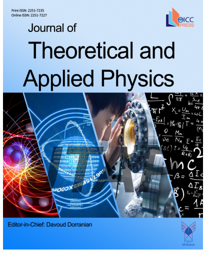

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Preparation of composite powder based on nano-TiO_2 and Cr_2O_3 using a spray dryer, for atmospheric plasma spraying, designed for HPAL systems

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Original Research

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Abstract:

In this study, composite coatings based on TiO_2 and TiO_2-Cr_2O_3 nanopowders were fabricated by air plasma spraying for High-Pressure Acid Leaching (HPAL) systems. Nanopowders were agglomerated in aqueous medium using polyvinyl alcohol and spray-dried into spherical granules. Coatings were deposited onto 12Kh18N10T stainless steel substrates. X-ray diffraction (XRD) analysis revealed rutile TiO_2 and Cr_2O_3 as the main crystalline phases, with minor Ti_2O_3. For TiO_2-only coatings, the XRD pattern showed predominantly rutile (R-TiO_2) and a small amount of anatase (A-TiO_2); brookite was absent. Rutile formation is attributed to high plasma spraying temperatures that promote anatase-to-rutile transformation. The coatings had dense microstructures with low porosity due to optimized powder preparation and spraying. Microhardness of TiO_2-Cr_2O_3 coatings reached 1015 HV, 40% higher than pure TiO_2 (723 HV). Tribological tests under a 3 N load and 500 m sliding distance showed a reduced friction coefficient from 0.98 to 0.65. The wear rate of TiO_2-Cr_2O_3 coatings was 4.2×10^{-5} mm^3/N.m, indicating enhanced wear resistance. These findings demonstrate that Cr_2O_3 addition and optimized powder processing yield harder, denser, and more durable coatings, suitable for harsh service conditions.

Keywords: Coatings; Plasma spraying; Agglomeration; Structure; Wear resistance; Microhardness

1. Introduction

Over the past two decades, metal seated ball valves (MSBV) have become the industry standard for hydrometallurgy. They provide tight and reliable shutoff, a crit-ical service that facilitates maintenance and promotes a safe working environment. A typical MSBV design for hydrometallurgy consists of a floating ball in contact with a fixed seat. The ball and seat consist of titanium or duplex stainless steel protected by a ceramic coating. The main function of the ceramic coating is to increase the bearing capacity and tribological characteristics of the base material, thus extending the ser-vice life of the equipment, especially during the ball movement phases [1–3].

There are two types of hydrometallurgical processes: Pressurized oxygen leach-ing (Pox) and pressurized acid leaching (HPAL) [4]. Both methods have been used to extract valuable metals, particularly nickel and cobalt, from ores for decades. Unlike POx, HPAL operates under high pressure, which combined with higher chloride con-tent creates a more corrosive environment (e.g., titanium is susceptible to crevice cor-rosion in HPAL) [5]. Based on Based on Velan Inc. experience with various coating mixtures at the Falconbridge (Canada) mines, a Cr_2O_3 ,experience with various coating mixtures at the Falconbridge (Canada) mines, a Cr_2O_3, POx optimized mixture cor-rodes prematurely when used in HPAL [6]. Since TiO_2 is relatively inert in this envi-ronment, it appears to be a promising choice for HPAL [7].

Thermal spray coatings have a wide range of applications, from space to medical applications, and are often applied to any substrate using appropriate site-specific techniques. A few basic criteria for coating application include adhesion, hardness, and thickness. A bonding layer is often applied to increase the adhesion of the func-tional layer to the sub-

strate material ref. TiO_2 and Cr_2O_3 or their combinations are ap-plied as coatings on titanium alloys used in industrial blade balls without any bonding layer. In [8], coatings ap-plied using powder agglomerated from nanoscale titanium oxide particles were investigated. Titanium oxide powder agglomerated from na-noscale particles showed better performance than sintered and milled commercial TiO_2 powder [9]. A recent study using a mixture of nano-TiO_2 and Cr_2O_3 powder showed even better results under laboratory conditions for dry and wet erosion [10].
However, due to the insufficient service life of ball valve parts used in hydro-metallurgy, particularly in HPAL, improvement of the applied coatings is still re-quired.
To solve the problems related to the development of wear-resistant coatings, TiO_2 and TiO_2/Cr_2O_3 based coatings were designed as the object of study in the present work. In order to achieve uniform and dense coatings, the samples were prepared by air-plasma spraying from agglomerated TiO_2 and Cr_2O_3 powders. This method allows the production of films with high mechanical and tribological properties and minimal defects and impurities.
In connection with the above, the aim of this work is to develop an air-plasma method of obtaining wear-resistant coatings TiO_2 and TiO_2/Cr_2O_3 on the surface of steel 12Kh18N10T, as well as to study the influence of technological parameters of spraying on the formation of the structural-phase state and tribological properties of these coatings.

2. Materials and methods

TiO_2 powder (Sulzer Metco, Amdry 6505) with a dispersity of $45 \pm 5\ \mu$m and Cr_2O_3 powder (Sulzer Metco, IKH 6003) with a particle size of $45 \pm 5\ \mu$m were used for spraying.
In the first step of this work, we prepared the required powder by agglomerations of TiO_2-Cr_2O_3 powders using a 1 S Attritor grade mill (Ohio, USA), to create a homogeneous structure with good mechanical properties during the spraying process.
Powder granulation was carried out in aqueous medium with the addition of polyvinyl alcohol and mixed in a 1 S Attritor ball mill for 36 hours (ball to powder mass ratio - 1:1, drum speed 150 rpm). Then it was placed in a special container and dried in a spray dryer (figure 1).
The process of granule powder production by spray drying is presented in the form of a scheme, where the prepared slurry of fine particles enters the spray tower. Under the pressure created in the atomizer, the slurry is atomized into droplets and dried by hot air. By changing the process parameters, it is possible to obtain spherical powder granules of the required size.
The quality of coatings in air plasma spraying depends on several factors: current, voltage and plasma gas flow rates. Of particular importance among these factors are the current strength and flow rate of working gas (Ar) and (H_2) [10]. In this regard, the parameters shown in Table 1 were selected for spraying.
Surface morphology was investigated by scanning electron microscopy (SEM) using backscattered electrons on a TESCAN VEGA scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDS). The phase

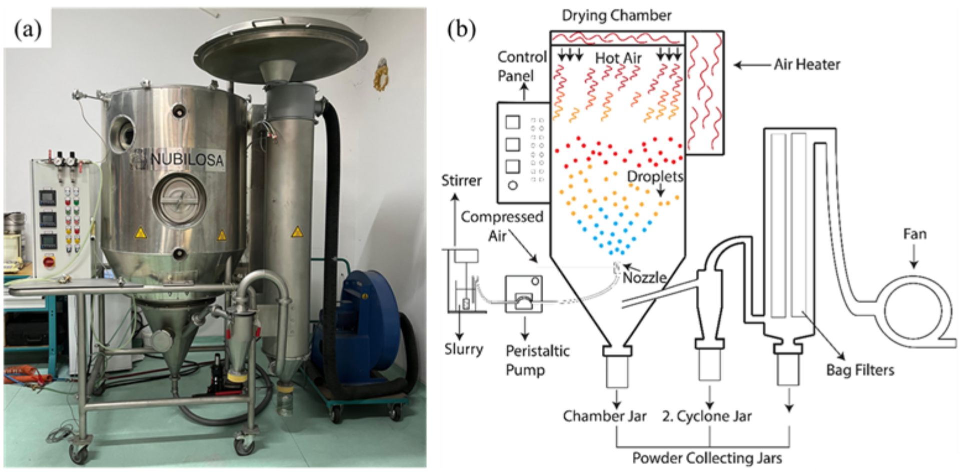

Figure 1. Spray dryer (Nubilosa) (a) and schematic of the spray dryer (b).

Table 1. Parameters of air plasma spraying.

Sample	Substrate	Powder	Powder flow rate, g/min	Current , A	Working gas	
					Argon (Ar) NLPM	Hydrogen (Hydrogen) NLPM
1	12Kh18N10T steel	TiO_2 – Milled and agglomerated	13	620	55	8
2	12Kh18N10T steel	TiO_2/Cr_2O_3 milled togetger than agglomerated	13	620	55	8

composition of the samples was studied by quantitative X-ray phase analysis on a RİGAKU D/MAX 2200 PC diffractometer using CuKα radiation. The microhardness of the samples was measured by Vickers method on the HVM Corporation instrument at 100 g load and 10 sec exposure time. Friction and wear tests were carried out on a CSM Instruments Tribometer, model THT (CSM Instruments, Switzerland), under a normal load of 3 N, a sliding speed of 25 cm/s, and a total sliding distance of 500 m. These parameters were selected based on preliminary tests and relevant literature data on ceramic-based coatings, in order to simulate moderate wear conditions typical for protective surface applications. The chosen conditions allow for measurable wear without causing catastrophic failure of the coating, thus enabling a reliable comparison of tribological performance. Each test was performed in dry sliding mode at room temperature.

3. Results and discussion

Figure 2 shows SEM images of powders obtained by spray drying and granulation methods and consolidated materials based on them. In both cases, agglomerates of different sizes are observed. The maximum size of agglomerates in TiO_2 powder, was $15-30$ μm; in TiO_2 powder -Cr_2O_3 , was $15-45$ μm. Agglomerates of TiO_2 -Cr_2O_3 powder are generally larger with a clear spherical shape, and in TiO_2 powder they are not only characterized by smaller sizes, but also have an irregular shape (agglomerates).

During the X-ray phase analysis it was found that the phase composition of the initial powder corresponds to the phase composition of the coatings. The main phase is titanium oxide with the chemical formula TiO_2, in addition, the phase contains a chemical compound with the formula TiO_2. In the system TiO_2-Cr_2O_3 it was also found that the phase composition of the initial powder corresponds to the phase composition of the coatings. As an example, figure 3 shows the diffractograms of the initial powder and coatings obtained by different regimes. Despite the fact that the heating temperatures of powder particles in the plasma jet are high, the rate of their crystallization on the substrate is also very high, so phase transformations during plasma spraying do not have time to take place. The broadening of diffraction peaks in the diffractograms of TiO_2 powder indicates its non-equilibrium state, whereas after spraying, the diffractogram may show narrower peaks, indicating a more ordered and equilibrium state of the material. This is because the spraying process often promotes the formation of a more ordered crystal structure and can lead to improved crystalline quality. Recrystallization, defect removal and lattice alignment can occur during the spraying process, which improves the crystal structure and reduces the width of diffraction peaks [11].

The data obtained by X-ray phase analysis are also confirmed by scanning electron microscopy (figure 4).

Figure 4, shows the SEM cross-sectional images of the coatings and mapping elements. At the interface betwen The coating thickness is about $\sim 100-150$ μm. During coating, microscopic pores were formed on the surface. These pores can be caused by irregularities in the application process such as improper temperature, humidity or composition of the starting material [12].

Figure 5 shows the results of microhardness of TiO_2-Cr_2O_3 ($HV_{0,1/10} = 1015$) coatings, which are significantly higher than those of TiO_2 ($HV_{0,1/10} = 723$). As explained in [13], in $TiO_2Cr_2O_3$ based coatings, the hardness values increase with increasing Cr_2O_3 content, whereas the presence of TiO_2 decreases the hardness of the coating and reduces its wear resistance. These data presented in the diagram and confirmed by the friction coefficients (figure 6) prove that the addition of Cr_2O_3 leads to an increase in the hardness of the coating and an improvement in its wear resistance [14].

As can be seen in figure 6, the coefficient of friction of $TiO_2Cr_2O_3$ coatings (0.65) is lower than that of TiO_2 coating (0.98) under dry friction. The relatively low coefficient of friction was achieved by the addition of Cr_2O_3, indicating better wear resistance of the coatings under the same test conditions. This is because the coefficient of thermal expansion of Cr_2O_3, which is about 4.2×10^{-5} mm^3/N.m, is lower compared to TiO_2, which is in the range of 7.9×10^{-5} mm^3/N.m. The difference in thermal expansion coefficient affects the temperature during tribological tests and consequently the coefficient of friction [15–20].

Figure 7, shows the surface wear traces of $TiO_2Cr_2O_3$ and TiO_2 coatings after tribological tests of the investigated ma-

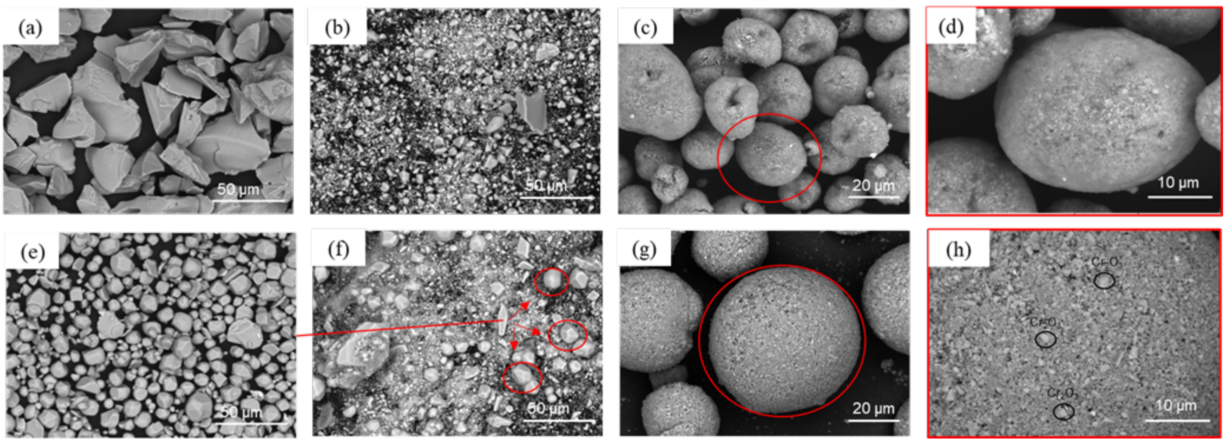

Figure 2. SEM images of powders: (a) TiO_2 powder (b) TiO_2 before agglomeration; (c) TiO_2 after agglomeration; (d) TiO_2 after agglomeration enlarged; (e) TiO_2 -Cr_2O_3 powder; (f) TiO_2-Cr_2O_3 before agglomeration; (g) TiO_2-Cr_2O_3 after agglomeration; (h) TiO_2-Cr_2O_3 after agglomeration enlarged.

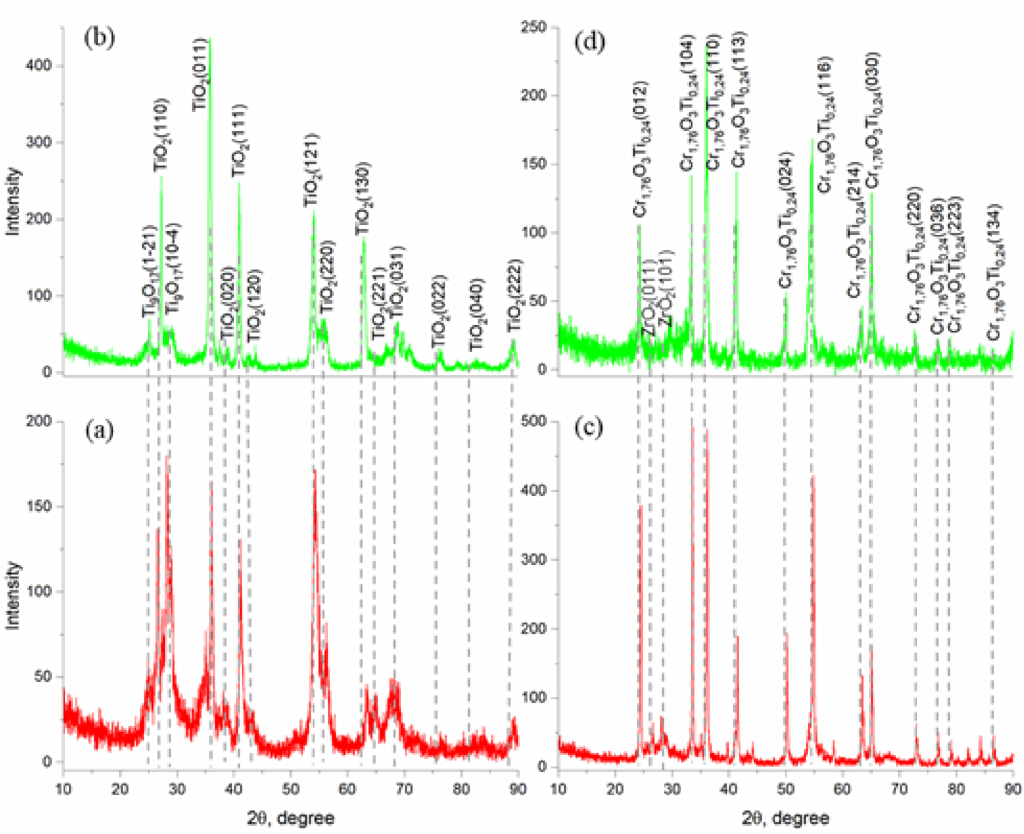

Figure 3. Results of X-ray phase analysis: (a) TiO_2 powder; (b) TiO_2 coatings; (c) TiO_2-Cr_2O_3 powder; (d) TiO_2-Cr_2O_3 coatings.

terial [21, 22]. A ZrO ball was used as a counter body. In tests using reciprocating dry sliding schemes, shear deformation, and non-uniform compressions of the coatings at the edge of the track are visible during the wear process. In the SEM images, in pure TiO_2, pronounced abrasive wear prevails: a wide, even furrow is formed with signs of polished friction and noticeable buckling ('squeezing') of the material at the edges. This corresponds to a high coefficient of friction ($\sim 0.9 - 1.0$) and indicates that the coating is rapidly deteriorating due to contact abrasion. The $TiO_2Cr_2O_3$ coating shows a 'softer' abrasive wear: The furrow width is smaller, and the wear itself is accompanied by the formation of microcracks and partial detachment of small ceramic fragments. This is consistent with the lower friction coefficient ($\sim 0.65 - 0.8$) and suggests that the presence of Cr_2O_3 increases the hardness and brittleness of the composite, reducing the effective contact area with the counter-sample and slowing down the overall wear.

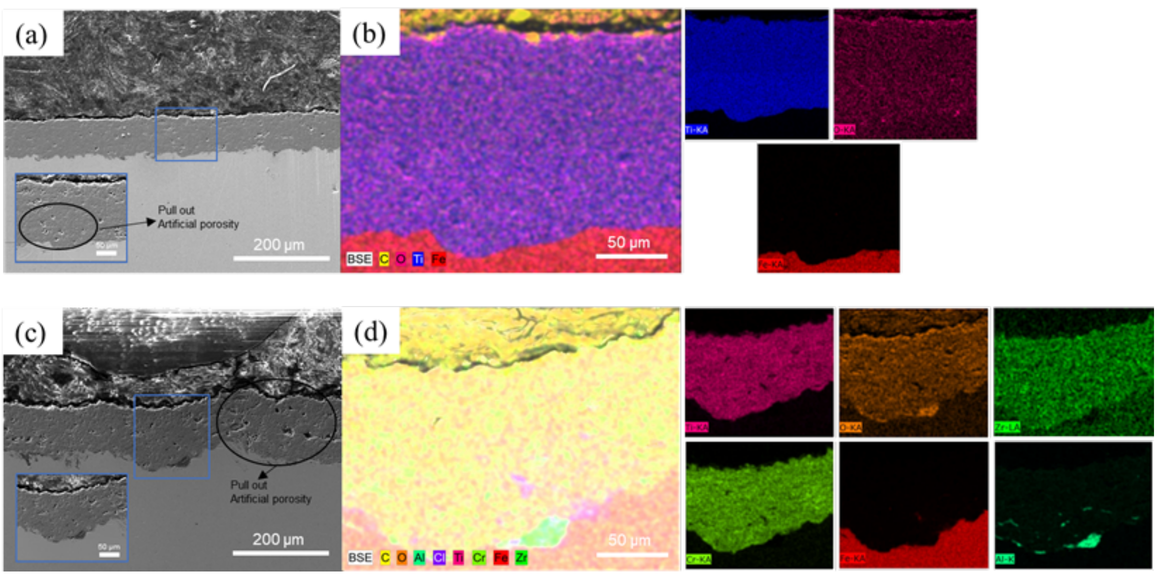

Figure 4. Cross section of coatings with the result of elemental mapping: (a,b) TiO_2; (c,d) TiO_2-Cr_2O_3.

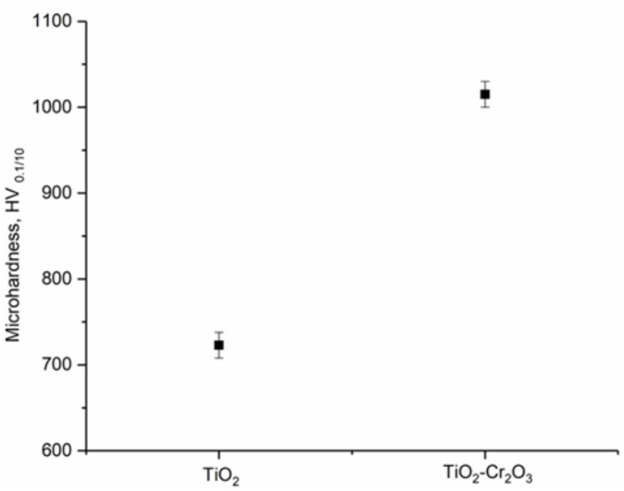

Figure 5. Hardness of coating the Cross-sectional Vickers.

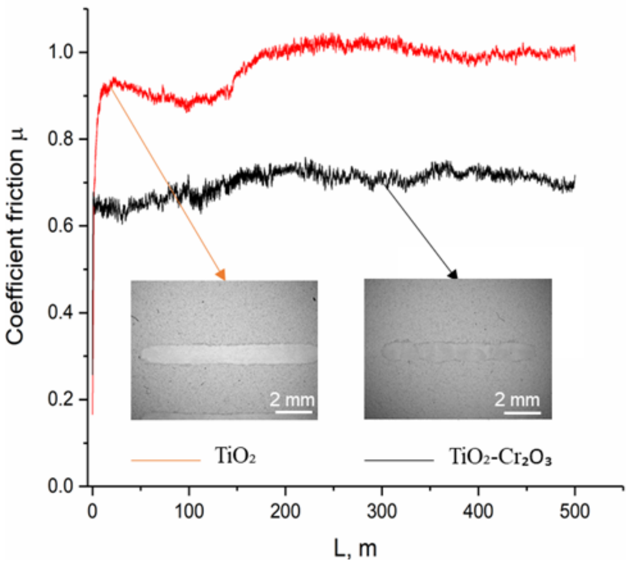

Figure 6. Dependence of the friction coefficient of coatings on the length of the friction path.

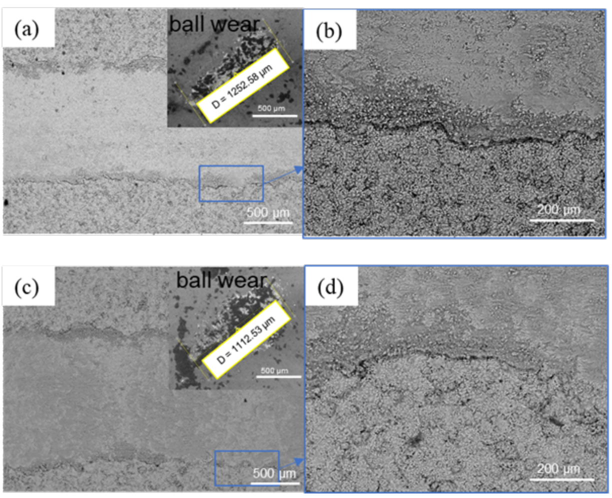

Figure 7. Morphology of the worn surface of the coatings: (a) and (b) TiO_2; (c) and (d) TiO_2 -Cr_2O_3.

4. Conclusion

Based on the research conducted, the following conclusions can be drawn:

1. The agglomeration of TiO_2 and TiO_2-Cr_2-Cr_2O_3 nanopowders resulted in agglomerates with different morphological characteristics. The agglomerates of $TiO_2Cr_2O_3$ powder exhibit larger sizes and distinct spherical shape, while the TiO_2 agglomerates have smaller sizes and irregular shape. These differences may affect the final properties of the materials and their application in different environments.

2. It is revealed that the phase composition of powder and coating is identical, the main phase is TiO_2. Plasma spraying improves the crystalline structure of the material by narrowing the diffraction peaks, which indicates a more ordered state. In the TiO_2-Cr_2O_3 system, the phase composition of the powder and coatings is similarly found to be consistent.

3. It was found that the microhardness of the developed coating based on TiO_2-Cr_2O_3, determined at an indenter loading force of 0.1 kg, is 30% higher than the hardness of the TiO_2 coating.

4. It was determined that the inclusion of Cr_2O_3 in the TiO_2-Cr_2O_3 coating leads to a significant decrease in the coefficient of friction (up to 0.65) compared to the TiO_2 coating (0.98). TiO_2-Cr_2-Cr_2O_3 based coating is more resistant to abrasion than TiO_2 coatings, therefore, more wear-resistant, less damaged under mechanical impacts.

In general, the addition of Cr_2O_3 to TiO_2-based coatings improves their mechanical and tribological properties, making such coatings more effective for high load and friction applications.

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Authors Contribution
Bauyrzhan Rakhadilov: Setup design, Data analysis, Draft writing. Zhangabay Turar: Conception, Setup design, Experiment, Data analysis, Draft writing, Finalizing the paper. Dauir Kakimzhanov: Experiment, Data analysis, Draft writing. Aidar Kengesbekov: Setup design, Experiment, Draft writing, Finalizing the paper.

Availability of data and materials
The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Conflict of interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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