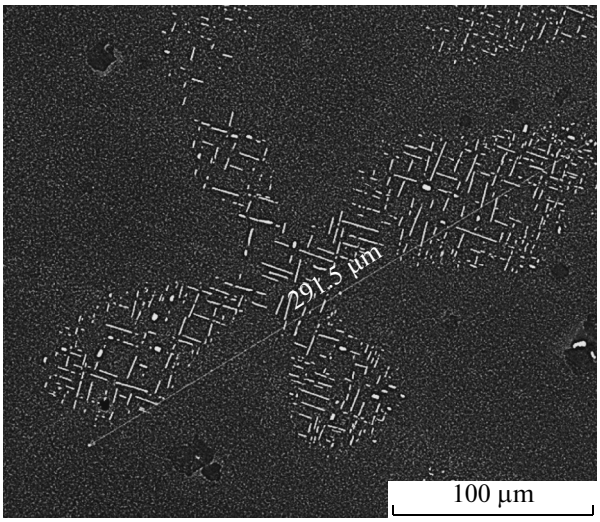

Fig. 6. TCP phases formed in dendrite arms in a single-crystal nickel superalloy.

formation of embrittling tcp phases, and the concentration of valence electrons in a γ matrix is calculated using this method.

Here, critical parameter $M(\bar{d})_\gamma$ calculated for the γ solid solution in an alloy should be lower than 0.93. However, the results of studying the last-generation alloys containing a significant number of elements, such as Re, W, Mo, and Ta, showed that this critical parameter should be lower, 0.905–0.93.

In alloys with a single-crystal structure, tcp phases mainly form in dendrite arms, which is clearly visible in Fig. 6.

Indeed, dendrite arms are significantly enriched in tungsten, rhenium, cobalt, and ruthenium due to dendritic segregation characteristic of casting, and the interdendritic space is enriched in aluminum, molybdenum, and tantalum.

The segregation coefficients of some elements (e.g., rhenium, tantalum, tungsten) reach high values, from 3.4 to 2.0 after casting and from 1.8 to 1.3 after homogenization under standard heat-treatment conditions.

Thus, upon casting of single crystals, the compositions of dendrite arms and the interdendritic space differ substantially from the average values.

It would not be expected that the NewPhacomp calculations hold true even if the alloy of an average composition should not form embrittling tcp phases. In other words, if harmful cp compounds do not form in the alloy of an average composition, this does not mean that embrittling tcp lamellae cannot form in dendrite arms (or in the interdendritic space) when a single crystal is formed from this alloy.

The idea that, as alloying is complicated, the NewPhacomp method can be rather inaccurate because of dendritic segregation was noted earlier [2]. The prob-

Segregation coefficients $K_s = C_{DA}/C_{IDS}$ for single-crystal nickel superalloys after casting in an UVNK-8P plant (DA, dendrite arm; IDS, interdendritic space)

Alloy	Al	Cr	Ti	Ni	Mo	W	Ta	Co	Re	Ru	Nb
CMSX-4	0.7	1.4	0.6	–	1.7	1.7	0.6	1.1	2.7	–	–
Rene no. 5	0.7	0.8	–	–	0.7	2.0	0.7	1.1	2.5	–	–
VZhM-1	0.7	1.2	–	–	1.2	2.1	0.5	1.2	3.4	–	–
ZhS-47	0.7	1.25	–	0.9	1.25	2.1	0.5	1.2	3.4	–	–
Alloy 52	0.7	1.43	–	0.83	1.25	2.8	0.38	1.4	6.8	1.2	–
Alloy 71	0.68	1.25	–	0.83	1.22	2.8	0.37	1.2	5.4	1.14	–
VZhM-4	0.7	1.0	–	–	0.9	2.1	0.4	1.2	5.9	1.2	0.55

lem is to correct the critical criterion of 0.93 so that the real change of the alloy composition in dendrite arms and the interdendritic space is taken into account. To this end, we analyzed available data on the dendritic segregation of elements in casting of various single-crystal nickel superalloys in UVNK-8P plants, which are widely used to produce gas turbine engine blades, or under solidification conditions that are similar to those in these plants (table) [5, 6].

The level of dendritic segregation depends on the following factors: the difference between the liquidus and solidus temperatures (the larger the difference, the larger the difference between the alloy compositions solidifying in dendrite arms and the interdendritic space); solidification conditions, namely, the higher the temperature gradient at the solidification front and the higher the front velocity, the smaller the dendrite arm spacing and, correspondingly, the degree of dendritic segregation; and the diffusion characteristics of alloying elements in solid and liquid states, since active diffusion processes occur in the layer adjacent to the solidification front from both liquid and solid phases.

An analysis of the tabulated data demonstrates that the segregation coefficients of alloying elements in different alloys cast in the same plants (or under the same solidification conditions) agree well with each other. This means that, among the three factors that determine dendritic segregation, the second and third factors, i.e., directional solidification conditions (temperature gradient at the growth front and the front velocity) and the diffusion characteristics of alloying elements, are likely to be most significant. Experimental results demonstrate that, since the segregation parameters of elements in different alloys coincide at a high accuracy under the same solidification conditions, their average values can be used to calculate the alloy compositions in dendrite arms or in the interdendritic space.

We performed this analysis for more than 200 alloys and calculated the values of $(M/\bar{d})_\gamma$ for the average compositions of alloys and for the compositions in dendrite arms and the interdendritic space.

It should be noted that the alloys have different levels of dendritic segregation after casting (high level) and heat treatment. In particular, the segregation coefficients of Re, Ta, and W in the ZhS47 alloy are 3.4, 0.5, and 2.1, respectively, after casing in an UVNK-9 plant, and these coefficients after homogenization of the alloy are significantly lower, 1.8, 0.9, and 1.3, respectively [5].

To find the group of segregation coefficients to be used to solve our problem, we consider the results [7] on studying the dissolution of the phases existing in a nickel superalloy that were obtained in RR Company (Figs. 7, 8).

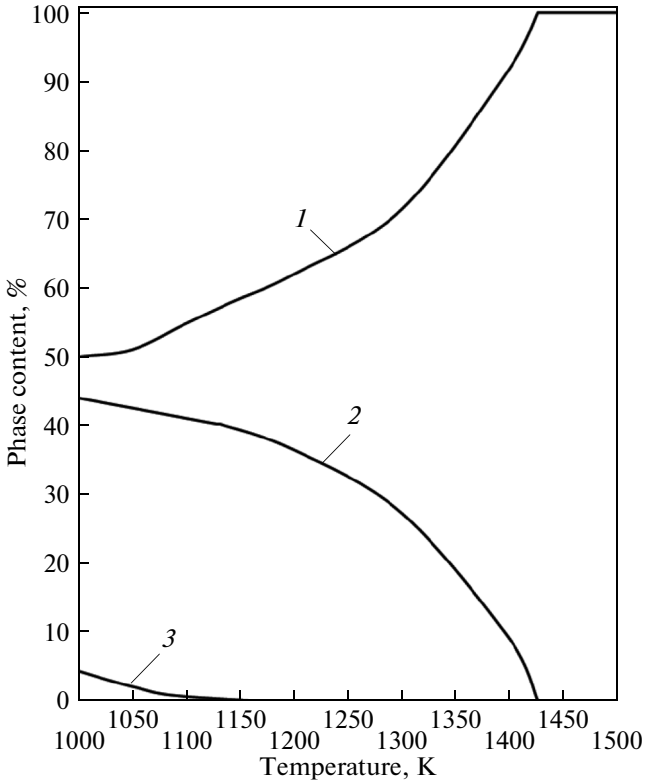

Fig. 7. Temperature dependences of the contents of the γ', γ, and σ phases (%): (*1*) γ matrix, (*2*) γ' phase, and (*3*) σ phase.

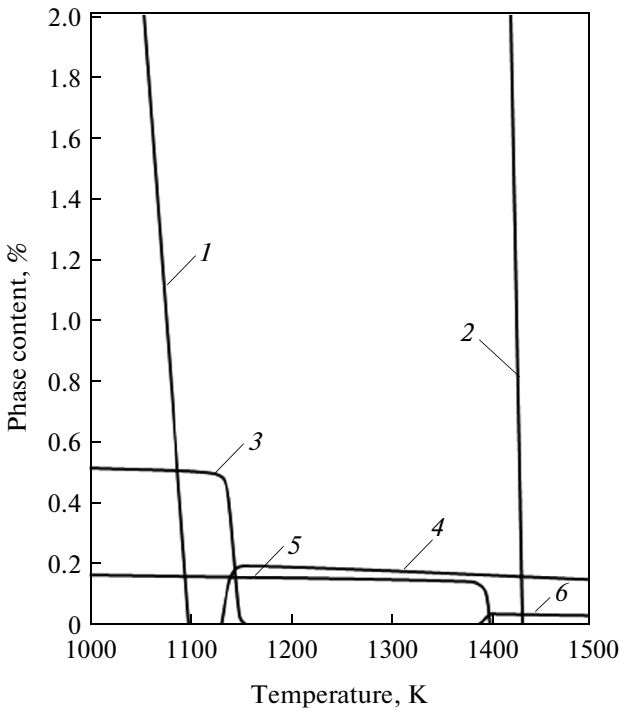

Fig. 8. Temperature dependences of the contents of the main phasesin the range 0–2%: (*1*) σ phase, (*2*) γ' phase, (*3*) $M_{23}C_6$ carbide, (*4*) MC carbide, (*5*) M_3B_2 boride, and (*6*) MB_2 boride.

The tcp σ phase is seen to completely dissolve at temperatures ≤900°C, whereas the dissolution of the γ' phase ends at ~1160°C.

This finding means that the σ phases are absent during heat treatment of alloys in the course of homogenization, since they dissolve in a matrix at a significantly lower temperature. The alloy compositions in dendrite arms and the interdendritic space become closer to each other during heat treatment. Here, we have to consider possible tcp-phase formation processes after heat treatment, which was done in this work.

Thus, we determined the values of $M(\bar{d})_\gamma$ for an average alloy composition and for the alloy volumes localized in dendrite arms and the interdendritic space after heat treatment.

As a result, we constructed models for the composition dependences of $M(\bar{d})_\gamma$ (average alloy composition), $M(\bar{d})\gamma_{DA}$ (alloy composition in dendrite arms), and $M(\bar{d})\gamma_{IDS}$ (alloy composition in the interdendritic space).

This means that $M(\bar{d})\gamma_{cr}$ should be calculated from the most dangerous concentration (in dendrite arms and the interdendritic space) rather than from the average alloy composition. In other words, we have

$$M(\bar{d})\gamma_{cr} = 0.93 - \Delta M(\bar{d})\gamma_{seg}, \quad (1)$$

where $M(\bar{d})\gamma_{cr}$ is the critical value above which tcp phases form;

$$M(\bar{d})\gamma_{seg.DA} = -0.00297 + 0.002033C_W - 0.00178C_{Al} + 0.000347C_{Ta} + 0.007817C_{Re}, \quad (2)$$

$$M(\bar{d})\gamma_{seg.IDS} = -0.06755 - 0.00205C_W + 0.01063C_{Al} - 0.00059C_{Ta} - 0.00158C_{Re}, \quad (3)$$

where C is the element concentration in the alloy (%).

Thus, we have

$$M(\bar{d})\gamma_{cr.seg.DA} = 0.933 + 0.0018C_{Al} - 0.002C_W - 0.00035C_{Ta} - 0.0078C_{Re}, \quad (4)$$

$$M(\bar{d})\gamma_{cr.seg.IDS} = 0.997 + 0.002C_W - 0.011C_{Al} + 0.0006C_{Ta} + 0.0016C_{Re}, \quad (5)$$

where $M(\bar{d})\gamma_{cr.seg.DA}$ and $M(\bar{d})\gamma_{cr.seg.IDS}$ are the critical values of parameter $M(\bar{d})\gamma$ estimated from the alloy element concentrations in dendrite arms (DAs) and the interdendritic space (IDS). If these values are exceeded, tcp phases form.

In this case, parameter $M(\bar{d})\gamma$ of an alloy is calculated by the well-known formula

$$M(\bar{d})\gamma = 0.717C_{Ni} + 1.9C_{Al} + 1.142C_{Cr} + 1.55C_{Mo} + 1.655C_W + 2.224C_{Ta} + 0.777C_{Co} + 2.117C_{Nb} + 2.27C_{Ti} + 3.02C_{Hf} + 1.267C_{Re} + 1.006C_{Ru}, \quad (6)$$

where C_i is the atomic fraction of a certain element in the γ matrix of the alloy.

An analysis of Eqs. (4) and (5) shows that dendrite arms are most dangerous for embrittlement because of the formation of tcp precipitates, since the allowable criteria for them are significantly lower than for the interdendritic space in most cases.

Rhenium is the main element that most actively decreases the allowable level of $M(\bar{d})\gamma$ in dendrite arms. Tungsten and tantalum also decrease this parameter and their contributions are lower by a factor of 4 and 20, respectively.

Thus, we developed a supplement to the NewPhacomp method, which takes into account the specific features of dendritic solidification in casting of single-crystal alloys and is suggested to be called LDN. Phacomp is a segregation supplement to the NewPhacomp method.

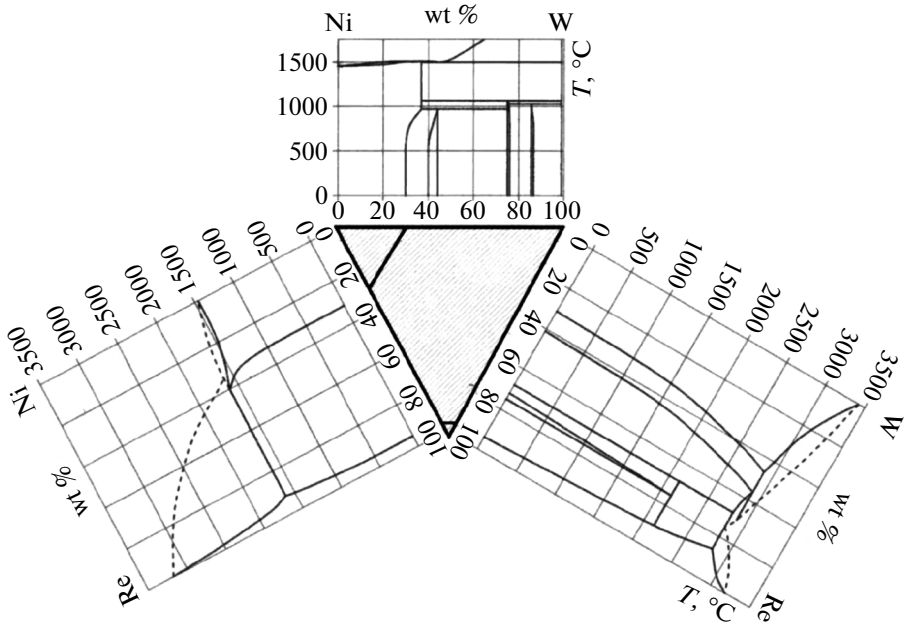

Fig. 9. Fragment of the ternary Ni–W–Re phase diagram.

In any case, the specific features of the structure of single-crystal alloys in the form of a pronounced dendritic structure and noticeable segregation heterogeneity call for a correction of the NewPhacomp method to ensure a more accurate prediction of the sensitivity of alloys to embrittlement because of the appearance of tcp compounds.

The next criterion introduced in the computer method of optimizing nickel superalloy compositions concerns the stability of a γ solid solution.

The main criterion of estimating the stability of a γ solid solution is known to be the danger of formation of tcp lamellar phases based on W, Cr, and Re in a γ matrix.

As was shown above, this criterion is based on the widely used NewPhacomp method [4]. This is true but not sufficient. The complication of alloying of modern nickel superalloys led to a substantial increase in the concentration of a large number of elements in the γ phase. This means that other phases can also precipitate apart from tcp phases. Therefore, it is necessary to develop a criterion to control and ensure structural and thermodynamic stability of a matrix.

As one of these criteria, we propose to introduce an additional parameter, namely, the limiting content of elements in a γ phase (Al + Ti + W + Mo + Re + Ta + Nb + Ru), which should not exceed 30%.

To corroborate this suggestion, we consider part of the ternary Ni–W–Re phase diagram (Fig. 9). Analysis of this diagram seems to be most convenient, since mutually dissolving (Ni–Co–Cr), which is one corner of the ternary diagram, are present in the γ solid solution of modern alloys.

The two other corners are represented by rhenium and tungsten, which are the most important alloying elements of modern nickel superalloys.

The other elements entering into the γ solid solution (Al, Mo, Ti, Nb, Hf, Ta) have low concentrations, and their total concentration narrows the homogeneity area of a nickel-based solid solution (to a first approximation, by the same value).

It is seen that the total limiting concentration of Re and W (and other elements entering into the γ solid solution, i.e., Al, Mo, Ti, Nb, Hf) should not exceed 30%; otherwise, phases Ni_4W (β phase), NiW (δ phase), W_2Re_3 (σ phase), and α-Re and their combinations would precipitate from the γ phase.

In this case, alloys undergo embrittlement, and the elements that cause high-temperature hardening of a γ matrix leave it.

The introduction of this criterion allowed us to significantly increase the results of determining the optimum compositions of next-generation nickel superalloys.

3. Strength parameters. These parameters are elastic modulus E; strength short-term characteristics σ_u^{20}, δ^{20}, and Ψ^{20}; long-term strength (smooth and notched specimens) $\sigma_\tau^{t^\circ C}$; low-cycle (10^4 cycles) and high-cycle (10^7 cycles) fatigue $\sigma_{-1_{(Ncycle)}}^{t^\circ C}$ (fatigue stress of smooth and notched specimens); and impact toughness KCV.

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(To be continued)

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