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# MATHEMATICAL MODELING OF MELTING TEMPERATURE RANGE AND PHASE COMPOSITION OF MULTICOMPONENT NICKEL ALLOYS

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**ABSTRACT**

Modern brazing filler metals for brazing high-temperature nickel alloys are complex alloys, where the components should provide the required level of strength, high-temperature resistance, high-temperature corrosion resistance and other service properties of brazed joints. However, establishing the optimum composition to obtain the desired set of properties is a non-trivial task, requiring considerable investment of time and money. The work is a study of applicability of the method of mathematical modeling of thermodynamic processes (CALPHAD) during development of multicomponent filler metals for brazing high-temperature nickel alloys. During performance of investigations, using CALPHAD computational procedure, melting temperature ranges were determined for a number of alloys of Ni–Cr–Co–Al–(Me)–Ta system. Calculated data were obtained on the influence of adhesion-active elements of groups IV and V of the periodic table on liquidus temperature and phase composition of the base nickel alloy. In particular, their impact on the quantity and thermal stability of γ′-phase and σ-phase was determined. Thermodynamic calculated data, obtained with application of mathematical modeling method, were used during development and investigation of a number of promising filler metals for brazing high-temperature nickel alloys, including single-crystal high-temperature nickel alloy ZhS-32VI.

**KEY WORDS:** brazing filler metal, brazing, high-temperature nickel alloys, mathematical modeling (CALPHAD), adhesion-active components, titanium, niobium, tantalum, γ′-phase, σ-phase

Service properties of gas-turbine engines and stationary units are largely determined by the properties of high-temperature nickel alloys (HTNA), which are the main material for turbine blade manufacture [1].

For a long time the required level of characteristics of casting HTNA was reached due to alloying of the nickel base by an ever greater number of components, the summary action of which had a positive influence on long-term strength, ductility, fatigue, oxidation resistance, etc. [1, 2]. Here, the empirical «trial and error» method had been the main method for a long time at development of high-temperature nickel alloys [3]. It is quite obvious, however, that in such a case, if more than 10–15 elements are used for alloying the nickel high-temperature alloys, it is rather difficult to find an optimum composition to obtain the sought complex of properties, as it requires considerable time and cost. In this connection, the methods of mathematical calculation and engineering of modern high-temperature alloys become a necessary tool [2–7].

The above-said is also valid at development of filler metals for brazing the high-temperature nickel alloys. As the modern nickel alloys may contain more than ten alloying elements, then the filler metals for their brazing, as a rule, are also complex alloys, which contain depressants and elements, ensuring the required strength, heat resistance, high-temperature corrosion resistance and other service properties of brazed joints [4, 8].

In a number of studies [6–11] it is noted that the modern programs of mathematical modeling of the thermodynamic processes are based on physical theories of thermal, diffusion and thermodynamic phenomena, which can adequately reflect the pattern of physicochemical processes taking place in multicomponent nickel systems, both at solidification (cooling), and at heating. The authors show that application of the calculation methods for thermodynamic processes allows plotting the constitutional diagrams for multicomponent systems in broad ranges of temperatures and concentrations, as well as calculating the type, volume fraction and composition of phases for equilibrium and nonequilibirum conditions of phase transformations.

In particular, the concept of CALPHAD method (CALculation of PHAse Diagrams) by prediction of stable phases, their composition, as well as thermodynamic properties in those areas of the phase diagram, where experimental data are absent, enables plotting the phase diagrams [12–14].

So, for Ni-based multicomponent alloys typical is a microstructure, which usually consists of solid solution (γ-matrix), dispersed particles of γ′-phase, carbides and topological close-packed phases (TCP). To determine the volume fraction of each of these phases, it is necessary to have an estimate of the energy Gibbs functions [3]. Thus, CALPHAD method combines all the exper-

imental data on phase equilibria in the system and all the thermodynamic data, obtained during performance of thermochemical and thermophysical investigations.

This is the most completely realized in JMatPro software package (Java-based Materials Properties) of Sente Software Company [15–19].

This software package is designed for modeling a wide range of properties of multicomponent systems on different base (Fe, Al, Ti, Ni, Co, etc.), contains specialized thermodynamic bases for modeling the processes of cooling (solidification) or heating of materials.

The objective of this study is determination of the possibility of prediction of the melting temperature range and phase composition of multicomponent nickel alloys by application of the methods of computational alloys design, namely the methods of computer thermodynamics (CALPHAD) in combination with the methods of statistical processing of the obtained results.

**Computational procedure.** For thermodynamic calculations of the melting range of the studied brazing filler metals, a special JMatPro program was used for modeling the properties of multicomponent steels and alloys. This software package allows performance of thermodynamic calculations for multicomponent systems, also on nickel base, with determination of the type, and volume fraction of the precipitating phases (γ-, γ′-, MC, $M_{23}C_6$, $M_6C$, $M_3B_2$, etc.), chemical composition of the phases and the temperature field of their existence.

Thermodynamic calculations are based on evaluation of energy Gibb's functions for each phase for the specified temperature [13]:

$$\Delta G = \Delta G_0 + \Delta G_i^m + \Delta G_i^{xs},$$

where $\Delta G_0$ is the phase free energy in its pure form; $\Delta G_i^m$ is the ideal energy from phase component mixing; $\Delta G_i^{xs}$ is the excess free energy from phase component mixing.

Free energy ($\Delta G_m$) for a multicomponent system can be represented by the following equation:

$$\Delta G_m = \sum_i x_i \Delta G_0^i + RT \sum_i x_i ln(x_i) + \\ + \sum_i \sum_{j \rangle i} x_i x_j \sum_v \Omega_v (x_i - x_j)^v,$$

where $x_i$ is the mole fraction of component $i$; $\Delta G_0^i$ is the free energy of the phase for pure component $i$; $T$ is the temperature; $R$ is the universal gas constant; $\Omega_v$ is the coefficient of interaction which depends on $v$ value (in practice, $v$ is usually not higher than 2) [13].

The base system for development of experimental filler metals for HTNA brazing was selected, allowing for the influence of each specific element on the properties of high-temperature nickel alloys. Ni–Cr–Co–Al– (Me) system is promising as a base. In view of the need to ensure the heat resistance, and high-temperature strength and to make the brazing filler metal composition close to that of the base metal, the base system alloys were additionally doped by tantalum, tungsten and molybdenum. Here, the limits of aluminium and tantalum content in experimental brazing filler metals were selected, proceeding from the considerations of ensuring the high-temperature strength of the alloy due to formation of the required volume fraction of the strengthening γ′-phase $Ni_3$ (Al, Ta, Ti). The content of niobium and titanium in the alloy was limited due to liquation susceptibility of these elements and local melting of interdendritic areas of the base material during brazing [2, 20].

**Discussion of the results.** During investigations a range of the values of liquidus and solidus temperatures was obtained, as well as the calculated phase composition of the experimental alloys. The calculated data were furtheron subjected to processing by statistical analysis methods, in order to plot the liquidus surfaces, which would allow assessment of the influence of the alloying elements on the melting temperature of the alloys of this system (Figure 1.)

So, for instance, it was determined that an increase of the quantity of tantalum from 2.5 to 10 wt.% in the base alloy allows lowering its liquidus temperature from 1371 to 1322 °C (Figure 2). The solidus temperature of the alloy here decreases from 1340 to 1261 °C. It is quite understandable that such a liquidus temperature is too high for the filler metal, which is designed for brazing the high-temperature nickel alloys.

Base metal alloying by zirconium almost does not change the liquidus temperature, but leads to a significant lowering of the solidus temperature — to 1060 °C (for an alloy with 2.5 wt.% Ta) and up to 991 °C (for an alloy with 10 wt.% Ta). Temperature lowering is related to formation of a low-temperature eutectic that contains zirconium and tantalum in its composition (Figure 3).

Doping of the base alloy by titanium and niobium leads to a significant lowering of melting temperature of the alloy. In this case titanium (Figure 4, curve *3*) has a stronger influence on lowering of the melting temperature than niobium does (Figure 4, curve *2*). However, temperature lowering to the required level can be achieved only at simultaneous addition of these elements and an increased tantalum content (Figure 4, curve *4*).

It is known that strengthening of γ-solid solution matrix by fine particles of γ′-phase ensures the required level of performance of the high-temperature nickel alloys at increased temperatures, due to slowing down of the dislocation movement. Therefore, during investigation of the microstructural components, special attention was given to studying the influence of alloying by the

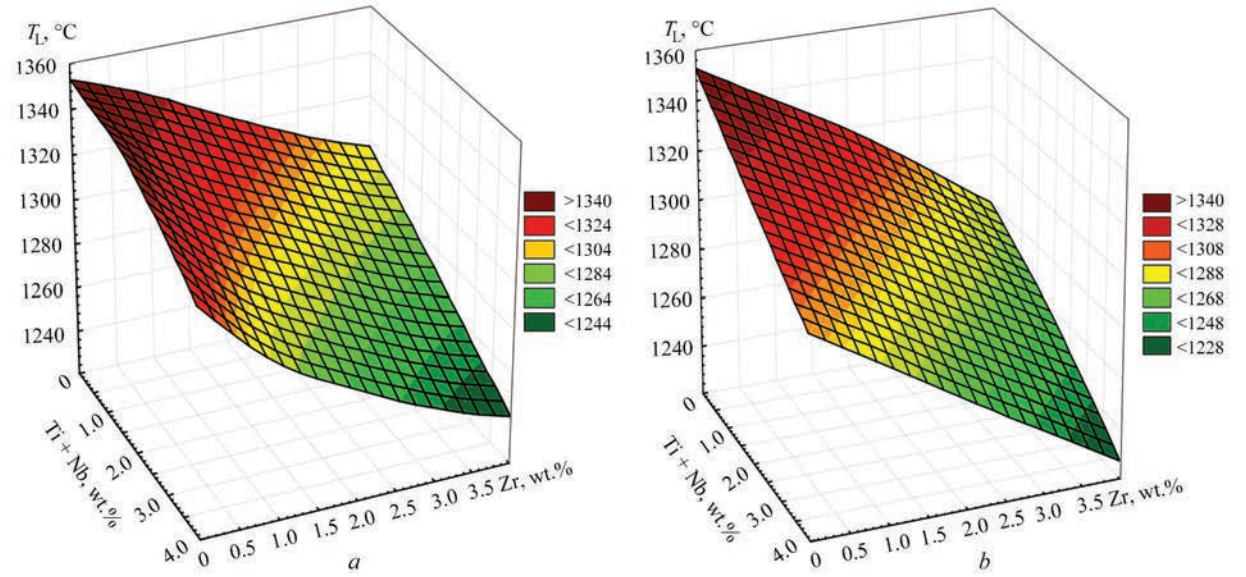


**Figure 1.** Liquidus surfaces of experimental brazing filler metals of Ni–Cr–Co–Al(Me:Ti, Nb, Zr) system with 5 (*a*) and 7.5 wt.% (*b*) tantalum

adhesion-active elements on formation of strengthening γ′-phase. This phase consists of $Ni_3Al$ intermetallics, and in addition to aluminium it may have titanium, niobium and tantalum in its composition [21].

In particular, when studying the influence of tantalum on the calculated quantity of γ′-phase, it was found that increase of the amount of tantalum (up to 10 wt.%) leads to an increase of the temperature range of γ′-phase existence (Figure 5), although this range still is somewhat smaller than in the commercial single-crystal alloy ZhS-32VI (Figure 5, curve *5*).

Additional alloying by titanium and niobium significantly increases (up 1100 °C) the temperature of the start of γ′-phase dissolution (Figure 6), even though it slightly decreases the range of its existence (to 1210–1225 °C) (Figure 6, curves *3* and *4*).

It should be also noted that additional alloying by γ′-forming elements promotes a slight lowering of the quantity of one of TCP phase varieties (σ-phase), and at simultaneous alloying by titanium and niobium the appearance of this phase is recorded only at temperatures above 600 °C. On the other hand, however, the maximum temperature of existence of this phase in the alloy also rises significantly to 1100 °C (Figure 7, curve *4*).

The attempts to additionally lower the quantity of σ-phase by addition of rhenium to the alloy, which is known to be a good σ-stabilizer [6], lead to shifting of the range of σ-phase existence from the temperatures of 600–1110 to 685–1180 °C (Figure 8).

Calculated data obtained using computer thermodynamics method were applied during development and investigation of a number of promising filler metals for brazing single-crystal high-temperature nickel alloy ZhS-32V1.

Thus, during investigations it was found that the method of mathematical modeling of thermodynamic process (CALPHAD) using JMatPro software package can be successfully applied during development of multicomponent filler metals for brazing high-temperature nickel alloys, in particular, for prediction of liquidus temperature and tentative phase composition that will allow considerable reduction of the cost of time and material resources.

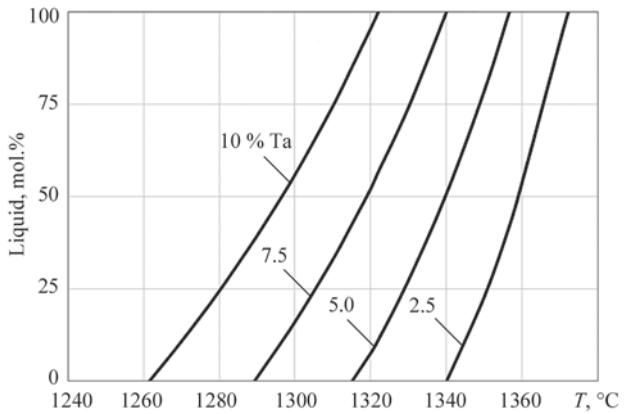


**Figure 2.** Dependence of melting range on the quantity of tantalum in the base alloy of Ni–Cr–Co–Al–(Me)–Ta system

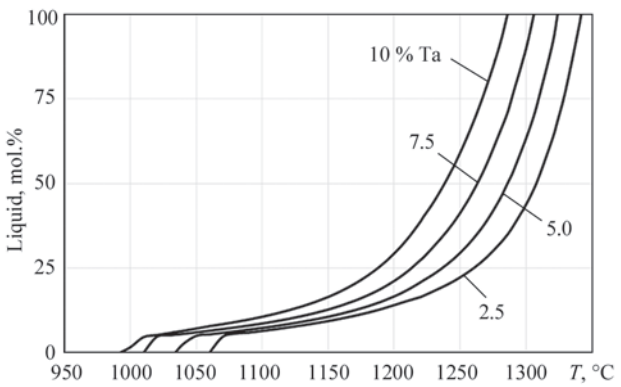


**Figure 3.** Dependence of melting range on alloying by tantalum and zirconium of the base alloy of Ni–Cr–Co–Al–Ta–2Zr system

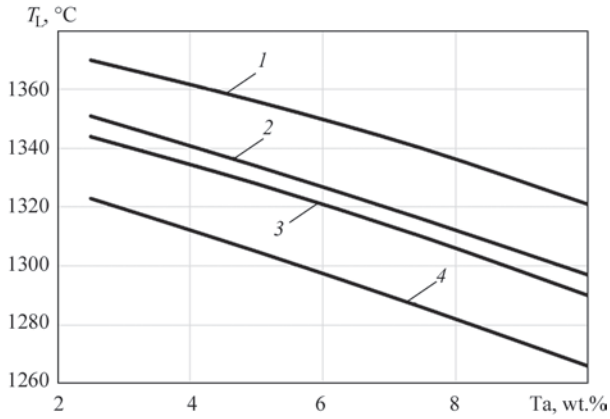


**Figure 4.** Dependence of liquidus temperature of the alloy of Ni–Cr–Co–Al–Me–(Nb, Ti) system on the content of adhesion-active components: *1* — Ta; *2* — Ta + 2 Nb; *3* — Ta + 2 % Ti; *4* — Ta + + 2 % Ti + 2 % Nb

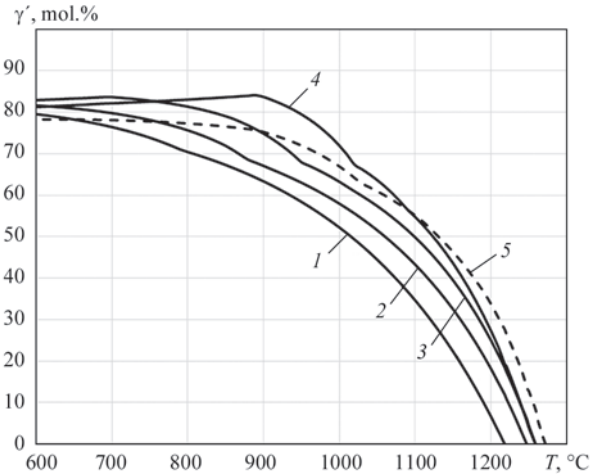


**Figure 5.** Dependence of volume percent of γ′-phase on Ta quantity in the base alloy of Ni–Cr–Co–Al– (Me) system: *1* — 2.5 % Ta; *2* — 5 % Ta; *3* — 7.5 % Ta; *4* — 10 % Ta; *5* — nickel alloy ZhS-32VI

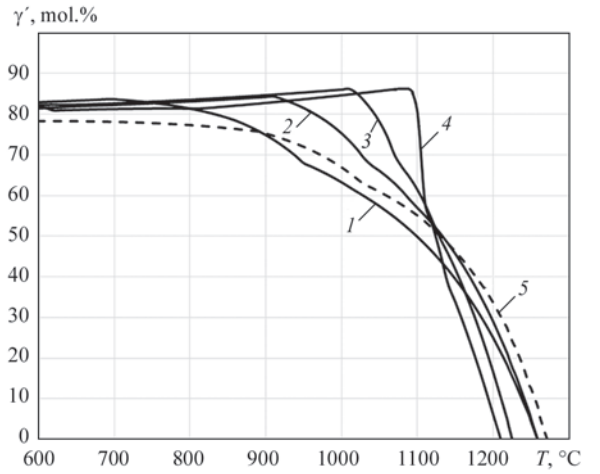


**Figure 6.** Dependence of volume percent of γ′-phase in the alloy of Ni–Cr–Co–Al–Ta–(Nb, Ti) system on the content of adhesion-active components: *1* — 7.5 % Ta; *2* — 7.5 % Ta + 2 % Nb; *3* — 7.5 % Ta + 2 % Ti; *4* — 7.5 % Ta + 2 %Ti + 2 % Nb; *5* — high-temperature nickel-alloy ZhS-32VI

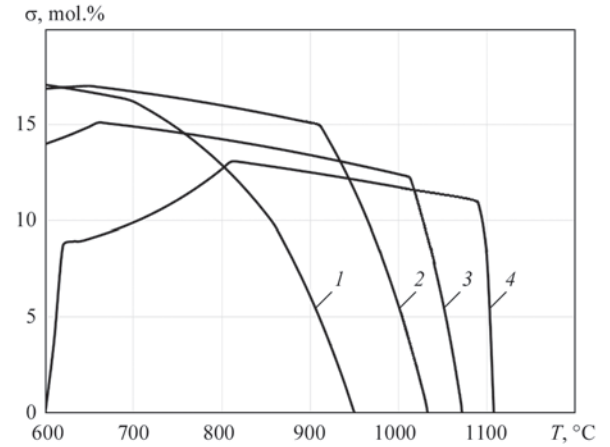


**Figure 7.** Dependence of volume percent of σ-phase in the alloy of Ni–Cr–Co–Al–Ta– (Nb, Ti) system on the content of adhesion-active components: *1* — 7.5 % Ta; *2* — 7.5 % Ta + 2 % Nb; *3* — 7.5 % Ta + 2 % Ti; *4* — 7.5 % Ta + 2 % Ti + 2 % Nb

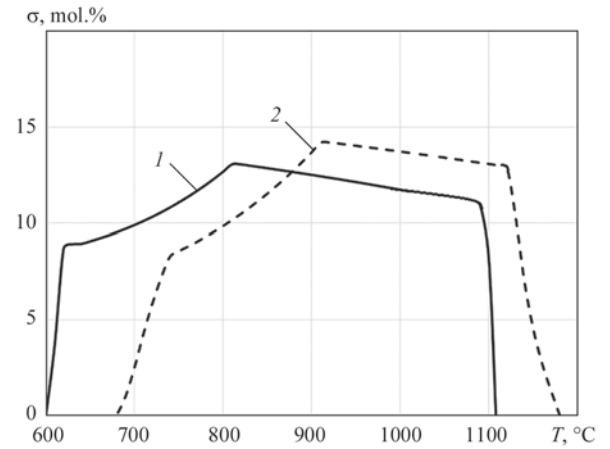


**Figure 8.** Dependence of volume percent of σ-phase in the alloy of Ni–Cr–Co–Al–Ta–(Nb, Ti) system on rhenium content: *1* — without rhenium; *2* — 2 % Re

## CONCLUSIONS

During performance of the investigations it was found that the method of computer modeling of the thermodynamic processes (CALPHAD) with application of JMatPro software package can be effectively used during development of multicomponent filler metals for brazing high-temperature nickel alloys, in particular, for prediction of the liquidus temperature and phase composition of the filler metal.

Proceeding from the conducted computational studies, it was established that:

- increase of the amount of tantalum from 2.5 to 10 wt.% in the base alloy of Ni–Cr–Co–Al–Ta system does not allow considerably lowering its liquidus and solidus temperatures;
- zirconium addition to the base alloy composition almost does not change the liquidus temperature of the base alloy, but it leads to an essential lowering of solidus temperature (991 °C). This is related to appearance of

a low-temperature eutectic in the alloy, which contains zirconium and tantalum in its composition;

● base alloy doping by titanium and niobium leads to a significant lowering of the alloy melting temperature. Here, the influence of titanium is stronger than that of niobium;

● additional alloying by titanium and niobium significantly increases (up to 1100 °C) the calculated temperature of the start of γ′-phase dissolution (Figure 6), although it somewhat decreases the range of its existence (to 1210–1225 °C);

● when studying the curves of the alloy microstructure, it was found that additional alloying by γ′-forming elements promotes a slight lowering of the quantity of σ-phase, and at simultaneous alloying by a certain quantity of titanium and niobium, the appearance of this phase is recorded only at temperatures above 600 °C;

● attempts to further lower the quantity of σ-phase, by adding rhenium to the alloy lead to shifting of the interval of σ-phase existence from 600–1110 to 685–1180 °C.

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## CONFLICT OF INTEREST

The Authors declare no conflict of interest

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