Effect of graphene and temperature on friction coefficient of nanocomposite Al₂O₃ / graphene

M A Pakhomov¹, V V Stolyarov¹, A M Mezrin² and E V Torskaya²

¹Mechanical Engineering Research Institute of RAS, Moscow, Russia
²Ishlinsky Institute for Problems in Mechanics of RAS, Moscow, Russia

Abstract. The paper presents the results of tribological tests of sintered nanocomposite ceramics with 1 wt.% graphene and without graphene at room and higher temperatures. It is shown that graphene decreases friction coefficient. With an increase in the test temperature, the friction coefficient increased on samples with and without graphene.

1. Introduction
Ceramics based on Al₂O₃ have many remarkable functional properties that make it possible to use it as a structure material [1]. These include high melting point, hardness, elastic modulus, corrosion resistance, etc. However, some disadvantages, such as high brittleness, lack of electrical conductivity, and a high friction coefficient, limit its application. Several physical approaches based on the refinement of the matrix and its alloying with various carbon additives, including nanotubes and fullerenes, give hope for the possibility of a significant improvement in these properties by modifying the structure of the ceramics under consideration [2, 3].

A relatively new modification method is the creation of a composite based on nanosized Al₂O₃ powder with the addition of 2D graphene [2]. It is assumed that the flake form of nanographene provides a large contact area between grains and promotes an increase in adhesive bonds. Also, the low electrical resistivity, layered structure, and length of graphene itself can significantly increase the conductivity and tribological properties of the composite [4]. Several studies of dielectric and tribological characteristics confirm a noticeable increase in the conductivity and wear resistance of the Al₂O₃ / graphene composite [5]. Note that most studies of the properties in the Al₂O₃ / graphene composite were carried out at room temperature. Only one paper presents the temperature dependence of the friction coefficient in the composite Al₂O₃ with carbon nanotubes [6]. At the same time, there is a need to use ceramic materials at higher temperatures, since their mechanical properties, as a rule, remain stable over a wide temperature range.

This study aims to evaluate the influence of graphene on the friction coefficient of Al₂O₃ nanoceramics at room and elevated temperatures under dry friction conditions.

2. Materials and methods
To obtain the advanced ceramic composites for the study, mixtures of alumina and graphene powders were used. For sample preparation, nanosized Al₂O₃ powder (45 nm) was obtained by means of the oxidation of aluminum in an air plasma jet. Graphene nanoplatelet powders (GNPs), supplied by Graphene-tech (Zaragoza, Spain), were produced with the ultrasonic exfoliation method. Graphene flakes with an average thickness of 3 nm (about 5 atomic layers) and square of 5 x 5 µm² were prepared. The morphology of the different starting powders is shown in figure 1. Al₂O₃ powder and 1 wt% GNPs...
were dispersed in ethanol and then mixed in an ultrasonic bath under mechanical stirring. After that, the powder mixture was dried at 78 °C for 1 h on a heating plate to completely remove all the dispersant. Finally, Al₂O₃-GNPs powders with nano particle sizes of alumina were sintered under vacuum with the spark plasma sintering technique (SPS, LABOX-625, SinterLand, Nagaoka City, Japan), where the powder was placed in a graphite die with an inner diameter of 15 mm. The sintering temperature was established at 1500 °C with a holding time of 10 min at the maximum temperature under an applied pressure of 50 MPa and a heating rate of 100 K/min. Afterwards, the sintered samples with 2 mm thickness were polished in order to complete measurement and analysis [7].

The ceramic discs Ø15 x 2 mm were used for the testing without lubrication in the air on a Cetr Umt-3 tribometer according to the "ball-disk" friction pattern with reciprocating motion. Test parameters were average speed in a cycle of 0,1 m / s, a load of 10N, frequency of 7,7 Hz, indenter amplitude of 6,5 mm. The material of the counter body was silicon carbide SiC as the Ø4 mm ball. The original sample was fixed in tooling with a high-temperature sealant, after which the working surface was subjected to grinding and polishing to achieve a roughness of Rₐ ≤ 0,04 μm. Roughness was measured on a Sensofar S Neox profilometer. The elastic modulus was determined by nanoindentation with a sphere-conical indenter with a curvature radius of 65 μm on the Nanoscan 4D nanoindenter. The friction tests were carried out at room temperatures and 300°C, for which the built furnace into the tribometer was used. Test duration at room temperature and 300°C was 10 000 and 3200 seconds, respectively.

Figure 1. FESEM images of the starting powders: (a) nanopowder Al₂O₃ and (b) graphene nanoplatelets (GNPs).

3. Experimental results

Figure 2 shows the results of measuring the friction coefficient of the ceramic samples at room temperature. The sample without graphene is characterized by the presence of numerous upward jumps on curve 1, which are practically absent for the sample with graphene on curve 2. It can be noted that the addition of graphene, already in the first 5 minutes, contributes to a noticeable decrease in the friction coefficient and its stabilization. Subsequently, the friction coefficient increases slightly.

Figure 2. Dependence of the friction coefficient on time at room temperature for ceramics without graphene (curve 1) and with 1wt.% graphene (curve 2).
In figure 3 the results of measuring the friction coefficient of the samples under consideration at the temperature of 300°C are shown.

![Figure 3](image)

**Figure 3.** Dependence of the friction coefficient on time at 300 °C for ceramics without graphene (curve 1) and with 1wt.% graphene (curve 2).

In this case, the addition of graphene also helps to reduce the average values of friction coefficient. However, the type of the curves differs from the curves at room temperature. Curve 1 becomes smoother, and on curve 2 in the first 5 minutes, the friction coefficient increases then decrease and stabilizes. Due to the high friction coefficient and stronger wear of the indenter, tests at elevated temperatures were shorter.

The average values of the friction coefficient and the roughness on the friction track for all test modes are presented in table 1.

**Table 1.** Average friction coefficient and roughness Rₐ on the friction track at different temperatures.

| Ambient temperature, °C | Friction coefficient | Roughness, µm |
|-------------------------|----------------------|---------------|
|                         | Graphene free        | With 1% graphene | Graphene free | With 1 wt.% graphene |
| RT                      | 0.54                 | 0.42           | 0.02          | 0.02                 |
| 300                     | 0.76                 | 0.68           | 0.5           | 0.1                  |

It can be seen that for both type of samples, an increase in the test temperature led to an increase in the friction coefficient.

It should be noted that the experimental curve for ceramics without graphene changes weakly with time; the friction coefficient is unstable, has peaks typical for friction in the presence of destruction acts at the microlevel. The initial values of the friction coefficient for both samples practically coincide, but the presence of graphene leads to a rapid decrease of the friction coefficient, that happens during the formation of a tribofilm. Over time, the value of the friction coefficient increases slightly, peaks appear, but still, it remains more than 20% lower (compared to ceramics without graphene). The process may be influenced by heat generation during friction since both interacting materials have low heat conductivity.

Figure 4 shows SEM images of wear tracks for ceramics without graphene and with 1 wt.% graphene at room temperature. It can be seen that the nature of the track wear is very different in the size and number of fracture sites.

In ceramics without graphene, the destruction is extensive, brittle, and has a predominantly grain-boundary character over the Al₂O₃ matrix grains (figure 4a). In contrast, in ceramics with graphene, the fractures are local and smoother (figure 4b).
Figure 4. Friction tracks at room temperature for ceramics: (a) - without graphene; (b) - with graphene 1 wt.%.

4. The discussion of the results

The latter assumption is partly confirmed by the test results at elevated temperatures. The curves shown in figure 2 were obtained at a shorter duration than at room temperature. This is due to a situation close to tearing at the end of this period. The presence of graphene somewhat reduces the average value of the friction coefficient (0.68 compared to 0.76), but the instability of the friction process does not allow us to regard this decrease as a significant advantage.

Measuring the elastic modulus by the nanoindentation method showed the data obtained for both materials are within the experimental error and the average can be taken equal to 406 GPa. The presence of tribofilms can lead to the appearance of a compliant layer on the surface of the friction track [8], which is identified during indentation. To test the assumption, measurements were carried out on smooth friction tracks obtained at room temperature. The obtained values of the curves are also within the error limits.

Estimation the modulus of inelastic bucking makes it possible to determine the initial parameters of the contact interaction before wear that are the same for both materials. The radius of the contact spot, calculated according to the theory of Hertz [9], is 33 μm, the maximum contact pressure is 4.38 GPa. Obviously, a sufficiently high pressure promotes rapid destruction at the pores that are stress concentrators at the micro level. The presence of graphene, which inevitably partially fills the pores and strengthens the material, somewhat slows down this process. Graphene, caught on the surface as a result of the destruction, forms a carbon nanofilm between rubbing ceramic surfaces that helps to reduce the coefficient of friction and wear at room temperature. At higher temperatures, the strength properties of oxide ceramics deteriorate [10]. It can be assumed, as a result of brittle fracture, larger particles of material are separated and enter the friction zone. It increases the wear track and prevents the formation of a carbon film between the rubbing surfaces. Indirect evidence of this fact is the significant roughness of the friction tracks obtained at high. At room temperature, for both samples, the roughness on the friction track was Rₐ = 0.02 μm. At 300 °C for a sample without graphene Rₐ=0.5 μm, for a sample with 1 wt.% graphene Rₐ = 0.1 obtained at high temperatures (table 1).

5. Conclusions

1) The addition of 1wt.% graphene to Al₂O₃ nanoceramics reduces the friction coefficient by 22% at room temperature and by 11% at elevated temperatures.

2) An increase in the test temperature from room temperature to 300 °C leads to an increase in the friction coefficient by 22 and 26%, respectively, in samples without and with graphene.

3) The mechanism of reducing the friction coefficient upon the introduction of graphene is associated with the formation of a lubricating carbon layer on the contact surface.
6. References

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