New heat resistant cobalt and nickel based sintered alloys strengthened by titanium carbide

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Abstract. Task of research is to study the properties of new sintered alloys in order to replace former used alloys XTN-61 and XTN-62 alloys. New materials should accede them by heat resistance but melting point should be higher. The properties of alloys obtained by powder metallurgy based on cobalt, nickel or heat-resistant alloy ZhS32-VI with titanium carbide in the range of 30–50% vol. were studied. Their structural researches were carried out and indicate uniform distribution of carbide particles. Porosity is present in all studied sintered alloys, but its value is controllable. It is shown that in terms of heat resistance at a temperature of 1100 °C, nickel alloys are dominated by alloys based on cobalt and ZhS32-VI. Porosity impact on heat resistance was estimated. Increase of porosity strongly reduces heat resistance. All studied alloys have melting temperature above 1300 °C. DSC and DTA tests indicate no unwanted additional effect during either heating or cooling. The properties of the obtained alloys give reason to recommend them for use in aircraft engine construction as a material to be covered to the contact faces of turbine blades top shrouds.

1. Introduction and literature review

The problem of increasing power, reliability and durability is given special attention in the creation, operation and repair of aircraft gas turbine engines. Their long service life is largely reduced due to the problem of resistance to the contact surfaces of the turbine rotor blades, which during operation are affected by high temperatures, high loads, high heating and cooling rates and corrosion-erosion products of fuel combustion. During long-term operation, the turbine blades wear out, first of all, on the bandage shelves. An effective way to increase the durability of the blades is to apply a wear-resistant material on the contact surfaces [1]. Developments in the creation of new generation gas turbine engines and modernization of existing ones, when with increasing resource the task of increasing power per unit mass of the engine, which, respectively, leads to increased operating temperatures and loads, require the creation of wear-resistant materials that would meet these increased requirements [2-5].

This paper compares the results of the study of the main characteristics of the developed alloys based on cobalt, nickel and heat-resistant alloy ZhS32-VI with titanium carbide, namely: melting point, heat resistance at maximum operating temperatures in order to present these materials for use in aircraft construction. As of today, one of the methods used for Motor Sich engines is the use of cast eutectic alloys as a material for various cladding processes. They are applied to the shroud friction surface. Namely, the cobalt based alloys XTH-61 and XTH-62 are the most widely used.

Recent decades refractory carbides are extensively used to strengthen metallic materials. Authors used TiC powders with 10-14 μm grain size was used. This improved the propertis of basic material, namely wear resistance. Steel 316L is also a very popular material as a matrix for TiC reinforced MMC's. In paper [6] the production technique – melt infiltration, TiC contend was 70-90 vol. %, grain size 4…10 μm. Sliding wear tests indicated a ratio between TiC grain size ond matrix-to-filler ratio. Coarser grain size promotes higher specific wear rate, increasing of binder content increases wear rate. Also, the formation of tribolayer with high O content was revealed. The predominant wear mechanism on the initial stage – two-body abrasive wear, being followed by three-body abrasive wear. But, at higher temperatures (was not studied in considered research) a tribo-chemical friction-induced layer will be formed in the early period of friction, and may protect the material from carbides spallation and abrasive action of nonoxidized TiC grain fragments. The researchers [7] used 2 wt. % TiC nanoparticles to significantly enhance mechanical properties of 316L austenitic stainless steel and have got promissing results.

TiC-Co composites were studied by Sun-A Jung [8]. The specimens were prepared by combination of high energy milling followed by liquid phase sintering. The TiC grain size was 7-10 μm. The importance of grain of TiC and matrix material were highlighted. Namely, fine powders of Co inhibit the TiC grain growth during sintering. Unfortunately authors did not do any tribological examinations. The fabricated Co and Co-based composites reinforced by TiC particles. They used the method of vacuum arc melting to fuse alloy constituents. Larger amount of TiC promoted coarsening of its grains. The sliding wear test gave promising results.

Concluding this part: TiC grains are worldwide used to strengthen metallic-based composites produced by versatile manufacturing methods.

2. The aim and objectives of research

The aim of this research is to develop new alloys with high melting point and oxidation resistance. To solve this task, we should do:

– DSC and DTA tests to determine melting point and to find possible additional effects unwanted during heating and cooling;

– to do heat resistance tests of all samples and to find impact of porosity, TiC content and other structural effects impact on heat resistance;

– to perform structural examinations in order to determine TiC distribution and structural integrity of fabricated alloys.

3. Materials and the methods

The objects of the study selected are three batches of alloys, the first of which is obtained from a mixture of powders of cobalt, titanium carbide and alloying elements - chromium, iron and aluminum, the second - from nickel, titanium carbide and the same alloying elements as in previous case. The third alloy is prepared from nickel heat-resistant alloy powder ZhS32-VI and titanium carbide. The samples were made by hot isostatic pressing on SPD-120 equipment from mixtures of powders of pure metals of fraction 5-20 μm: cobalt brand PK-1U, nickel brand PNE-1, chromium PAH 99H5, iron PZHV1, aluminum PA-0, titanium carbide standard TU 06173-74 and alloy ZhS32-VI (OST 1.90.126-85). To achieve the required heat resistance, the complex of alloying elements that are soluble in cobalt and nickel is selected by analogy with the alloy HTN-62, except for tungsten, the solid-soluble hardening of which is balanced by a sufficient amount of titanium carbide. Iron is introduced into alloys to stabilize the high-temperature more plastic modification of cobalt. To compensate for the free carbon in titanium carbide (1.5%), titanium hydride was introduced to eliminate the possibility of the formation of other carbides.

Microstructure studies were performed on an OLYMPUS IX70 optical microscope at magnifications x50 - 500 and by electron scanning microscopy (instrument JSM-6400 (JEOL Ltd), equipped with energy dispersion spectrometer) at magnifications x 1500 - 2000.

Heat resistance was determined by measuring the weight gin of the sample relative to its surface area. In the electric resistance furnace, each sample was placed in a separate crucible of alumina, heating to a temperature of 1100 °C in air was controlled by a thermocouple, exposure was 10 hours and cooling was performed with an oven. The procedure was repeated five times. The total exposure of the samples at 1100 ºC was thus 50 hours. The heat resistance of the alloys was determined after every 10 hours of annealing.

3. Results and discussion

The melting temperature of the developed alloys is important because it must meet the conditions of the technological process of manufacturing blades (1270 ° C - degassing and soldering), ie, in our case, taking into account possible deviations, must be higher than 1300 ° C. The composition of powder alloys with a titanium carbide content of 30, 40 and 50% vol., Based on cobalt, Nickel and alloy ZhS32-VI to study the microstructure, determine their melting point, heat resistance and wear resistance are given in Table 1

Thermal heating curves obtained by the method of DTA and DSC of powder alloys with a titanium carbide content from 30 to 50 vol.% indicate the possibility of creating composite materials based on cobalt, nickel and alloy ZhS32-VI, in which there are no transformations when heated to temperature melting. The absence of additional thermal effects when heated indicates the stability of the phase and structural composition of the obtained composite materials. At temperatures above the melting point, the alloys lose phase stability, as evidenced by the appearance of additional thermal effects during cooling. Comparison of the melting point of the samples of powder alloys on different bases does not reveal significant advantages. Thus, it was found that the melting point (solidus) of composite powder materials is not less than 1320 ± 10 ºC and does not depend on the content of titanium carbide in the range from 30 to 50% vol. and their basics.

Table 1. Chemical composition and melting point of alloys

№	Base, mass. %			TiC		TiH, mass.%	Alloying elements, mass.%			Tmelt., °C
	Co	Ni	ZhS32	% vol.	mass.%		Cr	Fe	Al	
74	55,5	-	-	30	17,84	1,16	19,6	2,95	2,95	1350
13	50,0	-	-	40	25,36	1,64	17,7	2,65	2,65	1320
14	43,83	-	-	50	33,8	2,2	15,51	2,33	2,33	1325
80	-	55,5	-	30	17,84	1,16	19,6	2,95	2,95	1330
6	-	50,0	-	40	25,36	1,64	17,7	2,65	2,65	1320
7	-	43,83	-	50	33,8	2,2	15,51	2,33	2,33	1320
100	-	-	81	30	19	-	-	-	-	1370
101	-	-	73	40	27	-	-	-	-	1355
102	-	-	64	50	36	-	-	-	-	1355

The correlation that exists between the resistance of materials to wear and their hardness was the reason for determining the latter. As measurements have shown, the Rockwell hardness of the test samples changes with increasing titanium carbide content from 52 HRC at 30% vol. TiC to 67 HRC at 60% vol. TiC. The hardness of composite powder materials of optimal composition (with a titanium carbide content of about 50% vol.) On the basis of cobalt is 67 HRC, nickel-based alloys - 64 HRC.

One of the most important factors determining the resistance of materials to wear is their structure, as well as the properties and quantitative ratio of its components. The heterogeneous structure of the studied alloys consists of evenly distributed dispersed inclusions of metal cobalt or Nickel alloy base and carbide. The structure of the alloys is quite fine-grained [9]; the particle size of the carbide fraction is mainly 5-10 μm. (Figure 1).

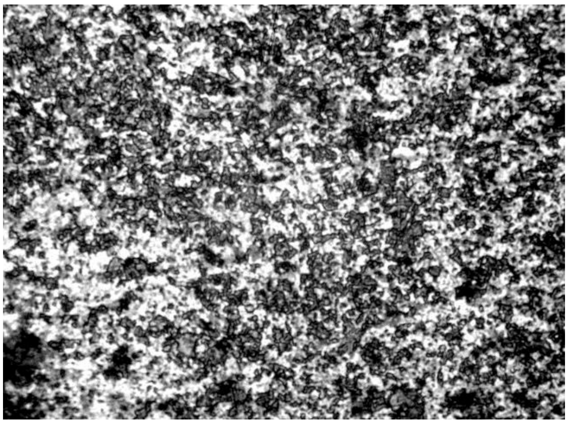


Figure 1. The microstructure of Co-based alloy containing 50 (vol) % of TiC.

Studies of the heat resistance of alloys have shown that the process of high-temperature oxidation initially (during the first 10 hours) proceeds rapidly, but after some time is established almost constant and insignificant rate of mass gain. With increasing content of titanium carbide in alloys, heat resistance decreases slightly. The most significant factor influencing the heat resistance of alloys is the porosity of manufactured alloys: with its increase, the indicators decrease regardless of the base of the alloy and the carbide content in it [10, 11]. This clearly demonstrates, for example, the dependence of the weight gains of the samples on the duration of exposure at 1100 ° C for alloys with the same content of titanium carbide (50% vol.), But with different porosity (Figure 2). Comparative analysis allows us to conclude that a more compact material has better heat resistance.

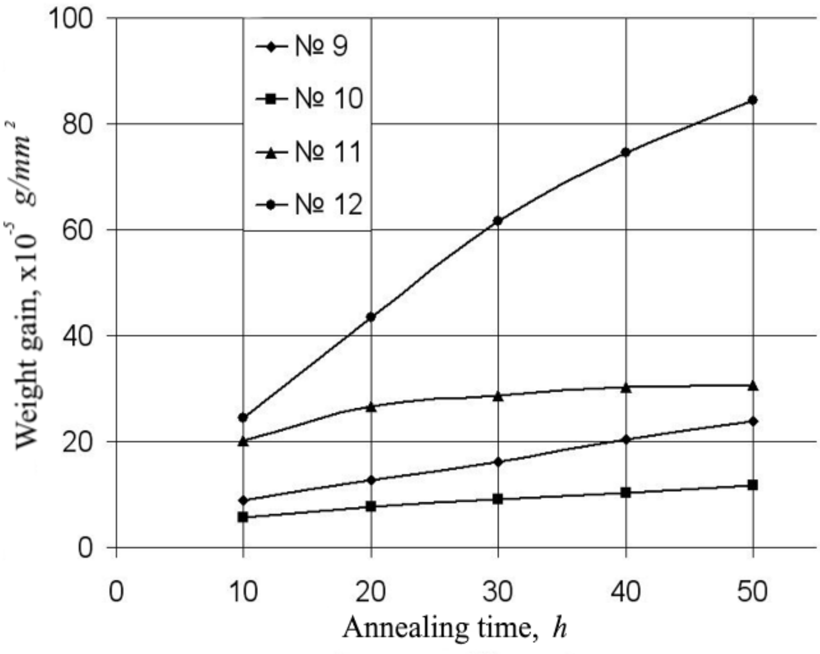
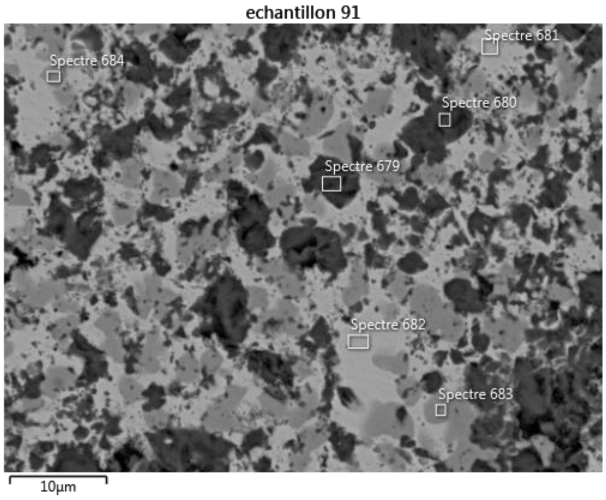


Figure 2. Oxidation kinetics of Co-based alloys $Co_{alloyed}$ – 50 % vol. TiC with dissimilar porosity: № 10 – 3,1%; № 9 – 6,0%; № 11 – 10,4%; № 12 – 28,0%.

The presence of a large number of pores facilitates the penetration of oxygen into the base material to a considerable depth. The width of the oxide layer in the near-surface zone can reach tens of microns. In addition, the inner surfaces of pores and cracks are also chemically exposed, ie the area of interaction with oxygen increases, as a result of which the heat resistance of the material decreases.

Investigation of the surface of a cobalt-based alloy with 50% vol. TiC after tests for heat resistance by electron scanning microscopy are shown in Figure 3.



№ of zone	Composition, mass.%					Note
	Co	Cr	Al	Fe	Ti	
679	2.06	1.08	0.1	0	96.76	(TiC)
680	1.95	0.84	0	0.28	96.93	
681	76.47	12.76	2.87	4.24	3.67	Light phase
682	78.32	12.9	2.87	4.17	1.74	
683	12.93	81.41	0	1.14	4.52	Grey phase
684	23.11	73.33	0.23	1.92	1.41	
	43.8	15.5	2.33	2.33	33.8 TiC+TiH	Nominal phase composition

Figure 3. Microstructure of 50% vol. TiC Co-bsed alloy: microstructure and chemical composition of phases.

The obtained results of oxidation kinetics of the objects of research - powder alloys based on doped Co, Ni and ZhS32-VI make it possible to compare them. Figure 4 shows the weight gain of alloys on different bases with the same content of titanium carbide (40% vol.) During annealing in air at a temperature of 1100 ° C.

The weight gain of nickel alloys remains the lowest during all fifty hours of testing. Of course, an additional influencing factor is the porosity of the samples, which is slightly different and adversely affects the oxidation processes. Nevertheless, of the three series of alloys, nickel-based powder composite materials are preferred.

The explanation for this may be the analysis of alloys of two similar systems - Ni - Cr and Co - Cr. The studied alloys based on cobalt and nickel are alloyed equally. At a high chromium content, when a Cr_2O_3 layer is formed, the oxidation rates in Co - Cr and Ni - Cr alloys are equated. But the adhesion of scale to cobalt is worse and therefore in practice the heat resistance of Co - Cr alloys is significantly lower [12].

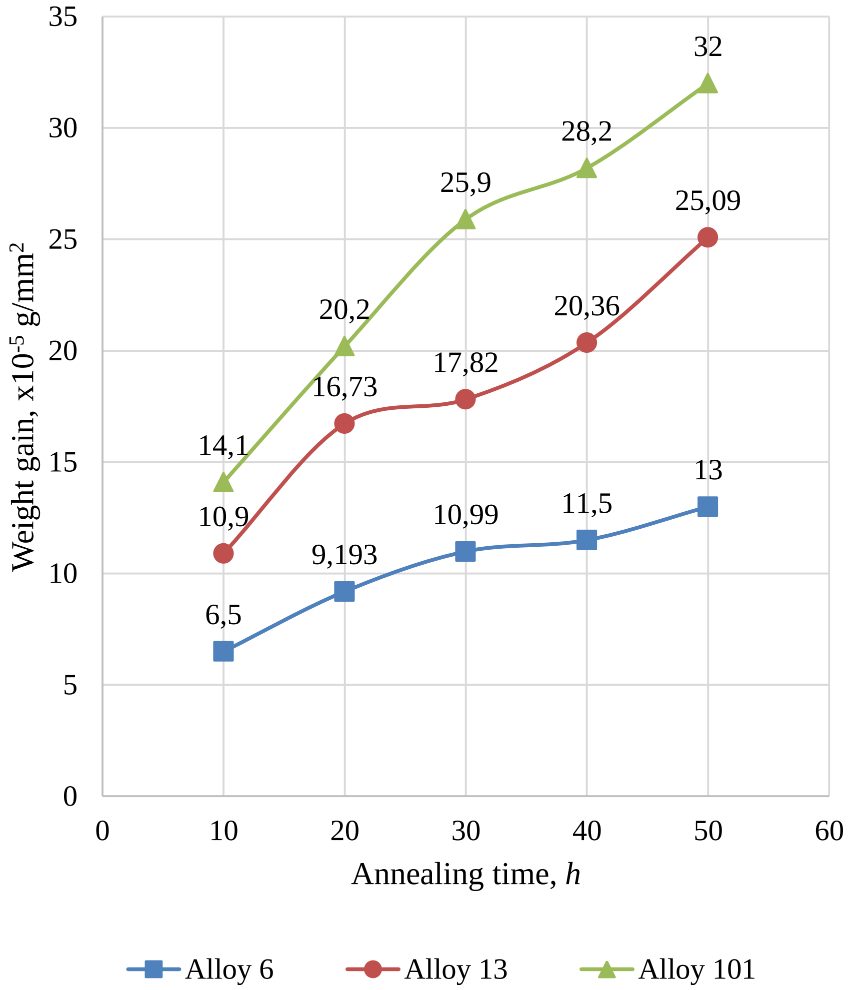


Figure 4. Heat resistance of powder alloys with 40 % vol. TiC based on: № 6 – nickel; № 13 – cobalt; № 101 – ZhS32-VI.

Alloys based on ZhS32-VI alloy, from which turbine blades are made, are the least heat-resistant, as the most important thing in the requirements for this alloy is heat resistance, and the surface of the blades is reliably protected by a heat-resistant coating. Therefore, heat resistance is not a defining characteristic of ZhS32-VI alloy, and, consequently, of powder alloys based on it. Nevertheless, the heat resistance of powder alloys based on ZhS32-VI was within acceptable limits.

Conclusions

New composite materials based on cobalt, nickel and heat-resistant alloy ZhS32-VI with titanium carbide have been created, which are made by hot isostatic pressing and can be used to protect the bandage shelves of GTE blades from wear.

It is shown that the melting temperature of alloys is 1320 ± 10 ° C, which is 50 degrees higher than the temperature of technological operations and does not depend on the carbide content.

The results of the study of the oxidation kinetics of alloys are analysed. As the heat resistance increases, they can be placed in the following order: alloys based on ZhS32-VI, cobalt-based, nickel-based. The heat resistance of alloys depends on the porosity of the material and is within the characteristics for other alloys for this purpose.

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