Tribological Properties of Al$_2$O$_3$ Coatings Obtained by Detonation

B K Rakhadilov$^{1,2,a}$, D B Buitkenov$^{1,2,b}$ and M K Rakhadilov$^{2,c}$

$^1$Sarsen Amanzholov East Kazakhstan University, Ust-Kamenogorsk, Kazakhstan
$^2$PlasmaScience LLP, Ust-Kamenogorsk, Kazakhstan

E-mail: $^a$rakhadilovb@mail.ru, $^c$bor1988@mail.ru
corresponding author: $^b$buitkenovd@mail.ru

Abstract. In the present work, the effect of the detonation-spraying mode on the tribological properties of Al$_2$O$_3$ coating was studied. It was found that a decrease in the delay time between shots is leading to an increase in the hardness and elastic module of Al$_2$O$_3$ coatings. The obtained values of the coefficient of friction showed that a decrease in the delay time between shots leads to a slight reduction in the coefficient of friction. It is determined that reducing the delay time between shots to 0.25 seconds leads to an increase in the resistance of coatings to abrasive wear. It was found that the main reason for the increase in hardness and wear resistance with a decrease in the delay time between shots to 0.25 s is associated with an increase in the volume fraction of the α-Al$_2$O$_3$ phase. It was found that increase in the volume fraction of the α-Al$_2$O$_3$ phase is caused by the secondary recrystallization $\gamma \rightarrow \alpha$, which occurs due to the heating of particles during coating formation, i.e. due to increase in temperature above 1100 °C in single spots of the coating when they are put each other.

1. Introduction

The method of detonation spraying of coatings has been widely used, as it can significantly increase the performance properties of parts, their service life. This is conditioned the fact that detonation coatings have significantly higher values of adhesion, wear resistance, and lower porosity than other types of gas-thermal coatings[1-3]. However, for a wider application of the detonation method for strengthening components and parts of equipment for the oil and gas industry, shipbuilding, metallurgy, gas turbine engineering, etc. it is necessary to significantly improve the properties of the obtained coatings. This is related to the fact that, as a rule, the components and parts of the above equipment operate under the simultaneous influence of various environment and loads, the values of which in many cases exceed the maximum permissible values for existing detonation coatings [4-6]. A significant increase in the properties of detonation coatings can be achieved by spraying various materials in several layers, which allows you to obtain coatings with special characteristics. This is possible when using gradient coatings made of the same material, which change the structure and properties of the coating depth. Such coatings have the necessary specified properties of the outer layers that are directly exposed to the external environment. In addition, compared to a multi-layer coating, they reduce the difference between the physical and mechanical characteristics of the coating and the base and, consequently, the stress jump that occurs when loading at the boundary of the interfaced layers. Despite the fact that scientific research on the production of detonation coatings with
different values of structure and properties in different layers (by coating cross-section) has been carried out for a long time, they have not been used in practice nowadays. This is obviously related to the fact that its realization requires carrying a complex of various research and development.

In connection with the above, this work aims to study the tribological properties of gradient coatings based on aluminum oxide.

2. Materials and research methods
A stainless steel 12Kh18N10T was chosen as the object of research. Corundum powders (α-Al₂O₃) were used to obtain aluminum oxide coatings. Powder particle size from 22-45 mµ. Before spraying coating, the samples were sandblasted.

The experiments were carried out based on the Scientific Research center "Surface Engineering and Tribology" of the Sarsen Amanzholov East Kazakhstan university of the industrial computer controlled detonation spraying complex CCDS2000 [7-9]. A general schematic diagram of the detonation spraying process is shown in figure 1. The action principle is as follows [8]. A mixture of gases is fed directly from the gas cylinders through the valve block 9, which enters the combustion chamber 3. At the same time, a powder sample is provided from the powder dispenser 11 into the space of the barrel 10 under pressure, then, thanks to the ignition device 4, ignition occurs. As a result, the mixture is detonated and moved towards the nozzle 14, where the particles being sprayed are picked up and accelerated along the way. As a result, we get the formed coating 12 on the substrate 13. The control unit 1 controls the entire spraying process, from the supply of combustible gases and powder dosing to the movement of the sprayed billet itself 13 using a 3D manipulator.

![Figure 1](image_url)

**Figure 1.** Schematic diagram of the computer controlled detonation spraying complex CCDS2000.

Preliminary results showed that the phase composition and properties of detonation coatings much depend on the technological parameters of spraying. Based on the preliminary results, we found that by varying the technological parameters of coating application, such as the percentage of barrel filling, the ratio of the gas mixture and the delay time between shots, it is possible to control the structure, phase and chemical composition and respectively the coating properties [10-13]. In this work was obtained Al₂O₃ coatings by varying the delay time between shots. In table 1 shows technological parameters of detonation spraying of Al₂O₃ coatings.
Table 1. Technological parameters of detonation spraying of Al$_2$O$_3$ coatings.

| Sample number | Ratio O$_2$/C$_2$H$_2$ | Barrel filling volume, [%] | Spray distance, [mm] | Shots number | Delay between shots, [s] |
|---------------|-----------------------|----------------------------|----------------------|--------------|-------------------------|
| 1             | 1,856                 | 63                         | 250                  | 20           | 1                       |
| 2             |                       |                            |                      |              | 0.75                    |
| 3             |                       |                            |                      |              | 0.5                     |
| 4             |                       |                            |                      |              | 0.25                    |

The phase composition of the samples was researching by X-ray diffraction analysis on an XPertPro diffractometer using CuKα-radiation. To determine the ratio of the main phases of the sample, the corundum number method (Reference Intensity Ratio – RIR) is used, which is destined for quantitative phase analysis of mixtures, when it is necessary to quickly estimate the composition of the study sample with low, but acceptable accuracy. This method is based on reference intensity ratios (RIR values) and particular coefficients [14]. The measurement of hardness and elastic modulus was determined by indenting on a nanohardmeter «NanoScan-4D compact» in accordance with GOST R 8.748-2011 and ISO 14577. The tests were carried out at a load of 100 mN. The tribological characteristics of the coatings were studied on a TRB tribometer using the «ball-disk» method. As a counterbody was used 3 mm diameter SiC ball. The study parameters were the same for the research samples: the run length was 81 meters, the load was 10N, and the speed was 3 cm / s, at room temperature [15]. Samples were tested for abrasive wear on an experimental installation for testing for abrasive wear by the scheme "Rotating roller-flat surface" in accordance with GOST 23.208-79.

3. Results and discussion

The values of elastic modulus and nanohardness calculated from the obtained curves are shown in table 2. Visible, that with a decrease in the delay time between shots, the hardness increases from 10.87 GPA to 16.33 GPA. The coatings elastic modulus also increases to 270.64 GPA. An increase in the elastic modulus indicates a decrease in plasticity and an increase in the strength of coatings. The reason hardness increase is probably related to secondary thermal hardening of coatings. Since, when the delay time between shots changes, the speed and temperature of the particles do not change, only the temperature of the applied coating layers changes during the spraying process. Thus, by reducing the delay time between shots of the detonation complex to the minimum possible value of CCDS2000, it is possible to obtain an Al$_2$O$_3$ coating with a hardness of 16.33 GPA and a young's modulus of 270.64 GPA.

Table 2. Results of Al$_2$O$_3$ coatings nanoindentation.

| Coating | Nanohardness, [GPa] | Young's modulus, [GPa] |
|---------|---------------------|------------------------|
| 1       | 10.87               | 207.70                 |
| 2       | 11.03               | 159.97                 |
| 3       | 11.72               | 206.48                 |
| 4       | 16.33               | 270.64                 |

Figure 2,3 shows the results of tribological tests of Al$_2$O$_3$ coating samples using the «ball-disk» scheme. The volume of wear characterized the wear resistance of the samples. The figure shows that with a decrease in the delay time between shots from 1 second to 0.75 and 0.5 seconds, it leads to a reduction in the wear volume. When the delay time between shots is 0.25 seconds, there is a significant reduction in the wear volume. The obtained values of the friction coefficient showed that a decrease in the delay time between shots leads to a reduction in the friction coefficient (figure 3). A decrease in the wear volume and the friction coefficient indicates an increase in the wear resistance of coatings.
Figure 2. Results of tribological tests of Al$_2$O$_3$ coatings by the ball-disk scheme.

Figure 3. Curves of the friction coefficient of Al$_2$O$_3$ coatings obtained by different spraying modes: the delay time between shots is 1 s (a), 0.75 s (b), 0.5 s (c), 0.25 s (d).
Figure 4 shows the abrasive wear results of testing Al$_2$O$_3$ coatings. The wear resistance of the samples was characterized by losing weight before and after the test. The results showed that reducing the delay time between shots to 0.25 seconds brings to an increase in the resistance of coatings to abrasive wear.

![Figure 4. Results of abrasive wear testing of Al$_2$O$_3$ coatings.](image)

Thus, by reducing the delay time between shots, the detonation spray method can be used as an additional source of energy for heating the applied coating layer. Reducing the delay time between shots leads to the fact that the temperature in individual spots of the coating when they are imposed on each other will consistently increase. The thermal effect of sputtering spots will be noticeable if the delay between spraying individual spots is minimal, approximately a few milliseconds.

X-ray diffraction research has shown that the highest content of the α-phase is achieved when coatings are formed with a delay between shots of about 0.25 s (figure 5). The increase in the volume fraction of the α-Al$_2$O$_3$ phase is caused by secondary recrystallization of γ→α, which occurs due to the warming of the particles during the formation of the coating, i.e., due to an increase in temperature above 1100°C in single spots of the coating when they are imposed on each other. Thus, by changing the delay time between shots, we can control the phase composition of coatings based on Al$_2$O$_3$ and respectively, the properties of coatings. The results obtained in the future allow us to get gradient coatings that have high adhesive strength and high surface hardness of the coating by changing the delay time between shots during the obtaining of coatings. Obtaining such coatings is provided by the surface layer of coatings consists of a large amount of α-Al$_2$O$_3$ phase, and the proportion of γ-Al$_2$O$_3$ phase increases as it approaches the substrate. Therefore, the denser γ-Al$_2$O$_3$ phase provides good adhesive strength of coatings to the substrate, and the α-Al$_2$O$_3$ phase, which is found in large quantities in the coating surface, offers high hardness and wear resistance.

Based on x-ray diffraction analysis, it can be claimed that the main reason for the increase in hardness and wear resistance with a decrease in the delay time between shots to 0.25 s is associated with an increase in the volume fraction of the α-Al$_2$O$_3$ phase. Modifications of the α and γ phases have different values of physical and mechanical properties. The modification of α-Al$_2$O$_3$ has a higher hardness and wear resistance, while γ-Al$_2$O$_3$ is relatively more plastic and provides a higher adhesion strength with substrate.
Figure 5. Diffractograms of Al$_2$O$_3$ coatings obtained by different spraying modes: delay time between shots-1 s (a), 0.75 s (b), 0.5 s (C), 0.25 s (d).

4. Conclusion

Analysis of the results shows that by reducing the delay time between shots can be obtained Al$_2$O$_3$ coatings with high hardness. By reducing, the delay time between shots to the lowest possible value for the CCDS2000 detonation complex was obtained Al$_2$O$_3$ coatings with a hardness of 16.33 GPA and a Young's modulus of 270.64 GPA. The obtained values of the friction coefficient showed that a decrease in the delay time between shots leads to a decrease in the friction coefficient. It was found that the main reason for the increase in hardness and wear resistance with a decrease in the delay time between shots to 0.25 s is associated with an increase in the volume fraction α-Al$_2$O$_3$ phase. X-ray diffraction research has shown that the highest content of the α-phase is achieved when coatings are formed with a delay between shots of about 0.25 s. The increase in the volume fraction of the α-Al$_2$O$_3$ phase is caused by secondary recrystallization of γ→α, which occurs due to the warming up the particles during the formation of coating, i.e., due to an increase in temperature above 1100°C in single spots of the coating when they are imposed on each other. Thus, by changing the delay time between shots, it is possible to control the phase composition of coatings based on Al$_2$O$_3$ and respectively the coating properties.

5. References

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