ISSN 1027-5495. Functional Materials, 28, No.1 (2021), p. 69-75.
doi:https://doi.org/10.15407/fm28.01.69

Dependence of properties of cobalt alloy HTN-62 on additional alloying

T.S.Cherepova[1], G.P.Dmitrieva[1], T.V.Pryadko[1], M.V.Kindrachuk[2], O.V.Tisov[2], O.I.Dukhota[2], A.O.Yurchuk[2], O.V.Gerasymova[2]

[1]G.Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine
[2]National Aviation University, Kyiv, Ukraine

Received August 20, 2020,

The paper presents the results of experimental studies of the dependence of melting temperature, phase composition, structure, and heat resistance (at 1100°C in the air) of the HTN-62 alloy on additional doping with molybdenum, titanium, hafnium, tantalum, cerium, and rhenium. Based on the experimental data obtained, the most promising doping elements providing the maximum heat resistance of the alloy were identified. The results of the study are a certain stage for further improving the heat resistance of alloys, ensuring their strength and performance under extreme operating conditions. The modified alloy can be successfully used to coat the contact surfaces of the upper shroud of turbine blades and aircraft engines.

Keywords: cobalt-based eutectic alloy, additional doping, heat resistance, melting point, rare-earth elements.

Залежність фізико-механічних властивостей серійного кобальтового сплаву ХТН-62 від додаткового легування. *Т.С.Черепова, Г.П.Дмітрієва, Т.В.Прядко, М.В.Кіндрачук, О.В.Тісов, О.І.Духота, А.О.Юрчук, О.В.Герасимова.*

Досліджено залежності температури плавлення, фазового стану, структури та опору окисненню при температурі 1100°C на повітрі сплаву ХТН-62 від додаткового легування молібденом, титаном, гафнієм, танталом, церієм та ренієм. На основі результату дослідження фізико-механічних властивостей додатково легованого сплаву ХТН-62 визначено найбільш перспективні легуючі елементи для забезпечення максимальної стійкості сплаву до окиснення. Результати дослідження є певним етапом подальшого підвищення жаростійкості сплавів даного призначення, забезпечення їх міцності і працездатності у складних умовах експлуатації бандажних полиць робочих лопаток авіаційних газотурбінних двигунів та можуть бути застосовані для розробки технології отримання і вибору матеріалів для практичного використання у реальних умовах роботи.

Исследованы зависимости температуры плавления, фазового состояния, структуры и сопротивления окислению при температуре 1100°C на воздухе серийного эвтектического сплава кобальта с карбидом ниобия ХТН-62, от дополнительного легирования молибденом, титаном, гафнием, танталом, церием и рением. На основе результата исследования физико-механических свойств дополнительно легированного сплава ХТН-62 определены наиболее перспективные легирующие элементы для обеспечения максимальной устойчивости сплава к окислению. Результаты исследования являются определенным этапом дальнейшего повышения жаростойкости сплавов данного назначения, обеспечения их прочности и работоспособности в сложных условиях эксплуатации бандажных полок рабочих лопаток авиационных газотурбинных двигателей и могут быть применены для разработки технологии получения и выбора материалов для практического использования в реальных условиях работы.

1. Introduction

Eutectic wear- and heat resistant materials have been continuously developed for decades [1–7]. The production of wear-resistant materials for aviation purposes, which could work under extreme operating conditions, is an urgent task; therefore, the results of this work are of particular importance and are a good basis for studying the factors influencing the physical and mechanical properties of new alloys. An important role in the development and production of alloys for aircraft gas turbine engines (GTE) has been retained by G.V.Kurdyumov Institute of Metal Physics of National Academy of Sciences of Ukraine (Kyiv). A set of cobalt-based alloys with carbide reinforcement (HTN-37 [8], HTN-61 [9, 10], HTN-62 [11, 12]) were developed and introduced into manufacturing processes at Ivchenko-Progress State Enterprise. Due to an increase in operating temperatures on new aircraft GTEs up to 1110°C (with possible overshooting up to 1150°C), it is very important to ensure high heat resistance of wear-resistant materials used for coatings on the wear surface of the upper blade shrouds. The melting point of these materials is required to be higher than 1300°C, since the procedure for removing gas from the blades requires heating to this temperature.

In order to further optimize the physical and mechanical properties of eutectic cobalt alloy XTH-62 (doped with chromium, aluminium, tungsten, and iron with niobium carbide as a strengthening phase), additional doping by molybdenum, titanium, hafnium, tantalum, rhenium, and cerium was carried out.

These alloying elements were selected based on the analysis of existing high-temperature materials and alloying systems already applied or promising for special wear-resistant materials for top shrouds or sealings of [13–15] turbine blades. Also, the effect of these elements on Co–NbC equilibrium was considered [16, 17].

2. Experimental

Alloy cast samples for examinations were made by electric arc melting with a non-consumable tungsten electrode. To prevent oxidation, the air from the furnace was evacuated and replaced by argon. The melting process was carried out on a copper water-cooled hearth. Chemical composition was studied by fluorescence X-ray spectral analysis on a VRA-20 spectrometer. The melting point was determined by thermal analysis (TA) using a VDTA-8M thermal analyzer and by the method of differential scanning calorimetry (DSK) using a Netzsch DSC 404 F1 Pegasus calorimeter. The contents of metallic components in alloys and in the oxide layer were determined by energy dispersion X-ray spectroscopy (EMF). Microstructural analysis (MSA) was done using an optical microscope "Neophot-32".

Heat resistance was determined on samples cut from ingots (using lathe) with high accuracy. The surface area of specimens was measured with an accuracy of 0.1 mm^2, weight was determined with an accuracy of $1\cdot10^{-4}$ g. For tests, the specimens were put into corundum crucibles and covered with a lid. The crucibles were placed into an electric furnace. The thermocouple was located closest to the samples for better temperature measurement accuracy. Annealing was performed with free air income into the crucibles. Heat resistance was determined as the weight gained by the specimen during annealing divided by the surface area of the specimen measured before the test. The annealing temperature was 1100°C. A test consisted of ten cycles, which included heating to 1100°C for one hour, isothermal annealing at 1100°C for 5 h, and cooling in the furnace turned off and closed. After every 10 h of the cycle, the samples were weighed together with the crucible, thus, the mass of the sample was measured after 10, 20, 30, 40, and 50 h of annealing. The maximum isothermal exposure time at 1100°C was fifty hours.

3. Results and discussion

The task of additional doping of the considered material is to modify, first of all, the Co-based solid solution. To solve this problem, it is necessary to apply an integrated approach — the alloy must retain its eutectic properties, and doping should not reduce the melting point of the alloy below 1300°C. Analysis of the content of doping elements in cobalt to increase the heat resistance [18–22] gives the following average ranges (wt. %): Mo: 4–6 %, Ta: 2–7.5 %, Hf: 0.2 %, Ti: 1–4 %, La or other REM: 0–0.5 %. Rhenium in the amount of 3–6 wt. % has recently been used in heat-resistant nickel alloys to increase their operating temperature [23].

It is difficult to calculate mathematically the optimal amounts of components in a high-alloy material. The complex of additional dopants was selected experimentally,

Table 1. Chemical compositions of the modified alloy HTN-62

No.	Component content, wt. %												
	Co	Cr	W	Al	Fe	Nb	Mo	Ta	Hf	Ti	Re	C	Ce
1	48.08	20	9.5	2	3	11.84		3.75				1.8	
2	48.08	20	9.5	2	3	11.84			3.75			1.8	
3	43.6	20	9.5	2	3	15.5					4.5	1.9	
4	48.1	20	9.5	2	3	15.5						1.9	
5	48.5	18	9	4	3	15.5	1.5					2	
6	52.0	20	6	3		15.5						2	
7	44.1	20	9.5	2	3	15.5		3.75				2.15	
8	44.1	20	9.5	2	3	15.5			3.75			2.15	
9	46.1	18	9.5	2	3	15.5				3.2		2.7	
11	46.1	19	10	4	3	15.5						1.9	0.5
12	43.5	18	9.5	2	3	15.5		3			3	2	0.5
13	47.0	19	6	3	—	15	1.5	3			3	2	0.5
15	48.2	20	9.5	2	3	15.5						1.8	
16	43.7	20	9.5	2	3	15.5					4.5	1.8	
17	45.2	20	9.5	2	3	15.5					3	1.8	
18	42.2	20	9.5	2	3	15.5					6	1.8	
20	45.7	18	9.5	2	3	15.5					4.5	1.8	
22	39.2	20	9.5	2	3	15.5					9	1.8	
23	49.7	14	9.5	2	3	15.5					4.5	1.8	

according to their influence on heat resistance. The additional introduction of titanium into the studied eutectic alloy is aimed to strengthen the Co-based solid solution. The maximum solubility of titanium in pure cobalt is 14 at. % (10.68 wt.%) at 1210°C. The solubility limit of titanium in the studied multicomponent alloy is 3.2 wt.% [24]. When titanium is added to cobalt in an amount that exceeds the solubility limit, undesirable intermetallic phases $TiCo_3$ and $TiCo_2$ appear. This makes the alloy brittle.

Little information is available on the use of hafnium as a dopant in cobalt-based alloys and its effect on heat resistance. This is due to the fact that the commercial use of hafnium is problematic due to its high cost. It is known that the maximum solubility of hafnium in cobalt is $\approx$ 4 wt. %. The use of tantalum (maximum solubility in cobalt $\approx$ 13 wt. %) may have a positive effect on the heat resistance, but may be accompanied by an increase in the density and cost of the alloy. Rhenium in cobalt-based alloys raises the melting point (solidus temperature), which is very valuable for alloys operating in aircraft engines. The addition of rhenium also increases the strength of cobalt-based alloys. The rhenium content in cobalt was determined from the Co–Re equilibrium phase diagram [17], and for the high-temperature modification of cobalt, it is limited by the peritectic reaction at 1550°C with 25 at. % Re. The solubility of rhenium in cobalt is unlimited. This allows free using if it an any quantity, but rhenium is a rare, precious metal, and its use is limited by economic feasibility.

Due to its high activity with respect to impurities, cerium refines, deoxidizes, and degasses alloys, thereby improving the mechanical properties of heat-resistant cobalt-based alloys at high temperatures. In addition, it refines the structure of the alloy thus increasing its strength. The modification of cast iron with cerium increases its wear resistance by about 2–3 times [26]. The additive 0.08–0.15 wt. % REM increases the bond strength of the oxide layer to the substrate and reduces the oxidation rate, promoting the formation of Cr_2O_3 and minimizing the formation of spinel-type oxide $CoCr_2O_4$ and oxide CoO. The introduction of REM in the amount of 0.03–0.07 % increases the heat resistance of nickel alloys by 1.5–2 times in the temperature range 800–1100°C [27]. Therefore, cerium was identified as a promising additional dopant to optimize the physical and mechanical properties of the HTN-62 alloy. The composition of the studied alloys is given in Table 1.

The results of the heat-resistance test and differential scanning calorimetry of mentioned in Table 1 alloys are given in

Table 2. Melting point and heat resistance of alloys

No	$T_{melt.}$, °C	Additional heat effect, °C	Weight gain, $\Delta m/s \times 10^{-5}$, g/mm^2				
			10 h	20 h	30 h	40 h	50 h
1	1310	1280	111.57	177.27	229.75	268.28	296.91
2	1310	1280	152.31	237.82	287.37	321.87	344.26
3	1315	1295	4.77	7.34	8.44	9.17	10.27
4	1315		4.12	15.34	22.07	28.43	32.55
5	1320	1300	11.76	12.67	11.76	27.14	33.93
6	1305	1250	146.81	224.4	283.05	318.38	339.51
7	1300		12.83	20.6	26.43	30.32	31.87
8	1302		7.08	15.69	22.27	27.34	33.92
9	1310		13.21	21.65	26.41	26.76	30.63
11	1300		47.77	85.99	113.83	129.61	144.15
12	1315		5.54	7.34	8.86	10.34	10.7
13	1310	1250	9.99	15.36	17.67	16.9	23.43
15	1315	1250	7.62	9.57	11.75	13.7	15.8
16	1305		4.84	6.29	7.74	10.16	12.1
17	1325	1300	5.0	5.76	6.76	8.76	10.5
18	1320	1270	10.44	11.41	13.15	15.08	17.02
20	1320		4.88	5.65	8.74	9.76	9.76
22	1315		3.0	3.0	3.47	3.7	3.94
23	1335	1305	5.05	5.05	7.07	10.11	10.36

Table 2. The results show that the melting point of alloys does not fall below 1300°C and remains close to the melting temperature eutectic alloy HTN-62 (alloy No. 15 in Tables 1 and 2). The thermal effect in the solid state at a temperature of 1250–1300°C is most likely caused by the presence in the alloys of intermetallic phases of cobalt with molybdenum, tantalum, hafnium or chromium, according to the phase equilibrium diagrams of cobalt with these metals. The heat resistance of the studied alloys with increasing annealing time at 1100°C in air depends on the content of alloying elements.

Analysis of the obtained experimental data allows us to conclude that the addition of titanium in an amount of ≈ 3 wt. % (alloy No. 9) below the solubility limit of titanium in cobalt, does not reduce the melting point of the base alloy, does not cause phase transformations, and slightly improves heat resistance.

The results of the study of alloys modified by hafnium indicate that the addition of 3 % Hf is excessive when the carbon content is sufficient to form NbC. This alloying does not lower the melting point but changes the phase composition by the formation of intermetallic phases with cobalt or chromium. This is evidenced by the additional heat effect at a temperature of 1280°C. As a result, the heat resistance of the alloyed sample is significantly reduced (alloy No. 2). However, when the carbon content exceeds the amount enough for the formation of NbC carbide (alloy No. 8), the excess of carbon stimulates the formation of carbides (Nb, Hf)C preventing the formation of intermetallic compounds; this leads to the fact that the melting point and heat resistance of such an alloy are not lower than that of HTN-62. Thus, it was found that the addition of hafnium in an amount close to the maximum solubility limit in a Co-based solid solution without simultaneously increasing the carbon content is impractical. Another negative factor when alloying HTN-62 with a large amount of hafnium can be an increase in the cost of the alloy.

It has been proven that the simultaneous addition of 3.75 % Ta to the alloy and the reduction of niobium content, which is not balanced by the appropriate amount of carbon to form a sufficient amount of carbide in the eutectic alloy (alloy No. 1), does not lower the melting point of the alloy. But with a lack of carbon, when the amount of Ta exceeded the limit of solubility in Co, an intermetallic compound Co_2Ta was formed in the experimental alloy. As a result, the alloy was brittle, and the thermal heating and cooling curves showed an additional thermal effect due to the presence of an intermetallic phase in the alloy. The result is significant oxidation at high temperatures. For sample No. 7 (with increased carbon content sufficient to form carbides (Ta, Nb)C), high-temperature differential thermal analysis (HTDTA) showed the disappearance of the additional thermal effect associated with the formation of an intermetallic compound. The melting point of the alloy does not decrease. The heat resistance of the alloy remains almost the same as in the alloy HTN-62 (No. 2 in the Tables 1 and 2). The solubility of tantalum in cobalt is insignificant. An increase in the tantalum content and a decrease in the content of Nb at a lower carbon content leads to a decrease in the amount of formed carbides. Thus, doping with tantalum in an amount of less than 4 wt. % is not promising, but in a larger amount is impractical.

A small amount of molybdenum (alloy No. 5) to strengthen the cobalt-based solid solution does not significantly affect either the melting temperature or heat resistance, but the thermal effect in the solid state at about 1300°C indicates the presence of an additional phase (along with the solid solution and niobium carbide), which according to preliminary data contains chromium. It was found that the addition of both molybdenum and rhenium to the base alloy (alloy No. 13) also leads to the formation of an intermetallic phase, but significantly improves the heat resistance (Table 2).

The studies indicate that 0.5 % Ce has no effect on the melting point of the alloy. Cerium showed high activity in relation to harmful impurities, namely to deoxidation and degassing of the alloy, strengthening of the alloy by structure refinement; we consider, that the addition of cerium in an amount of 0.5–1.0 wt. % is promising for improving the technological and mechanical properties of the alloy.

The choice of rhenium as a doping element is explained by its use in heat-resistant nickel alloys for gas turbine blades in the amount of 3–6 wt. %. It is used to increase the structural stability of γ-solid solution and dispersion of γ′-phase during decomposition of the supersaturated solid solution [23, 28]. The properties of eutectic alloys are structure-sensitive, so the ability of rhenium to disperse the phases, both metallic and carbides, should be used. Rhenium was additionally introduced to the alloy HTN-62, in amounts of 1, 3, 4. 5, 6, and 9 %, slightly varying the content of primary alloying elements — chromium, tungsten, aluminium, and carbon (alloys No. 3, 16, 17, 18, 20, 22, 23). Analysis of the properties (Table 2) allows us to consider rhenium as the most promising element among studied here. The effect of rhenium on heat resistance is shown in Fig. 1.

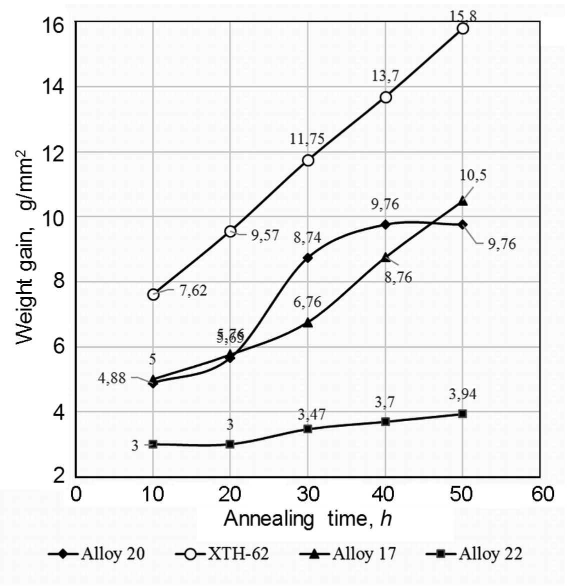

Fig. 1. Weight gain Δm/s, $\times 10^{-5}$, g/mm^2, for alloys with dissimilar rhenium content (t = 1100°C, τ = 50 h).

At the same time, it was found that in the alloys modified with rhenium, the chromium content should be reduced from 20 % to 18 % to prevent the formation of intermetallic compounds (forming below 1305°C and containing Co, Cr and Re). Simultaneous doping with rhenium, tantalum and cerium (alloy No. 12) almost three times improves the heat resistance of the HTN-62 alloy at a temperature of 1100°C. But addition a small amount of molybdenum somewhat reduces the achieved effect (alloy No. 13).

The first indicator of the suitability of alloys to protect the contact surfaces of the turbine blades in a modern large gas turbine engine is the melting point. Rhenium has the highest melting point among metals considered (3186°C), therefore, the melting point of alloys doped with rhenium is 1315–1330°C (Table 2), that is the highest among the studied alloys.

Simultaneous doping with rhenium, tantalum and cerium (alloy No. 12) almost three times improves the heat resistance of

XTH-62 alloy at a temperature of 1100°C. But addition a small amount of molybdenum somewhat reduces the achieved effect (alloy No. 13).

The first indication of the suitability of alloys for use as a material to protect the contact surfaces of the turbine blades of a modern large gas turbine engine is the melting point. Rhenium has the highest melting point among metals considered (3186°C), therefore its use to improve melting temperature of studied alloy XTN-62 is most promising. The melting point of alloys doped with rhenium is 1315–1330°C (Table 2), and is the highest among the studied alloys. According to current study, it varies from 1305°C to 1335°C. Rhenium-modified alloys have phase stability, as evidenced by the lack of additional effects on the heating and cooling curves or they are insignificant. As an example, the thermograms of alloy No. 20 (Fig. 2) are given. The alloy melting point (solidus) is 1319°C, and solidification (liquidus) temperature is ~ 1329°C. The melting interval of studied alloys is 20–30 degrees.

Comparison of the main properties of the modified HTN-62 alloy for wear protection of the contact surface of gas turbine engine blades gives reason to consider the most promising additional doping with 3–9 wt.% rhenium. However, it does not exclude the possibility of using titanium, hafnium, tantalum, cerium for this purpose. The obtained experimental results on the influence of additional doping on the physical and mechanical properties of the wear-resistant alloy HTN-62 are of great practical importance and expand the possibilities of optimizing cobalt-based alloys.

4. Conclusions

The analysis of the effect of modification of the HTN-62 alloy with titanium, hafnium, tantalum, molybdenum, cerium and rhenium on its physical and mechanical properties allows us to draw the following conclusions:

— titanium (in quantities below solid solubility limit) does not affect heat resistance of the alloy, does not reduce the melting temperature and may be used for strengthening the solid solution;

— doping with hafnium does not lower the melting point and does not change the heat resistance at a temperature of 1100°C if the carbon content is not sufficient to form the carbide (Hf, Nb)C;

— molybdenum in small quantities does not reduce the heat resistance, and together with rhenium significantly improves the oxidation resistance at 1100°C;

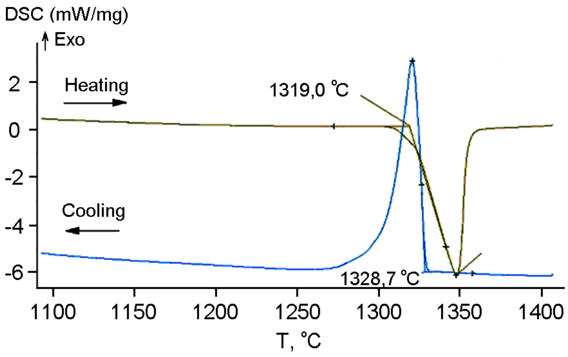

Fig. 2. Heating and cooling curves of alloy HTN-62 modified with 4.5 % Re (alloy No. 20).

— addition of with tantalum up to 4 wt.% to improve the heat resistance requires an increase in the carbon content, accompanied by an increase in density, which is undesirable for the alloy for aviation purposes;

— 0.5 % Ce has no effect on the melting point of the alloy, but due to its deoxidizing, degassing and refining action, it is recommended to add cerium in the amount of 0.5–1.0 % for improving the mechanical and technological properties of the alloy;

— rhenium in an amount of 1 to 9 wt. % improves the heat resistance at 1100°C at least four times without lowering the melting point and is the most optimal component for doping.

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