# Influence of Alloying Elements on the Composition of Primary Carbides in the Ni−11.5Cr−5Co−3.6Al−4.5Ti−7W−0.8Mo−0.06C System

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In this work, theoretical modelling of the thermodynamic processes of the release of excess phases is carried out using the CALPHAD method. As well as a practical study of the structure and distribution of chemical elements in carbides, depending on alloying using scanning electron microscopy. It has been established that in typical carbides, for the system Ni−11.5Cr−5Co−3.6Al−4.5Ti−7W−0.8Mo−0.06C, there is a tendency to degeneration and phase reactions depending on the level of alloying with the given elements. The mathematical dependences of the influence of alloying on the temperature of precipitation (dissolution) of carbides and the change in the chemical composition of the alloy on the content of elements in carbides are established. The obtained dependences were experimentally confirmed using scanning electron microscopy on nickel-based superalloys.

**Key words:** superalloy, carbides, modelling, tantalum, scanning electron microscopy.

У цій роботі проведено теоретичне моделювання термодинамічних процесів виділення надлишкових фаз методою CALPHAD, а також практичне вивчення будови та розподілу хемічних елементів у карбідах залежно від леґування за допомогою сканувальної електронної мікроскопії. Встановлено, що у типових карбідах для системи Ni−11,5Cr−5Co−3,6Al−4,5Ti−7W−0,8Mo−0,06C спостерігається тенденція до деґрадації та фазових реакцій залежно від рівня леґування заданими елементами. Встановлено

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математичні залежності впливу леґування на температуру виділення (розчинення) карбідів та зміни хемічного складу стопу від вмісту елементів у карбідах. Одержані залежності були експериментально підтверджені за допомогою сканувальної електронної мікроскопії на жароміцних стопах на основі ніклю.

**Ключові слова:** жароміцні стопи, карбіди, моделювання, тантал, сканувальний електронний мікроскоп.

## 1. INTRODUCTION

The most important step in improving the structure of superalloys was the production of materials without any grain boundaries at all, that is, single crystals. That required not only the modernization of the directional crystallization technology in order to grow single crystals with a given orientation, but also the development of special compositions of superalloys, as well as their heat treatment modes [1−6]. Since there are no grain boundaries in single crystals, there is no need to introduce elements that strengthen them into the alloy. This circumstance has significantly simplified the system for alloying superalloys for growing single crystals. In addition, using the anisotropy of physical and mechanical properties, it is possible to choose such a rational orientation of the single crystal (axial or azimuthal) relative to the direction of action of the main stresses, which would provide the best mechanical properties and the maximum service life of the product [7−13].

The role of carbides is very complex in nickel-based superalloys. They influence on mechanical properties depending on their morphology and distribution. Single crystals alloys are characterized by the presence of primary carbides of spherical, block or script-like morphology [14−19]. The main method for studying such fine structures is x-ray spectroscopy, which fully makes it possible to determine the main characteristics of the fine structure [20−24].

The aim of this work is to study the specifics of the influence of alloying elements on the distribution of various types of carbides in the structure, their topology and morphology, as well as their composition for a multicomponent system such as Ni−11.5Cr−5Co−3.6Al−4.5Ti−7W−0.8Mo−0.06C using the computational prediction method CALPHAD (passive experiment) versus data obtained by scanning electron microscopy (SEM) (active experiment).

## 2. MATERIAL AND RESEARCHTECHNIQUE

Modelling of thermodynamic processes occurring during crystallization

(cooling) or heating in the structure of alloys was carried out by the CALPHAD method [25, 26].

Modelling of these processes allows for computational prediction and comparative assessment of the effect of alloying elements in carbides of different types on their distribution and phase composition in the alloys under study. Calculations were carried out for each investigated composition individually with a stepwise introduction of a specific alloying element into a fixed composition of a multicomponent system.

Depending on the alloying system of the alloy, the results obtained by modelling the crystallization process make it possible to calculate the temperatures and the amount of precipitated types of carbides, as well as their chemical composition.

In the multicomponent alloying system (Ni−11.5Cr−5Co−3.6Al−4.5Ti−7W−0.8Mo−0.06C) the range of variation of the elements was chosen from considerations of the maximum and minimum amount of the element introduced into the superalloys. Thus, for the study were selected carbide-forming elements in the following alloying ranges: carbon (0.02−0.2)%; hafnium (0.1−2.5)%; niobium (0.1−4)%; titanium (1−6)%; tantalum (0.5−12)% by weight.

The alloy crystallization process was simulated 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 precipitation 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 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 UVNK-8P high-gradient unit for directional (mono) crystallization in special ceramic blocks with pre-installed starting crystals in accordance with the serial technology. The required cooling rate was provided by immersing the cast molds into a liquid metal crystallizer (aluminium melt) at a rate of 10 mm/min. To obtain a given crystallographic orientation, we used starting crystals (seeds from an alloy of the binary system Ni−W), which had deviations from the main crystallographic direction [001] by an angle 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 kept in a crucible at a metal overheating temperature of 1620°C for 8…10 minutes. The samples were poured under the following parameters: pouring temperature 1580°C; lower heater temperature 1610°C; the temperature of the upper heater was 1580°C. The 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 the REM-106I scanning electron microscope with an energy-dispersive x-ray spectral microanalysis system. This method was used to study the 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 instrument program. The relative error of the method is ±0.1% (by weight). The calculation results of the type of carbides and their chemical composition were compared with the experimental data obtained using electron microscopy.

The obtained values were processed in the Microsoft Office software package in the EXCEL package. The obtained dependences have rather high coefficients of determination $R^2 \geq 0.9$ and can be used for predictive calculations of the indicated characteristics with a relative error of ±3.1%.

## 3. RESEARCH RESULTS AND DISCUSSION

The study of phase separation during crystallization of the investigated alloy in the temperature range (1600–20°C) showed that the most probable is the separation of the main phases in the following order: $\gamma$—solid solution; primary carbides; eutectic $\gamma + \gamma'$; type $\gamma'$ intermetallic compound based on (Ni$_3$Al). As known [27–30], primary carbides have a high decomposition temperature and well harden alloys at elevated operating temperatures. The main elements that make up their composition are titanium, tantalum, hafnium, and niobium. In this regard in the future modelling and experimental study of the distribution of these elements will be carried out.

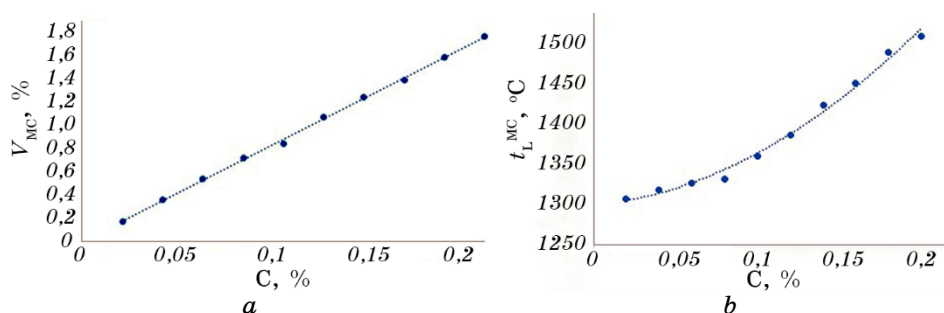It was found that the dependences of the dissolution (precipitation)



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

**TABLE 1.** Dependences of the temperature of dissolution (precipitation) of carbides and the content of alloying elements in primary carbides on the content of alloying elements in the alloy.

| Alloying element | Dissolution (precipitation) temperatures of carbides, °C | The amount of carbides ($V$) and the content of elements in carbide ($C$), % wt. |
|---|---|---|
| C | $t_\text{L}^\text{MC} = 1818.18(C)^2 - 188.18(C) + 1299$ | $V_\text{MC} = 8.8758(C) - 0.0013$ |
| Ta | $t_\text{L}^\text{MC} = 1.672(C_\text{Ta})^2 - 15.173(C_\text{Ta}) + 1349.8$ | $C_\text{Ta} = -0.7427(C_\text{Ta} \text{ in alloy})^2 + 15.668(C_\text{Ta} \text{ in alloy}) + 0.189;$ $C_\text{Ti} = 57.135e^{-0.182}(C_\text{Ta} \text{ in alloy});$ $C_\text{W} = 32.103e^{-0.35}(C_\text{Ta} \text{ in alloy})$ |
| Ti | $t_\text{L}^\text{MC} = 0.7677(C_\text{Ti})^3 - 6.7459(C_\text{Ti})^2 + 10.757(C_\text{Ti}) + 1342$ | $C_\text{Ta} = 1.3478(C_\text{Ti} \text{ in alloy})^2 - 14.527(C_\text{Ti} \text{ in alloy}) + 89,293;$ $C_\text{Ti} = -0.6788(C_\text{Ti} \text{ in alloy})^2 + 8.8497(C_\text{Ti} \text{ in alloy}) + 2,6473;$ $C_\text{W} = -0.4277(C_\text{Ti} \text{ in alloy})^2 + 3.4424(C_\text{Ti} \text{ in alloy}) + 1.7964$ |
| Hf | $t_\text{L}^\text{MC} = -6.6371(C_\text{Hf}) + 1325.2$ | $C_\text{Hf} = 24.526\ln(C_\text{Hf} \text{ in alloy}) + 68.343;$ $C_\text{Ta} = -14.96\ln(C_\text{Hf} \text{ in alloy}) + 19.696;$ $C_\text{Ti} = 1.8744(C_\text{Hf} \text{ in alloy})^{-1.111}$ |
| Nb | $t_\text{L}^\text{MC} = 5.8807(C_\text{Nb})^2 - 23.849(C_\text{Nb}) + 1329.7$ | $C_\text{Ta} = -0.8811(C_\text{Nb} \text{ in alloy})^2 - 0.6181(C_\text{Nb} \text{ in alloy}) + 52.036;$ $C_\text{Ti} = 0.7664(C_\text{Nb} \text{ in alloy})^2 - 7.5143(C_\text{Nb} \text{ in alloy}) + 28.911;$ $C_\text{Nb} = -0.5051(C_\text{Nb} \text{ in alloy})^2 + 12.876(C_\text{Nb} \text{ in alloy}) - 0.7022$ |

of MC carbides and the amount of MC carbides on the carbon content have a complex character (Fig. 1) and are optimally described by dependencies (Table 1).

Thermodynamic modelling showed the dependence of the temperature of the carbide liquidus on titanium alloying (Fig. 2). An extremum is observed at 5% Ti in the alloy. This is associated with 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 up to 31% (Table 1). At the same time, the tantalum content in the carbide decreases to the level of 50%.

An increase in the tantalum content in the alloy leads to the appearance of an extremum of temperatures of the carbide liquidus at Ta content of 7% in the alloy, which is associated with the formation of the σ-phase in the alloy (Fig. 3, *a*). When tantalum is added into the alloy, a change in the base of MC carbides from titanium to tantalum is observed (Fig. 3, *b*). The transition of MC carbide to tantalum-based carbide leads
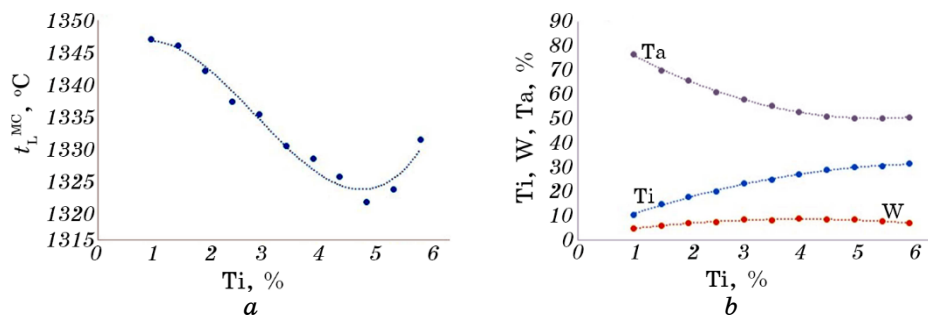
**Fig. 2.** Temperature dependence of the dissolution of carbides of the MC type (*a*); the amount of tantalum, titanium, and tungsten in the MC carbide (*b*) versus the titanium content in the alloy.

to an increase in interatomic bonds, which contributes to an increase in the temperature of dissolution (precipitation) of carbide (Fig. 3, *a*). At the same time a decrease in the indicated dependences (Table 1) is observed in the content of titanium and tungsten.

It was found that hafnium decreases the temperature of dissolution (precipitation) of primary carbides (Fig. 4), which is described by a linear relationship (Table 1). When the content of hafnium is more than 0.1%, the morphology of the carbide changes. Ti-based carbide is converted to Hf-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.

Niobium has an ambiguous effect on the temperatures of carbide formation (Fig. 5), decreasing to a concentration of 2% and increasing at a higher content. The minimum on the dependence of the carbide liquidus disappears with an increase in niobium in carbide to 22% and a predominance of titanium in MC. With an increase in the concentration of
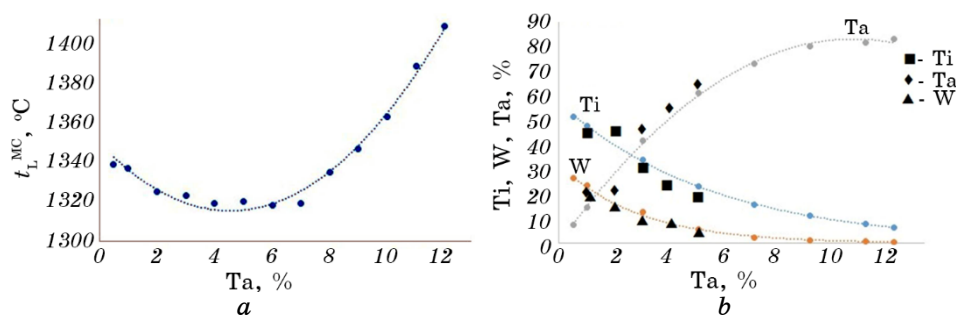


**Fig. 3.** Temperature dependence of the dissolution of MC type carbides (*a*) and the amount of tantalum, titanium and tungsten in MC carbide (*b*) on the tantalum content in the alloy (■, ▲, ♦ —points obtained experimentally (Table 2)).

**TABLE 2.** Changes in the compositions of primary carbides depending on the tantalum content in the alloy of the Ni–11.5Cr–5Co–3.6Al–4.5Ti–7W–0.8Mo–0.06C system.

| Method of obtaining results | Element content, % by weight | | | | | | |
|---|---|---|---|---|---|---|---|
| | Ti | Ta | Cr | Co | Mo | W | C |
| 0% Ta | | | | | | | |
| Calculated | 55.66 | – | 0.6 | – | 0.14 | 28.69 | 14.92 |
| Experimental | 57.7 | – | 0.28 | 0.3 | 3.5 | 23.3 | 14.92 |
| 1% Ta | | | | | | | |
| Calculated | 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 |
| 2% Ta | | | | | | | |
| Calculated | 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 |
| 3% Ta | | | | | | | |
| Calculated | 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 |
| 4% Ta | | | | | | | |
| Calculated | 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 |
| 5% Ta | | | | | | | |
| Calculated | 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 |

niobium over 3.5% carbide is formed the base of which is dominated by niobium. This leads to changes in the forces of interatomic bonds and an increase in the temperature of dissolution (precipitation) of carbide.

The results of calculating the phase composition obtained according to the dependences (Table 1) were further compared with the experimental data obtained using electron microscopy in the microprobe mode on a scanning electron microscope REM-106I. Figure 6 shows the typical morphology of carbides depending on the amount of tantalum in the alloy. It was found that carbides are precipitated 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. 6).

The chemical composition of carbides was determined experimentally by x-ray spectral microanalysis with the help of which the intensity of x-ray radiation was recorded depending on the energy (keV). It was found experimentally that the composition of carbides includes titanium, tantalum, tungsten, molybdenum, cobalt, and chromium in the
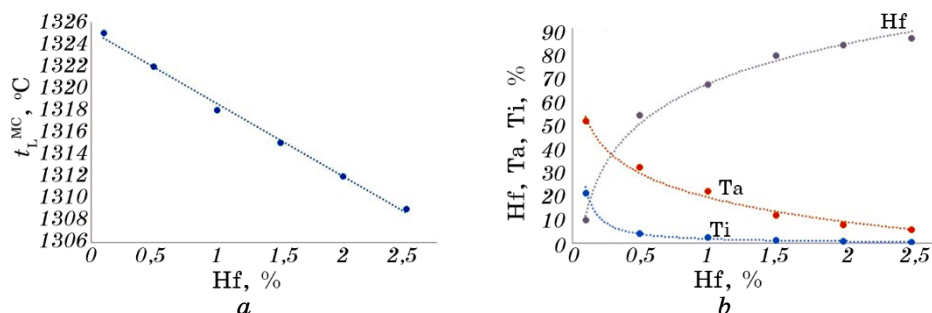
**Fig. 4.** Temperature dependence of the dissolution of MC carbides (*a*) and the amount of tantalum, titanium and hafnium in MC carbide (*b*) on the content of hafnium in the alloy composition.

following ratios with the calculated values (Table 2). The errors in determining the elements by this method did not exceed ±1% by weight.

Table 2 shows that the calculated and experimental data are in good agreement with each other for almost all elements. It was found that when the alloy contains 4% Ta, the carbide base changes from titanium to tantalum (the tantalum concentration in the carbide exceeds 50%). A decrease in the amount of tungsten in the carbide is less than 10% and an increase in chromium and molybdenum up to 1%, which is explained as the interchangeability of these elements in the crystal lattices. An increase in tantalum to 5% in the alloy increases its concentration in the carbide by more than 60% and reduces the titanium to below 20%. Such a distribution of elements in carbides can be associated with the properties of the material, in particular, in the work [31] it is indicated that the alloy obtains optimal properties with the introduction of 4% Ta. This is explained not only by a change in the carbide composition, but also by the occurrence of other structural transformations in the alloy.

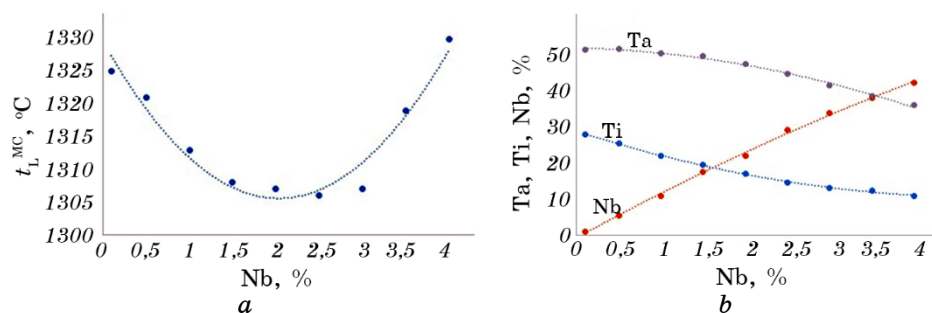Thus, the calculated data obtained by the CALPHAD method for



**Fig.5.** Temperature dependence of the dissolution of carbides of the MC type (*a*) and the amount of tantalum, titanium and niobium in the MC carbide (*b*) on the content of niobium in the alloy composition.
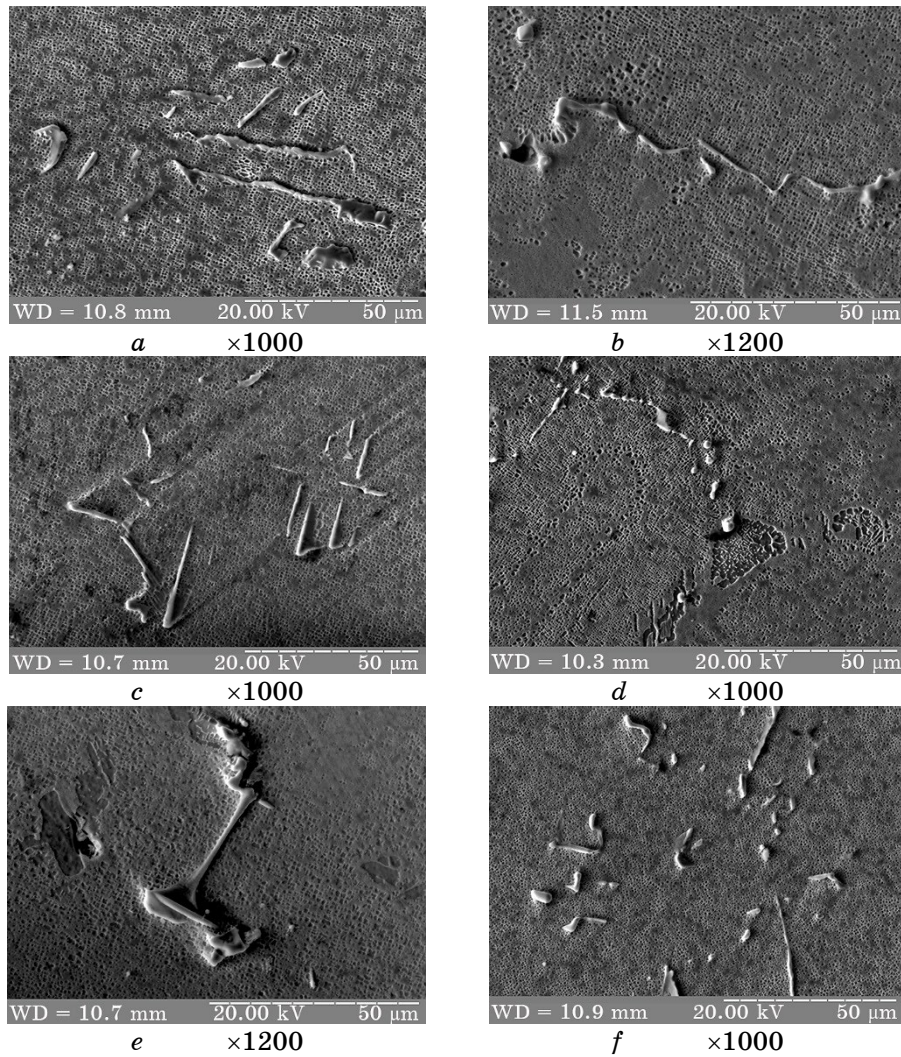
**Fig. 6.** Typical morphology of carbides in the alloy structure of the Ni−11.5Cr−5Co−3.6Al−4.5Ti−7W−0.8Mo−0.06C system: *a*—0% Ta; *b*—1% Ta; *c*—2% Ta; *d*—3% Ta; *e*—4% Ta; *f*—5% Ta.

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

## 4. CONCLUSIONS

Based on an integrated approach for the multicomponent system Ni−

11.5Cr−5Co−3.6Al−4.5Ti−7W−4Ta−0.8Mo−0.06C new regression models have been obtained, that make it possible to adequately predict the chemical composition of carbides from the chemical composition of the alloy.

1. Dependences of the influence of alloying elements on the temperature of dissolution (precipitation) of carbides were established. It was shown that the temperature dependences vary with the element content and closely correlate with the thermodynamic processes occurring in the system, that is, the curves exhibit extrema accompanying a change in the stoichiometry of carbides or the precipitation of new phases.

2. It was found that with an increase in the concentration of titanium over 5% and tantalum over 7%, the σ-phase is formed in the alloy, which reduces the mechanical properties. Hafnium content of more than 0.1% leads to a change in the carbide base from titanium to hafnium, which reduces the temperature of carbide formation (dissolution). The introduction of niobium of about 2% reduces the temperature of formation (dissolution) of carbides to a minimum. However, when the concentration of niobium in the carbide is more than 20%, the carbide liquidus begins to increase.

3. A comparative assessment of the calculated results obtained by the CALPHAD method and the experimental data obtained by the x-ray spectroscopy method has been carried out. The results obtained for determining the type and chemical composition of carbides are consistent with each other.

4. The optimal content of tantalum in this system has been determined, which should be from 4% to 7%. Introducing tantalum in an amount of less than 4% is impractical due to the fact that titanium remains in the carbides as a base and more than 7% due to the formation of the σ-phase and a decrease in the properties of the alloy.

## ACKNOWLEDGEMENTS

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