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HEAT RESISTACE OF THE POWDER COBALT ALLOYS REINFORCED WITH NIOBIUM OR TITANIUM CARBIDE

Heat-resistance of powder cobalt alloys at 1100 °C has been studied. These alloys have been designed for the protection of GTE blade platforms from wear and prepared by hot compaction of cobalt, chrome, aluminum, and iron powders and niobium or titanium carbides. Heat resistance of the alloys containing carbides between 30 and 70% (vol.) depends on the type of carbide: the alloys with titanium carbide have a higher heat-resistance as compared with the alloys containing niobium carbide. The most significant factor affecting the heat-resistance of alloys is porosity: as it increases the parameters decrease regardless of the type and content of carbide. The optimum composition of powder heat-resistant alloy containing titanium carbide with a melting point above 1300 °C, to be used in the aircraft engine industry has been established.

Keywords: cobalt alloys, niobium carbide, titanium carbide, and heat resistance.

The service life of aircraft gas-turbine engine (GTE) depends on reliability and durability of the crucial parts of hot gas path, such as Z-lock and nozzle buckets whose contact surfaces intensively wear down in the aggressive environment, at high temperature and varying loads acting for a long while. Shrouding of blades in turbine rotors increases time between repair of GTE. During the operation, the contact surfaces of platforms suffer from friction, vibrating shocks, collisions, and high-temperature oxidation. As a result, the edges of platforms wear down, with a gap appearing between them. A platform wear of 0.5 mm causes almost a tenfold increase in vibrating stress of blade airfoil, which can lead to a fatigue breakdown of the airfoil and a failure of the engine as a whole. The reinforcement of platforms by coating them with more wear-resistant material as compared with the blade material, enables extending the service life of blades between repairs. In this case, the repair is made by replacing the welded pads instead of the blades. Nowadays, for this purpose, wear-resistant alloys KhTN-61 and KhTN-62 designed by the Institute of Physics of Metals of the NAS of Ukraine [1, 2] are used. These alloys are eutectic composites where the volume share of reinforcing carbide is limited with composition of eutectic system [3]. To increase the share of reinforcing carbide component and to enhance significantly the alloy wear resistance one can create an artificial composite by powder metallurgy technique.

This research is aimed at creating powder alloys based on cobalt, with carbide reinforcement. At this stage, it means to ensure their high wear resistance as one of key requirements for protective coatings of platform edges within the whole range of operating temperature that can reach 1100 °C and melting point ≥1300 °C, which meets the blade manufacturing process (1270 °C — gas removal and brazing).

Increasing heat resistance of eutectic cast alloys based on Co—NbC is ensured by impurity doping complex [4—8]. New powder alloys used for protection of platform edges are in contact with high-temperature combustion products containing a large amount of oxygen. Therefore, they should have a high resistance to oxidation. The impurities for raising heat resistance of cobalt powder alloys have been selected on the basis of previous studies. The key element is chrome that gives required resistance to oxidation and hot corrosion, with aluminum used for additional increase in heat resistance. All impurities have higher sensitivity to oxygen as compared with cobalt. The use of hot compaction technique has enabled comparing the alloys reinforced with niobium and titanium carbides that are the most resistant to oxidation amongst the refractory metal carbides [9].

On the basis of research results, the optimal complex of impurities and the effect of niobium and titanium carbides on heat resistance of cobalt powder alloys have been established.

MATERIALS AND METHODS OF RESEARCH

The researchers used multicomponent alloys consisting of reinforcing carbides of niobium and titanium and Co—Cr—Fe—Al. The content of chrome, iron, and aluminum ensures required heat resistance of alloys.

For preparing powder alloys, pure powdered cobalt PK-1U, chrome PAKh99H5, aluminum PA-0, and iron PZhV1.71 powders and carbides of respective standard were used. The initial size of the major part of particles (approximately 50%) is 5—10 μm; the share of particles smaller than 5 μm is 25%, and that of particles bigger than 10 μm accounts for 20%.

The samples were prepared by the powder metallurgy technique that foresees grinding of powder mixes in a planetary mill at a ratio powder : steel balls = 1 : 5, in acetone, during 30 min. After

Table 1

Composition and Porosity of Alloys Studied

Sample no.	Content, weight. %								Porosity, %
	NbC		TiC		Cr	Al	Fe	Co	
	vol. %	weight. %	vol. %	weight. %					
1	30	27.0	—	—	17.7	2.66	2.66	49.98	1.0
2	40	36.5	—	—	15.39	2.31	2.31	43.49	4.4
3	50	46.5	—	—	12.97	1.95	1.95	36.63	5.0
4	70	61	—	—	8.0	1.2	1.2	22.6	4.2
5	—	—	30	19.0	19.6	2.95	2.95	55.5	25.0
6	—	—	30	19.0	19.6	2.95	2.95	55.5	3.2
7	—	—	30	19.0	19.6	2.95	2.95	55.5	18.0
8	—	—	40	27.0	17.7	2.66	2.66	49.98	10.0
9	—	—	50	36.0	15.51	2.33	2.33	43.83	6.0
10	—	—	50	36.0	15.51	2.33	2.33	43.83	3.1
11	—	—	50	36.0	15.51	2.33	2.33	43.83	10.4
12	—	—	50	36.0	15.51	2.33	2.33	43.83	28.0
13	—	—	50	36.0	15.51	2.33	2.33	43.83	3.4
14	—	—	60	45.5	13.21	1.98	1.98	37.33	9.5
15	—	—	60	45.5	13.21	1.98	1.98	37.33	4.4
16	—	—	70	56.5	10.54	1.58	1.58	29.8	25.0
17	—	—	70	56.5	10.54	1.58	1.58	29.8	6.7

the milling, the share of particles smaller than 5 μm increased up to 48%, while that of particles having a size of 5—10 μm grew up to 38%. The powder mixes were baked in graphite molds, in hydraulic press, at a temperature of 1300—1400 °C, under a load of 2—3 kN. The samples were compacted at ambient temperature, under a load of about 1 MPa. As temperature reached hot compaction temperature and pressure came to 15—50 MPa, the samples were kept under these conditions for 20—30 min. The content of carbide in alloys ranged from 30 to 70% (vol.). The actual specific weight of samples prepared was measured by hydrostatic weighting with the use of analytical balance AD-200 in order to find porosity from the formula

$$\Pi = \left(1-\frac{\rho_{actual}}{\rho_{calculated}}\right)\times 100\%. \tag{1}$$

For neutralizing free carbon that is always present in the carbides (approximately 1.5% C for TiC and 1.0% for NbC) in order to prevent the formation of fusible chrome eutectic system Co—$Cr_{23}C_6$, titanium hydride was added to the alloys. During the alloy compaction, as temperature increases, it decays thereby preventing titanium oxidation, with free titanium reacting with excessive carbon into carbide.

Table 2

Alloy Melting Pont and Heat Resistance

No.	Melting point, °C	Increase in weight, $\Delta m \times 10^{-5}$, g/mm^2				
		10 hours	20 hours	30 hours	40 hours	50 hours
1	1340	81.36				
2	1320	75.82				
3	1320	112.75				
4	1270	222.03				
5	1340	13.505	18.0	20.25	24.4	28.6
6	1350	4.098	6.831	18.85	24.04	28.96
7	1240	12.634	19.35	25.0	30.9	36.8
8	1320	18.39	29.502	37.55	40.99	48.27
9	1270	8.971	12.69	16.19	20.34	23.84
10	1325	5.6	7.67	9.14	10.32	11.8
11	1315	20.16	26.703	28.61	30.25	30.79
12	1280	24.479	43.48	61.7	74.47	84.36
13	1250	11.42	15.38	18.4	21.44	23.77
14	1325	32.55	38.936	49.79	57.02	64.89
15	1260	6.86	9.35	11.22	13.3	14.97
16	1200	37.065	67.15	84.57	94.5	103.2
17	1300	29.27	44.058	58.26	67.82	78.55

Table 3

Temperature of Commencement of Carbide Active Oxidation [9]

Carbamide	TiC	ZrC	HfC	VC	NbC	TaC	Cr_3C_2	Mo_2C	WC
T, °C	1200	1100	900	800	600	650	130—1400	900	800

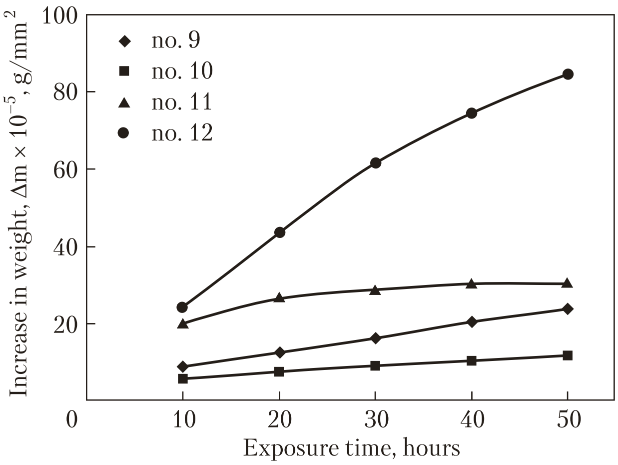

Fig. 1. Heat resistance of powder alloy Co_{doped} — 50% TiC of various porosity: no. 10 — 3.2%; no. 9 — 6.0%; no.11 — 10.4%; and no.12 — 28.0%

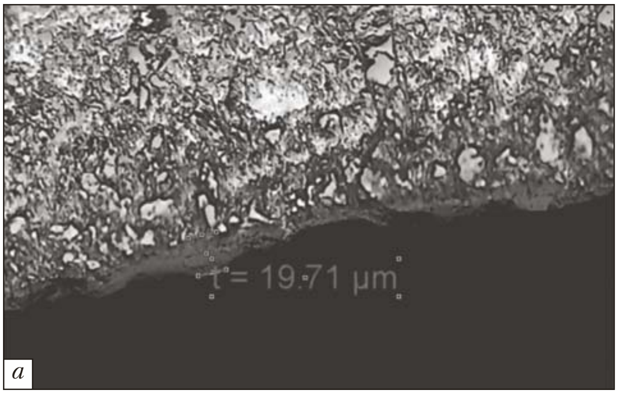

Fig. 2. Oxidation of alloy no.10 at 1100 °C: *a* — formation of surface amorphous oxides; *b* — oxidation in the area of crack formation

The cast alloy samples had approximately the same size and were cut from blanks by the electro-spark technique. Having measured their surface area and weight, the researchers put them into a stone oven, in aluminum oxide crucibles. Each sample was in individual crucible. The heating in electric resistance furnace up to a temperature of 1100 °C in air was controlled by a thermocouple. The samples were kept at these conditions for 10 hours and cooled together with the furnace. The procedure was repeated five times. Totally, the samples were kept at 1100 °C during 50 hours. Heat resistance was determined as increase in the sample weight every 10 hours of annealing divided by its surface area. The phase transformation temperature (commencement and end of melting, start and end of crystallization, solid phase transformations) was found by the differential thermal analysis with the help of VDTA-8M device. The samples having a diameter and height of 5 mm were cut of central part of mold by the electro-spark technique.

The microstructure was studied sing optical microscope OLYMPUS IX70 with a magnification of ×50—500 and by ESM technique (JSM-6400 (*JEOL* Ltd) equipped with EDS) with a magnification of ×1500 — 2000.

THE RESEARCH RESULTS

In order to study wear resistance of compacted powder alloys based on cobalt with niobium or titanium carbides at a temperature of 1100 °C, samples of the following composition have been prepared (Table 1).

The melting point of alloys was measured by the differential thermal analysis method in order to exclude the alloys melting under 1300 °C. The alloy thermograms show that the cobalt alloys reinforced with carbides neither contain fusible phases nor undergo phase transformations under the melting point (1300—1350 °C depending on carbide type), which testifies to the fact that there are no additional effects on them, except for the alloys with high content of carbide, for which it is difficult to reach an equilibrium sta-

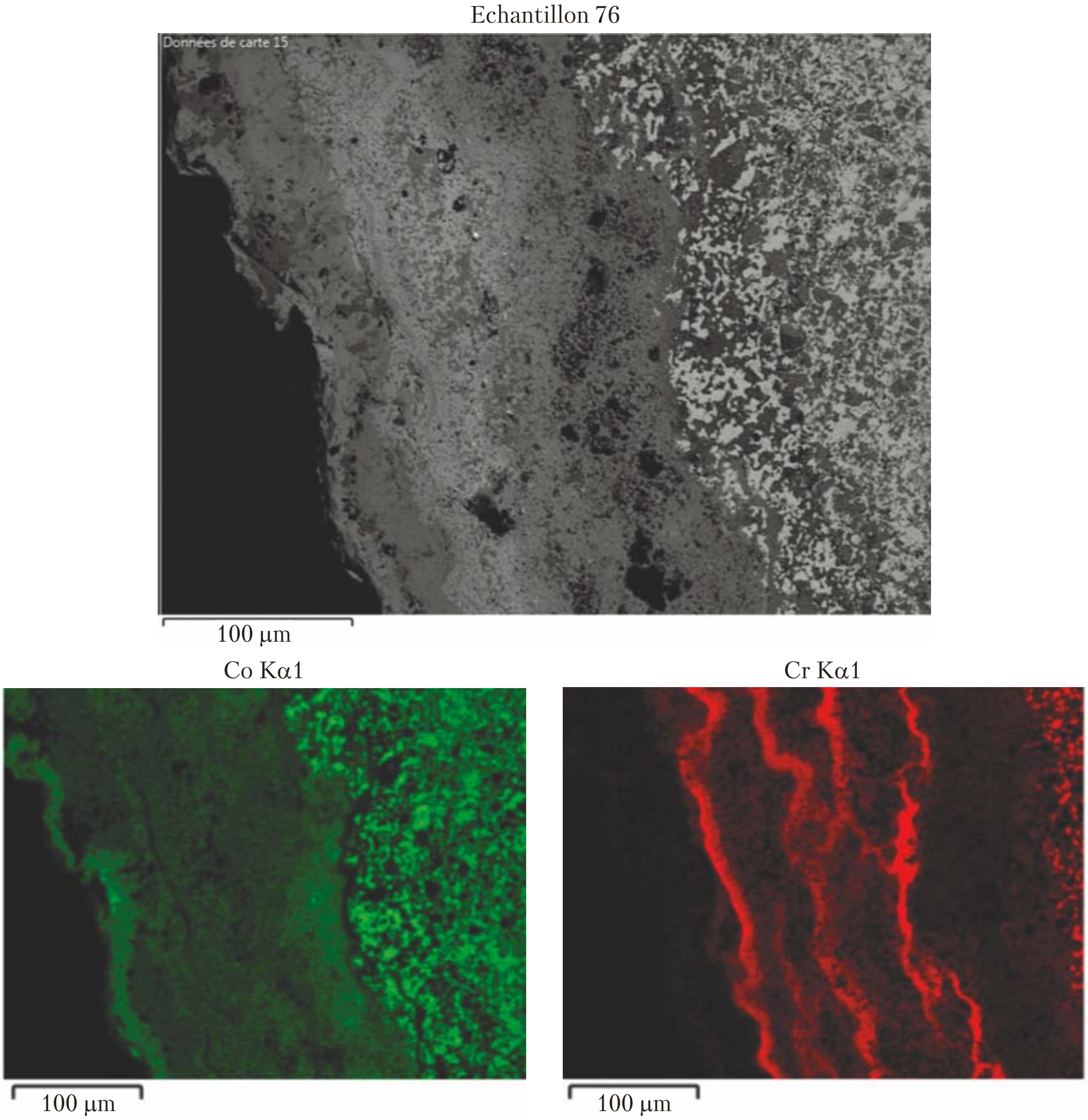

Fig. 3. Microstructure and qualitative content of oxidative layer for alloy no.10 (see the next page as well)

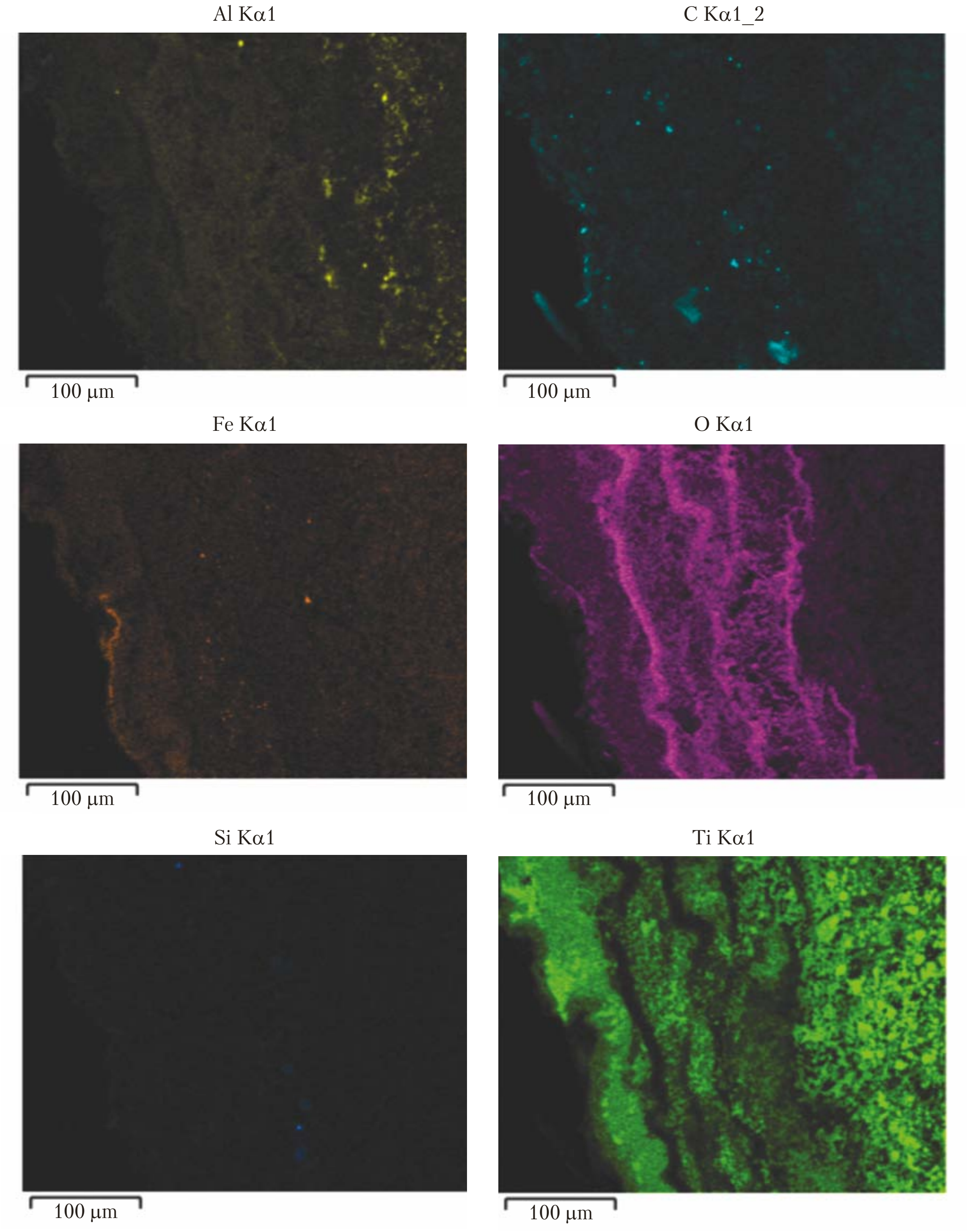

Fig. 3. Continuation

te. However, these alloys keep their shape up to 1400 °C, which is important in terms of their application.

Heat resistance of the cobalt alloys with niobium and titanium carbides obtained by the hot compaction method is given in Table 2.

The compacted alloys with titanium carbide have showed higher heat resistance as compared with that of alloys containing niobium carbide. The further experiments with the latter (over 10 hours) were inexpedient because of very poor results. Doped cobalt being the same base metal for the alloys with both carbides, the difference in heat resistance is caused by resistance to oxidation of metals themselves.

Carbides were chosen on the basis of data concerning oxidation resistance of carbides of IVa—VIa subgroup metals [9]. Table 3 shows temperature of commencement of carbide active oxidation.

Chrome carbide Cr_3C_2 is known to possess the highest resistance to oxidation, with titanium carbide being the second behind it. However, in titanium carbide, unlike other carbides, at high temperature, TiO_2 phase is formed due to diffusion of titanium cations through lattice points. This slows down oxygen dissolution in titanium carbide and raises resistance of titanium carbide to oxidation as compared with other carbides.

It has been decided to use titanium carbide for reinforcement of powder alloys since its hardness is 2—3 times higher than that of chrome carbide, its melting point is 1.5—2 times higher and its resistance to oxidation is twice as much than those of niobium carbide [9, 10].

The study of heat resistance of alloys with titanium carbide has showed that high-temperature oxidation, at the beginning (during the first 10 hours), goes quickly but later, in a little while, the weight starts to grow with a very small almost fixed rate. The most important factor effecting the alloy heat resistance is porosity: as it increases the parameters go down irrespective of type and content of carbide. One can see this from the dependence of weight growth rate on duration of exposure at 1100 °C for the alloys with the same content of titanium carbide (50% vol.) and different porosity (Fig. 1).

The comparative analysis has showed that the more compacted is material the higher is its heat resistance. Large number of pores facilitates oxygen penetration into the base material to a large depth. The width of oxidized near-surface layer can reach dozens of microns (Fig. 2, *a*). In addition, inner surfaces of pores and cracks undergo chemical reactions as well (Fig. 2, *b*), i.e. the area of contact increases, with heat resistance of the material deteriorating.

The ESM study of alloy surface after heat resistance trials have showed a significant oxidized layer in the near-surface layer (Fig. 3, see color inset). The map of sample's edge shows that main elements involved in oxidation are chrome, titanium, and cobalt. It should be noted that the higher is content of element, the more intensive is color.

According to the data of X-ray analysis, the main components of minor traces of cinder remaining in the crucible after the heat resistance trials are rutile TiO_2, cobalt-titanium oxide $CoTi_2O_5$, cobalt-chrome oxide $CoCr_2O_4$, and iron-titanium oxide $FeTiO_3$.

To summarize the results, it should be pointed out that the powder alloys based on doped cobalt with titanium carbide possess an acceptable heat resistance and a melting point higher than 1300 °C and can be used as wear- and heat-resistant material for protecting the GTE blade platforms. These alloys can be used by various application techniques such as: brazing, microplasma powder deposit welding, micro-discharge and diffusion-reaction deposit welding (elaborated in cooperation with the Paton Electric Welding Institute).

CONCLUSIONS

1. The cobalt alloys with titanium carbide content ranging from 30 to 70% (vol.) for protection of GTE blade platform edges have higher heat resistance as compared with the ones with niobium carbide.

2. Heat resistance of the powder alloys with titanium carbide at 1100 °C corresponds to that of ZhS-32 alloy, which testifies to their high protective properties. The lowest gain in weight for the alloy with 50% vol. TiC amounts to nearly 118 g/m^2 per 50 hours. The melting point of powder alloys reaches 1320 °C.

3. Porosity is an important factor effecting heat resistance of the powder alloys with niobium and titanium carbides: as it grows the parameters go downward irrespective of type and content of carbide.

REFERENCES

1. *Pat. Ukrai'ny N 8240A*. Splav na osnovi kobal'ta. Shurin A.K., Dmytrijeva G.P., Cherepova T.S. ta in. [in Ukrainian].
2. *Pat. Ukrai'ny na korysnu model' N 39450*. Splav na osnovi kobal'tu. Shurin A.K., Cherepova T.S., Andrijchenko N.V., Zamkovyj V.Je. [in Ukrainian].
3. Shurin A.K., Dmitrieva G.P., Matjushenko N.I., Maksjuta I.I., Cherepova T.S. Vysokotemperaturnaja solevaja korrozija kobal't-karbidnyh jevtekticheskih splavov. *Zashhita metallov*. 1990, 26(4): 659—661 [in Russian].
4. *Supersplavy II. Zharoprochnye metally dlja ajerokosmicheskih i promyshlennyh ustanovok*. Per. s angl. Red. Sims. Ch.T. Moskva: Metallurgija, 1995 [in Russian].
5. Zharoprochnye splavy na osnove kobal'ta dlja primenenija v gazovyh turbinah. *Mater. Sci. and Eng.* 1987 — 88. R. 11—19 [in Russian].
6. Reznik I.D., Sobol' S.N., Hudjakov V.M. *Kobal't*. Moskva: Mashinostroenie. 1995, T. 1. 1996. T.2 [in Russian].
7. *Physical Properties of Materials, Materials Engineering — Materials Selector — 1987*. dec. 1986. v. 103. N T — 12. P. 81—83.
8. Cherepova T.S., Dmytrijeva G.P., Nosenko A.V, Semyrga O.M. Znosostijkyj splav dlja zahystu kontaktnyh poverhon' robochyh lopatok aviacijnyh dvyguniv vid okyslennja pry vysokyh temperaturah. *Nauka innov.* 2014, 10(4): 22—31 [in Ukrainian].
9. Vojtovich R.F. *Okislenie karbidov i nitridov*. Kyiv: Nauk. dumka, 1981 [in Russian].
10. *Enciklopedija neorganicheskih materialov*. Kyiv, 1977. T. 1. [in Russian].

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ЖАРОСТІЙКІСТЬ ПОРОШКОВИХ КОБАЛЬТОВИХ СПЛАВІВ, ЗМІЦНЕНИХ КАРБІДАМИ НІОБІЮ АБО ТИТАНУ

Досліджено характеристики жаростійкості при температурі 1100 °С порошкових кобальтових сплавів, розроблених для захисту бандажних полиць робочих лопаток ГТД від зношування. Сплави отримані методом гарячого пресування порошків кобальту, хрому, алюмінію, заліза, карбіду ніобію або титану з вмістом карбідів в межах від 30 до 70% (об.). Встановлено, що сплави з карбідом титану переважають за жаростійкістю сплави з карбідом ніобію. Суттєвим фактором, який впливає на жаростійкість сплавів, є пористість: з її збільшенням показники знижуються незалежно від виду та вмісту карбіду. Встановлено оптимальний склад порошкових жаростійких сплавів з карбідом титану з температурою плавлення вищою за 1300 °С для застосування в авіаційному двигунобудуванні.

Ключові слова: сплави кобальту, карбід ніобію, карбід титану, жаростійкість.

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ЖАРОСТОЙКОСТЬ ПОРОШКОВЫХ КОБАЛЬТОВЫХ СПЛАВОВ, УПРОЧНЕННЫХ КАРБИДАМИ НИОБИЯ ИЛИ ТИТАНА

Исследованы характеристики жаростойкости при температуре 1100 °С порошковых кобальтовых сплавов, разработанных для защиты бандажных полок рабочих лопаток ГТД от износа. Сплавы получены методом горячего прессования порошков кобальта, хрома, алюминия, железа, карбида ниобия или титана с содержанием карбидов в пределах от 30 до 70% (об.). Установлено, что сплавы с карбидом титана превосходят по жаростойкости сплавы с карбидом ниобия. Существенным фактором, влияющим на жаростойкость сплавов, является пористость: с ее увеличением показатели снижаются независимо от вида и содержания карбида. Установлен оптимальный состав порошковых жаростойких сплавов с карбидом титана с температурой плавления выше 1300 °С для применения в авиационном двигателестроении.

Ключевые слова: сплавы кобальта, карбид ниобия, карбид титана, жаростойкость.

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