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Improvement of chemical composition, structure and mechanical properties of heat-resistant chromium-nickel alloy

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Abstract. A thermodynamic analysis of a multicomponent system of the Cr-Ni alloy (Cr-32Ni-1,5W-0,25V-0,5Ti) with small additions of refractory metals was carried out. The microstructure and phase composition of the base alloy (I) and alloy with additional alloying (II) were studied. The effect of additives on the mechanical properties of the Cr-Ni alloy at 20, 900 and 1080 °C was shown. The microstructure of alloys I and II was studied in the fracture zone of samples after tensile tests at different temperatures. We studied the effect of small additives on the microstructure of alloys and changes in the morphology of the structural components (phases) as a function of temperature and degree of deformation.

1. Introduction

Development and improvement of hot-strength and heat-resistant materials is one of the key issues of metal science. The use of new modern materials is a necessary condition for achieving the required tactical, technical and operational characteristics of material for space application. Extreme operating conditions of products are forced to tighten the requirements to the level and stability of the properties for materials being developed [1].

High-temperature chromium-based alloys due to significant high-temperature strength at temperatures above 1000 °C, thermal stability and high corrosion resistance are promising substitutes for nickel alloys for aerospace and power engineering application [2].

At present, high-temperature Cr-based alloys has a limited employing in industry. The known alloy Cr- (31-35) Ni (1-3) W- (0.1-0.4) V- (0.05-0.3) Ti mass. % used to manufacture fuel decomposition chambers and nozzle of satellite's thrusters that operate in an impulse power setting.

However, from the point of view of the ongoing update of the requirements to mechanical properties and high-temperature strength, particularly, the potential of the existing alloy is almost exhausted and its further improvement is required.

The grain boundaries are the "weakest" elements of the structure in polycrystalline alloys in terms of creep resistance and a tendency to embrittlement. It is known that the properties of grain boundaries depend on their chemical composition that differs from the average chemical composition of the alloy due to segregation phenomenon [3]. Low-alloying is a well-known hardening method at which the structure and properties of alloys are changed due to local formation on borders of grains and sub-grains of the strengthening phases with limited solubility in α-γ solid solutions of alloy. The specific state of the grain boundaries facilitates and intensifies the diffusion and self-diffusion processes of various elements in polycrystalline metals that proceeds more actively in boundary zones than in grain volume. The low alloying additives introduced into the alloy can change the diffusion rate in the volume and along the grain boundaries, approximating the grain boundaries state in a thermodynamic and kinetic relation to the peculiar grain volume state [4].

The effect of low alloying on the properties of alloy can be explained by means of the theory of internal adsorption in metals according to which the defective parts in the bulk of structure are enriched with atoms of the dissolved component (with low impurity, in particular) that leads to a decrease of surplus defect energy [5]. Adsorption enrichment, occurring predominantly in the inter-crystalline sections, creates an uneven distribution of properties in different parts of the volume of metal. With low alloying additives, such unevenness becomes particularly significant. Intercrystallite boundaries form a continuous, unified and very branched netting, so low alloying additions seem to reinforce the matrix of alloy.

The high temperature strength of Cr-Ni alloy mainly depends on creep strength of the nickel phase at high temperature [2]. So it is of interest to harden this phase to improve the high temperature strength of the alloy.

In paper [6] the results of a first principles theoretical research of alloying elements effect on cohesive properties of high temperature superalloys are presented. The authors [6] showed that such low alloying elements as Zr, Hf, Ta and Nb promote increasing of cohesive strength and work of grain boundaries separation, as well as tend to segregate to the grain boundaries.

In accordance with Ref. [7] when alloying of Cr-Ni alloy by low alloying elements of refractory metals (up to 0.2% mass) is observed increase in tensile strength of alloy at simultaneous decrease in elongation.

It should be noted that current literature data confirm the increase in the high-temperature strength of the chromium-nickel alloy, however, the mechanism for strengthening the Cr-based and Cr-Ni-based alloys were studied insufficiently.

In accordance with the foregoing, the aim of this paper is to thermodynamically analyze the phase distribution of small additions of refractory metals in a chromium-nickel alloy, as well as to study the effect of these additives on the microstructure of the alloy and the properties of the material.

In this paper, we undertake the thermodynamic analysis of the phases distribution of low alloying refractory metals in a Cr-Ni-base alloy, as well as the impact of these additives on a microstructure and the mechanical properties of material.

2. Materials and experimental techniques

Base (I) and experimental with low alloying of refractory metals (II) alloys were chosen as the materials to be studied. Both alloys have been smelted in a vacuum induction furnace with the subsequent electroslag refining. The chemical composition (Table 1) was determined on a glow discharge spectrometer on a Leco GDS 850 unit.

Table 1. Chemical composition of alloys, % mass.

	Cr	Ni	W	V	Ti	Ta	Nb	Zr	Hf
Alloy I	62,0	34,9	2,0	0,28	0,4	-	-	-	-
Alloy II	63,7	32,8	2,0	0,3	0,45	0,15	0,16	<0,002	<0,002

Calculation in the program Thermo-Calc was carried out with reference to an alloy containing low alloying additives of refractory metals. The temperatures chosen for the calculation corresponded to the temperatures of the tensile test.

Tensile tests of the samples were carried out on a Zwick Z050 test machine at temperatures of 20, 900 and 1080 °C.

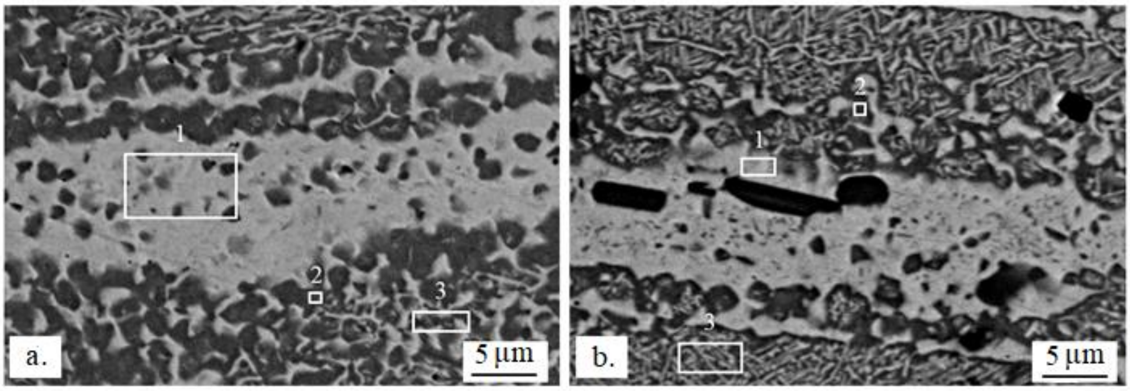
The microstructure was studied before and after tensile tests with use an electronic scanning microscope (SEM) JEOL JSM 6610LV, equipped with the system Oxford Instruments Advanced AZ tec to X-ray microanalysis (MRSA). Samples for metallographic studies were prepared by mechanical polishing.

The program "Thermo-Calc" with the TCNI8 database was used for thermodynamic calculations; TCSNi-based Superalloys Database [8]. The program is based on the model of equilibrium thermodynamics that takes into account the change in the thermodynamic activity of the alloy components in phases that exist in an equilibrium state. Thus, the calculations use the temperature, pressure, chemical potential of the components to determine the chemical composition of the equilibrium phases in the alloy [9].

3. Results and discussion

By calculations it has been established that the low-alloying additives of refractory metals are mainly dissolved in the γ-Ni phase with a FCC lattice. Niobium and tantalum in minimal amounts are present in Ni_3M intermetallides.

To confirm the results of the calculations, using SEM for metallographic specimens, the microstructure of the alloys after extrusion and annealing was studied. The analysis in various areas of specimens was carried out. The specimens were selected from three different parts of the rod: the sagging end, the middle and the inlet end. Figure 1 shows typical photographs of the microstructure and the results of MRSA analysis.



Спектр	Содержание элемента, масс. %				
	Cr	Ni	W	V	Ti
1	43,14	53,35	2,43	0,49	0,59
2	93,15	4,87	1,98	-	-
3	70,20	26,68	2,85	-	0,27

Спектр	Содержание элемента, масс. %						
	Cr	Ni	W	V	Ti	Nb	Ta
1	46,97	47,45	2,85	0,42	0,74	0,37	1,2
2	87,94	10,79	1,26	-	-	-	-
3	69,27	28,12	2,31	0,30	-	-	-

Figure 1. Typical microstructure of alloy I (a) and alloy II (b) after hot extrusion and annealing, × 3000 and characteristic MRSA spectra

As a result, studies have found that tantalum and niobium are located predominantly in the nickel γ-phase and it is consistent with the results of the calculation. Niobium partially present in the form of nitride.

Both alloy's samples were analyzed by XRF. The X-ray diffraction maximum method established increasing of lattice period of γ-phase (Ni) in alloys with low alloying, while the lattice period of α-phase (Cr) did not change. Figure 2 shows the diffractograms.

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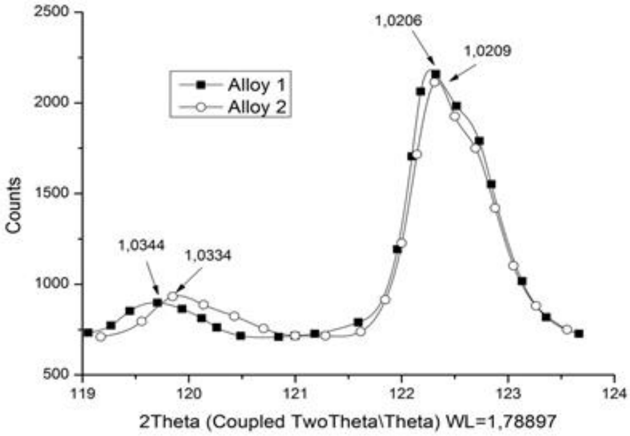

Figure 2. Diffractograms of Alloy I and Alloy II

The observed results lead us to the conclusion that low alloying refractory elements dissolve in a γ-solid solution, and their distribution over the lattice is fairly uniform.

The results of the tensile tests are presented in the Table 2. Figure 3 shows exterior of the samples after tensile tests at a temperature of 1080 °C.

Table 2. Mechanical properties of alloys I and II at different temperatures

	T = 20 °C		T = 900 °C		T = 1080 °C	
	δ	$\sigma_в$	δ	$\sigma_в$	δ	$\sigma_в$
Alloy I	20	1182	24	374	136	89
Alloy II	17,5	1224	12,3	384	20,2	137

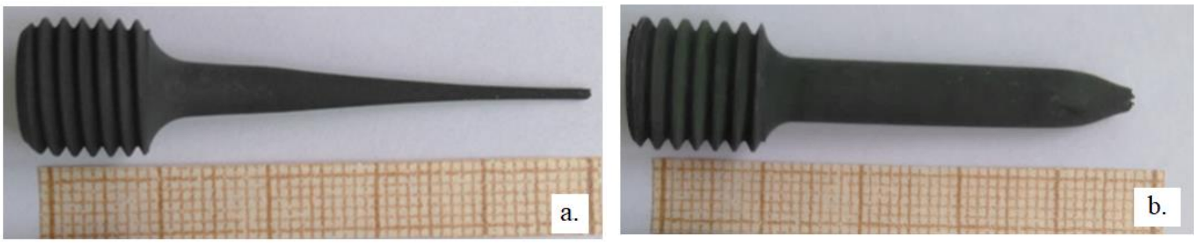

Figure 3. Exterior of the samples after tensile tests at a temperature of 1080 °C

Tensile tests showed that low alloying of refractory metals significantly increase the tensile strength ($\sigma_в$) from 89 MPa (Alloy I) to 137 MPa (Alloy II). At the same time the elongation (δ) had decreased from 136% (Alloy I, Fig 3a) to acceptable level for structural materials 20% (Alloy II, Fig.3b).

Samples for studying the microstructure after tensile tests were taken from the fracture zone (Fig. 4). The SEM showed that with temperature increase the morphology of the phases also significantly changed. Although at test temperature of 20 °C the difference in the microstructure of the alloys is insignificant, with temperature increase in alloy I take place coarsening of the secondary precipitations of γ-Ni solid solution in α-Cr solid solution due to the dynamic recrystallization [10] (Fig. 4c, e). However, in an alloy II disperse precipitates of γ-Ni are smaller in size than in alloy I.

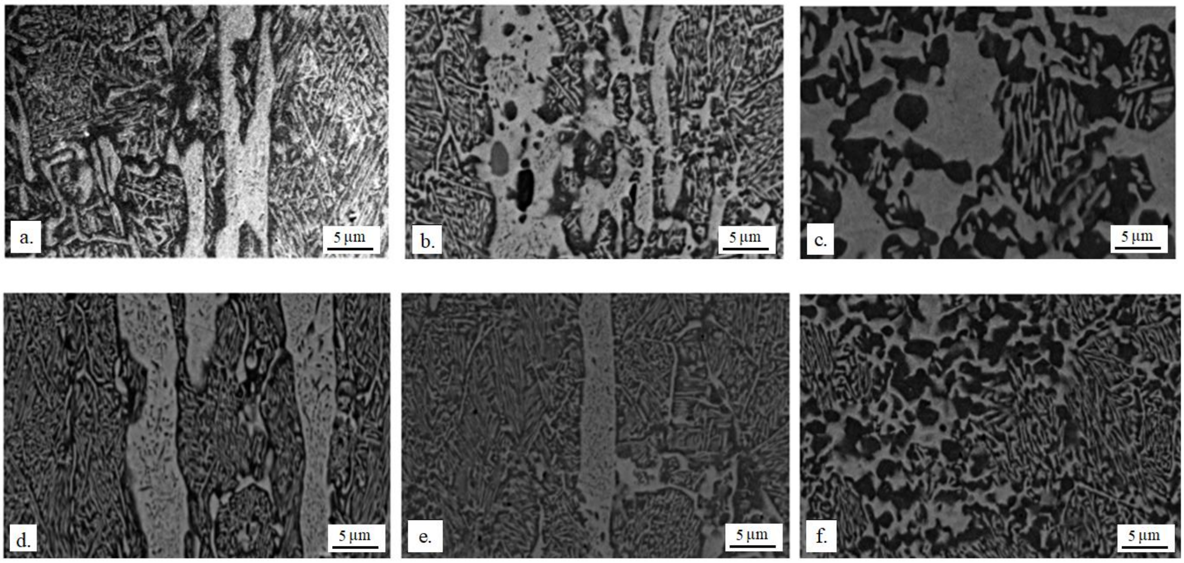

Figure 4. Microstructure of alloys after tensile tests at a temperature: a, d - 20 ° C; b, e - 900 ° C; c, f - 1080 ° C

It may be result of increasing the stability of the alloy structure due to segregation low alloying Ta, Nb, Hf and Zr at the interphase boundaries and slow down of their dissolution with increasing temperature.

4. Conclusions

Low-alloying additives of refractory metals is an effective way to improve the high temperature strength of the chromium-nickel alloy.

Thermodynamic calculations in Thermo-Calc show that low-alloying additives of refractory metals are mainly dissolved in the γ-Ni phase with a FCC lattice.

Tensile tests show that low alloying of refractory metals significantly increase the tensile strength from 89 MPa to 137 MPa and decrease the elongation from 136% to acceptable level for structural materials 20%

The X-ray diffraction maximum method established increasing of lattice period of γ- Ni phase in alloys with low alloying, while the lattice period of α- Cr phase did not change. The observed results lead us to the conclusion that low alloying refractory elements dissolve in a γ-solid solution, and their distribution over the lattice is fairly uniform.

We assumed that increasing in stability of alloy structure is connected with a segregation low alloying Ta, Nb, Hf and Zr at the interphase boundaries and slow down of their dissolution with increasing temperature.

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