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Modelling the composition of carbides in nickel-based superalloys of directional crystallization

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ABSTRACT

Purpose: The specifics of the influence of alloying elements on the chemical composition of various types of carbides, their topology and morphology for a multicomponent system of the type Ni-5Cr-9Co-6Al-1Ti-11.7W-1.1Mo-1.6Nb-0.15C using the calculation method CALPHAD. It is shown that the obtained dependences closely correlate with thermodynamic processes occurring in the system.

Design/methodology/approach: This work presents the results of studies of the distribution of chemical elements in the composition of carbides, depending on their content in the system.

Findings: It was found that the influence of alloying elements on the composition of carbides is complex and is described by complex.

Research limitations/implications: An essential problem is the prediction of the structure and properties of heat-resistant alloys without or with a minimum number of experiments.

Practical implications: The obtained dependences can be used both for designing new heat-resistant alloys and for improving the compositions of industrial alloys.

Originality/value: The value of this work is that the obtained dependences of the influence of alloying elements on the dissolution (precipitation) temperatures and the distribution of elements in carbides in the alloy of the Ni-5Cr-9Co-6Al-1Ti-11.7W-1.1Mo-1.6Nb-0.15C.

Keywords: Nickel-based superalloys of directional solidification, Alloying system, CALPHAD method, Structure, Composition of carbides

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MATERIALS

1. Introduction

Numerous studies and statistical data on aircraft breakdowns due to engine failure have shown that the main reason for the destruction of the blades of gas turbine engines (the most loaded engine parts) is their rupture along grain boundaries oriented perpendicular to the main tensile stresses from centrifugal forces. This served as an impetus for the development of directional crystallization technology, which ensures the production of blades with a columnar structure, the grain boundaries of which are oriented parallel to the main axis of the blade. The blades with a columnar structure have a longer service life on the engine, in contrast to blades with an equiaxial structure. Nickel-based superalloys are used for the manufacture of directional solidification rotor blades. The main phases of such alloys are a solid solution based on nickel and a strengthening phase based on the Ni_3Al intermetallic compound with a superstructure of the $L1_2$ type (γ'-phase); in addition, there are carbides of the MeC, $Me_{23}C_6$, and M_6C types, which are precipitated at the boundaries and within grains in the form of dispersed inclusions [1,2].

The role of carbides is very complex in nickel-based superalloys. They affect mechanical properties depending on their morphology and distribution. Fine blocky particles at the grain boundary can have a reinforcing effect, inhibiting the sliding of the boundaries, thereby improving creep and tensile strength. On the other hand, if they are present in the form of continuous films at the grain boundaries, they have a detrimental effect on the plasticity [3,4].

The objective 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 multi-component system such as Ni-5Cr-9Co-6Al-1Ti-11.7W-1.1Mo-1.6Nb-0.15C using the calculated prediction method CALPHAD.

2. Materials and test methods

Modelling of thermodynamic processes occurring during crystallization (cooling) or heating in the structure of alloys was carried out by the CALPHAD method [5].

In the multicomponent alloying system (Ni-5Cr-9Co-6Al-1Ti-11.7W-1.1Mo-1.6Nb-0.15C), which corresponded to the average composition of the ZhS-26VI alloy, the range of variation of the elements was chosen for reasons of maximum and the minimum amount of an element introduced into superalloys. Thus, for the study, carbide-forming elements were selected in the following alloying ranges: carbon (0.02-0.2)%, titanium (1-6)%, niobium (0.1-4)%, molybdenum (1-6) %; tungsten (1-16)% by weight.

The obtained values were processed in the Microsoft Office software package in the EXCEL package by the least squares method with obtaining correlation dependences of the "parameter-property" type and obtaining trend lines with mathematical equations of regression models that optimally describe these dependences. The obtained dependences have sufficiently high coefficients of determination $R^2 \geq 0.85$ and can be used for predictive calculations of the indicated characteristics with a relative error of ± 3.9%.

3. Influence of elements on the phase composition of the composition

The study of phase precipitation during the crystallization of the investigated alloy in the temperature range (1600-20°C) showed that the most probable for the ZhS-26VI alloy is the precipitation of the main phases in the following order: carbides of the MC type; γ - solid solution; eutectic γ + γ'; intermetallic compounds of the γ'-phase type based on (Ni_3Al); carbides of the M_6C type.

It is known [1,6,7] that MC carbides are formed in the process of crystallization (solidification) in the form of discrete particles in the intergrain and intragranular space, as well as in the interdendritic regions. Carbides of the MC type are formed in a liquid due to strong segregation of carbon, when its amount is higher than 0.05%, as well as at temperatures slightly below the solidification temperature of the alloy. In carbide reactions in alloys, they serve as the main source of carbon. In order of decreasing stability in superalloys, carbides are arranged in the series HfC, TaC, NbC, TiC. Carbides of this type are very stable at low temperatures, but at higher temperatures tend to be converted (degraded) into different types of secondary carbides. Carbides of the M_6C type are formed at temperatures of 815-980°C in alloys with a higher content of refractory elements of tungsten and molybdenum. Mostly they stand out along the grain boundaries. Compared with carbides of the $M_{23}C_6$ type, M_6C carbides are more stable at high temperatures [8]. The formation of carbides M_6C and $M_{23}C_6$ occurs according to the well-known reaction:

$MC + \gamma \rightarrow M_6C + \gamma'$; [8]

Figure 1a,b shows that in the structure the volume fraction of both primary MC carbides and secondary M_6C carbides depends on the carbon content in the alloy composition and is optimally described by linear and parabolic functions (Tab. 1). It is shown that with an increase in the carbon content in the alloy, the volumetric amount of carbides of both types' increases. However, upon reaching a concentration of 0.12% C, the amount of secondary carbide decreases, which is explained by the lack of carbon for the simultaneous formation of two types of carbides. At the same time, it is shown in (Fig. 1c) that the effect of carbon on the temperature t_L^{MC} of dissolution (precipitation) of MC carbides has a rather complex character and is optimally described by a quadratic polynomial (Tab. 1). The effect of carbon on the temperature of dissolution (precipitation) of secondary carbide M_6C is described by a directly proportional relationship (Fig. 1d)

Table 1.
Polynomial dependences of the temperature of dissolution (precipitation) of carbides and the content of alloying elements in carbides on the content of alloying elements in the alloy

Alloying element	Dissolution (precipitation) temperatures of carbides, °C	Content of elements in carbide, wt.%
C	t_L^{MC},°C =8.2576(C)-0.0513 t_L^{M6C},°C=-300.28(C,)^2 +86.296(C)-0.6652	V_{MC} = -511.36(C)^2+ 217.95(C)+1350.5 V_{M6C} = 77.879 (C)+1163.7
Ti	t_L^{MC},°C = 80.491·(C_{Ti})+1268.8; t_L^{M6C},°C=-8.7956 (C_{Ti})^3 + 73.727(C_{Ti})^2-180.3(C_{Ti}) +1294.6	**carbides MC**: C_{Ti}=-1.0679(C_{Ti} in alloy)^2 +12.85(C_{Ti}in alloy +8.9873; C_{Nb}=2.1679(C_{Ti} in alloy)^2 -21.36(C_{Ti}in alloy +67.653; C_W=-1.048(C_{Ti} in alloy)^2 +8.2623(C_{Ti} in alloy)+8.6829
Nb	t_L^{MC},°C = 1.2382·(C_{Nb})^2-8.3294·(C_{Nb})+1381; t_L^{M6C} ,°C =-0.907 (C_{Nb})^2 -3.7649(C_{Nb}) + 1182.6	**carbides MC**: C_{Nb}=-5.3041(C_{Nb} in alloy)^2 +42.301(C_{Nb} in alloy)+6.8364; C_{Ti}=1.5703(C_{Nb} in alloy)^2 -14.836(C_{Nb} in alloy)+40.095; C_W=3.9361(C_{Nb} in alloy)^2 -27.475(C_{Nb} in alloy)+51.534
Mo	t_L^{MC},°C = -0.8252·(C_{Mo})^2+ 0.2308·(C_{Mo})+1371.5; t_L^{M6C} ,°C = -10.163 (C_{Mo})^2 +114.4(C_{Mo}) + 1052.3	**carbides M_6C**: C_{Mo}= 4.7305(C_{Mo} in alloy)+ 3.7976; C_W= -4.3064(C_{Mo}in alloy)+ 64.09
W	t_L^{M6C} ,°C = 49.214(C_W) + 595.07	**carbides MC**: C_{Nb}= 0.2444(C_W in alloy)^2 -4.2089(C_W in alloy)+65.006; C_W=-0.1951(C_W in alloy)^2 3.9132(C_W in alloy)-3.1815; **carbides M_6C**: C_{Mo}= -0.7443(C_W in alloy)+ 16.973; C_W= 1.3639($C_W$in alloy)+ 45.03

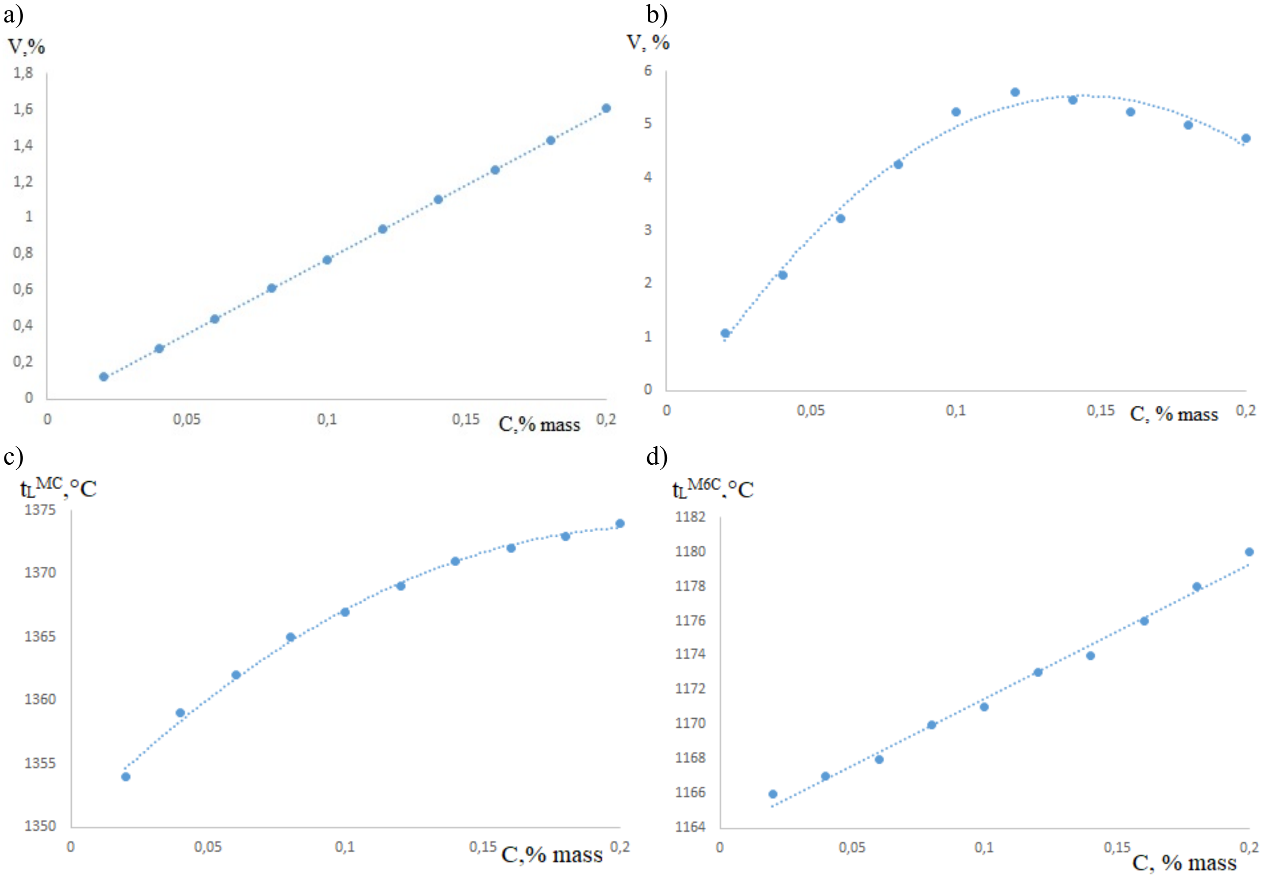

Fig. 1. Change in the amount of carbides of type MC (a), M_6C (b) and the temperature of dissolution of carbide MC (c), M_6C (d) as a function of carbon content in the alloy

It is known [2,9,10] that titanium is contained in the majority of superalloys. Titanium is present not only in the composition of the strengthening γ'-phase, but is also a strong carbide-forming element, on the basis of which MC carbides are formed. In the alloying system under study, the primary niobium-based carbide also contains elements such as titanium, tungsten, molybdenum, and chromium. It was found that titanium affects not only the temperature of dissolution (precipitation) of the primary carbide MC, but also the analogous temperature of formation of the secondary carbide M_6C (Fig. 2). It was found that the dependencies are complex and are optimally described by linear and cubic polynomials (Tab. 1).

It was found that with an increase in the titanium content in the alloy, its concentration in the MC carbide also increases to 48.53 by weight (Fig. 1c), which is optimally described by a parabolic function (Tab. 1). At the same time, the tungsten content in carbide increases within (15.5-20)%, while molybdenum and chromium decreases within (1.45-0.5)% and (1.14-0.48)% by weight, respectively. The niobium content in carbide decreases with increasing titanium from a concentration of 49.6 wt.%. up to 17.4 wt.%, which leads to the degeneration of the carbide MC. So, at a concentration of more than 2% by weight Ti in the alloy, in MC carbide, the titanium content prevails over the niobium content, which is indirectly manifested at the temperature of dissolution (precipitation) of the secondary carbide by a minimum. In turn, at a titanium concentration of 4.5% wt. In the alloy, P- and μ-phases are formed, which belong to topologically close-packed (TCP) phases, which cause a decrease in the temperature of dissolution (precipitation) of the secondary carbide (Fig. 2b).

A change in the titanium content in the alloy does not affect the chemical composition of the secondary carbide. The average content of alloying elements in M_6C carbide is at the level: 61.5W-15.6Ni-9Cr-7.7Mo-3.8Co-1.85C-0.55Nb.

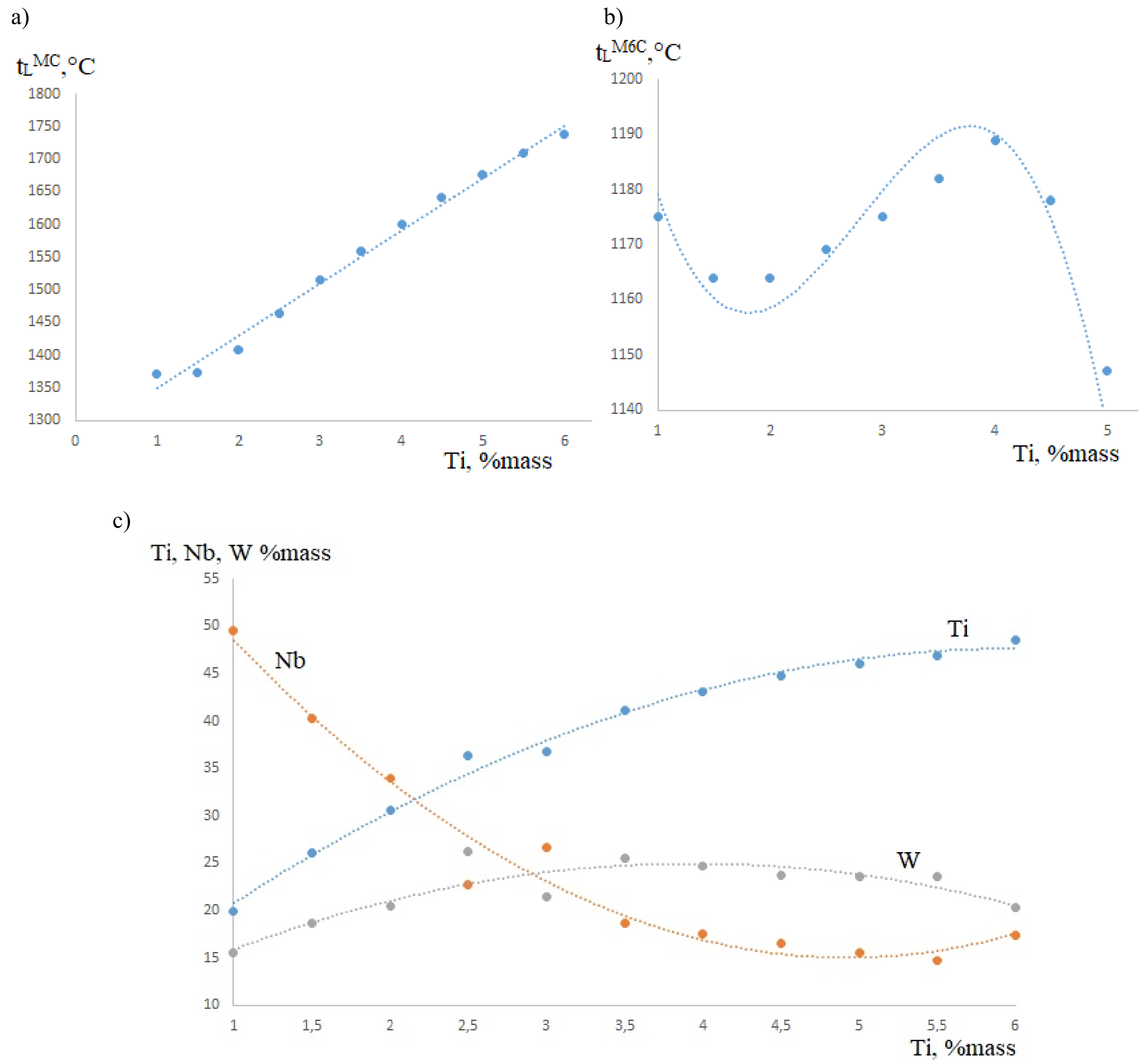

Fig. 2. Dependence of the temperature of dissolution (precipitation) of carbides of the type MC (a), M_6C (b) on the amount of titanium, tungsten and niobium in the primary carbide (c) on the content of titanium in the alloy

Niobium, as a strong carbide-forming element, with titanium forms primary MC carbide on a mixed basis [3,11,12]. Niobium affects the temperatures of carbide formation (Fig. 3a,b), lowering them according to parabolic dependences (Tab. 1), which is explained by changes in the interatomic bond forces in these precipitates.

It is shown in (Fig. 3c) that with an increase in the niobium content in the alloy above 1% by weight, its concentration in the primary carbide increases and exceeds the concentration of titanium and tungsten. Thus, the titanium content in MC carbide decreases from 36.7 wt.%. up to 6.25 wt.%, and tungsten from 47wt.%. up to 3.75% by weight, which leads to the formation of niobium-based carbide.

A change in the niobium content in the alloy does not affect the chemical composition of the secondary carbide. The average content of alloying elements in M_6C is at the level: 61.8W-15.9Ni-7.9Cr-8.23Mo-3.8Co-1.85C-0.52Nb.

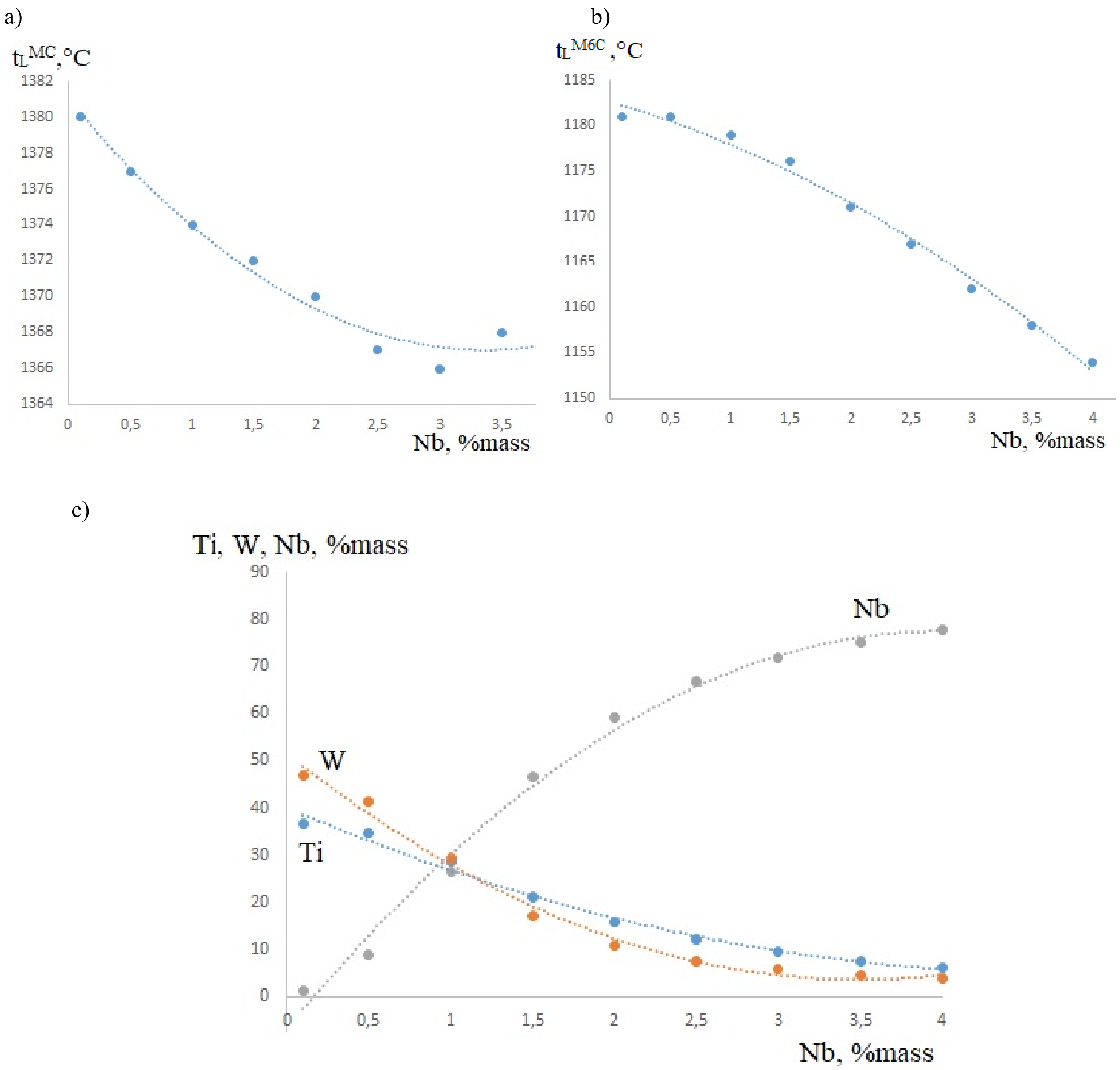

Fig. 3. The dependence of the temperature of dissolution of carbides MC (a),M_6C (b), the amount of titanium, tungsten and niobium in the primary carbide (c) of the niobium content in the alloy

Molybdenum, one of the elements that participates in the formation of secondary carbides and on its basis can form carbides of the M_6C[13-17] type, while molybdenum can be a part of the $M_{23}CS_6$ carbides. Since only M_6C carbides are formed in the investigated composition, the effect of molybdenum on them will be considered later. Figure 4 show that molybdenum has a complex effect on the temperature of dissolution (precipitation) of carbides. The temperature of dissolution (precipitation) of primary carbides decreases according to the parabolic dependence with an increase in the amount of molybdenum (Tab. 1), and for secondary carbides, an increase in temperature is observed according to the parabolic dependence. This behaviour is explained by a change in the strength of interatomic bonds in the secondary carbide, due to an increase in alloying with refractory molybdenum.

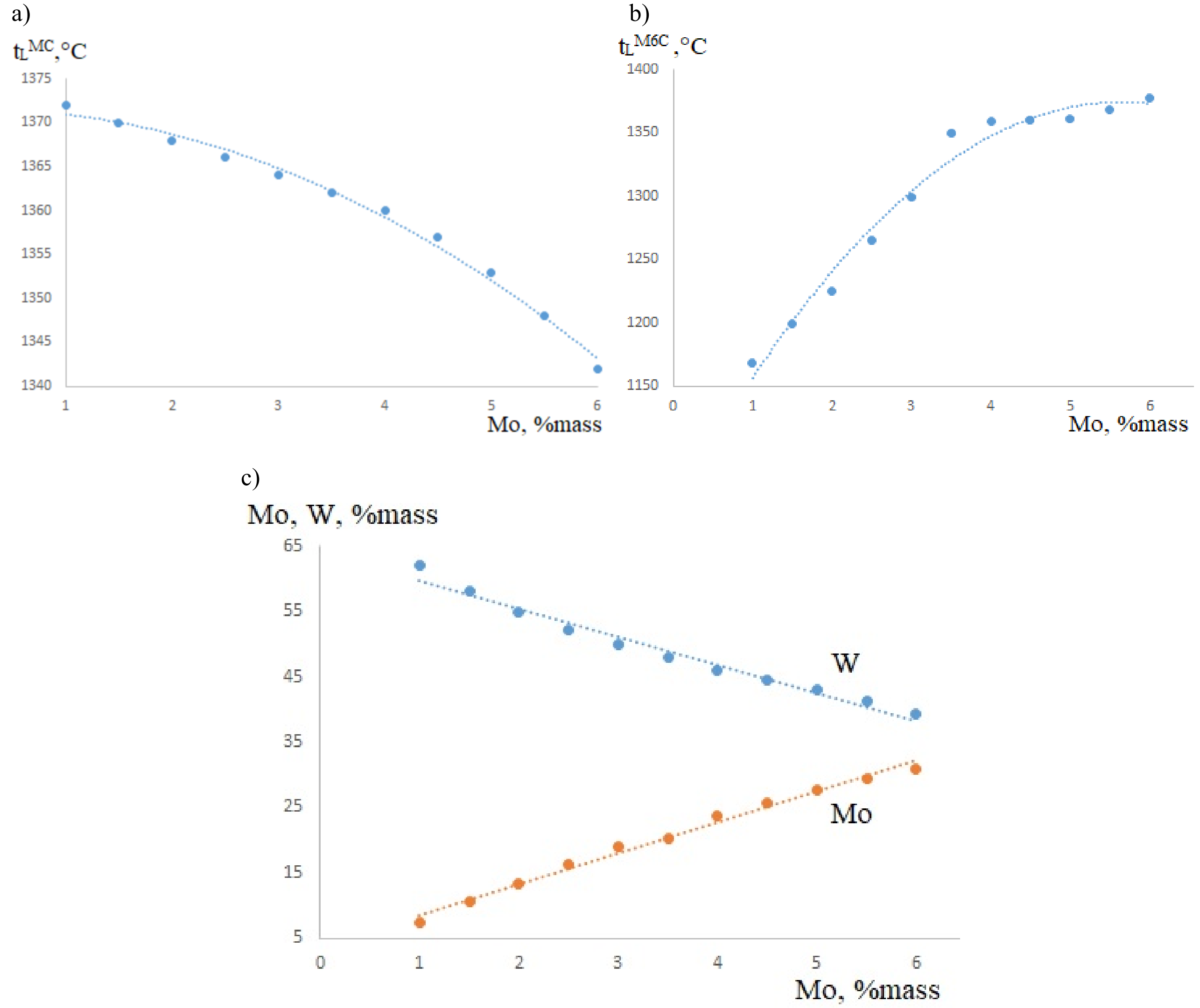

Fig. 4. The dependence of the temperature of dissolution of carbides MC (a),M_6C (b), the amount of tungsten and molybdenum in the secondary carbide (c) of the molybdenum content in the alloy

Molybdenum does not affect the chemical composition of the primary carbide, the average composition of which is at an average level of 46.7Nb-22.3Ti-15.3W-12.3C-2.6Mo-0.8Cr. However, when the content of molybdenum is more than 4%, the carbide degenerates. The composition of M6C carbide changes significantly with an increase in the amount of molybdenum in the alloy. In addition to the fact that the content of molybdenum in the carbide increases and the tungsten content decreases (Fig. 4c), the appearance of the μ-phase is observed at a concentration of more than 4%, which reduces the strength characteristics of the alloy.

Tungsten is introduced into the composition of heat-resistant alloys in order to increase the temperature level of phase transformations, and, consequently, the heat resistance of the alloy [18]. The tungsten content in superalloys is within a fairly wide range of 1-16% by weight. A further increase in the tungsten content significantly increases the probability of precipitation of phases in the TCP structure. Tungsten has practically no effect on the temperature of dissolution (formation) of MC carbide and has a linear effect on the temperature of dissolution (formation) of M_6C carbide (Fig. 5) (up to a concentration of 10% tungsten, M_6C carbide is not formed).

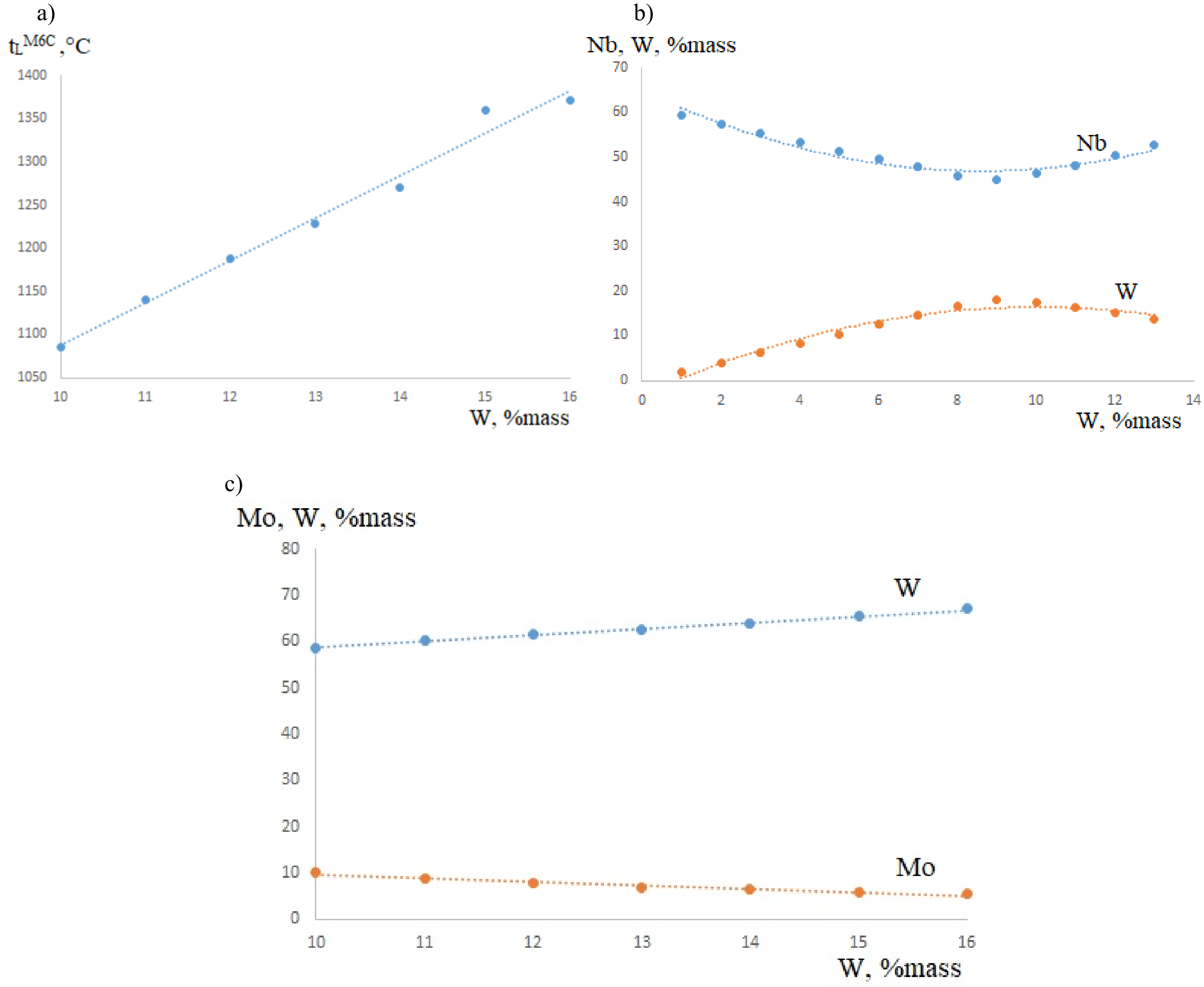

Fig. 5. The dependence of the temperature of dissolution of carbides M_6C (a), the amount of tungsten and niobium in the primary carbide (b), the amount of tungsten and molybdenum in the secondary carbide (c) of the tungsten content in the alloy

An increase in the concentration of tungsten in the alloy leads to a decrease in the concentration of niobium in MC carbide and a simultaneous increase in tungsten, which obeys the parabolic law (Tab. 1). The extreme on the curves (Fig. 5b) correspond to a concentration of 10% W, which is associated with the appearance of M_6C carbides in the structure. Upon reaching 13% W, the primary carbide degenerates.

The change in the concentration of alloying elements in the secondary carbide obeys a linear law (Tab. 1). In this case, the tungsten content increases by 10%, for molybdenum, nickel and chromium it decreases by 5%, 3%, and 2%, respectively. Thus, the secondary carbide approaches the tungsten-based monocarbide.

Typical morphology of primary carbides, which is most often found in the structure of alloys of this class in the form of blocks and hieroglyphs (Fig. 5a,b). Carbides of the M_6C type in this alloy are present in block form (Fig. 5c,d). The most preferable is the block type of secondary carbide precipitation, since in this case we have a lower level of stress concentration with the matrix.

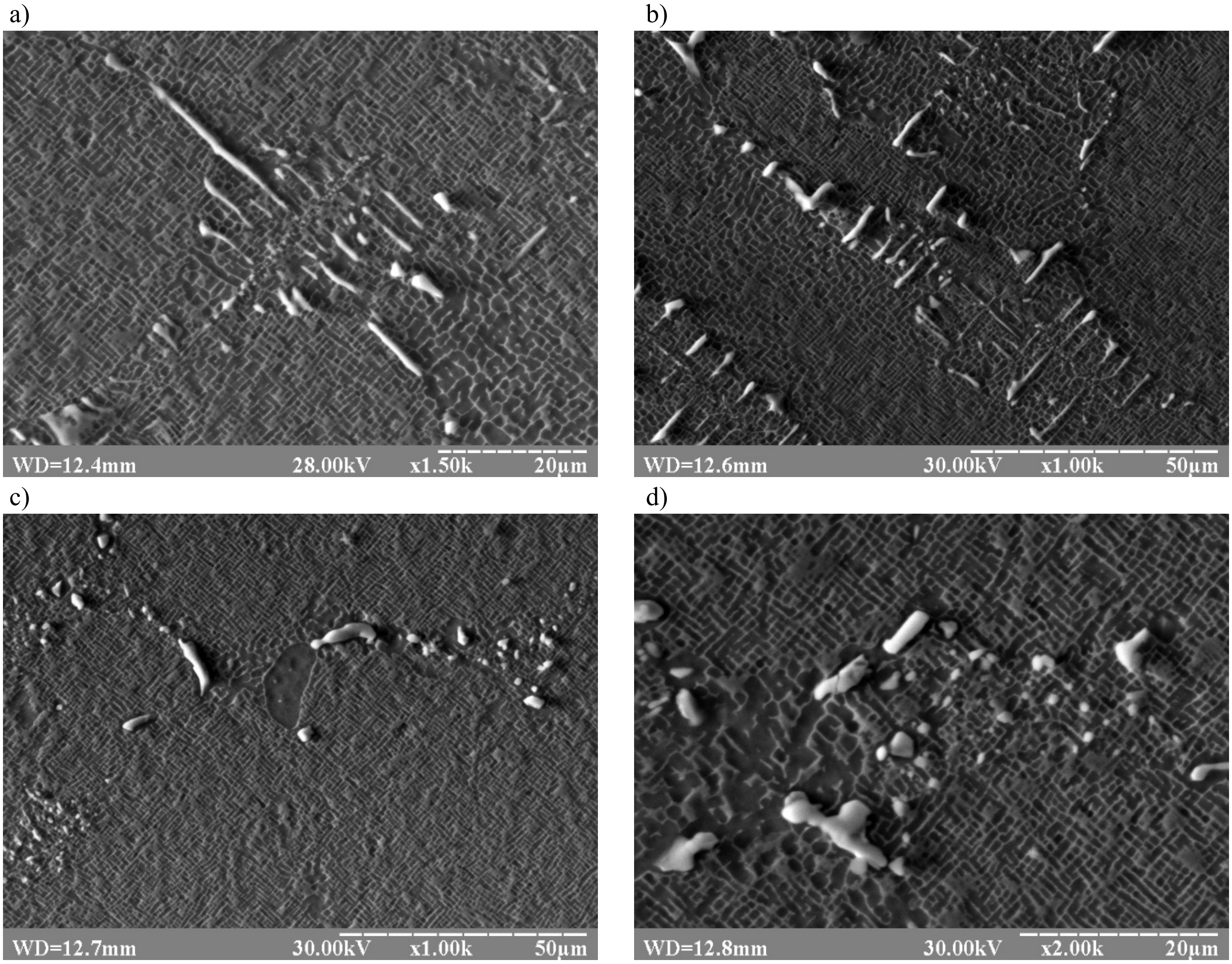

Fig. 5. Typical morphology carbides in the structure of superalloy ZhS 26

4. Conclusions

On the basis of an integrated approach, computational and experimental, for multicomponent superalloys, new regression models were obtained that allow to adequately predict the chemical composition of carbides by the chemical composition of the alloy, this made it possible to solve the problem of calculating the prediction of the composition of carbides by the chemical composition of the alloy, which was confirmed by the obtained experimental data.

Dependences of the influence of alloying elements on the temperature of dissolution (precipitation) of carbides in the alloy of the Ni-5Cr-9Co-6Al-1Ti-11.7W-1.1Mo-1.6Nb-0.15C system have been established. It is shown that changes in the course of the curves of the temperature dependence on the element content closely correlate with the thermodynamic processes occurring in the system, that is, the curves exhibit extrema accompanying the change in the stoichiometry of carbides or the precipitation of new phases.

It is shown that with an increase in the total concentration of carbide-forming elements, the chemical composition of carbides also becomes more complex. It was found that with an increase in the carbon content in the alloy, the volumetric amount of carbides increases. However, upon reaching a concentration of 0.12% C, the amount of secondary carbide decreases, which is explained by the lack of carbon for the simultaneous formation of two types of carbides. At a concentration of more than 2% wt. Ti in the alloy, in MC carbide, the titanium content prevails over the niobium content, which is indirectly manifested at the temperature of dissolution (precipitation) of the secondary carbide by a minimum. In turn, at a titanium concentration of 4.5% wt. In the alloy, P- and μ-phases are formed, which belong to TCP - phases, which causes a decrease in the temperature of dissolution (precipitation) of the secondary carbide. With an increase in the niobium content in the alloy above 1% by weight, its concentration in the primary carbide increases and exceeds the concentration of titanium and tungsten. An increase in the content of molybdenum over 4% is accompanied by the appearance of the μ-phase, which reduces the strength characteristics of the alloy. An increase in the concentration of tungsten in the alloy leads to a decrease in the concentration of niobium in the MC carbide and a simultaneous increase in tungsten. At 10% W, M_6C carbide is formed, and at 13% W, the primary carbide degenerates.

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