

## EFFECT OF OXIDATION ON ABRASIVE WEAR BEHAVIOUR OF TiC-BASED CERMETS IN SiO<sub>2</sub> MEDIUM

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**Abstract:** *The aim of the current study was to investigate the effect of oxidation on 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. The paper should facilitate the optimisation of TiC-Ni-Mo cermets selection for room and high temperature wear applications.*

*Key words: cermet, oxidation, abrasion.*

### 1. INTRODUCTION

High efficiency of thermal processes in energy applications is available at elevated temperatures. The ashes that are present in flowing hot gases act as abrasive provoking the competition and interaction between the oxidation and abrasion processes [1]. Tungsten free cermets with Ni and Mo binder are able to perform at high temperatures in wear applications [2]. It was reported 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 decrease in properties is associated with formation of brittle intermetallic phases [3]. Molybdenum takes part in formation of core-rim structure of TiC-MoC double carbides that leads to the increase of carbide phase content (comparing to the initial composition) during sintering [4].

Above 500 °C, MoO<sub>3</sub>, begins to volatilise and as the temperature increases above 770 °C, the volatilisation rate becomes extremely rapid [5].

The aim of the current study was to investigate the effect of oxidation on abrasive wear behaviour of TiC-NiMo cermets in SiO<sub>2</sub> medium with emphasize on initial metal powders content and share of molybdenum.

### 2. EXPERIMENTAL DETAILS

TiC-NiMo cermets were produced at Tallinn University of Technology by means of a conventional powder metallurgy routine described elsewhere [4]. The chemical composition of initial powders, density and mechanical properties of cermets tested are summarised in Table 1 and further described in [4].

Grade	Binder content*, wt %	Density, g/cm <sup>3</sup>	Hardness, HV <sub>10</sub>	R <sub>TZ</sub> , MPa	K <sub>IC</sub> , MPa m <sup>1/2</sup>
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

Table 1. Chemical composition of initial powders, density and mechanical properties of studied cermets

The densities of the samples were measured using Archimedes approach. Transverse rupture strength was determined in 3-point bending test arrangement. Palmqvist method was applied for fracture toughness evaluation. The number inside the marking of grades multiplied by 10 indicate the initial weight content of metal powders (Ni and Mo). The grades having marking without letters at the end, with A and B have the proportions (by weight) of molybdenum and nickel in initial powders as 4:1, 2:1, 1:1 accordingly (4 shares of Mo are mixed with 1 share of Ni during preparation of T2 grade, for example).

Microstructural examination of specimens was conducted by using 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 analyzer (XRD, CuK $\alpha$  - radiation). Distribution of elements in oxide film was studied at the edges of craters produced by *kaloMax* ball cratering device.

The recently developed tester described elsewhere [6, 7] was used for studying of 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 5 hour test was close to 600 °C per hour.

The oxide layers were observed and qualitative rating of resistance to scratching and to grinding after holding at 900 °C was made. Manual scratching by rounded plastic stick with minimal possible force not exceeding 0.01 N was made to evaluate the adhesion of the oxide layers to the substrate. Evaluation of oxide resistance to grinding was made by diamond grinding disc with mean size of diamond grains 125-160  $\mu\text{m}$ .

The sample cleaning procedure before and after wear tests was selected to facilitate the removal of abrasive but being not very aggressive to the oxide scales. Specimens were ultrasonically cleaned for 2 minutes 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 indicate that the specimen has gained the weight during the test. Tests series were repeated three times and results averaged. The procedure for conversion of wear rate into  $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$  units is given elsewhere [6].

### 3. RESULTS

#### 3.1. Cermets oxide properties

The ultrasonic cleaning done before and after oxidation tests facilitate the removal of oxide scales that has insufficient adhesion to substrate. It was found that the change of mass during 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 Figure 1.

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

Feature / parameter	Description
Size of specimen (L x W x H), mm	25 x 15 x 5
Number of specimens tested simultaneously in same abrasive, pcs	18
Speed of specimen movement, $\text{m s}^{-1}$	0.05
Abrasive, properties	SiO <sub>2</sub> , 0.2 ÷ 0.3 mm, rounded, $\rho$ 2150 $\text{kg m}^{-3}$ , 700g per test
Mean pressure of abrasive toward the sample, $\text{N m}^{-2}$	253
Duration of test, hours	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

Table 2. Main parameter of abrasive wear test

	T2	T3	T4	T5	T6
-	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	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	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 ( $K_o$ ), $\times 10^{-3} \text{mg cm}^{-2} \text{h}^{-1}$	
	I After 15 min. at 900°C	II After 5 h. at 900°C	III After 5 h. at 900°C	IV 700°C	V 900°C	
	1 - Oxide retain integrity 2 - Some oxide is removed 3 - Sufficient peeling 4 - Catastrophic peeling	1 - Oxide retain integrity 2 - Some oxide is removed 3 - Sufficient peeling 4 - Catastrophic peeling	1 - Very hard to remove 2 - Hard to remove 3 - Easy to remove 4 - Removed at once			

Figure 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.

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

The oxide layers formed on T2, T2A, T4B and T6 grades after 15 minutes and 5 hour has exhibited high resistance to scratching and grinding and are highlighted by hatch in Figure 1. The oxidation rates of these materials are sufficiently high 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 has shown the presence of TiO<sub>2</sub>, NiO, Mo<sub>3</sub>C<sub>2</sub>, SiO<sub>2</sub> with free carbon and MoO<sub>2</sub> found only on 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 outer part of 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 surface. T6B cermet having the same binder content as T6 but with maximum share of molybdenum has oxide that is easy removed when it reaches critical thickness. The content of Ti in thin

oxide layer was almost the same high as in substrate. It was also found that in addition to the variation of elements concentration through the oxide thickness 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 same Ni:Mo share in order to study the effect of binder content and Ni:Mo share. The choice of the wear and oxidation test temperatures was influenced by the oxidation kinetic of 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 Figure 2.

At temperatures below 400 °C the oxidation of metal binder is minimal. T4, T4A and T4B have the lowest wear rates in their groups at room temperature. At 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.

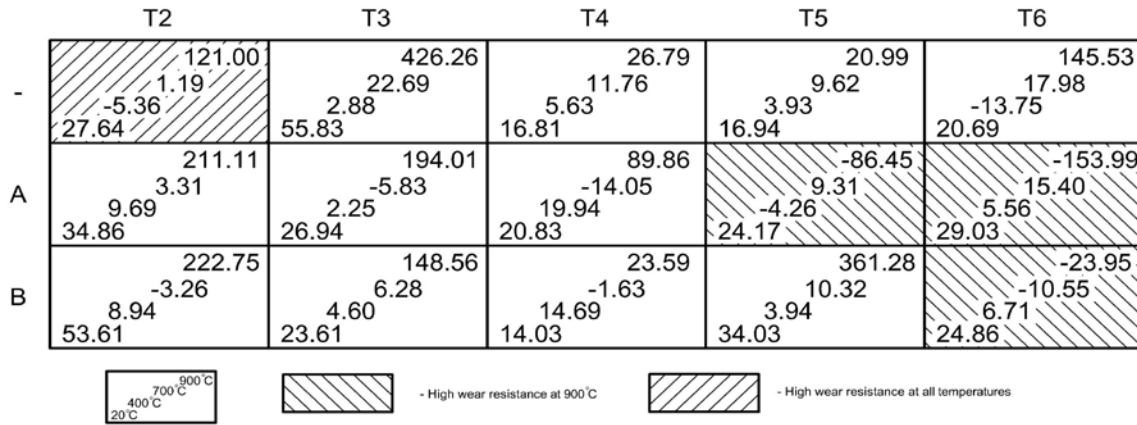


Figure 2. Mapping of wear rate ( $W_{AO}$ ) of TiC-NiMo cermets at various temperatures in SiO<sub>2</sub> abrasive.

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

Materials enabling to achieve lowest wear rate have optimal mechanical properties. Under conditions of low intensity wear the ability of material to resist initiation and development of cracks is of minor importance (fracture toughness). Softening of metallic phases and oxide layer properties starts to play more important role in formation of tribolayer. The common rule that the hardest material always has the lowest wear rate is not feasible under these conditions. The results of 20 °C, 400 °C and 900 °C tests shows opposite tendency when materials with 40 and 50 wt % of initial metal content with low hardness are showing the best wear performance.

### 3.3. Effect of oxidation on abrasive wear rate

The effect of oxidation on abrasive wear rate can be calculated according to the method proposed elsewhere [6].

The effect of oxidation on high temperature wear rate is the difference between wear rate  $W_{AO}$  and corrosion (oxidation) rate  $K_O$  normalized by absolute value of corrosion rate:

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

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

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

1. Corrosion dominated mode is characterized by domination of 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 characterised by aggressive abrasion able to remove oxide.
4. Fourth mode is possible when wear rate is lower than corrosion. In this case oxide film is improved by abrasive action

The map showing the effect of oxidation on wear of the studied cermets is presented in Figure 4. Materials with low NiMo content and low share of Mo in initial metal powder (4:1 share of Ni:Mo) are mainly exhibiting mode 3.a in SiO<sub>2</sub> 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.

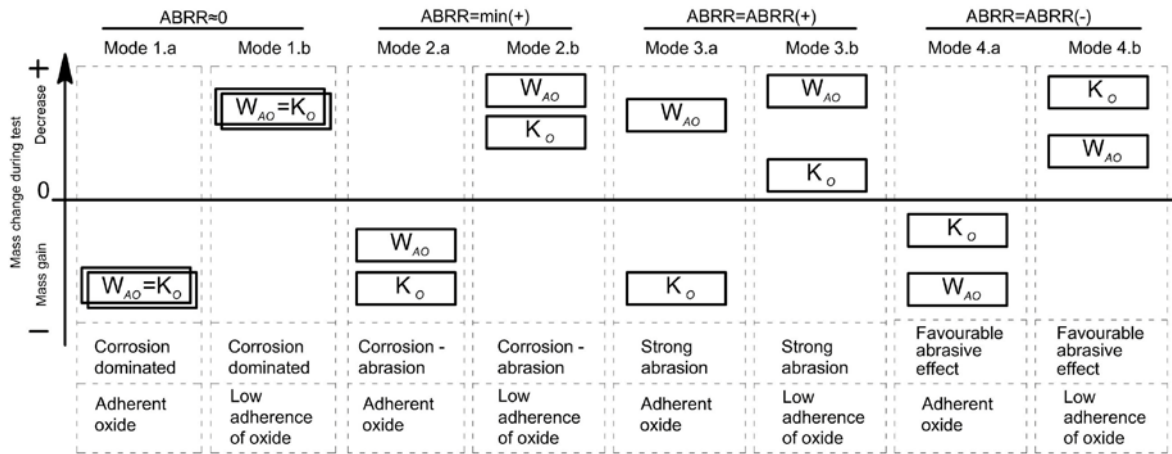


Figure 3 High temperature abrasive wear regimes

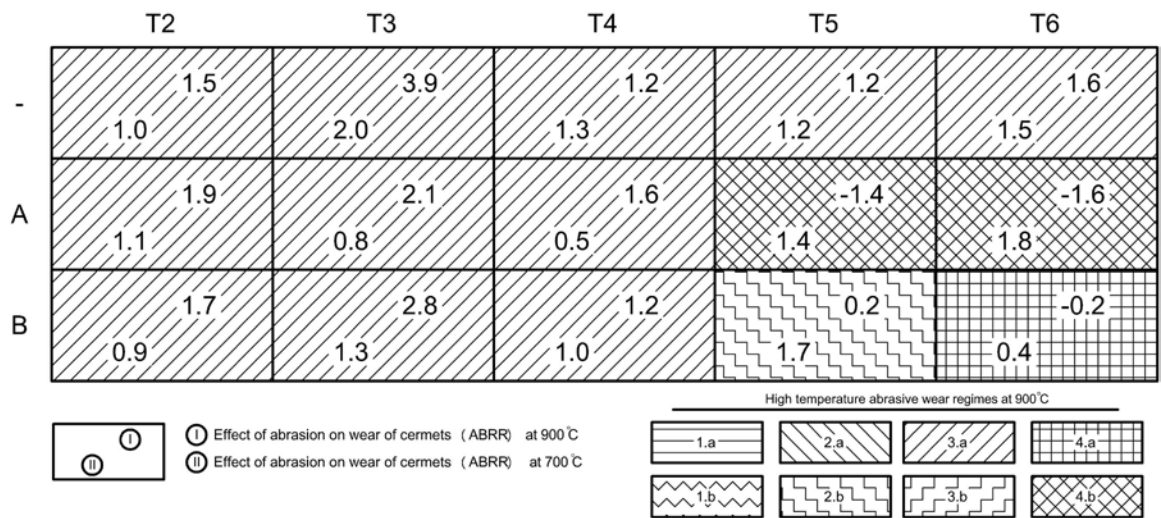


Figure 4. Effect of oxidation and abrasion on wear of TiC-NiMo cermets at various temperatures in SiO<sub>2</sub> abrasive.

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 accordingly). The wear and oxidation rates for T5B are very close to each other at 900 °C (2.b mode) indicating low adherence of oxide layer and that abrasion has almost no effect on high temperature material deterioration (process is mainly controlled by oxidation). The improper oxide layer do not always lead to high wear rate. T5A, T6A and T6B exhibit 4.b and 4.a modes of high temperature abrasive wear respectively. Oxide 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 shows mass gain in wear conditions at same temperature. That means that the material has surface layer with tendency of stable growing.

Authors propose that protective mechanism is associated with formation of tribolayer enriched by SiO<sub>2</sub> particles assisted by sufficiently high (3.27 [8]) volume ratio between oxide and reacted metal (Pilling-Bedworth ratio) for molybdenum. In addition, the abrasive action regulate (decrease) the thickness of oxide reducing the risk of peeling.

#### 4. FURTHER RESEARCH

It is required to make higher intensity (with harder and more angular abrasive than SiO<sub>2</sub>) and cyclic (repetition of heating and cooling regimes) tests to prove the unique property of T5A, T6A and T6B of tribolayer formation enabling protection of base material.

#### 5. 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).
2. TiC-NiMo cermets mainly exhibit 3.a mode of abrasive wear at 900°C (Figure 4) that means that the oxide has sufficient adhesion to substrate but is removed by abrasive action.
3. The method for measuring and describing materials (cermet in particular) resistance to high temperature abrasive wear of low intensity and effect of oxidation is updated comparing to [6, 7].

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