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RESEARCH PAPER

# MODELING OF CARBIDE FORMATION IN ALLOY OF THE Ni-Cr-Co-W-Mo-Al-Ti-C SYSTEM

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## ABSTRACT

Theoretical modeling of thermodynamic processes of separation of carbide phases was carried out, as well as a practical study of the structure and distribution of chemical elements in carbides. Based on an integrated approach for the Ni-Cr-Co-W-Mo-Al-Ti-C system, new regression models were obtained that make it possible to predict the chemical composition of carbides based on the chemical composition of the alloy. The relationships between the chemical composition of the alloy and the chemical composition of the phases have been established. 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:** nickel-based superalloy, carbides, distribution alloying elements, TCP- phase.

## INTRODUCTION

The required level of physical, mechanical and operational properties of modern heat-resistant nickel alloys is ensured by a rather complex alloying system [1-8]. Quite effective ways to improve the complex properties of existing alloys are known, such as modification and other technological methods for improving the structure and quality indicators of the material of finished products [9–16]. However, it is possible to influence the properties by changing the chemical composition of the structural components without significantly changing the composition of the alloy. For example, it has been shown that changes in the chemical composition of carbides lead to changes in their shape, size and dissolution temperature [17-19]. In turn, this leads to an increase in the performance properties of the experimental compositions.

The purpose of this work is to study the specific influence of alloying elements on the formation of carbides in the structure, their shape and the possibility of isolating TCP- phases for a system of the Ni-Cr-Co-W-Mo-Al-Ti-C type using the CALPHAD calculation prediction method in comparison with data obtained by scanning electron microscopy.

## MATERIAL AND METHODS

Modeling of thermodynamic processes of phase formation was carried out for the Ni-Cr-Co-W-Mo-Al-Ti-C system in which each element was changed step by step within the limits given in **Table 1**. In a multicomponent alloying system, the range of varying elements was chosen for reasons of maximum and the minimum amount of element introduced into the nickel-based superalloy. 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 variations in the content of chemical elements in the Ni-Cr-Co-W-Mo-Al-Ti-C system

| Element content, % by weight | | | | | | |
|---|---|---|---|---|---|---|
| C | Cr | Co | Al | Ti | Mo | W |
| 0.01-0.2 | 1.0-35.0 | 0.5-19.0 | 0.5-6.25 | 1.0-6.0 | 0.1-6.0 | 1.0-16.0 |

Process modeling allows for computational prediction and comparative assessment of the influence of alloying elements on the composition of carbides of different types, 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 likely allocation of the amount and type of carbides in the structure, as well as their chemical composition after modeling the crystallization process. The obtained dependencies have fairly high coefficients of determination $R^2 \geq 0.9$ and can be used for predictive calculations.

The composition of carbides 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 alloy structure's morphology and chemical composition of precipitated carbides. To test the theoretical dependencies, the industrial alloy ZhS3DK (**Table 2**) was chosen, which belongs to the system under study.

**Table 2** Chemical composition of ZhS3DK alloy

| Element content, % by weight | | | | | | |
|---|---|---|---|---|---|---|
| C | Cr | Co | Al | Ti | Mo | W |
| 0.1 | 11.7 | 9.0 | 4.4 | 2.9 | 4.2 | 4.2 |

The conversion of qualitative values into quantitative analysis was carried out automatically using the device program. The relative error of the method is ±0.1% (by mass).

## RESULTS AND DISCUSSION

In the Ni-Cr-Co-W-Mo-Al-Ti-C 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: γ - solid solution; carbides (type TiC, $M_{23}C_6$); eutectic γ+γ′; type γ′ intermetallic compound based on ($Ni_3Al$). It has been established that primary carbides have a high decomposition temperature (1350...1450°C), which makes it possible to strengthen alloys at elevated operating temperatures. It has been established that the temperature of dissolution (separation) of MC carbides practically does not change depending on the carbon content (1300±50°C), as well as for carbides of the $M_{23}C_6$ type (1000±50°C). However, the number of carbides in the alloys of the system increases (**Fig. 1**).

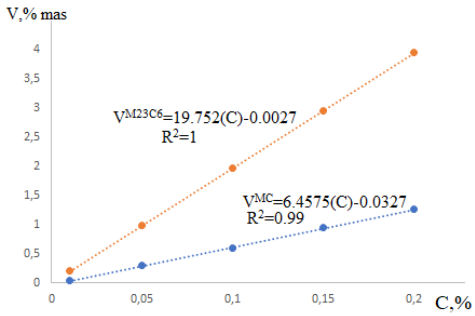



**Fig. 1** Dependence of the number of carbides on the carbon content in the alloy composition

When Ti is introduced into the alloy, in the above-mentioned limits, it leads to a change in the composition of MC carbides (**Fig. 2**) (an increase in the titanium content and a decrease in the amount of tungsten and molybdenum). An increase in the titanium content in the alloy by more than 4% leads to the precipitation of the P-phase, which is a TCP- phase and significantly reduces the performance properties of the alloys.

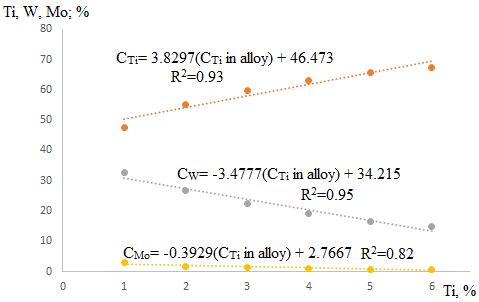



**Fig. 2** Dependence of the amount of titanium, tungsten and molybdenum in MC carbides on the titanium content in the alloy

Molybdenum has virtually no effect on the change in the chemical composition of carbides MC and $M_{23}C_6$. The introduction of more than 4% Mo into the alloy leads to the formation of M6C carbide, the basis of which is molybdenum, however, already at 6% Mo, the TCP- phase appears in the alloy (P-phase, which nucleates on this carbide), which reduces the performance properties.

Tungsten does not affect the dissolution (precipitation) temperature of MC and $M_{23}C_6$ carbides; it is at the level of 1340±10°C and 1050±10°C, respectively. An increase in the concentration of tungsten in the alloy leads to a change in the content of alloying elements in MC carbides (**Fig. 3**). In this case, the concentration of titanium in the carbide decreases, and tungsten increases. However, already at 5% W, $M_6C$ carbide (35% W, 27% Mo and other elements) is formed in the alloy, which can serve as a center for the formation of TCP- phases. The content of molybdenum and chromium in MC carbide is reduced to minimum values. Tungsten has virtually no effect on the chemical composition of $M_{23}C_6$ carbides.

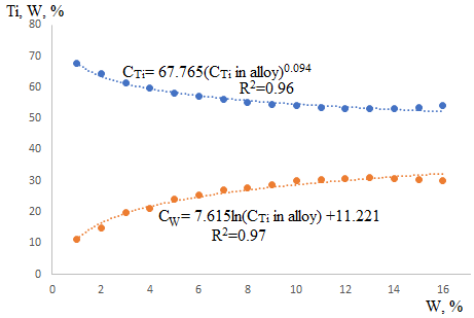



**Fig. 3** Dependence of the amount of titanium and tungsten in MC carbides on the tungsten content in the alloy

Chromium is an element that influences the formation of $M_{23}C_6$ carbides; on its basis, it has virtually no effect on the temperature of dissolution (precipitation) of carbides (1000±50°C). It was found that when the chromium concentration changes in this system, the following dependencies are observed (**Fig. 4**).

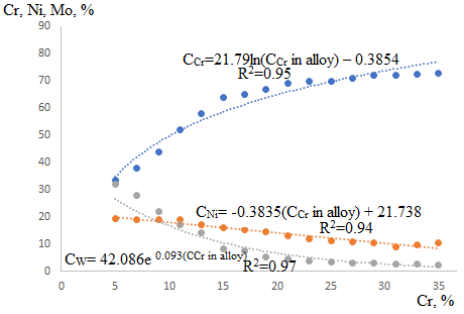
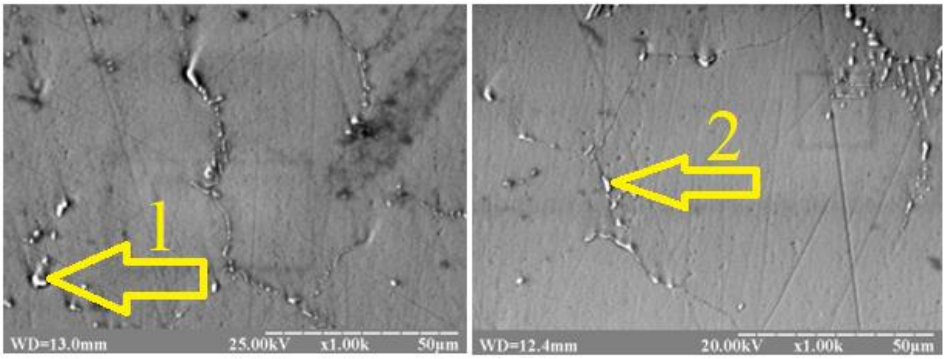



**Fig. 4** Dependence of the amount of chromium, nickel and tungsten in $M_{23}C_6$ carbides on the chromium content in the alloy

Up to 5% chromium concentration, the presence of carbides of the MC and $M_6C$ types is observed in the alloy, however, when the concentration exceeds 5% Cr, carbide $M_{23}C_6$ is formed. The introduction of more than 10% chromium leads to the disappearance of $M_6C$ carbide and the formation of three TCP phases (P, σ and μ-phases) at 15% Cr, which will significantly reduce the performance properties of the alloy. The cessation of chromium dissolution in the system is observed at a concentration of 25% Cr, which leads to the formation of α - a chromium-based solid

solution and an even greater decrease in the properties of the alloy.

The results of the calculation of the phase and chemical composition, according to the obtained dependencies, were subsequently compared with experimental data obtained using electron microscopy in microprobing mode on a scanning electron microscope, REM-106I. The morphology of carbides in the structure of the ZhS3DK alloy (which belongs to the system under study) is presented in **Fig. 5**. Carbides of the $M_{23}C_6$ type are located along the grain boundaries in the form of separate blocks and plates; carbides of the MC type in this alloy are present in block form and they are located inside the grains.




a ×1000 b ×1000

**Fig. 5**. Morphology of carbides in the structure of the ZhS3DK alloy and points of chemical analysis

The chemical composition of carbides was determined experimentally by the method of X-ray spectral microanalysis, with the help of which the intensity of X-ray radiation was recorded depending on the energy kEv. It has been experimentally established that the composition of carbides includes titanium, tungsten, molybdenum, nickel and chromium in the following proportions in comparison with the calculated values (**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 and molybdenum in MC carbide and chromium and nickel in $M_{23}C_6$ carbide are observed. Such values may be caused by an increased content of these elements in the alloy, segregation processes, or instrument errors. Thus, the calculated data for determining the type and chemical composition of carbides showed good convergence and agreement with experimental data obtained by electron microscopy.

**Table 3** Chemical composition of carbides calculated from the obtained dependences and obtained experimentally by X-ray spectral microanalysis at 20°C

| Method of obtaining results | Element content, % wt. | | | | | | |
|---|---|---|---|---|---|---|---|
| | Ti | W | Mo | Cr | Ni | Co | C |
| Estimated composition MC | 58.65 | 23.63 | 1.28 | 0.83 | - | - | 15.68 |
| Estimated composition $M_{23}C_6$ | - | 1.5 | 18.38 | 57.36 | 13.43 | 4.3 | 5.03 |
| Experimental composition MC (Fig. 5, point 1) | 56.4 | 25.6 | 2.76 | 0.6 | - | - | 15.6 |
| Experimental composition $M_{23}C_6$ (Fig.5, point 2) | - | 0.9 | 17.6 | 58.9 | 14.7 | 3.1 | 5,05 |

## CONCLUSIONS

1. Based on an integrated approach for the Ni-Cr-Co-W-Mo-Al-Ti-C system, new regression models have been obtained that make it possible to adequately predict the chemical composition of carbides 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 a change in the stoichiometry of carbides or the precipitation of new phases.

2. It has been established that when the concentration of titanium increases to more than 4%, molybdenum to more than 6% and chromium to 15%, the formation of TCP- phases (P, σ and μ-phases) is possible, which reduces the performance properties of the alloy. Also, when more than 25% chromium is introduced, a chromium-based solid solution is formed in the alloy, which reduces the properties of the alloy (mechanical and corrosion).

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 gave good convergence and can be proposed for predicting structural components both in industrial alloys and in the development of new materials.

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