

Fatigue behaviour of Plasma Sprayed Titania and Chromia Coatings

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Abstract. Cr₂O₃ and TiO₂ powders were deposited by atmospheric plasma spray (APS) on steel substrates. Microstructural analysis of the coatings showed typical lamellar structure with good coating quality. Fatigue strength was studied by using cyclic testing (measuring with an in-house-built apparatus the strength of the coated systems under a wide range of impact cycles) and static loading tests (Vickers tests standards with 600N and 1500N) measuring the adhesion properties of the coatings. In low cycles (1×10^3) Titania coatings exhibited better strength, while at intermediate (4.5×10^5) and high (1×10^6) number of impact cycles, both Chromia and Titania coatings exhibited quite similar strength characteristics. At low impact force the thickness of the coatings plays critical role with better performance obtained by Chromia coatings. During static loading both coatings exhibited similar characteristics at the crater diameter but with larger crater depth for Titania. Chromia coatings exhibited higher strength resistance than Titania coatings with better mechanical properties and coating structure.

1 Introduction

The coating technology has the advantage of combining two dissimilar materials to improve, in a synergistic way, the performance of the whole. Plasma spray, one of the most common deposition techniques for thick coatings, is characterized by a set of unique features, such as the wide range of materials, homogeneous coatings, fine microstructures, high deposition rate and a process being performed in any conceivable environment [1, 2]. The purpose of this study is to study the fatigue properties of Cr₂O₃ (Chromia) and TiO₂ (Titania) coatings. Chromium oxide (Cr₂O₃) based materials have been used to improve the scuff resistance [3, 4] and enhance corrosion resistance [5]. Plasma sprayed Titania (TiO₂) coatings are used in applications like bearings and pump seals and are characterized by sufficient microhardness (approx. 8GPa), relatively high density and adhesion to metallic substrates [6, 7].

A rather limited number of research studies have been carried out on the fatigue behaviour of plasma sprayed coated specimens with conflicting findings relative to the

influence of coatings on the fatigue life either enhancement [8,9] or debit [10,11]. Some studies investigate the effect of substrate preparation prior to coating deposition, such as shot peening or grit blasting, which are considered as residual stress contributors mitigating fatigue debits incurred by coating application [12] or attempt to isolate the coating's influence on fatigue life [13].

Considering that coating properties are highly dependent on their processing parameters [14, 15], some works try to assess the coating process parameters on the fatigue behaviour of thermally sprayed coated specimens [11, 16].

This paper focuses on the fatigue behaviour of chromia and titania plasma sprayed coatings, introducing a unique fatigue tester and seeks to address the relation of coating application and structure on their fatigue behaviour in an effort to elucidate prior findings. This work is a part of a wider research work on the wear and mechanical properties of these coatings.

2 Experimental

A commercially available chromia (METCO 106) and titania powder (AMPERIT 782) were deposited on the surface of structural steel substrates (0.60%wt C, 0.40%wt Si, 0.75%wt Mn, 0.035%wt P and 0.0035%wt S). The chromia powder (Cr_2O_3 : 95%, TiO_2 : 4.25%, Fe_2O_3 : 0.25%, SiO_2 : 0.5%, Al_2O_3 : 0.25%, all other: 0.5%) had particle size -90+11 μm and angular/blocky morphology while the also angular/blocky titania powder (TiO_2 : 99%, Fe_2O_3 : 0.25%, SiO_2 : 0.3%) had particle size distribution of -90+45 μm . Fatigue test specimens were prepared with 45mm (L), 35mm (W), and 2.5mm (H).

Prior to the APS, the steel substrates were grit blasted by alumina with 0.8-1 mm grain sizes to achieve roughness of approximately $R_a=8\mu\text{m}$. After sandblasting, samples were cleaned in an ultrasound bath with acetone for 5 min and dried with compressed air. Cleaned samples were vacuum packed and conserved in a dryer at 60°C until coating deposition.

Nickel Aluminide (METCO 404NS) powder was used as bond coating with a thickness of 80 μm . The thicknesses of the deposits in each specimen were 100 μm , 200 μm , 250 μm , 350 μm respectively.

The coatings were deposited by APS gun (FST SG-100 80kW) fitted to a KUKA robotic arm. The spraying conditions are shown in Table 1.

Table 1. Spraying parameters

Spraying Parameter	Cr_2O_3	TiO_2	Ni-Al bond coat
Voltage (V)	37,5	38,5	50
Current (A)	600	500	450
Pressure Argon (psi)	120	120	120
Pressure Hydrogen (psi)	11	11	9
Spraying distance (mm)	100	100	100
Spray rate (mm/sec)	450	450	450
Step (mm)	5	5	5

A B071 Olympus optical microscopy and JEOL JSM-63000 scanning electron microscope were used for the microstructural analysis. X-ray diffraction (XRD) analysis was performed (Cu K α radiation with a wave length of 1.5418 \AA).

Fatigue strength of the chromia and titania coatings was studied using cyclic and static loading. Cyclic testing was performed using an in-house-built fatigue tester (Fig. 1) applying 1×10^3 , 4.5×10^5 and 1×10^6 impact cycles. The force was constantly monitored using a HBM Type U3 50KN load cell connected to a computer. The fatigue tester provided sinusoidal impact of amplitude 100N and 250N at 50Hz.

After the fatigue tests, the diameter of the remaining imprints was investigated by means of an optical AmScope microscope, while the depth of the remaining imprints was measured using a Taylor Hobson PRECISION roughness tester. The coatings adhesion were studied under static loading using a Mitutoyo Hardness Testing Machine. For the investigations, the hardness Vickers test specifications were taken into consideration. Briefly, the Vickers test is characterized by the indentation of a conical indenter with angle $\alpha=136^\circ$ onto the specimen. For the Vickers tests, two indentation loads were implemented, 600N and 1500N.

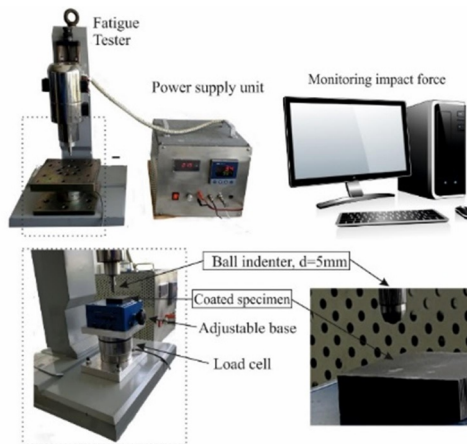


Fig. 1. Fatigue tester and experimental procedure

3 Results and discussion

3.1 Coatings microstructure

Fig. 2 shows that the micrograph of chromia coating which appears with the typical, for plasma sprayed deposits, lamellar structure. The microstructure exhibited some interlamellar defects and intra-lamellar cracks, attributed to splat quenching. The black spots are rounded pores, due to gas entrapment and imperfect stacking between splats. Porosity was measured approximately to 7%. No unmelted particles were found, the coating is rather homogeneous and coating-bond coating-substrate interfaces reveal good cohesion.

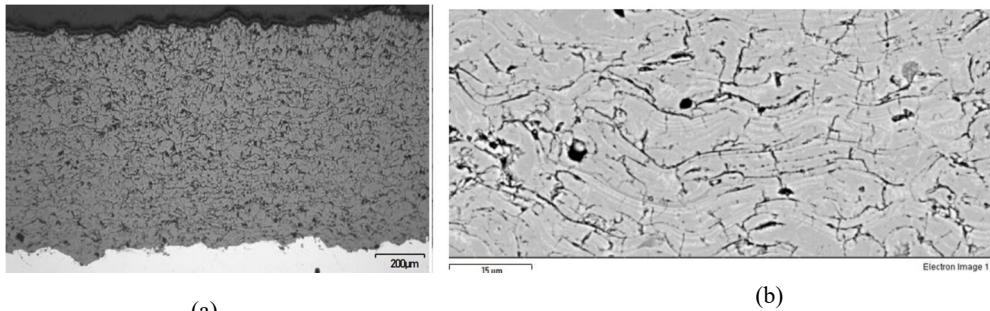


Fig. 2. Optical (a) and SEM (b) micrographs of Cr₂O₃ APS coatings

In the layered structure of the chromia coating light coloured stringers are observed (Fig. 2b), which are attributed to sub-stoichiometric chromium oxide (CrO₂) [17]. The presence of this phase in the coating was not confirmed by the X-ray diffraction of the as-plasma-sprayed Cr₂O₃ coating (Fig. 3b), indicating small volume fraction of the CrO₂ suboxide. EDS analysis revealed metallic Cr areas within particles and variable Cr/O ratios (Fig. 3). No changes of crystallographic structure of Cr₂O₃ during spraying were observed. The crystallographic structure remained as α -Cr₂O₃ (eskolait) without signs of other crystalline or amorphous phases. As observed by others [7,18-19] at plasma temperatures, a reduction of Cr₂O₃ to Cr occurs leading to small amounts of other phases, like Cr₃O₄, CrO, CrO₂, along with oxidation of chromium thus leading to a stable eskolaite phase.

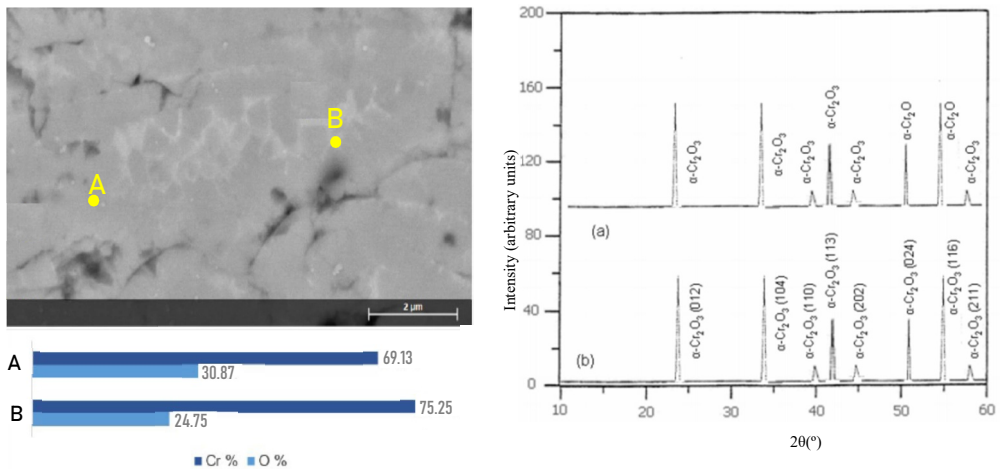


Fig. 3. SEM Cr₂O₃ coating with EDS analysis and XRD patterns of Cr₂O₃ powder (a) and coating (b)

Fig. 4 shows the cross section of the titania coating which also exhibits acceptable porosity (~6%), good coating integrity and scattered transverse cracks emanating either from interconnected pores or local thermal stresses. XRD analysis of the titania coating shows presence of rutile only, while the titania powder exhibits phases of rutile along with anatase and magneli which are transformed during spraying to rutile, as reported and elsewhere [20, 21]. According to literature metastable anatase transforms to stable rutile phase above 620°C, while magneli phase undergoes oxidation to form rutile phase under similar condition [22, 23].

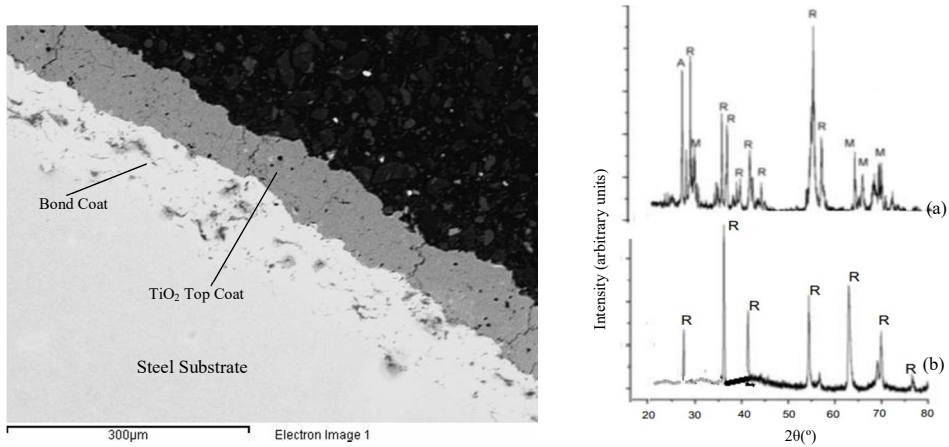


Fig. 4. Titania APS Coating (left) and XRD patterns of TiO₂ powder (a) and coating (b)

3.2 Fatigue results

Fig. 5 shows imprint diameter as function of impact cycles for 100N indentation force. It is obvious that the increase in coating thickness increases the overall durability of both types of material. The significant observation is that chromia coatings exhibit better strength characteristics than their titania counterparts. In addition, the increase in strength for chromia coatings as function of the thickness increase is more intense than the one obtained by titania coatings.

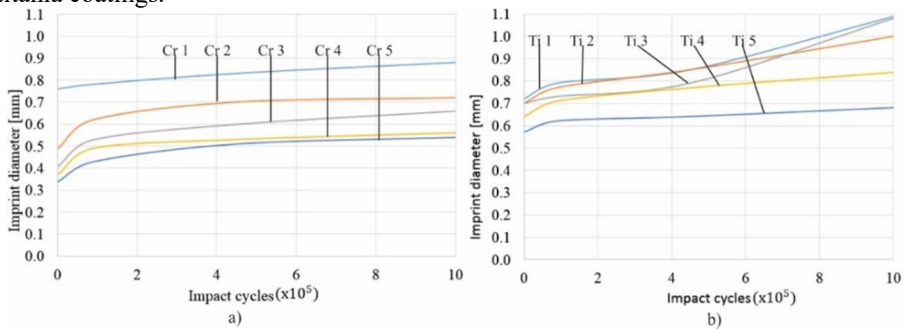


Fig. 5. Imprint diameter obtained at 100N indentation force for (a) chromia and (b) titania coatings

Fig. 6 shows the results for the imprint diameter obtained at 250N. The results here tell another story. Despite that the small differences between the two types during high cycling fatigue, the titania coatings are characterized by better strength at the very low cycling fatigue loading. The story begins to change at 4.5×10^5 impact cycles where the chromia coatings reach the performance of their titania counterparts. At very high cycling fatigue loading, the extent of the imprint gets stabilized. The phenomenon is more intense for titania coatings which is attributed to strain hardening [24].

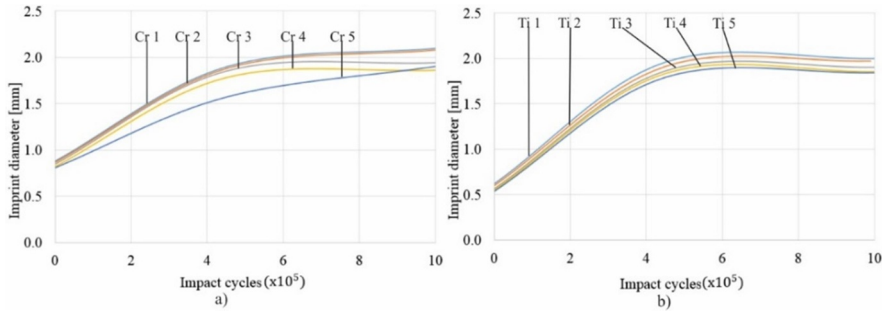


Fig. 6. Imprint diameter obtained at 250N indentation force for (a) chromia and (b) titania coatings

At very low cycling fatigue tests at 250 N indentation force as it is shown in Fig. 7 the Chromia coatings exhibited slightly better mechanical strength than titania coatings [25]. At middle impact cycles range, the first two titania specimens are characterized by shallower imprints than their counterparts. Although the fourth and fifth chromia imprints indicated that the specimens are characterized by higher resistance than the titania coatings. Taking into consideration the first four specimens from each category, the titania coated specimens exhibit higher strength against the indentation loads [26].

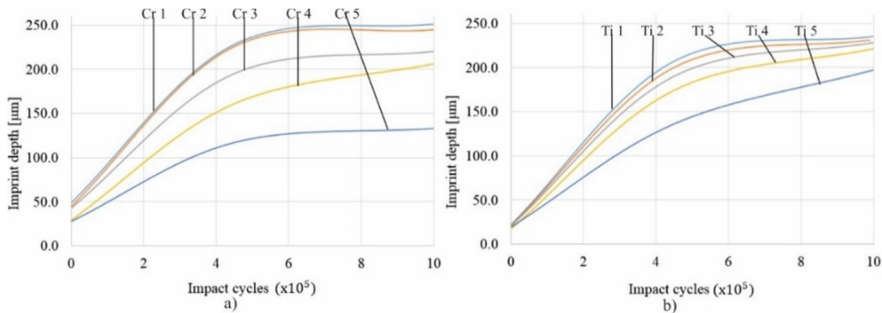


Fig. 7. Imprint depth obtained at 250N indentation force for (a) chromia and (b) titania coatings

Fig. 8 shows the remaining imprints at 4.5×10^5 and 10×10^5 impact cycles for the chromia and titania coatings with impact force of 100N. The first notation is that in agreement with Fig 5, the remaining imprints at the 1×10^6 impact cycles are slightly larger than those obtained where the number of impact cycles was set equal to $4,5 \times 10^5$. Furthermore, the size of the imprints left on coated substrates for 4.5×10^5 impact cycles, indicate that indeed the difference between chromia and titania coatings is distinct. In addition, one may observe that when moving from specimen 1 to 5 (for chromia) and 10 to 6 (for titania) for impact cycles equal to 4.5×10^5 , the extent of the imprint decreases. Although this observation is very much less distinct for titania coatings as can be verified by Fig. 5b. When the number of impact cycles was set equal to 1×10^6 , the differences in extent of the remaining imprints for chromia coatings when moving from specimen 1 to 5 gets more intense, than the one observed on titania. This also can be clarified by Fig. 6, since the data expressed by Y-axis vary in shorter bounds than those obtained for chromia.

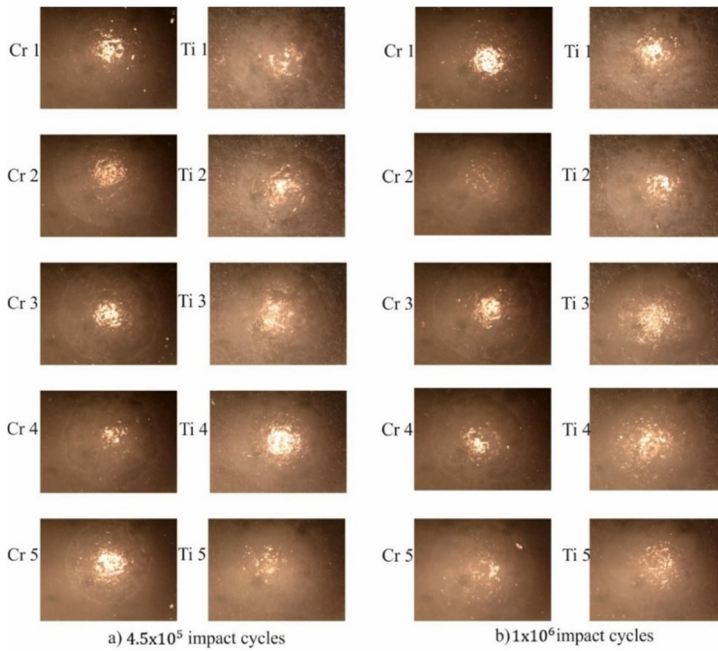


Fig. 8. Comparison for both types of specimens at 4.5×10^5 impact cycles, and 10×10^5 impact cycles at 100N impact force

Fig. 9 indicates the extent of the imprint diameter for both chromia and titania coatings, while Fig. 10 represents the imprints at on the chromia and titania coatings after the 600N and 1500N static load. The imprints are characterized by a conical shape with pressure tip in the middle as a result of the conical indenter. In Fig. 9a can be noticed that the imprint depth left on titania coatings is quite larger than the chromia coatings after 600N indentation force [27]. The difference in imprint depth between the two types of coatings exhibits a decrease after the introduction of 1500N indentation force. Investigating the remaining imprint diameter, the results indicated that all chromia and titania specimens exhibited similar deformation characteristics in radial direction after 600N of indentation load. According to the Vickers test findings, the coatings that can withstand the most desired static load resistance are the chromia.

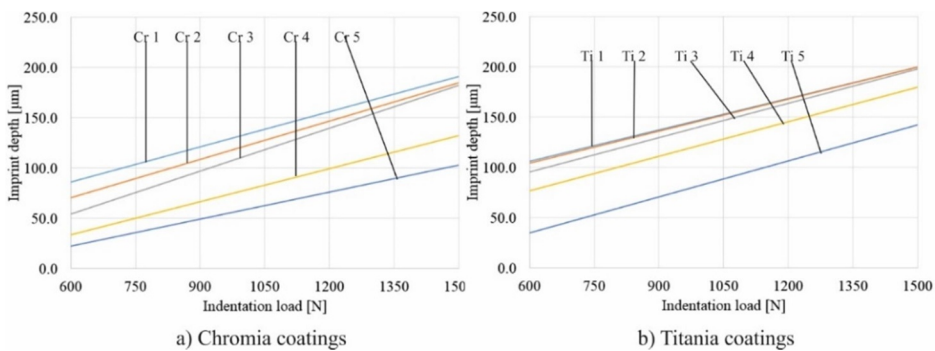


Fig. 9. Imprint depth after 600N and 1500N static loading for a) chromia and b) titania coatings

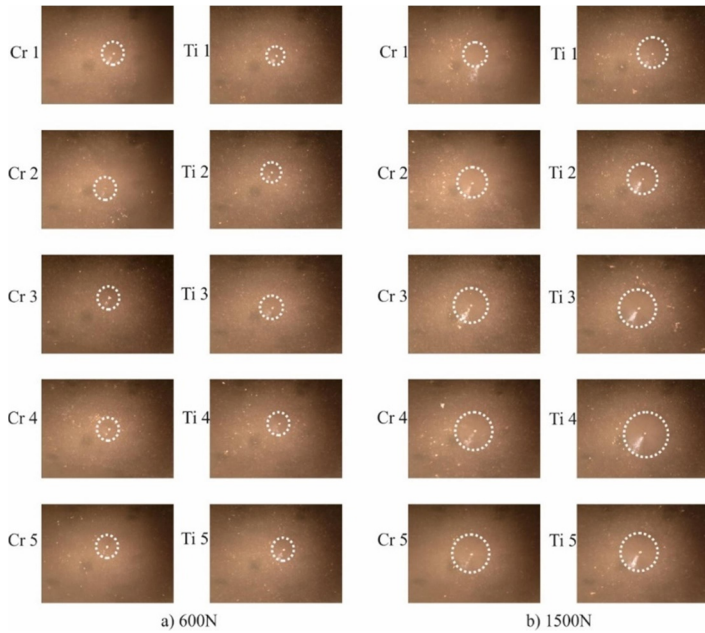


Fig. 10. Imprints on chromia and titania coatings a) After 600N and b) After 1500N static load

4 Conclusions

Chromia (Cr_2O_3) and titania (TiO_2) powders were deposited by atmospheric plasma spraying (APS) on the surface of carbon steel with an intermediate layer of Ni-Al bond APS coating. The coating microstructures exhibited typical lamellar structure, with porosity within quality limits.

XRD of titania coating revealed that anatase and magneli phases, which were traced in the TiO_2 powder, had transformed upon spraying into rutile phase while no phase transformation observed during spraying for the chromia coating.

Cyclic fatigue tests were conducted, using an in-house-built test apparatus for 1×10^3 , 4.5×10^5 and 1×10^6 impact cycles under the two different cases of 100N and 250N impact force by measuring the imprints diameters.

The mechanical strength of five chromia and five titania plasma sprayed coatings was investigated by means of cyclic and static loading test conditions. The static tests were employed according to Vickers tests standards with 600N and 1500N indentation loads.

In low number of cycling fatigue tests (1×10^3) at 250N impact force titania coatings exhibited better strength, while at 4.5×10^5 impact cycles, both types of coatings exhibited quite similar strength characteristics. Quite similar characteristics also obtained at high number (1×10^6) of impact cycles, where the difference of both types of coating imprints' diameter are much less than before.

The imprint depth at 100N cyclic fatigue test exhibited similar results. For both types of coatings, at low impact force the thickness of the coatings plays critical role with better performance obtained by chromia coatings.

The parameters that are affecting the mechanical strength and behaviour of the specimens are the substrate material, the bonding layer between coating and substrate, the different thicknesses of the specimens, the adhesion properties of the coating materials which is depended on the amount of porosity and the strain hardening mechanism after cyclic loading. The combination of the above parameters can explain the different behaviour of the specimens. The most important parameter for the evaluation of the

mechanical strength and behaviour of the specimens, is the strain hardening mechanism which is different under various parameters, cyclic loads and number of impacts.

During static loading, at 600N and 1500N both types of coatings exhibited similar characteristics at the crater diameter but with greater damage (larger crater depth) for titania. Summarizing all the above, chromia coatings exhibited higher strength resistance than titania coatings with better mechanical properties and coating structure. The reason for this behaviour is because of the two intensive static loads that affect both substrate and coating materials and without any strain hardening within coating, the specimens demonstrate typical strength behaviour.

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