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Influence of Doping on Physicochemical Properties of Eutectic Alloy of Cobalt with Niobium Carbide

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The influence of doping on the physicochemical properties of cobalt alloy with niobium carbide NbC is determined on the basis of experimental studies. As established, a doping with a complex of elements including chromium, aluminium, tungsten and iron, reduces the melting point from $(1410 \pm 10)^\circ\text{C}$ to $(1320 \pm 10)^\circ\text{C}$, does not affect the phase composition and structural state, but significantly increases the oxidation resistance at a temperature of 1100°C . The optimum content of alloying elements is established to impart increased heat resistance to a natural composite based on cobalt with niobium carbide.

Key words: eutectic, cobalt, niobium carbide, alloying, heat resistance, oxidation resistance.

На основі експериментальних досліджень визначено вплив легування на фізико-хімічні властивості сплаву кобальту з карбідом ніобію NbC. Встановлено, що легування Хромом, Алюмінієм, Вольфрамом та Ферумом знижує температуру топлення з $(1410 \pm 10)^\circ\text{C}$ до $(1320 \pm 10)^\circ\text{C}$, не впливає на фазовий склад та структуру евтектичного сплаву, і сприяє суттєвому підвищенню опору окисненню за температури 1100°C . Встановлено оптимальні межі легування означеними елементами для надання евтектичному природному композиту на основі кобальту з карбідом ніобію високої жаростійкості.

Ключові слова: евтектика, кобальт, карбід ніобію, легування, жаростій-

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1. INTRODUCTION

A prerequisite for the development of industrial cast eutectic alloys with high strength, heat resistance, hardness, wear resistance is the study of crystallization parameters and properties of eutectic metal alloys with phases of embodiment that meet the conditions of dispersed and composite hardening. Eutectic alloys of quasi-binary metal systems with phases of embodiment, for example with carbides of refractory metals of IV and V group PSE, are natural composites, in which the strong and plastic metal component (cobalt solid solution) and finely differentiated carbide crystals creating conditions for composite reinforcement [1, 2].

The eutectic alloys retain its properties up to 0.9 of the melting point temperatures. Due to the combination of soft and hard phases, regular structure and the reinforcing effect of a sufficient number of reinforcing carbide crystals, quasi-binary eutectic alloys have high wear resistance in a wide range of temperatures. Determining the conditions of eutectic crystallization and studying the unique properties of eutectic composites opens up the possibility of creating new alloys in different areas and directions of use [3, 4]. One of such composites is the eutectic alloy based on cobalt with niobium carbide.

Conditions for eutectic crystallization the alloy of quasi-binary section of Co–NbC of the ternary system Co–Nb–C are established in our own studies [5, 6]. The composition of the eutectic is determined by the physical conditions of thermodynamic equilibrium of the system components, according to which the alloy of eutectic composition contains two phases—solid solution based on cobalt and niobium carbide in an amount of 12–13% mass., in which dissolved $\approx 8\%$ cobalt at a melting point of $(1410 \pm 10)^\circ\text{C}$. The advantage of eutectic alloys over dispersion-strengthened is the possibility to obtain high properties of strength and hardness in the cast state, without heat treatment and at much higher temperatures. Quasi-binary eutectic alloys in the cast state have essential strength at high temperatures. At temperatures below 0.5 of the melting point they are inferior to the strength of dispersed alloys, but above 0.5 of the melting point, with a sufficient volume fraction of the carbide phase, have a significant advantage and are promising to create on their basis heat-resistant, heat-resistant, wear-resistant alloys for mechanical engineering [7–9]. Acquisition of these properties by eutectic alloys can be achieved by optimal doping, which affects the crystallization parameters. The aim of the study was to select the optimal complex of alloying components and determine the ef-

fect of such doping on the physical and mechanical properties of the eutectic alloy based on cobalt with niobium carbide.

2. EXPERIMENTAL DETAILS

Alloys to study the effect of doping on the properties of the eutectic alloy of cobalt with niobium carbide were made in a laboratory electric arc furnace with a non-consumable tungsten electrode on a cooled copper hearth by multiple re-melting in purified argon to achieve their maximum homogenization. For the production of alloys were used: cobalt brand K1 (98.5%); niobium brand N6Sh-00 (99.98%); spectrally pure graphite MG-1 (99.96%); chromium electrolytic brand ERC (99.96%); aluminium brand A-995 (99.995%); tungsten brand WA (99.95%); Armco iron (99.84%). The chemical composition of the alloys, determined by fluorescence X-ray spectral analysis on a VRA-30 spectrometer, coincides with the nominal composition within an error of $\pm 0.3\%$.

The phase transformation temperature was determined by differential scanning calorimetric (DSC) with the apparatus Netzsch DSK 404 F1 Pegasus with a heating and cooling rate of $300^\circ\text{C}/\text{h}$.

X-ray phase analysis (X-ray diffraction) was performed on a DRON-3M diffractometer in standard CuK_α radiation.

Refinement of the crystal structure of the defined phases was performed by the Rietveld method using the Maud program. Metallographic studies were performed using light microscopy (microscope 'Neophot-32').

The structure, distribution of components and chemical composition of the phases of the alloys were determined by the EDAX method on the equipment Super probe 733 (JEOL LTD, Tokyo, Japan).

Samples for heat resistance tests were cut from castings by spark cutting or turned on a lathe, measured their surface area with an error of $\pm 0.1 \text{ mm}^2$, placed in a corundum crucibles, covered with a lid, weighed with an error of $\pm 0.01 \text{ g}$ and oxidized in air at 1100°C . Tested in five stages, each of which consist in heating to 1100°C for 1 h, isothermal test for 10 h, and subsequent cooling with an furnace. Heat resistance was determined by increasing the mass of the sample after every 10 h of annealing, related to its initial surface area ($\Delta m = (m_n - m_0)/s$).

3. RESULTS AND DISCUSSION

Doping gives the eutectic composite the desired properties, but changes the crystallization parameters of the eutectic, so you need a balanced approach to the choice of alloying elements. Analysis of the alloying

limits for industrial cobalt-based alloys on [10–14] is summarized in Table 1. Metals of the fourth group of PSE were undesirable to alloying elements, because they have high chemical activity, which creates certain problems in melting in refractory crucibles. Molybdenum and vanadium reduce the resistance to oxidation of cobalt-based alloys; tantalum is almost never used in aviation materials.

In this work, based on the analysis of the influence of alloying elements on the properties of cobalt industrial alloys, the number of alloying elements in the alloy of eutectic composition of cobalt with niobium carbide was limited to four—chromium, aluminium, tungsten and iron.

According to the experimental data obtained in this work, the compatible solubility of aluminium and tungsten at a solidus temperature reaches almost 8% mass. and 26% mass., respectively. For operating temperatures of aviation materials in the range of 900–1200°C, it was found that the solubility of aluminium and tungsten is reduced to $\approx 6\%$ Al and $\approx 23\%$ W for a temperature of 1200°C, and to $\approx 4\%$ Al and $\approx 20\%$

TABLE 1. Preferable alloying elements in industrial cobalt alloys.

Element	Doping limits, % mass.	Average content in alloys, % mass.
Cr	18.5–33	20–25
C	0–2.5	0.2–1
W	0–20	6–10
Ni	0–30	3–20
Fe	0–30	2–4
Mo	0–10	4–6
Mn	0–1.4	0.5–1.2
Ta	0–7.5	2–7.5
B	0–0.4	0.01–0.03
Hf	0–0.5	0.2
Si	0,1–2	0.3–1
Nb	0–16	1–3
Al	0–15	0,5–3.5
Ti	0–4	1–4
Y	0–0.5	0–0.5
V	0–9.5	8–9.5
La	0–0.08	0.08
Be	0–0.03	0.03
Zr	0–2.25	0.2

W for a temperature of 900°C, respectively (Fig. 1). Thus, both aluminium and tungsten reduce each other's solubility in cobalt.

The choice of chromium as an alloying element is explained by the fact that it increases resistance to oxidation at high temperatures, forming on the surface of cobalt alloys a protective layer of oxidation-resistant chromium oxide Cr_2O_3 , and at the same time increases its strength at high temperatures. The solubility of chromium in cobalt exceeds 35% [17]. In the studied eutectic alloys was introduced chromium in an amount of from 5 to 25%. The optimal chromium content was determined to be 18–20%, because at a content of $\geq 20\%$ Cr the stability of the phase composition of the alloy was disturbed by the appearance of the third phase based on σ -phase CoCr, and at a content of $\leq 18\%$ Cr the effect of chromium on heat resistance of the studied alloys was insufficient. Further studies were performed on an eutectic doped alloy of cobalt with niobium carbide, which contained 18–20% chromium.

Addition to the cobalt-based alloy with aluminium and tungsten of such components as chromium, niobium and carbon to create an alloyed eutectic alloy obviously will change the established solubility. The investigation was conducted in two stages for established that condition. At the first stage, the solubility of aluminium and tungsten in the cobalt base of a eutectic alloy with niobium carbide, in other words, in alloys of the Co (Al, W) + NbC system without chromium was established. Microstructure and local X-ray spectral analyzes showed that the solubility of aluminium in the cobalt base solid solution of such alloys increases from $\approx 5\%$ to 6.5% in the temperature range from 900°C to the melting point. Solubility of tungsten reaches $\approx 20\%$ at a temperature of 1200°C. Up to 6% of cobalt is soluble in the carbide component of alloys.

Chromium is a component that significantly affects the characteristics of the eutectic alloy, primarily on the properties of the cobalt metal base. Therefore, the aim of the second stage of investigation was to

Fig. 1. The field of the cobalt-based solid solution at temperatures of 900°C, 1200°C and on the solidus surface.

establish the limits of the existence of a solid solution based on cobalt doped with aluminium, tungsten and chromium in the presence of niobium and carbon, in an amount sufficient for the formation of niobium carbide in alloys. The field of the cobalt-based solid solution for the multicomponent system Co (Al, W, Cr) + NbC at a temperature of 1100°C are presented in Fig. 2.

Thus, the presence of aluminium as an alloying element in the test alloy should be limited to 5%, and the tungsten content should not exceed 16%. In addition, the high density of tungsten requires limiting its use in aviation materials.

A small amount of iron (optimally 3%) was added to the alloy to stabilize the phase transformation of cobalt ($\alpha \rightleftharpoons \epsilon$), but such doping has little effect on the basic properties.

According to the Technical Conditions for alloys used as heat-resistant and wear-resistant alloys to protect against wear of the contact surfaces of gas turbine blades, alloying should not reduce the melting point of the alloy below 1300°C. Its structure and phase composition must remain thermo stable; heat resistance at a temperature of 1100°C must be higher than the heat resistance of existing alloys for this purpose.

The calculation of the component contribution of alloying elements

Fig. 2. Solubility limit of aluminium and tungsten in a solid solution on cobalt-based in the eutectic alloy system Co(Al, W, Cr) + NbC at a temperature of 1100°C (●—composition of single-phase alloys, ■—composition of two-phase alloys).

to the melting temperature of the eutectic alloy was performed. It was taken into account that: the alloying elements are soluble mainly in solid solution; the effect of insignificant dissolution of some elements in niobium carbide ($T_{\text{liq}} \approx 3600^\circ\text{C}$) can be neglected; melting point Co—1495°C; melting point of the eutectic alloy 1410°C;

$$T_{\text{sq.alloy}} = T_{\text{Co}} + \frac{dT_{\text{Co-Al}}}{dx_{\text{Co-Al}}} X_{\text{Al}} + \dots$$

The effect of doping with chromium, tungsten, aluminium and iron on the melting point and oxidation rate eutectic alloy of cobalt with niobium carbide according to the study, shows Table 2 and Fig. 3. Slightly higher calculated values of melting temperatures of alloys can be explained by the dissolution of some alloying elements in niobium carbide and their lower content in solid solution (εCo).

From the obtained experimental data it follows that the melting point of the eutectic alloy due to doping reduced to 1300–1320°C in comparison with 1410°C for unalloyed eutectic alloy Co–NbC. The amount of iron in the alloy come to nothing more than 3% mass., because when the iron content in larger quantities (4–6%), the resistance of alloys to oxidation at 1100°C decreases. Optimal properties of heat resistance and melting point temperature are inherent in alloys, the complex of alloying elements which contains 18–20% Cr, 8–9% W, 2–3% Al, 2–3% Fe, 1.8–1.9% C and $\approx 15\%$ Nb. The heat resistance of the alloy doped with the specified complex of elements is dominated by the heat resistance of the serial alloy HTN-61 [18], which is used to protect

TABLE 2. Melting point and oxidation resistance at 1100°C of doped eutectic alloys of cobalt with niobium carbide.

No. *	Composition, % mass.					Melting point, °C		Mass gain, g/mm ² ·10 ⁻³ , during annealing, hours				
	Cr	W	Al	Fe	C	Calc.	Exp.	10	20	30	40	50
1	20	7.5	3.3	4.0	1.9	1308.62	1310	1.2	2.02	2.61	3.12	3.5
2	20	7.0	2.0	—	1.8	1294.68	1320	0.85	1.64	1.56	2	1.85
3	18	9.0	3.5	3.0	1.7	1333.49	1315	0.7	1.14	1.29	1.32	1.05
4	20	12	2.5	3.0	1.6	1315.88	1300	0.48	0.82	1.2	1.56	1.15
5	18	9.0	2.0	3.0	1.9	1315.71	1315	0.73	0.82	1.11	1.2	1.05
6	20	7.5	3.5	6.0	1.8	1309.37	1315	1.4	2.52	3.45	4.16	4.5
7	18	10	3.0	1.5	1.9	1332.32	1300	0.9	1.56	2.1	2.2	2.3
HTN-61	20	7.0	2.0	—	1.8	—	1320	0.85	3.3	5.58	7.6	9.85

*All alloys based on cobalt and contain 14–15% Nb.

Fig. 3. Oxidation rate at 1100°C of doped eutectic alloys of cobalt with niobium carbide.

against wear of the contact surfaces of the working blades of the gas turbine engine at JSC Motor Sich.

An important requirement for eutectic cast wear-resistant and heat-resistant composites is the thermal stability of the structure and phase composition to a temperature close to the melting point (solidus). The microstructure of the eutectic alloy is characterized by the presence of carbide crystals with a small thickness and a small distance between them, as well as a number of primary crystals of niobium carbide as a phase that begins and conducts crystallization (Fig. 4, *a*). Doping re-

Fig. 4. Microstructure of cobalt-based alloys with niobium carbide: unalloyed alloy of eutectic composition (*a*); doped eutectic alloy (*b*).

duces the melting point of the eutectic composition alloy and is accompanied by a corresponding thermodynamic shift of its composition towards a decrease in the volume fraction of the carbide component. The alloy, which had a eutectic structure in the unalloyed state, becomes slightly hypereutectic. And as a result of increasing the carbide content acquires a structure with a slightly higher content of primary small crystals of niobium carbide (Fig 4, *b*), which increases hardness and wear resistance. The strength of the metal component of the eutectic alloy decreases faster with increasing temperature than the carbide. Therefore the strength of the composite as a whole depends on the volume of crystals of the embodiment phase—carbide. Hardness and wear resistance of the eutectic alloy is also determined in the first approximation by the volume fraction of the embodiment phase. So an alloy with a slightly hypereutectic structure is more preferable for creating a wear-resistant industrial eutectic composite based on it.

According to X-ray diffraction phase composition of alloyed alloys remains stable when heated to the melting point of the eutectic component and contains (Fig. 5):

- solid solution based on (ϵ Co), Pearson symbol hP_2 , space group P_63/mmc , prototype Mg, lattice parameters $a = 0.2530$ nm, $c = 0.4098$ nm;
- solid solution based on (α Co), Pearson symbol $cF4$, space group $Fm3m$, prototype Cu, lattice parameters $a = 0.33532$ nm;
- niobium carbide, Pearson symbol $F23$, space group $Fm3m$, prototype C_5V_6 , lattice parameters $a = 0.444974$ nm.

According to the obtained experimental data, the volume fraction of niobium carbide in the doped alloy is about 16% , which should provide it with high properties of resistance to high-temperature wear. The cobalt base of the investigated alloy in the cast state is 84.2% and is

Fig. 5. Diffractogram of cast doped eutectic alloy Co–NbC.

Fig. 6. Qualitative analysis of phase composition in doped eutectic alloy of cobalt with niobium carbide according to EDAX.

mainly represented by a solid solution based on low-temperature hexagonal modification of cobalt in the amount of 78.8%. The solid solution based on the cubic modification of cobalt is only 5.4% by volume of the metal base. The parameters of the crystal lattice of the h.c.p. of the solid solution of the investigated alloy are increased by comparison with pure cobalt (ϵ Co): $a = 0.2507$ nm $c = 0.4069$ nm), and niobium carbide is reduced (NbC: $a = 0.4470$ nm [19]. This phase composition is preferred for cast eutectic industrial composites such as HTN-61.

The qualitative distribution of alloying elements in the phase components of the eutectic alloy in the cast state was study by the EDAX method (Fig. 6). According to it, the carbide phase in addition to niobium and carbon contains a carbide-forming element—tungsten, but aluminium and chromium are present mainly in the metal component of the eutectic alloy (Fig. 7). Based on the obtained experimental data,

Fig. 7. Quantitative analysis of phase composition in doped eutectic alloy of cobalt with niobium carbide according to EDAX.

there is reason to believe that the complex of alloying elements used is optimal for conditions of complete dissolution of 18–20% chromium and 2–3% aluminium in cobalt, while the tungsten content is 8–9% higher than the solubility limits in solid solution, as a result, it is present in the niobium carbide.

Doping of eutectic alloy of cobalt with niobium carbide by a complex of elements consisting of 18–20% Cr, 2–3% Al, 9–10% W and $\leq 3\%$ Fe (% mass.) may be recommended to provide an alloy of high heat resistance at a temperature of 1100°C under conditions thermal stability of phase composition and structure.

4. CONCLUSION

The optimal complex of alloying elements for the eutectic alloy of cobalt with niobium carbide is recognized: 18–20% chromium, 2–3% aluminium, 9–10% tungsten and $\leq 3\%$ iron (% mass.). Doping with the specified complex of alloying elements:

- does not change the phase composition of the eutectic alloy;
- increases the amount of carbide in the microstructure of the alloy;
- does not reduce the melting temperature below 1300°C, leaving it within the Specifications for wear-resistant aircraft alloys;
- increases the heat resistance at 1100°C more than twice in comparison with the heat resistance of the wear-resistant at 1050°C serial alloy HTN-61, which is used to protect against wear of the contact surfaces of the gas turbine blades at JSC Motor Sich.

The results obtained in this work should become the basis for the creation of new heat-resistant and wear-resistant foundry composites for the needs of aircraft engineering, and for improving the technological modes of industrial melting of the alloy in the form of ingots, powder or tapes.

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