

OXIDATION RESISTANCE OF TITANIUM AND CHROMIUM CARBIDE-BASE CERMETS

Jüri PIRSO and Jakob KÜBARSEPP

Tallinna Tehnikaülikooli materjalitehnika instituut (Department of Materials Technology, Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn, Eesti (Estonia)

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Abstract. The influence of chemical composition of TiC- and Cr₃C₂-base cermets on the resistance to oxidation during prolonged exposure to high-temperature (800 and 900°C) air was studied. It was found that in the temperature range of 800–900°C, the oxidation of Cr₃C₂-base cermets exceeds that of TiC-base ones 30–50 times. This process follows the logarithmic kinetics. The parabolic rate law was observed during the oxidation of TiC-base cermets. Alloying of TiC–NiMo cermets by NbC and VC contribute considerably to the increase in oxidation resistance (up to 5 times). Among TiC-steel cermets, alloys with low TiC content and high oxidation resistant chromium-silicon steel binder had the highest oxidation resistance.

Key words: oxidation, titanium carbide, chromium carbide, cermets, hard metals, carbide phase, binder-phase.

1. INTRODUCTION

Titanium carbide, in particular, chromium carbide-base cermets (hard metals) are well known because of their high resistance to oxidation [1–4]. The latter has the highest oxidation resistance among hard metals. To improve oxidation resistance of TiC- and Cr₃C₂-base cermets, alloying (modifying) by different elements could be used. At the same time, information about the influence of alloying elements on the oxidation resistance is scanty.

This paper focuses on the influence of chemical composition of titanium and chromium carbide-base cermets on the resistance to oxidation during prolonged exposure to high-temperature air.

2. MATERIALS AND EXPERIMENTAL DETAILS

Oxidation is known to be a uniform process [5]. Therefore we may assume that thickness of an oxide film is proportional to the increase in the

specimen weight. Therefore we used the traditional method of measuring oxidation by determining weight gain ΔG (mg/cm^2) of specimens.

The kinetics of oxidation was determined at 800 and 900°C. Using ground test pieces $5 \times 15 \times 20$ mm with mass *ca* 8 gr, measurements of weight gain were taken periodically – after heating during 1, 3, 6, 12, 24, 48, 72, and 96 h, followed by open air cooling. Such experimental feature creates thermal stresses of oxide protective scales after every specific interval of time, but at the same time, it simulates a cyclic mode of operation, frequently occurring in engineering service (e.g., turbine blades, oil sprayers).

Three different groups of cermets were investigated:

Cr_3C_2 -Ni and Cr_3C_2 -NiCr;

TiC-NiMo;

TiC-steel.

The binder content in the Cr_3C_2 -base cermets investigated was 10–30 mass % and in TiC-NiMo ones 20–60 mass %. Chromium content in Cr_3C_2 -NiCr binder-phase was 20 mass %. The ratio Ni:Mo in TiC-NiMo cermets was 4:1, 2:1 and 1:1. Some grades of such cermets were modified by different refractory compounds: VC, NbC, Cr_3C_2 , TiB_2 , TiN, and SiC. The content of alloying compounds in TiC-NiMo cermets was 1, 3, 5, 10, and 15 mass %.

The content of steel binder in steel-bonded hard metals (SBH) was 30–60 mass %. According to oxidation resistant steel binder composition, SBH can be classified into four groups (content of alloying elements in binder in mass %):

TiC-FeSi2

TiC-FeCrSi21 1.5

TiC-FeCrNi22 16

TiC-FeCrNi22 26.

The first two groups of SBH have heat-treatable steel binder with martensitic structure after hardening, and the two latter ones have an austenitic non-heat-treatable binder. Some grades of such corrosion resistant SBH were additionally alloyed (mass % in binder) by silicon (1.5 or 3), copper (1.5 or 3) and molybdenum (5 or 10).

All Cr_3C_2 - and TiC-base cermets were sintered in a vacuum. The porosity of cermets was 0.1–0.8 vol. % depending on the composition.

3. RESULTS AND DISCUSSION

Pilling and Bedworth classify oxidisable metals into two groups: those that form protective oxide scales and those that do not [6]. If the Pilling-Bedworth ratio (volume of 1 mol of oxide/volume of 1 mol of metal) is < 1 , the oxide scales provide no efficient barrier to the penetration of gas to the metal surface. If the ratio is > 1 , the protective scale will shield the metal, and oxidation can proceed only by solid state diffusion. If the ratio is much greater than 2 and the scale is growing at the metal/oxide interface, the large compressive stresses developed in the oxide may cause the scale to crack and spall off.

Oxide scale content is a necessary but not a sufficient condition for providing resistance to oxidation. For protective purposes, the scale adhesion in the metal/oxide interface and stresses in scales that can damage the scale are of great importance.

In engineering practice, changes in temperature have a great effect on the stress state of metals and their oxides. Therefore, oxide protective scales fail because of the stresses created by cooling from the oxidation temperature. Thus, in the case of cyclical heating, oxidation of metals as well as cermets is higher than that at constant temperature [7].

3.1. Cr₃C₂-base cermets

During heating in air at 700–1000°C, an oxide film consisting of oxides CrO₂, Cr₃O₈ and Cr₂O₃ is formed [7]. A mixed oxide NiCr₂O₄ is usually formed when Cr₃C₂-Ni cermets are oxidised [3]. Considerable oxidation of such hard metals begins at 800°C and is accompanied by burning out of carbon. In that process, chromium carbides with decreased carbon content – Cr₇C₃ and Cr₂₃C₆ – are formed under oxide films.

Our experiments show that oxidation resistance of Cr₃C₂-Ni cermets depends on binder content (Fig. 1) – the rate of oxidation increases with the increase of metallic binder content of an alloy. At the first stage of oxidation, NiO film forms, followed by the formation of a mixed oxide NiCr₂O₃ layer. Similar results have been described in [7]. Consequently, in oxidation resistance, chromium carbide is superior to the binder-phase. On the specimens from chromium carbide, a thin green-colour chromium oxide Cr₂O₃ film forms after 0.5 h heating. According to petrographical analysis [7], a double-layer oxide film forms on the chromium carbide. The outer green-colour layer has coarse-crystalline structure (grain size 10–20 μm). The inner dark layer is fine grained (grain size 2–7 μm), in large numbers also containing crystals of chromium carbides Cr₃C₂, Cr₇C₃ and Cr₂₃C₆.

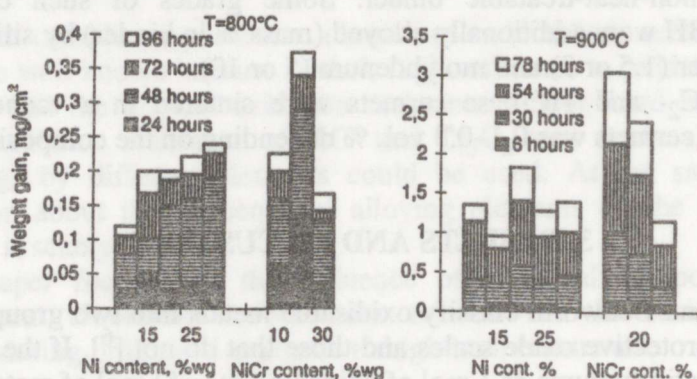


Fig. 1. Weight gain in air at 800 and 900°C for Cr₃C₂-Ni cermets as a function of binder content.

Unexpectedly, the oxidation resistance of cermets with Ni-Cr binder is inferior to that of cermets with Ni-binder (Fig. 1). It may be attributed to the developing higher growth stresses during oxidation and thermal

stresses during cooling from the reaction temperature. Both may result in partial loss of oxidation protection. An increase in temperature up to 900°C raises the oxidation factor to nearly ten. At such a high temperature, no relationship between oxidation resistance and binder content of Cr_3C_2 -Ni cermets exists. It can be explained by the equalisation of oxidation rates of carbide and binder-phases.

3.2. TiC-NiMo cermets

Resistance to oxidation of TiC-base cermets is by 30–50 times less than that of Cr_3C_2 -base ones (Fig. 2). It can be attributed, in particular, to the formation of oxide scales of less tightness during oxidation of TiC-base cermets. As is known, already at 500°C, oxidation of titanium carbide begins [8]: decrease in lattice parameter of TiC from 4.324 Å to 4.320 Å is an evidence of titanium oxycarbide formation. Oxidation at such a low temperature is also accompanied by the formation of porous rutile TiO_2 with a relatively low protection ability.

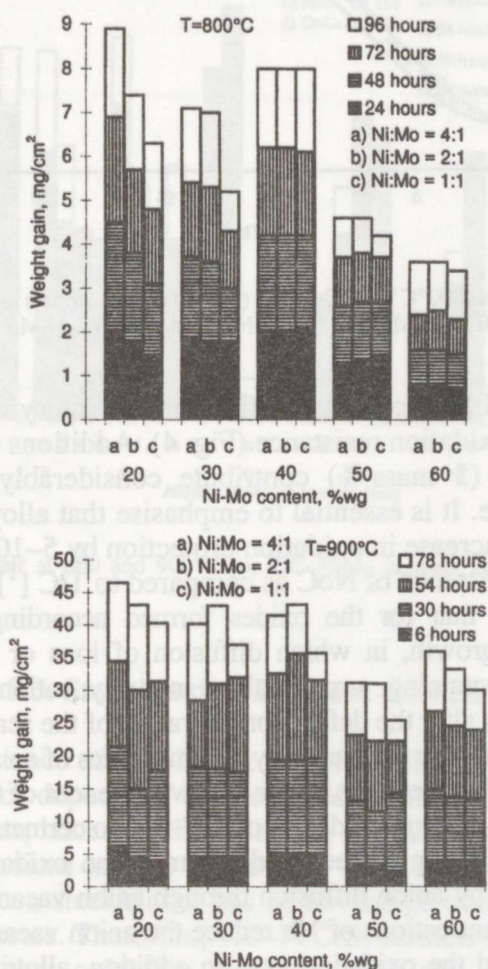


Fig. 2. Weight gain in air at 800 and 900°C for TiC-NiMo cermets as a function of binder content and ratio Ni:Mo.

Results of the present study confirm that during oxidation of TiC–NiMo cermets, the parabolic rate law is observed (Fig. 3). An increase in the binder content is accompanied by an increase in the resistance to oxidation. Consequently, oxidation resistance of TiC is at a disadvantage in relation to NiMo binder. A small increase in oxidation resistance is observed due to Mo content increase of cermets. The tight adherent mixed oxide NiMoO₄ film tends to resist a rapid oxidation up to 940°C [9].

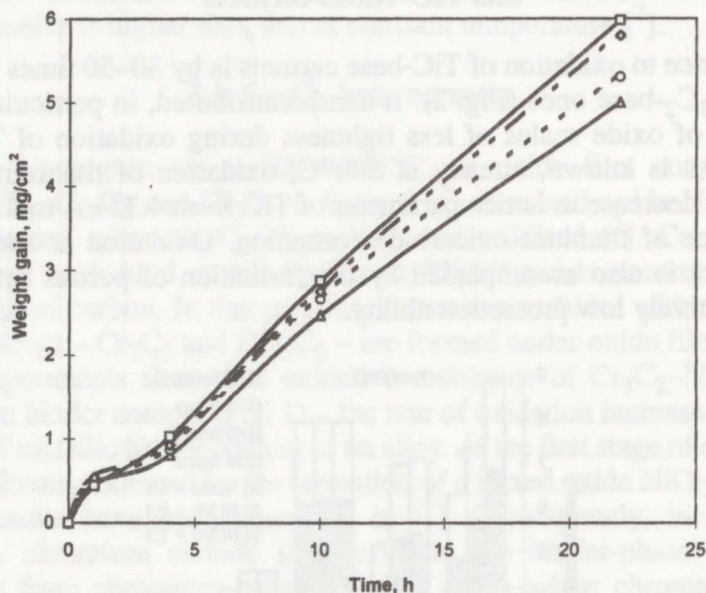


Fig. 3. Weight gain in air at 800°C for TiC–NiMo (Ni:Mo = 4:1) cermets as a function of time. □ – 50TiC–NiMo; ◊ – 60TiC–NiMo; ○ – 70TiC–NiMo; Δ – 80TiC–NiMo.

Alloying TiC–NiMo cermets by different refractory compounds has a marked effect on oxidation resistance (Fig. 4). Additions of NbC (up to 10 mass %) and VC (5 mass %) contribute considerably to the gain in oxidation resistance. It is essential to emphasise that alloying additions of NbC result in the increase in oxidation protection by 5–10 times in spite of lower oxidation resistance of NbC as compared to TiC [1].

It is known [5] that for the oxides formed according to the Wagner mechanism (scale growth, in which diffusion of ions or electrons is rate-controlling) and containing wrong-valent impurity cations, soluble in the oxide, the impurities alter the defect concentration of the scale. Consequently, the oxide growth rate may be altered by the impurities of an alloy. An increase or decrease in oxidation depends on the relative valences of the cations and on the type of an oxide. During oxidation of TiC–NiMo cermets, evidently a film of *n*-type semiconducting mixed oxide forms. The oxidation rate of such oxides is controlled by anion diffusion through anion vacancies. In this case, additional high valent cations of Nb reduce the anion vacancy concentration of mixed oxide and the oxidation rate. In addition, alloying elements with smaller ion size (size of Nb ions is less than that of Ti and Ni) contribute to sinterability and therefore to tightness of the protective oxide layer [9].

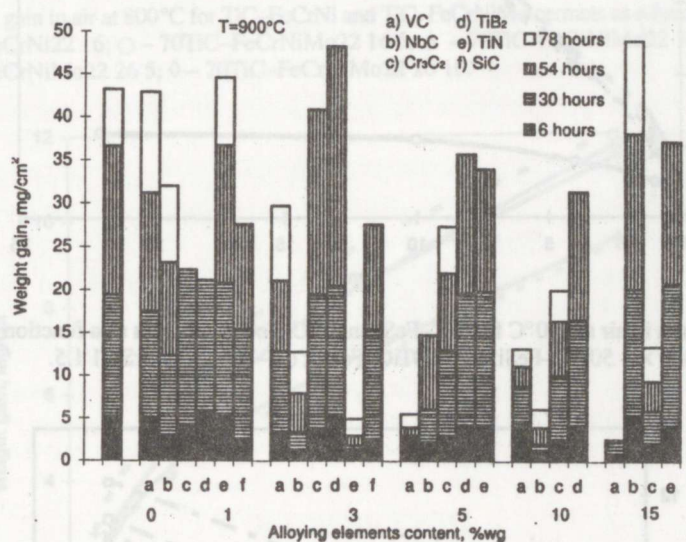
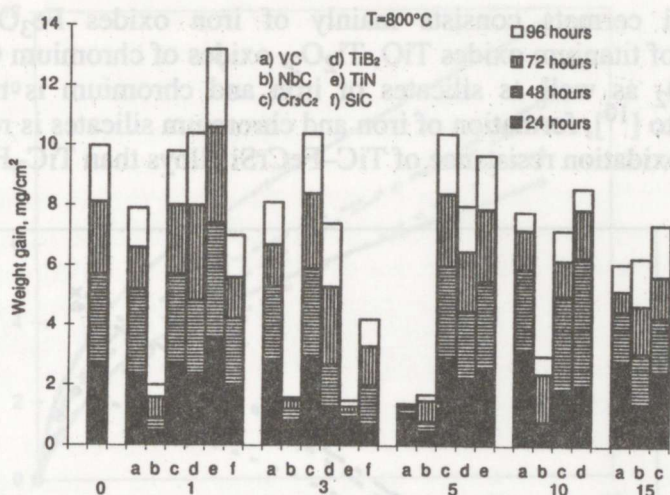


Fig. 4. Weight gain in air at 800 and 900°C for TiC–NiMo cermets as a function of alloying compound content.

3.3. Steel-bonded TiC-base cermets

Oxidation resistance of TiC–FeSi cermets and that of TiC–NiMo alloys is nearly equal, not depending on the binder content (cf. Figs. 3 and 5). The latter can be explained by the oxidation resistance of the binder phase close to that of titanium carbide at 800°C.

Chromium-silicon steel binder has an advantage over titanium carbide in oxidation resistance. Therefore, TiC–FeCrSi cermets have (at equal TiC content) much higher oxidation resistance than that of TiC–FeSi hard metal (Fig. 5). According to petrographical analysis, the oxide film of

TiC-FeCrSi cermets consists mainly of iron oxides Fe_3O_4 , Fe_2O_3 . Formation of titanium oxides TiO , Ti_2O_3 , oxides of chromium Cr_2O_3 and silicon SiO_2 as well as silicates of iron and chromium is much less. According to [10], formation of iron and chromium silicates is responsible for higher oxidation resistance of TiC-FeCrSi alloys than TiC-FeCr ones.

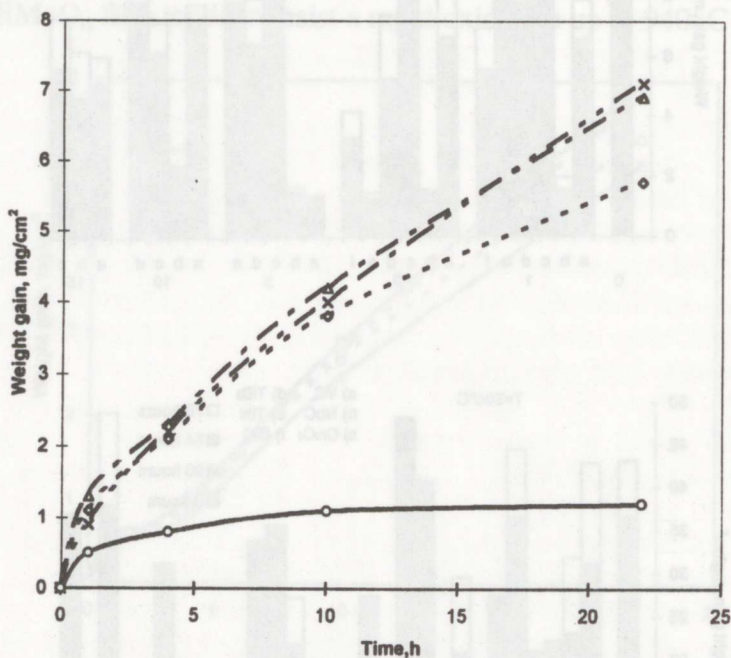


Fig. 5. Weight gain in air at 800°C for TiC-FeSi and TiC-FeCrSi cermets as a function of time. Δ - 40TiC-FeSi2; \times - 50TiC-FeSi2; \diamond - 60TiC-FeSi2; \circ - 40TiC-FeCrSi21 1.5.

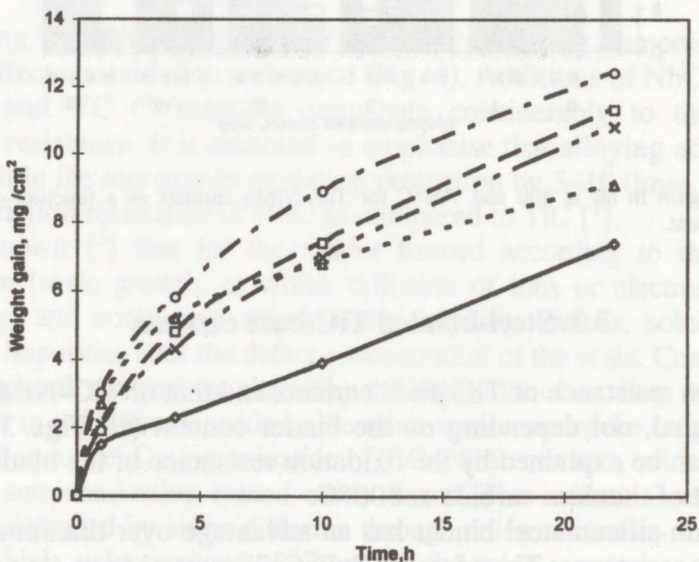


Fig. 6. Weight gain in air at 800°C for TiC-FeCrNiSi and TiC-FeCrNi cermets as a function of time. \square - 70TiC-FeCrNiSi22 16; \diamond - 70TiC-FeCrNiSi22 16 1.5; Δ - 70TiC-FeCrNiSi22 16 3; \times - 70TiC-FeCrNiSi22 26 1.5; \circ - 70TiC-FeCrNiSi22 26 3.

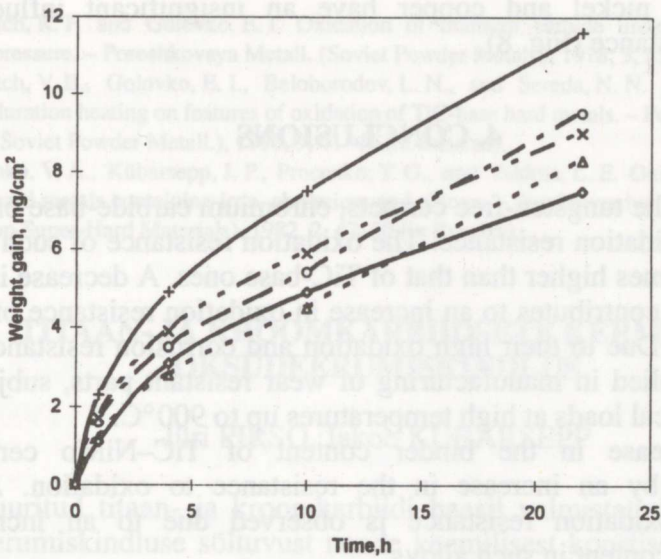


Fig. 7. Weight gain in air at 800°C for TiC-FeCrNi and TiC-FeCrNiMo cermets as a function of time.
 + - 70TiC-FeCrNi22 16; ○ - 70TiC-FeCrNiMo22 16 5; △ - 70TiC-FeCrNiMo22 16 10;
 × - 70TiC-FeCrNiMo22 26 5; ◇ - 70TiC-FeCrNiMo22 26 10.

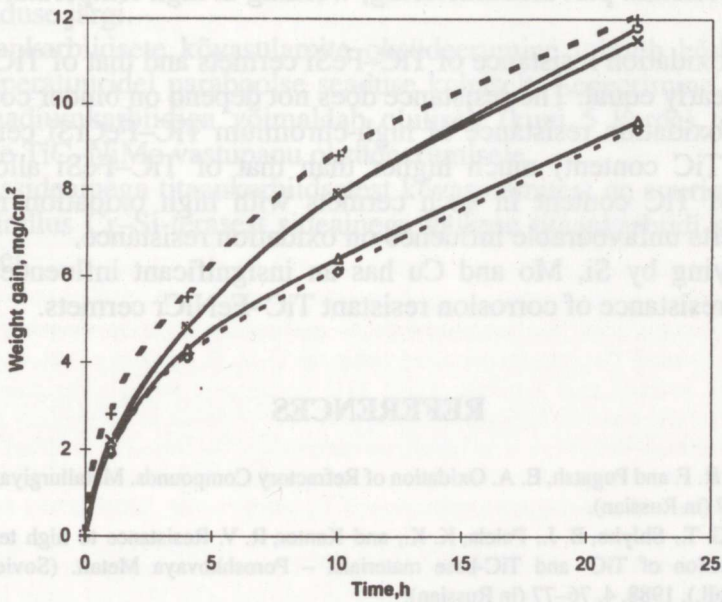


Fig. 8. Weight gain in air at 800°C for TiC-FeCrNi and TiC-FeCrNiCu cermets as a function of time.
 ○ - 70TiC-FeCrNi22 16; ◇ - 70TiC-FeCrNiCu22 16 1.5; △ - 70TiC-FeCrNiCu22 16 3;
 × - 70TiC-FeCrNiCu22 26 1.5; + - 70TiC-FeCrNiCu22 26 3.

An increase of TiC content in cermets with high oxidation resistant FeCrSi binders exerts an unfavourable influence on the resistance to oxidation (cf. Figs. 5-8). A relatively small increase in oxidation resistance at 800°C is observed because of silicon and molybdenum additions in corrosion-resistant TiC-FeCrNi cermets (Figs. 6 and 7).

Additions of nickel and copper have an insignificant influence on oxidation resistance (Fig. 8).

4. CONCLUSIONS

1. Among the tungsten-free cermets, chromium carbide-base ones have the highest oxidation resistance. The oxidation resistance of such cermets is by 30–50 times higher than that of TiC-base ones. A decrease in binder phase content contributes to an increase in oxidation resistance of Cr_3C_2 -base cermets. Due to their high oxidation and corrosion resistance, these alloys are applied in manufacturing of wear resistant parts, subjected to wear and static loads at high temperatures up to 900°C.

2. An increase in the binder content of TiC–NiMo cermets is accompanied by an increase in the resistance to oxidation. A small increase in oxidation resistance is observed due to an increase of molybdenum content in such alloys.

3. Additions of NbC and VC contribute considerably to the increase in oxidation resistance (up to 5 times) of TiC–NiMo cermets. Because of their high oxidation resistance, TiC–NbC–NiMo cermets are used for tool and wear resistant part manufacturing, working at high temperatures up to 800°C.

4. The oxidation resistance of TiC–FeSi cermets and that of TiC–NiMo ones are nearly equal. The resistance does not depend on binder content.

5. The oxidation resistance of high-chromium TiC–FeCrSi cermets is (at equal TiC content) much higher than that of TiC–FeSi alloys. An increase of TiC content in such cermets with high oxidation resistant binder exerts unfavourable influence on oxidation resistance.

6. Alloying by Si, Mo and Cu has an insignificant influence on the oxidation resistance of corrosion resistant TiC–FeNiCr cermets.

REFERENCES

1. Voitovitch, R. F. and Pugatsh, E. A. Oxidation of Refractory Compounds. Metallurgiya, Moscow, 1979 (in Russian).
2. Dzodziev, G. T., Shlyko, B. J., Palela, K. K., and Kantor, R. V. Resistance to high temperature oxidation of TiC- and TiC-base materials. – Poroshkovaya Metall. (Soviet Powder Metall.), 1988, 4, 76–77 (in Russian).
3. Grigoryeva, V. V. and Klimenko, V. N. Chromium Carbide-base Alloys. Ukrainian Academy of Sciences, Kiev, 1961 (in Russian).
4. Golovko, E. I., Voitovitch, V. B., Sereda, N. N., and Beloborodov, L. N. Kinetics of oxidation of TiC–NiMo cemented carbides. – Poroshkovaya Metall. (Soviet Powder Metall.), 1990, 4, 89–93 (in Russian).
5. Birks, H. and Meier, G. H. Introduction to High Temperature Oxidation of Metals. Edward Arnold, London, 1983.
6. Pilling, N. B. and Bedworth, R. E. The oxidation of metals at high temperature. – J. Inst. Metals, 1933, 29, 529–582.
7. Gorbato, I. N., Yurtshenko, V. S., Sötshev, I. G., Pashchenko, V. A., and Bovkun, G. A. Investigation of oxidation resistance of hot-pressed chromium–carbide-base cermets. – Poroshkovaya Metall. (Soviet Powder Metall.), 1980, 6, 71–74 (in Russian).

8. Voitovitch, R. F. and Golovko, E. I. Oxidation of titanium carbide under different oxygen pressure. – Poroshkovaya Metall. (Soviet Powder Metall.), 1978, 3, 55–61 (in Russian).
9. Voitovitch, V. B., Golovko, E. I., Beloborodov, L. N., and Sereda, N. N. Influence of long-duration heating on features of oxidation of TiC-base hard metals. – Poroshkovaya Metall. (Soviet Powder Metall.), 1990, 9, 41–46 (in Russian).
10. Lavrenko, V. A., Kübarsepp, J. P., Procenko, T. G., and Valdma, L. E. Oxidation of TiC-base hard metals containing iron, chromium and silicon. – Sverkhтвердые Материалы (Soviet J. on Super-Hard Materials), 1982, 2, 47–50 (in Russian).

TITAAAN- JA KROOMKARBIIDSETE KERMISTE OKSÜDEERUMISKINDLUS

Jüri PIRSO, Jakob KÜBARSEPP

On uuritud titaan- ja kroomkarbiidi baasil valmistatud kõvasulamite oksüdeerumiskindluse sõltuvust nende keemilisest koostisest pikaajalisel kuumutamisel õhu käes temperatuuril 800 ja 900°C. Temperatuuriintervallis 800–900°C ületab kroomkarbiidi baasil kõvasulamite oksüdeerumiskindlus 30–50 korda titaankarbiidsete kõvasulamite oma, kusjuures Cr₃C₂ baasil kõvasulamite oksüdeerumine toimub 800°C juures logaritmilise seaduse järgi.

Titaankarbiidsete kõvasulamite oksüdeerumine toimub kõikidel uurimistemperatuuridel paraboolse seaduse kohaselt. Legeerimine nioobium- ja vanaadiumkarbiidiga võimaldab oluliselt (kuni 5 korda) tõsta kõvasulamite TiC–NiMo vastupanu oksüdeerumisele.

Terassideainega titaankarbiidsetest kõvasulamitest on suurim oksüdeerumiskindlus Cr–Si-terasest sideainega väikese titaankarbiidi sisaldusega sulamitel.