

Effect of oxidation on abrasive wear behaviour of titanium carbide based composites in silica medium

Maksim Antonov, Irina Hussainova, Jüri Pirso, Kristjan Juhani
and Mart Viljus

Department of Materials Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086
Tallinn, Estonia; Maksim.Antonov@ttu.ee

Received 27 September 2010, in revised form 26 October 2010

Abstract. The aim of the study was to investigate the effect of oxidation on the behaviour of TiC-based cermets with Ni-Mo binder under low intensity wear conditions in silica sand medium. Three types of material performance maps were constructed: oxidation rate map, wear rate map and map showing the effect of oxidation on wear. Discussion on the performance of cermets is based on oxidation, wear, SEM, EDS and XRD results. It is shown that cermets behaviour is highly influenced by microstructure (Ni, Mo content and Ni:Mo ratio) and oxidation kinetic. The paper should facilitate the optimization of TiC-Mo₂C-Ni cermets selection for room and high temperature wear applications.

Key words: cermet, oxidation, abrasion, titanium carbide.

1. INTRODUCTION

High efficiency of thermal processes in energy applications is achieved at elevated temperatures. The ashes that are present in flowing hot gases act as an abrasive, provoking the competition and interaction between the oxidation and abrasion processes [¹]. Tungsten-free cermets with the Ni and Mo binder are able to perform at high temperatures in wear applications [²].

It is known that the molybdenum has positive effect if added to the TiC-Ni cermet system by improving the wettability of phases, decreasing the number of microstructural defects and increasing the interphase bond strength and phase uniformity. The possible deterioration in properties is associated with the formation of brittle intermetallic phases [³]. Molybdenum addition results in the formation of the three-phase core-rim structure composite TiC-Mo₂C-Ni that leads to the increase of the carbide phase content (comparing to the initial composition) during sintering [⁴].

At high temperature, the working conditions of different types of oxides, developed on the surface of the specimens, affect the material reliability to a great extent. For example, volatilization of MoO_3 , started at 500°C , results in a rapid mass and composition change as the temperature increases above 770°C [5].

The aim of the current study was to investigate the effect of oxidation on the abrasive wear behaviour of $\text{TiC}-\text{Mo}_2\text{C}-\text{Ni}$ cermets in SiO_2 medium with an emphasize on the initial metal powders content and the share of molybdenum.

2. EXPERIMENTS

$\text{TiC}-\text{Mo}_2\text{C}-\text{Ni}$ cermets were produced at the Powder Metallurgy Laboratory, Tallinn University of Technology by means of a conventional powder metallurgy routine described elsewhere [4]. The chemical composition of initial powders, the density and mechanical properties of cermets tested are summarized in Table 1 and also described in [4].

Density of the materials was measured using the Archimedes approach. Transverse rupture strength was determined in the 3-point bending test arrangement. Palmqvist method was applied for fracture toughness evaluation.

Designation of the materials was made as follows: the number in the grade designation multiplied by 10 indicates the initial weight content of metal powders (Ni and Mo). The grades having marking without letters at the end, with A and B

Table 1. Chemical composition of initial powders, density, hardness HV_{10} , transverse rupture strength R_{TZ} and fracture toughness K_{IC} of studied cermets

Grade	Binder content*, wt %	Density, g/cm ³	Hardness, HV_{10}	R_{TZ} , MPa	K_{IC} , MPa m ^{-1/2}
T2	16Ni 4Mo	5.47	1400	1010	11.9
T2A	13Ni 7Mo	5.50	1515	990	11.8
T2B	10Ni 10Mo	5.54	1650	730	11.3
T3	24Ni 6Mo	5.74	1300	1210	17.3
T3A	20Ni 10Mo	5.77	1415	1180	15.5
T3B	15Ni 15Mo	5.68	1590	1090	10.4
T4	32Ni 8Mo	6.04	1170	1450	18.6
T4A	26Ni 14Mo	6.02	1270	1320	18.3
T4B	20Ni 20Mo	6.03	1360	890	14.4
T5	40Ni 10Mo	6.40	990	2180	22.6
T5A	34Ni 16Mo	6.42	1150	1600	22.9
T5B	25Ni 25Mo	6.34	1340	1120	13.2
T6	48Ni 12Mo	6.50	810	2450	N/A
T6A	40Ni 20Mo	6.54	950	2270	N/A
T6B	30Ni 30Mo	6.62	1180	1300	N/A

* The rest is TiC .

have the proportions (by weight) of nickel and molybdenum in initial powders as 4:1, 2:1, 1:1, respectively (4 shares of Ni are mixed with 1 share of Mo during preparation of T2 grade, for example).

Microstructural examination of the specimens was conducted by a scanning electron microscope (SEM) *Zeiss EVO MA15* supplied with energy dispersive X-ray spectroscopy (EDS) – *INCA* analyzer. Phase composition was studied with the help of *Siemens Bruker D5005* X-ray analyser (XRD, CuK α – radiation). Distribution of elements in the oxide film was studied at the edges of craters produced by the *kaloMax* ball cratering device.

A recently developed tester, described elsewhere [^{6,7}], was used for studying of the oxidation-abrasive wear interactions. The sample is fixed between two disks and the couple of disks is rotated inside the chamber with abrasive. The main parameters of the test are given in Table 2. The heating and cooling rate of a 5-hour test was close to 600°C per hour.

The oxide layers developed during the test were microstructurally characterized. Materials resistance to scratching and grinding after holding at 900°C was ranked. Manual scratching by rounded plastic stick with minimal applied force not exceeding 0.01 N was performed to evaluate the adhesion of the oxide layers to the substrate. Evaluation of oxide resistance to grinding was made by the diamond grinding disk with a mean size of diamond grains 125–160 μm .

The sample cleaning procedure before and after wear tests was selected to facilitate the abrasive particle removal, but not very aggressive to the oxide scales. Specimens were ultrasonically cleaned for 2 min in acetone and weighed before and after the tests to the nearest of 0.01 mg using GR-202, A&D Instruments balance. The results of oxidation and abrasive wear tests are expressed in $\text{mg cm}^{-2} \text{ h}^{-1}$ to compare rates and calculate the effect of oxidation on wear. The negative sign of wear or oxidation rate indicates that the specimen has gained the weight during the test. Test series were repeated three times and results averaged. The procedure for conversion of the wear rate into $\text{mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ units is given elsewhere [⁶].

Table 2. Main parameter of the abrasive wear test

Feature/parameter	Description
Size of the specimen ($L \times W \times H$), mm	$25 \times 15 \times 5$
Number of specimens tested simultaneously in the same abrasive, pcs	18
Speed of the specimen movement, m s^{-1}	0.05
Abrasive, properties	SiO_2 , 0.2–0.3 mm, rounded, $\rho 2150 \text{ kg m}^{-3}$, 700 g per test
Mean pressure of the abrasive toward the sample, N m^{-2}	253
Duration of the test, h	5 h
Duration of sliding inside abrasive during one turn of disks, deg	98° out of 360°
Temperature, °C	20, 400, 700, 900
Environment	Air

3. RESULTS

3.1. Cermets oxide scale properties

The ultrasonic cleaning done before and after oxidation tests facilitates the removal of oxide scales that has insufficient adhesion to the substrate. It was found that the change of mass during the oxidation test at 400 °C is untraceable. The oxidation rates at 700 and 900 °C and resistance to scratching and grinding of cermets oxidized at 900 °C are given in Fig. 1.

The spread of studied cermets oxidation rates at high temperature is sufficiently large (from -15.48 to -47.42 and from -19.78 to 311.66×10^{-3} mg cm $^{-2}$ h $^{-1}$ for 700 and 900 °C oxidation tests, respectively).

Conditions for the formation of oxide at 700 °C are more favourable and oxide remains attached to the surface. Grades T5B, T6A and T6B have the lowest oxidation rate at 700 °C. The mass loss of T5A, T5B and T6A grades at 900 °C indicates that oxides scale formed has been lost at one of the stages of oxide growth, cooling or ultrasonic cleaning.

The oxide layers formed on the surface of T2, T2A, T4B and T6 grades after 15 min and 5 h has exhibited high resistance to scratching and grinding and are highlighted by hatch in Fig. 1. The oxidation rates of these materials are sufficiently higher comparing to other cermets tested in the present study.

The SEM/EDS and XRD examinations of the surfaces after oxidation and wear at 900 °C revealed the presence of TiO₂, NiO, Mo₃C₂, SiO₂. Free carbon and MoO₂ was found only on the surfaces of cermets with high binder content. Distribution of elements inside the oxide layer studied with ball cratering method has revealed that the concentration of Ni and Mo is usually the highest in the outer part of the oxide while the concentration of Ti is the lowest. T6 cermet with highest Ni content (48 wt %) has thick oxide layer with almost Ti-free outer

	T2 (Ni, Mo) - 20 wt %	T3 (Ni, Mo) - 30 wt %	T4 (Ni, Mo) - 40 wt %	T5 (Ni, Mo) - 50 wt %	T6 (Ni, Mo) - 60 wt %
- Ni:Mo - 4:1	2 1-2 1-2 -30.43 -238.60	4 4 3 -23.76 -145.59	2 4 2 -41.51 -109.46	1-4 4 2-3 -38.89 -98.17	1 1-2 1-2 -36.02 -266.24
A Ni:Mo - 2:1	2 2-3 2 -30.86 -241.18	2-4 3-4 3 -28.71 -183.12	4 4 2-3 -27.31 -149.03	4 4 3-4 -25.48 208.39	4 4 3-4 -18.28 260.22
B Ni:Mo - 1:1	1-2 3-4 2 -27.74 -327.96	3-4 4 2-3 -21.29 -82.69	2 2-3 2 -47.42 -128.39	4 4 3-4 -15.48 311.61	2-3 4 2-3 -17.63 -19.78

Resistance to scratching after oxidation		Resistance to grinding after oxidation		Oxidation rate (Ko), $\times 10^{-3}$ mg cm $^{-2}$ h $^{-1}$
	I After 15 min at 900 °C 1 Oxide retain integrity 2 Some oxide is removed 3 Sufficient peeling 4 Catastrophic peeling		II After 5 h at 900 °C 1 Oxide retain integrity 2 Some oxide is removed 3 Sufficient peeling 4 Catastrophic peeling	III After 5 h at 900 °C 1 Very hard to remove 2 Hard to remove 3 Easy to remove 4 Removed at once
				IV 700 °C V 900 °C

Fig. 1. Mapping of oxide properties and oxidation rate of TiC-NiMo cermets. Materials with sufficient resistance to scratching and grinding (rating is lower than 4) are highlighted by hatch.

surface. T6B cermet having the same binder content as T6 but with maximum share of molybdenum has oxide that is easily removed when it reaches the critical thickness. The content of Ti in the remaining oxide layer was almost as high as in the substrate. It was also found that in addition to the variation of elements concentration throughout the oxide layer the top surface has zones with different elemental content. The formation of oxide zones with different content initially goes by replication of the carbide-metal topography of substrate materials with evolution during further growth.

3.2. Wear rates of cermets

It is of interest to find the grades with minimal wear rate within each group of the same Ni:Mo share in order to study the effect of the binder content and Ni:Mo share. The choice of the wear and oxidation test temperatures was influenced by the oxidation kinetics of the binder and ceramic phases in air environment. The wear rate (W_{AO}) is calculated according to the method described elsewhere [6,7]. The wear rates at 20, 400, 700 and 900°C are given in Fig. 2.

At temperatures below 400°C the oxidation of the metal binder is minimal. T4, T4A and T4B have the lowest wear rates in their groups at room temperature. At the temperature of 400°C, when softening of metallic phases take place, the T6, T5A and T5B are the most suitable cermets for protection against wear in their groups.

At 700°C, when oxidation of the metal phase is intensive, T2, T4A and T6B have the lowest wear rates. If the temperature and oxidation rates are increased (900°C), the T5, T6A and T6B grades show the lowest wear rates in their sub-groups with the same Ni:Mo share.

Mechanical properties of cermets are to be considered. Under conditions of mild wear the ability of the material to resist nucleation and development of cracks is of minor importance (fracture toughness). Softening of the metallic

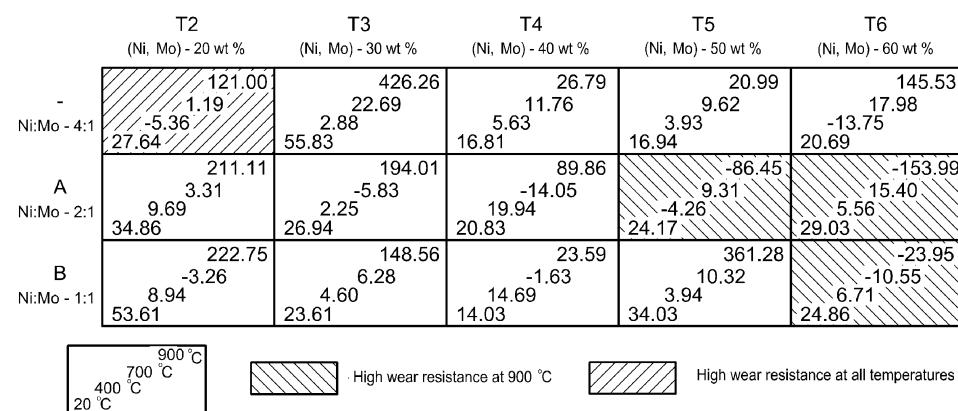


Fig. 2. Mapping of the wear rate (W_{AO}) of TiC-NiMo cermets at various temperatures in SiO_2 abrasive.

phases and oxide layer properties start to play more important role in the formation of the tribolayer. The common rule that the hardest material always has the lowest wear rate is not feasible under these conditions. The results of 20, 400 and 900°C tests show opposite tendency while materials with 40 and 50 wt % of initial metal content with low hardness show the best wear performance.

3.3. Effect of oxidation on the abrasive wear rate

The effect of oxidation on the abrasive wear rate can be calculated according to the method proposed elsewhere [6,8]. The effect of oxidation on the high temperature wear rate $ABRR$ is the difference between the wear rate W_{AO} and corrosion (oxidation) rate K_O , normalized by absolute value of the corrosion rate:

$$ABRR = \frac{W_{AO} - K_O}{|K_O|}. \quad (1)$$

The modes of the high-temperature abrasive wear, depending on oxide properties, are extended comparing to [6], taking into account the situations when sample can loose mass during the corrosion test accompanied with ultrasonic cleaning due to insufficient adhesion (Fig. 1).

Four possible modes are proposed depending on the intensity of oxidation, adherence of the oxide and success of the abrasive action (Fig. 3).

1. Corrosion dominated mode is characterized by the domination of the oxidation process. Abrasive wear influence on oxidation is ineffective.
2. Corrosion–abrasion mode with prevailing corrosion is characterized by prevailing role of oxidation and some effect of abrasion.
3. Abrasion–corrosion mode is characterized by aggressive abrasion able to remove oxide.
4. Fourth mode is possible when wear rate is lower than corrosion. In this case the oxide film is improved by abrasive action.

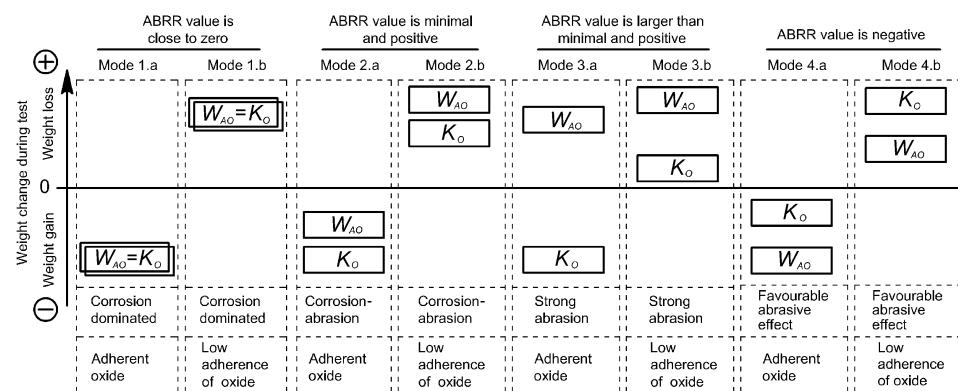


Fig. 3. High temperature abrasive wear regimes.

The map showing the effect of oxidation on wear of the studied cermets is presented in Fig. 4. Materials with low NiMo content and low share of Mo in initial metal powder (4:1 share of Ni:Mo) mainly exhibit mode 3.a in SiO_2 medium. During abrasive wear of these cermets at high temperature the oxide layer has sufficient adhesion to substrate but it is removed by abrasive action.

The oxide layer of T3, T3A and T3B cermets was less resistant against abrasive action (ABRR value is 3.9, 2.1 and 2.8 at 900°C , respectively). The wear and oxidation rates for T5B are very close to each other at 900°C (2.b mode), indicating low adherence of the oxide layer and that abrasion has almost no effect on the high temperature material deterioration (this process is mainly controlled by oxidation).

The improper oxide layer does not always lead to a high wear rate. T5A, T6A and T6B exhibit 4.b and 4.a modes of high temperature abrasive wear, respectively. Oxides formed on T5A and T6A grades have low resistance to scratching and grinding and these grades exhibited mass loss during oxidation tests at 900°C (oxide layer peel off). However, these materials show mass gain in wear conditions at the same temperature. That means that the material has surface layer with a tendency of stable growth.

The authors assume that the protective mechanism is associated with the formation of tribolayer enriched by SiO_2 particles, assisted by sufficiently high (3.27 [9]) volume ratio between oxide and reacted metal (Pilling–Bedworth ratio) for molybdenum. In addition, the abrasive action regulates (decreases) the thickness of oxide reducing the risk of peeling.

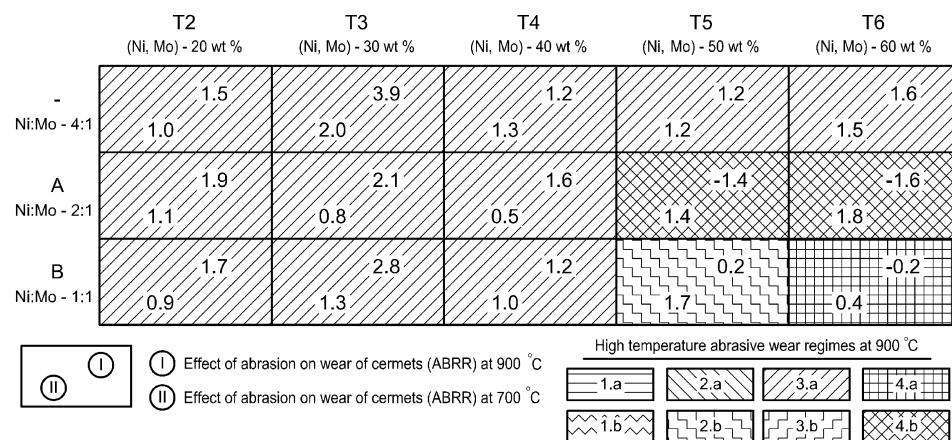


Fig. 4. Effect of oxidation and abrasion on wear of TiC-NiMo cermets at various temperatures in SiO_2 abrasive.

4. CONCLUSIONS

1. It is found that the protection of the cermet surface is possible through the formation of the tribolayer based on entrapping of abrasive particles (4.a and 4.b modes). The best wear performance of TiC-based cermets with Ni-Mo binder at 900°C is obtained for high initial content of metal powders and high share of molybdenum (T5A, T6A and T6B).
2. TiC-Mo₂C-Ni cermets mainly exhibit 3.a mode of abrasive wear at 900°C (Fig. 4) that means that the oxide has sufficient adhesion to the substrate but is removed by abrasive action.
3. The updated method [⁶⁻⁸] for measuring and describing materials (cermet in particular) resistance to high temperature abrasive wear of low intensity and effect of oxidation is assessed.
4. In further research it is required to make higher intensity (with harder and more angular abrasive than SiO₂) and cyclic (repetition of heating and cooling regimes) testing of TiC-based cermets with high initial content of metal powders and high share of molybdenum (T5A, T6A and T6B) to prove favourable tribolayer formation enabling protection of the base material.

ACKNOWLEDGEMENTS

The authors wish to thank R. Traksmaa from the Centre for Materials Research of Tallinn University of Technology for help with sample analysis. The research was supported by the Estonian Science Foundation (grants Nos. 8211 and T062).

REFERENCES

1. Wang, B.-Q. and Luer, K. The relative erosivity of limestone, dolomite and coal samples from an operating boiler. *Wear*, 1998, **215**, 180–190.
2. Antonov, M., Hussainova, I., Pirso, J. and Volobueva, O. Assessment of mechanically mixed layer development during high temperature erosion of cermets. *Wear*, 2007, **263**, 878–886.
3. Brookes, K. Nano carbides make for low temperature sintering. *Metal Powder Report* (online magazine www.metal-powder.net) 2009 October, 26–32.
4. Hussainova, I. Effect of microstructure on the erosive wear of titanium carbide based cermets. *Wear*, 2003, **255**, 121–128.
5. Shreir, L. L., Jarman, R. A. and Burstein, G. T., eds. *Corrosion. Metal and Environment Reactions*. Butterworth-Heinemann, 2000.
6. Antonov, M. and Hussainova, I. Experimental setup for testing and mapping of high temperature abrasion and oxidation synergy. *Wear*, 2009, **267**, 1798–1803.
7. Antonov, M., Hussainova, I., Kimmari, E. and Juhani, K. Verification of new 1000C tester designed for investigation of wear-corrosion properties of advanced materials for high temperature applications. In *Proc. 6th International Conference of DAAAM Baltic Industrial Engineering* (Küttner, R., ed.). Tallinn University of Technology, Tallinn, 2008, 395–399.

8. Antonov, M., Hussainova, I. and Kübarsepp, J. Oxidation-abrasion of TiC-based cermets. *Wear*, 2010. Forthcoming.
9. Bradford, S. Fundamentals of corrosion in gases. In *Metals Handbook*, 9th ed., vol. 13. American Society for Metals, 1987, 61–76.

Oksüdeerimise mõju titaankarbiidkermiste kulumisintensiivsusele liivakeskkonnas

Maksim Antonov, Irina Hussainova, Jüri Pirso, Kristjan Juhani
ja Mart Viljus

Molibdeeni lisamine TiC-Ni-kermiste koostisele võimaldab modifitseerida kermiste mikrostruktuuri ja tõsta mehaanilisi omadusi; samas on olemas oht habraste intermetalsete faaside tekkeks, samuti hakkab molibdeen kõrgel temperatuuril (alates 500°C) aurustumma. Artiklis on uuritud oksüdeerimise mõju volframivabade kermiste kulumise intensiivsusele madala abrasiivse toimega keskkonnas temperatuuridel 20, 400, 700 ja 900°C. Katsetulemuste põhjal koostati kolme tüüpi kaardid: 1) oksüdeerimise hindamise kaart, 2) kulumise intensiivsuse kaart, 3) oksüdeerimise mõju abrasiivse kulumise intensiivsusele hindamise kaart. Enamikul uuritud TiC-Mo₂C-Ni-kermiste oksiididel on hea adhesioon põhimaterjaliga, kuid nõrk vastupidavus abrasiivsele toimele. On leitud, et liivakeskkonnas kulutamisel on võimalik tekitada kermistele abrasiivosakesi sisaldav triboloogiline kaitsekiht.