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HIGH TEMPERATURE OXIDATION OF DOUBLE CARBIDE BASED HARD ALLOYS

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Summary. Dependences of the oxidation kinetics in air of titanium and vanadium carbide based hard alloys with a nickel-chromium binder and the structure, phase and chemical composition of the formed scale in the temperature range 800–1100 °C were found. The regularities of the oxidation process were determined by the weight method, the main kinetic characteristics were calculated.

Key words: hard alloy, titanium and vanadium carbide, high temperature oxidation, kinetic, scale.

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Statement of the problem. The field of application and the service temperature range of titanium carbide based hard alloys can be broadened by establishing the temperature conditions under which they maintain their exploitation stability. Since the heat resistance of alloys can be changed by reducing the rate of oxygen diffusion into the depth of the products due to the formation of dense protective oxide layers, the intended addition of certain chemical elements and compounds to the basic composition is a promising field of research.

Analysis of available researches. Titanium carbide is the most appropriate for use as a carbide base of wear-resistant and heat-resistant hard alloys both from an economic point of view and the level of physical and mechanical properties [1]. It has a high melting point, microhardness, relatively low density, and is well wetted by binding metals used in alloys manufacturing. In this regard, despite lower strength and toughness compared with tungsten cobalt hard alloys, titanium carbide based alloys are effectively used as materials for cutting and stamping tools, structural parts operating under intense friction conditions and high temperatures [2–4].

One of the ways to improve their properties, titanium carbide based alloys heat resistance in particular is the improvement of their chemical composition by carbide base alloying adding the components, which form protective oxide layers, into the composition of the metal binder. That is vanadium carbide forms a complete solid solution with titanium carbide and is an inhibitor of carbide grains growth, which results in the improving of the mechanical properties of double carbide based alloys [5, 6].

The carbide base and metal binder of titanium carbide based alloys are oxidized in different ways and at different temperatures. Oxidation of the metal binder starts at the temperature 500 °C, while that of the carbide base – at 800–900 °C [7], and alloys based on tungsten carbide are intensively oxidized at least at the temperature 700 °C [8–12].

It is known that nickel, chromium and aluminum are promising from the point of view of increasing heat resistance due to formation of protective layers, which consists of their oxides and spinel-type compounds [13, 14]. Both for the high-entropy AlCoCrFeNi alloys, which are used as a metallic binder in titanium carbide/carbonitride based alloys, it is shown that high

concentration of Cr and Al causes a passivation effect [15], Cr and Ni [16] being of similar effect. Aluminum in the amount of 1 (wt.) % increases oxidation resistance and forms an oxide barrier up to the temperature 900°C, but at 1100 and 1300°C the oxide layers are not dense enough and oxidation resistance decreases [17]. Aluminum is added to hard alloys as metal [15], intermetallic Ni₃Al [18, 19], aluminum nitride AlN [20, 21]. In titanium carbide based hard alloys, the latter is treated as the anti-recrystallization adding. During sintering process, aluminum nitride is decomposed, and the formed aluminum diffuses into the binder, which results in its dispersion strengthening with the formation Ni₃Al(Ti) compound.

Despite the available investigations on the oxidation of titanium carbide/carbonitride based hard alloys, they almost deal with the alloys of the TiC/Ti(C,N)-metal binder type. However, the behavior of double/multi-carbide based hard alloys at high temperatures is not studied enough. Besides most of the papers deal with the process of high-temperature long time oxidation of hard alloys – 20, 100 or more hours, but the initial stage of oxidation is not studied enough, when the alloys adjustment to the environment and the protective scale layer is formed. However, to understand the kinetics and mechanism of alloys oxidation in the early stages makes possible to predict their behavior under conditions of long time high-temperature oxidation.

Thus, the problem of developing hard alloys with improved physical, mechanical properties and service characteristics for operating at high temperatures is up to time.

The objective of the paper is to determine the regularities of chemical composition impact on the high-temperature oxidation kinetics of TiC-VC-Ni-Cr-AlN hard alloys, morphology, phase and chemical composition of oxidation products.

The task of the research is to study the effect of vanadium carbide and nickel-chromium binder on the high-temperature oxidation kinetics in the temperature range 800–1100°C, the scale microstructure and its chemical and phase composition.

Materials and methods of the research. Titanium and vanadium carbide based hard alloys with a nickel-chromium binder were prepared by the powder metallurgy method, which includes such basic technological operations as making homogeneous mixture of the appropriate composition, bilateral cold pressing and high-temperature sintering in vacuum. The optimal regims of technological process were established as a result of previous studies [22].

To obtain alloys, powders of carbides with a non-stoichiometric composition of TiC_{0.96}, VC_{0.88}, binder metals with the main component content of at least 99.8%, aluminum nitride AlN_{0.97} were used. Iron is added to the alloy as a result of grinding while obtaining the homogeneous mixture. To study the influence of chemical composition of alloys on their heat resistance, vanadium carbide-free alloys and those with 2 and 5% VC, with different contents of Ni-Cr alloys, taking into account the optimal amount of components from the point of view of their influence on mechanical properties, were prepared (Table 1).

Table 1

Chemical composition of the studied alloys

No	Content of components (wt.)%					Additive density, g/cm ³
	TiC	VC	Ni	Cr	AlN	
1.	80.0	–	13.5	4.5	2.0	5.25
2.	78.0	2.0	13.5	4.5	2.0	5.26
3.	75.0	5.0	13.5	4.5	2.0	5.28
4.	83.0	5.0	7.5	2.5	2.0	5.10
5.	69.0	5.0	18.0	6.0	2.0	5.48

Cylindrical specimens of 8 mm diameter and 10 mm height and relative density of 0.98–0.99 were used for the study, which excludes the presence of through porosity and its influence on oxidation rate.

Investigation of heat resistance was carried out by the weight method in the isothermal conditions in air. The influence of vanadium carbide on the heat resistance of alloys has been studied at the temperatures 800 and 1050 °C for 24 hours, and the influence of nickel-chromium binder has been investigated at the temperatures 900, 950, 1000 and 1100 °C for 3 hours. Oxidation kinetic curves were analyzed using the STATISTICA 10 software package.

The scale microstructure was studied using the electron microscope «Camscan 4-DV», and its micro-X-ray spectral analysis was carried out. The morphology of the alloys was studied using a MIM-10 microscope. X-ray phase analysis of oxidation products was performed on a DRON-4 diffractometer in monochromatic $\text{CuK}\alpha$ radiation.

Results of the research and discussion. To compare the alloys resistance to high-temperature oxidation, their oxidation kinetic curves were analyzed. Quantitative evaluation of heat resistance was carried out according to by the value of weight gain g (mg/cm^2) depending on the time and temperature of oxidation.

Figure 1 presents the kinetic curves of alloys oxidation based on titanium carbide and on a double carbide base with similar content of metallic binders – 18 (wt.%) and 2 (wt.%) aluminum nitride at the temperatures 800 and 1050 °C in different coordinates.

At both temperatures, the titanium carbide based alloy, compared with the alloy of 5 (wt.%) VC, the weight gain is greater – by 2.2 times at the temperature 800 °C, and by 1.33 times at the temperature 1050 °C. The greatest heat-resistant happened to be in the alloy with 5 (wt.%) VC the greatest weight gain being 1.97 mg/cm^2 at the temperature 800 °C and 25.07 mg/cm^2 at the temperature 1050 °C in 24 hours.

Comparison of oxidation value of the studied alloys with titanium carbonitride based alloy testified that they are more resistant to oxidation [23]. Thus, the value of weight gain of the titanium carbonitride based alloy increase at the temperature 800 °C during 3 hours of oxidation varies within 2–3 mg/cm^2 , while for the researched alloys such values of weight gain are demonstrated after 24 hours.

Linear, parabolic and logarithmic equations were used to analyze the oxidation kinetic curves, the last being the most proper to describes accurately the oxidation process of the alloys under study (Fig. 1 c, d).

$$g = k \ln (t/t_0 + 1), \quad (1)$$

where g is the weight gain (mg/cm^2),

k is the oxidation rate constant (mg/cm^2),

t is the oxidation time at constant temperature (min),

t_0 is heating time to the researching temperature (from 45 to 70 minutes) (min).

After appropriate transformations, we obtained a linear equation:

$$y = b_0 + b_1 x, \quad (2)$$

where $x = \ln(t+t_0)$; $b_0 = -k \ln t_0$.

The corresponding regression equations were obtained, which made it possible to calculate oxidation rate constants.

The regularities of oxidation of TiC-based alloys with 5 (wt.%) VC and different metallic binder content at the early stages of oxidation (up to 3 h) are presented in Fig. 2.

At all temperatures, the highest heat resistance was demonstrated by alloy 5 with 24 (wt.%) NiCr, which contains 6 (wt.%) Cr and whose the weight gain during 3 hours does not exceed 16 mg/cm².

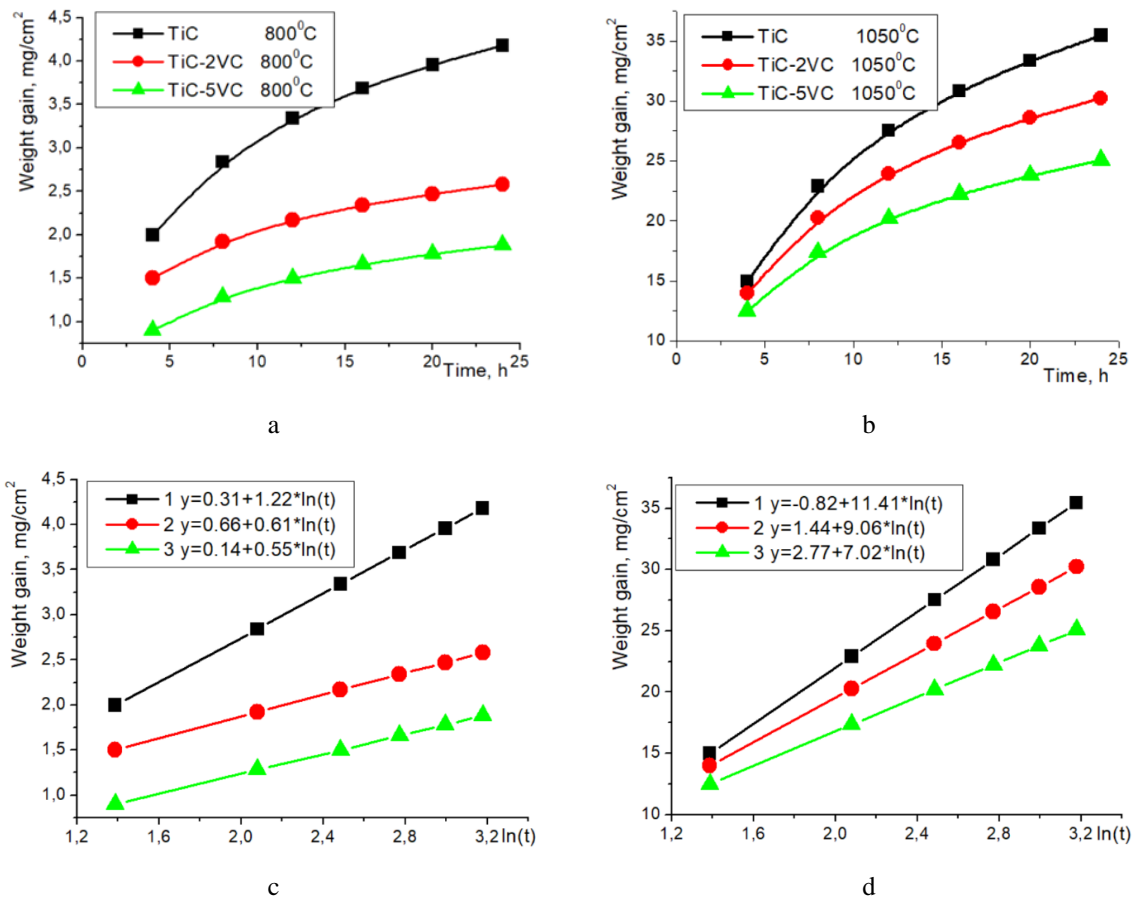


Figure 1. Dependence of the weight gain of TiC-NiCr-AlN alloys (1), TiC-2VC-NiCr-AlN (2), TiC-5VC-NiCr-AlN (3) at the temperatures 800 (a, c) and 1050 °C (b, d)

Table 2 presents the values of oxidation rate constants of alloys 3-5 calculated from equation (1) at different temperatures.

Table 2

Oxidation rate constants of alloys 3–5 at the studied temperatures

Alloy	Content of metal binder, (wt.) %	Oxidation rate constant (mg/cm ²) at different oxidation temperatures, °C			
		900	950	1000	1100
3	10	1.71	3.11	6.04	11.72
4	18	1.57	2.92	5.49	10.38
5	24	1.19	2.42	4.54	7.81

As it can be seen from Table 2, with the increase of metal binder content and, respectively, the content of chromium in it, the value of oxidation rate constant decreases at all temperatures of the study. For all alloys, starting from a temperature 1000 °C,

intensification of oxidation process and changing the logarithmic law of oxidation to a linear one were observed (Fig. 2): after 125 minutes of oxidation for alloys with 10 and 18 (wt.%) NiCr, and after 95 minutes for an alloy with 24 (wt.%) NiCr.

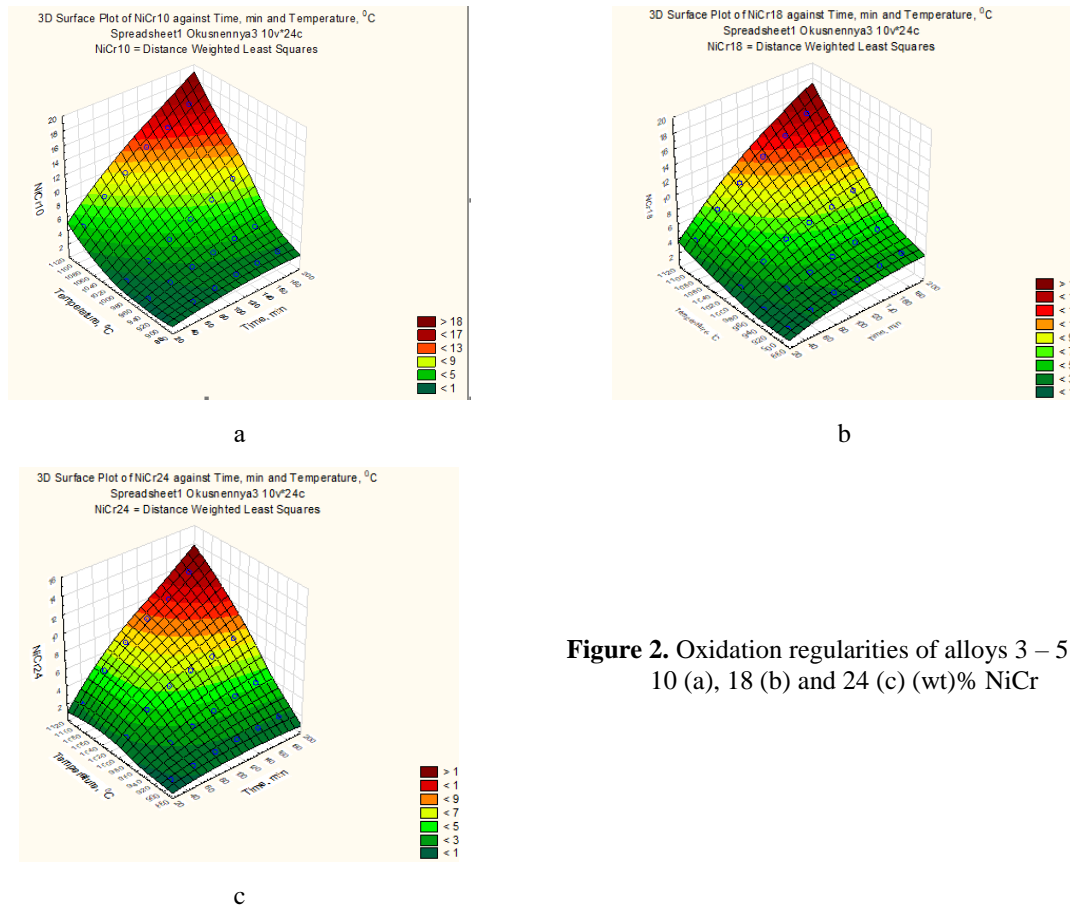
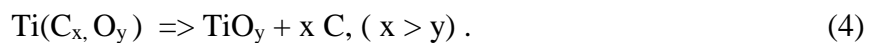


Figure 2. Oxidation regularities of alloys 3 – 5 with 10 (a), 18 (b) and 24 (c) (wt.%) NiCr

Oxidation occurs by diffusion of oxygen and counterdiffusion of titanium (Ti^{+4}) and binding elements. Oxygen advance into the crystal lattice of carbides forming the oxycarbide solid solutions of titanium and vanadium. When concentration of oxygen in the oxycarbide phases increases, they can be decomposed in two ways:



Titanium release occurs unevenly along the carbide grains, which have a typical core/rim structure. Oxycarbide phases have defects both in the metalloids and in the metallic sublattice, so both free metal and carbon can be released.

Effective activation energy in the temperature range 900 – 1000 °C does not depend on the chemical composition and for alloys 3–5, in fact it is the same – 157, 155 and 166 kJ/mol, respectively. For all alloys, the effective activation energy is in 1.5...1.6 times lower than for pure titanium carbide (250 kJ/mol).

If decomposing of oxycarbide occurs according to the equation 4, the oxidation process is probably controlled by carbon burning. The effective activation energy of carbon combustion in the temperature range up to 1300 °C is 100 kJ/mol, which is close to the effective activation energy of alloys 3 and 4 in the temperature range 1000 – 1100 °C – 96.3, 92.5 kJ/mol.

As two opposite processes take place during oxidation – the value increasing of weight gain due to the formation of oxide layers and evaporation of some elements and the formation of gaseous products of oxidation, in order to evaluate the heat resistance of alloys, in addition to kinetic dependencies, scale thickness, its morphology and chemical composition were taken into account.

As it can be seen from Fig. 1, for alloys with different contents of vanadium carbide at the temperature 800 °C, the value increasing of weight gain is insufficient, blue-violet colors of runoff, which specify the lower titanium oxides – TiO, Ti₂O₃, were observed on their surface. X-ray analysis testified the presence of these oxides, as well as traces of lower vanadium oxides VO. The scale adheres tightly to the base of the specimens.

As the temperature rises to 1050 °C, the scale becomes brown, it is less dense, has a larger thickness and drop-shaped formations, but its delamination from the base of the sample was not observed. The scale is two-layered – the inner layer contains lower titanium and vanadium oxides, and the outer layer has rutile TiO₂, higher vanadium oxide V₂O₅, iron oxide Fe₂O₃. Drop-shaped formations are rutile of 1–3 microns particles. In addition, a small amount of gaseous product of carbon oxidation is likely to be formed.

The scale structure of alloys containing 5% VC, 2% AlN and different content of nickel-chromium binders is presented in Fig. 3.

From Fig. 3 it can be seen that in alloy 5 with 24 (wt.) % NiCr, the scale is two-layered, which is conventional for the titanium carbide oxidation [7]. In the alloys containing less metallic binder, an intermediate loose layer of low density was found. Scale layers differ in size and grain size. For all alloys, the inner layer is dense, fine-grained, of 44...60 μm thickness, while the total scale thickness in alloy 5 is approximately 260 μm, and in alloys 3 and 4 it is 280 μm. Meanwhile, as compared with the temperature 1000 °C, the scale thickness increased by 2.4, 3.5, and 4.4 times for the alloys with 10, 18, and 24 (wt.) % NiCr, respectively. When the content of metallic binder is greater, the total scale thickness decreases due to the reduction of the outer layer and disappearance of the intermediate layer, which testifies the oxidation process retardation.

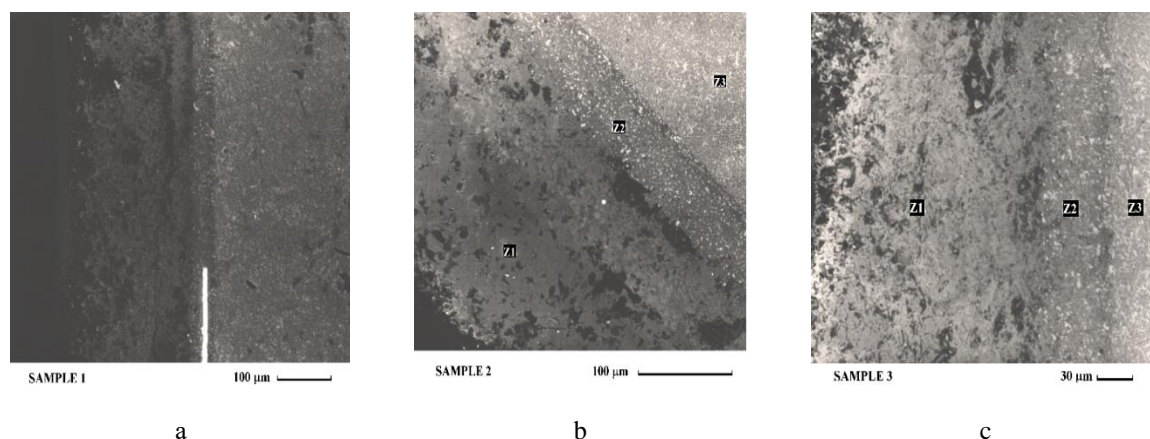


Figure 3. Cross-sections of alloys scale with 10 (a), 18 (b) and 24 (wt.) % NiCr binder (c), obtained at the oxidation temperature 1100 °C for 3 hours

The results of X-ray phase analysis for the alloy with 18 (wt.) % NiCr, in which the intermediate layer is clearly visible, are presented on Table 3.

It was established that, in addition to the main phase of rutile (TiO₂) with a P4/mnm (C4) lattice, spinel of the NiTiO₃ type was found in the outer layer. In the intermediate

layer, besides rutile and spinel, Ti_2O_3 and traces of V_2O_5 were found. Ni and TiO trases were found in the inner layer at the boundary with the intermediate layer, and spinel was not available on the boundary with the base of the alloy. Moreover, such phases as TiC and Ni have appeared.

Table 3

Phase composition of oxidation products of alloy 4 at the temperature 1100 °C

Alloy	Content of metal binder, (mass)%	Scale layer				Alloy base
		Outer	Intermediate	Internal (boundary with intermediate layer)	Internal (boundary with alloy base)	
4	18	TiO ₂ , NiTiO ₃	TiO ₂ , Ti ₂ O ₃ , NiTiO ₃ , traces V ₂ O ₅ ,	TiO _{2-x} , NiTiO ₃ , traces Ni, TiO	TiO _{2-x} , TiO, TiC, Ni,	(Ti,V)C, Ni, traces Cr ₇ C ₃ , Fe ₃ C

The results of micro-X-ray spectral analysis of alloy 3 with 10 (wt.%) NiCr binder scale (as the least heat-resistant), formed after three hours at the temperature 1100 °C, are presented on Table 4.

As it can be seen from the presented results, the outer layer is formed by the diffusion of metal to the outer phase boundary, and the inner layer is formed through the outer layer by the diffusion of oxygen through it. Composition of the binder changes due to the preferential oxidation of titanium and the different rate of diffusion of binder components into the outer layers of the scale. Due to the fact, that the pseudo-light phase, saturated with nickel is insufficient (up to 42.9%), no nickel oxide was found in the outer layer of nickel oxide by X-ray method. In the same layer, a dark phase was found, in which, beside titanium, there was found significant amount of vanadium, aluminum and iron.

Table 4

Distribution of elements in the scale layers of alloy 3 from 10 (wt.) % NiCr, oxidation temperature 1100 °C

Layer	Point of analysis	Content of elements, (at.) %						
		Ti	V	Ni	Cr	Al	Fe	O
Internal	Light phase	7.271	0.644	87.28	0.086	0.168	3.456	1.091
	Gray phase	70.511	5.014	11.97	2.924	0.517	1.08	7.985
External	Pseudo-light phase (little)	43.55	3.65	42.9	1.585	1.323	2.42	5.565
	Light phase	80.52	5.18	2.427	0.437	0.422	1.062	9.96
	Gray phase	62.95	6.12	18.11	0.472	0.93	2.95	8.46

The structure of the inner layer of scale looks like oxycarbide core and is similar to the initial structure of the alloys carbide base. Oxidized carbide grains (Ti,V)C and their conglomerates, as well as oxides of the alloy components, were observed at the boundary between the scale and the base of the alloy (Fig. 4).

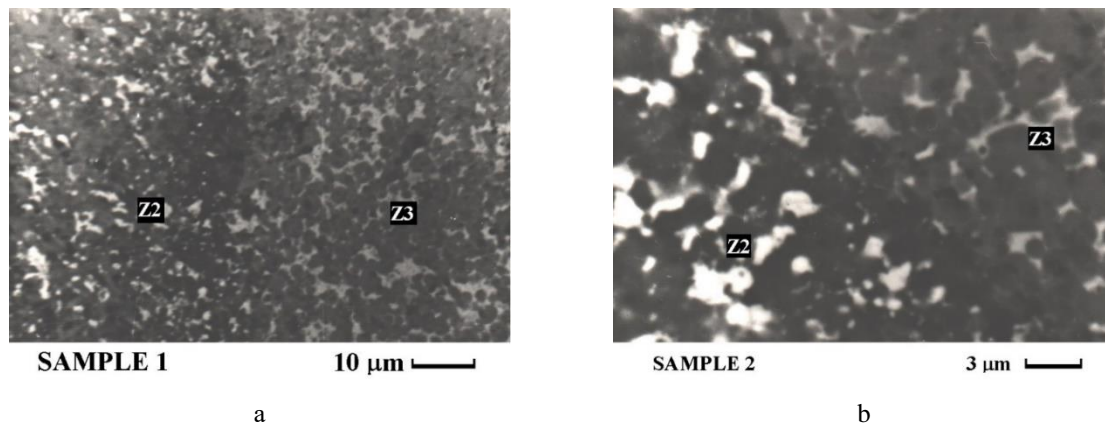


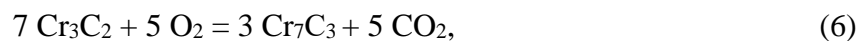
Figure 4. Boundary surface between the inner scale layer and the alloy base of alloys 3 and 4 with 10 and 18 (wt.) % NiCr obtained at an oxidation temperature 1100 °C for 3 hours

In the inner layer, nickel is available as metallic round inclusions (Fig. 4, Table 3) and NiTiO₃ spinel.

It is known [24] that in double carbide based alloys, the component being of higher similarity to oxygen is oxidized in the inner part of oxidation zone while still in the metal phase. Due to this, when the temperature rises, an entire inner layer of scale is formed and the heat resistance increases. Thus, the increase of chromium content in the binder from 2.5 to 6 (wt.)%, which is found in the internal oxidized layer, result in the decrease in the rate of oxygen diffusion to the material base. Oxidation, when chromium is available occurs according to the following reactions:



under incomplete oxidation lower carbides are formed:



These processes are likely to take place during the oxidation of alloys with 6 (wt.)% chromium in the binder. The heat resistance improvement is achieved by means of binder metals due to their passivating effect, when the diffusion of oxygen into the scale and the counterdiffusion of titanium atoms is more complicated. The release of CO and CO₂ gases results in formation of porosity, which reduces the alloys heat resistance.

Cations diffusion with a valency of 3 and higher in rutile occurs due to the internodal mechanism. The presence of vanadium, chromium, and aluminum increases the number of internodal Ti⁴⁺ cations, while the number of oxygen vacancies increases, the diffusion of which is the controlling stage during sintering of rutile. In this way, an internal barrier layer based on carbides of titanium, vanadium and chromium is formed, which reduces the diffusion of titanium and oxygen and slows down the formation of the outer scale layer. The rate of oxidation is determined by the processes in the inner layer on the surface of oxide-carbide phases, since the outer layer does not possess protective properties.

All studied alloys are heat-resistant up to the temperature 900 °C, they can be used for long-term operation at 800–900 °C and for short-term work at 1000–1100 °C. An alloy with 24 (wt.)% NiCr binders is heat-resistant even at the temperature 1100 °C, since in this case the

amount of chromium is sufficient to form a protective scale layer and the oxidation process is controlled by the diffusion of titanium and oxygen through the chromium oxide layer.

Comparison of the obtained results with the data in [10, 12, 13, 23] regarding the oxidation of tungsten carbide based, carbide based and titanium carbonitride based alloys, testifies that the investigated alloys are more heat resistant. Alloys of the TiC-VC-Ni-Cr-AlN system are heat-resistant up to the temperature 1100 °C and can be used for the manufacture of cutting tools operating at high cutting speeds, wear-resistant parts for operation in the oxidizing environments at extremely high temperatures, etc.

Conclusions. It is found that the alloy based on titanium carbide, compared to the alloy with 5 (wt.%) VC, has in 2.2 and 1.33 times higher the value increasing of weight gain at oxidation temperatures 800 °C and 1050 °C respectively.

Despite the metal binder content, the oxidation of the TiC-VC-Ni-Cr-AlN system alloys at the initial stage (up to 3 hours) to the temperature 1000 °C is described by logarithmic equation. At the temperature 1100 °C, for alloys with 10 and 18 (wt.%) NiCr binders after 95 minutes, and with 24 (wt.%) after 125 minutes, the logarithmic law of oxidation changes to a linear one. In the temperature range 800–1000 °C, the effective activation energy of the alloys is almost the same 157, 155 and 166 kJ/mol and is 1.5...1.6 times lower than the effective activation energy of pure titanium carbide. At higher temperatures the effective activation energy decreases to 79 kJ/mol as the NiCr content of binder increases.

As a result of oxidation, a two-layered scale is formed in all alloys with the inner layer thickness 44...59 μm, and the thickness of the outer layer is in 3.7–5.4 times larger, and in the alloy with 24 (wt.%) NiCr connections, it is the smallest and is equal to 260 microns.

The phase composition of the oxidation products was found – the outer layer contains TiO₂ and NiTiO₃, the inner layer contains TiO^{2-x}, TiO, TiC, Ni.

TiC-VC based alloys with 24 (wt.%) NiCr binder are heat resistant up to 1100 °C and more heat resistant than tungstate cobalt and titanium carbide/carbonitride hard alloys.

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ВИСОКОТЕМПЕРАТУРНЕ ОКИСНЕННЯ ТВЕРДИХ СПЛАВІВ НА ПОДВІЙНІЙ КАРБІДНІЙ ОСНОВІ

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Резюме. Встановлено взаємозв'язок між кінетикою окиснення на повітрі твердих сплавів на основі карбиду титану і ванадію з нікель-хромовою зв'язкою в інтервалі температур 800–1100 °С та структурою, фазовим та хімічним складом утвореної окалини. Ваговим методом встановлено

закономірності процесу окиснення, на їх основі розраховано кінетичні характеристики – константу швидкості окиснення й ефективну енергію активації. Мікроструктурні дослідження окалини та мікрорентгеноспектральний аналіз проводили з допомогою електронного мікроскопа. Морфологію окалини сплавів досліджували металографічним методом аналізу. Рентгенівський фазовий аналіз продуктів окиснення проводили на дифрактометрі ДРОН-4 у монохроматичному $\text{CuK}\alpha$ випромінюванні. Показано, що при обох температурах окиснення сплав на основі карбіду титану, порівняно із сплавом з 5 (мас.)% VC, має більший питомий приріст маси – при температурі 800 °C в 2,2 рази, а при температурі 1050 °C – в 1,33 рази. При температурах до 1000 °C на початковій стадії кінетика окиснення всіх сплавів добре описується логарифмічним рівнянням. При температурі 1100 °C відбувається інтенсифікація процесу окиснення логарифмічний закон змінюється на лінійний після 95 хвилин (для 24 (мас.)% нікель-хромової зв'язки) і 125 хвилин (для 10 і 18 (мас.)% зв'язки). Константа швидкості окиснення має найменші значення при усіх температурах для сплаву з 5 (мас.)% VC і 24 (мас.)% Ni-Cr зв'язки. У сплавах виявлено двошарову окалину, основною фазою зовнішнього шару є рутил TiO_2 . У внутрішньому шарі виявлено хром, який перешкоджає дифузії кисню в основу сплаву, а також NiTiO_3 . Досліджувані сплави є більш жаростійкими порівняно зі сплавами на основі карбіду вольфраму та карбіду/карбонітриду титану. Їх можна використовувати для роботи в умовах окиснення на повітрі до температури 1100 °C.

Ключові слова. Тверді сплави, карбіди титану і ванадію, високотемпературне окиснення, кінетика, окалина.

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