Wear mechanisms maps of Si$_3$N$_4$/carbon nanotube nanocomposites

Zs Koncsik, MB Maros, L Kuzsella, A Kovacs
University of Miskolc, Hungary

E-mail: metkzs@uni-miskolc.hu

Abstract. Silicon nitride-based nanocomposites with different amount (0, 1, 2 wt%) of multiwall carbon nanotubes (MWCNT) have been prepared by hot isostatic pressing. Tribological tests were carried out at room temperature, in dry sliding condition using pin-on-disc test apparatus, applying different normal loads and sliding speeds. Wear phenomena was analysed by scanning electron microscopic investigations of the wear tracks. Based on the controlling wear mechanisms and wear types two-dimensional wear mechanisms maps were created for all composition of the investigated ceramic nanocomposites.

1. Introduction
Silicon nitride ceramics are known as a group of one of the strongest structural ceramics. Their monolithic and even reinforced types possess an advantageous combination of mechanical and other physical properties. They have low density, low thermal expansion, thermal shock resistance, corrosion resistance, and appropriate hardness and strength even at high temperatures. Their application as tribological material, especially at high temperatures is widely known. Nowadays Si$_3$N$_4$ nanocomposites with different types of carbon additives have been created with the aim of producing electrically conductive materials with reasonable mechanical and electrical properties [1, 2]. The microstructural and electric properties of these carbon added nanocomposites have already been investigated by many authors [3, 4, 5, 6]. However details relating to their tribological performance – e.g. processes controlling the friction and wear behavior of these novel materials in various wear systems – have not been exactly clarified [7, 8, 9].

The basic aim of the current research work is to investigate the wear mechanisms of Si$_3$N$_4$ ceramic composites containing different amount of MWCNT applying pin-on-disc wear test methods.

2. Experimental work
2.1. Test and evaluation methods
Pin-on-disc wear tests were carried out using a CETR-UNMT1 high-precision micro-nano surface tester, according to the standard ISO 20808 [10], applying different normal loads: 10 N, 40 N, 80 N, different sliding velocity: 10 mm/s, 100 mm/s, 200 mm/s, at constant sliding distance: 100 m and sliding radius: 3 mm. SiC ball was used as counterpart with $r = 5.545$ mm radius. Wear tests were carried out in dry conditions at ambient atmosphere.

The main objectives of the research work were to describe and identify the controlling wear mechanisms and wear types occurred in the investigated different tribo-systems, based on which wear mechanisms maps for the investigated materials could be created. These 2D maps are able to visualize
the controlling wear mechanism regions of the given tribo-system as a function of the applied load, $F$ and the sliding velocity, $v$.

The first step of creating these type of maps is the adequate systematization of wear mechanism and wear types, a question that is rather confusing and incomplete in the current technical literature. Therefore a new classification system of tribological processes has been worked out (Fig.1.) and published [11, 12]. Beside our aim for providing a suggestion for classification the definitions of the wear mechanisms and wear types are also given and well differentiated.

![Figure 1. Classification of tribological processes](image)

(M: mechanical, T: thermal, E: environmental)

To create a two-dimensional wear mechanisms map the following steps have been taken:
1. assigning the numerical value of the corresponding test parameters, i.e. the normal load and the sliding velocity pairs;
2. scanning electron microscopic investigation of the wear track produced in a tribo-system with the given test parameter combination;
3. morphological analyses of the wear track and identification of related wear mechanisms and wear types;
4. choosing the controlling wear mechanism(s) and wear type(s) for the given tribo-system. The wear mechanisms and wear types may change during the tribological process, therefore we usually able to identify only the main appearing tribological phenomena from which the controlling wear mechanism and wear type should be chosen;
5. creating two-dimensional diagrams of wear mechanisms, and wear types as a function of the applied load and sliding velocity, and determining their validity ranges.

2.2. Material characterisation

Test specimens were produced by the Research Institute for Technical Physics and Materials Science, Department of Ceramics and Nanocomposites Budapest, Hungary. The chemical compositions of the investigated samples are listed in Table 1. The initial powder mixtures were milled in water in a high-speed HDDM type attritor mill using zirconia balls for 5 hours, with 3000 rpm. After drying the dust,
screening was applied with 100 µm sieve. Green samples were obtained by cold pressing at 200 MPa. Sintering process was carried out at 1700 °C, for 3 hours, with 20 MPa pressure, in high purity N₂-gas.

Table 1. Chemical composition and measured density of the samples

| Samples     | Chemical composition, [wt %] | Density, [g/cm³] |
|-------------|------------------------------|------------------|
|             | Si₃N₄ | Al₂O₃ | Y₂O₃ | MWCNT |             |
| 0% MWCNT    | 90   | 4     | 6    | 0     | 3.434      |
| 1% MWCNT    | 89   | 4     | 6    | 1     | 3.386      |
| 2% MWCNT    | 88   | 4     | 6    | 2     | 3.293      |

The experimental work was executed on these 3 types of specimens on 3-3 samples for each composition. The initial disc shape samples with the diameter of \( \phi \) 27.3 … 27.6 mm and height of 2.2 … 2.3 mm are shown in Fig. 2.

XRD analyses proved that beside the presence of the initial compounds and phases of the ceramic materials formation of new phases during sintering have occurred. Relating to the basic Si₃N₄ matrix material a SiAlON complex phase has formed, while relating to the Y₂O₃ sintering aid, it reacted with the ZrO₂ (a residuum from the zirconia milling balls) and formed a complex ZrYO phase.

![Initial samples](a) 0% MWCNT, (b) 1% MWCNT, (c) 2% MWCNT

**Figure 2.** The initial samples used for the wear tests

3. Test results, wear mechanism mapping

High (magnification: 300×) and low (magnification: 50×) resolution pictures were taken by scanning electron microscope to describe the wear process of the samples and of the tribo-systems.

Analyzing the wear tracks evolved in the different tribo-systems the controlling wear phenomena were identified. In each cases, i.e. for the monolithic and even for the composite samples three different dominant wear mechanisms could be identified, in addition four different wear types occurred in case of the monolithic samples, while five different ones were observed in case of the composite samples, which were identified according to the own classification system presented in Fig. 1.

Table 2 contains the regions of controlling wear mechanisms and wear types indicating the measured ranges of the related steady state friction coefficients, while Fig. 3 illustrates the two dimensional wear mechanisms/wear types maps of the investigated materials. The main characteristics of the different regions of the wear behavior are as follows:

**Region I.:** Delamination of thin silicon-hydroxide tribofilm occurs by plastic deformation, due to unidirectional shearing of surface. In this case a new, plastically deformed hydroxide layer is forming, while under the surface pores can be overlapped, forming cracks. Due to repeated loading of surface the cracks will propagate and smaller-larger platelets will erupt from the surface by fatigue wear. The steady state friction coefficients ranged from 0.43 to 0.46.

**Region II.:** Due to plastic shearing of a more massive hydroxide film the newly developed sheets can overlap and stack on each other. In addition, due to the SiC counterpart traces of grooving in the plastically deformed surface layer can be observed. In general the best wear performance accompanied with the lowest frictional coefficient falling into the range of 0.36-0.43.

**Region III.:** At higher normal loads or sliding speeds an intensive tribofilm formation of surface complexes is possible due to thermochemical reaction between sliding surfaces. This new tribofilm forms a continuous coating on the surface, which is mostly an oxide film and its physical properties...
will basically influence the wear process. The higher normal load and frictional heat results in amore expressed plastic deformation, and abrasive wear increasing the friction coefficient up to 0.42-0.58.

Region IV.: Melt wear occurs, as very high temperature between the sliding surfaces occur, so some \( \mu m^2 \) of the surface can melt and operate as lubricant, with friction coefficient of 0.49-0.54.

Region V.: Massive tribo-chemical film formation is followed by fatigue wear due to repeated load, by applying high normal loads and low sliding velocity. The pores being present due to the MWCNT particles enhances the crack initiation and propagation, with a friction coefficient range of 0.43-0.46.

**Table 2.** The controlling wear mechanisms, wear types and the steady state friction coefficient values

| Region | Controlling wear mechanism | Main wear types | \( \mu \) steady state |
|--------|---------------------------|-----------------|----------------------|
| I.     | plastic deformation       | weak hydroxide film formation, fatigue wear, delamination | 0.43-0.46 |
| II.    | plastic deformation       | hydroxide film form, layer stacking, growing | 0.36-0.43 |
| III.   | tribo-chemical wear, plastic deformation, | strong, oxide film formation, abrasive wear | 0.42-0.58 |
| IV.    | tribo-chemical wear, plastic deformation, | strong, oxide film formation, melt wear | 0.49-0.54 |
| V      | tribo-chemical wear, brittle fracture | massive tribofilm formation followed by fatigue wear and delamination | 0.43-0.46 |

![Figure 3. Wear mechanisms/wear types maps of the investigated materials](image)

In case of monolithic samples the ranges I. – IV. appeared, while in case of composite samples the range V. additionally occurred. In general the plastic deformation as a controlling wear mechanism turned up in the I-IV.regions, while in region V. the massive tribofilm formation was accompanied by a brittle fracture. The wear maps of samples containing 0 and 1 wt% MWCNT were very similar. The only difference was observed in the loading range of 40-80 N at low (v=10 mm/s) sliding velocity where a new wear regime, i.e. the Region V. appeared for the samples containing 1 wt% MWCNT.

This happened at the expense of Regions III., as well as of the ability for plastic deformation. In case of samples containing 2 wt% MWCNT the area of Region II. is enlarged, demonstrating that this amount of MWCNT can serve as a solid lubricant lowering the friction coefficient and the wear damage. At the same time with an increasing MWCNT content the Region I. is changed by region V. at the low sliding speeds. It can be explained by the higher sensitivity to surface cracking due to the higher porosity developing during sintering caused by the insufficient dispersion of the MWCNT particles in the matrix. Increasing the sliding velocity at higher loads the temperature of the contact area is increasing and a more massive tribofilm formation can be experienced. The fatigue wear is...
changed by a more intensive plastic deformation resulting in abrasive wear. At the highest loads (F = 80 N and v = 200 mm/s) the oxide film formation process is competing with a melt wear process.

4. Summary
A novel proposal for classification and description of wear processes – such as wear mechanisms and wear types – has been worked out. Using this classification a systematic analysis of wear mechanisms controlling the wear damage process of monolithic and MWCNT reinforced Si₃N₄ ceramics was completed investigated in different pin-on-disc test conditions. The observations have been summarized in two-dimensional wear maps as a function of applied load and sliding velocity.

For the monolithic and even for the composite samples three main wear mechanisms – plastic deformation, tribochemical wear and brittle fracture could be identified – while five different wear types – tribofilm formation, fatigue wear, delamination, abrasive wear and melt wear – appeared. Each of the investigated materials showed more or less plastic deformation, but MWCNT composites due to the more porous matrix tended to brittle fracturing at low sliding speeds and high loads.

The most advantageous wear behavior is represented by the Region II. wear tribofilm of good plastic deformation capability and low friction coefficient provides to realize the lowest wear damage. Si₃N₄ ceramics containing 0 and 1 wt% MWCNT possess a very similar wear mechanism maps, while in case of 2 wt% MWCNT composites the carbon additive could serve as a solid lubricant.

The composed 2D wear maps can contribute to a more easy and purposeful tribological application of these new composites, and can help a more reliable prediction of their wear behavior.

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