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Properties of Alumina-Based Coatings Deposited by Plasma Spray and Detonation Gun Spray Processes

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Alumina, Al_2O_3 + 3 to 40 wt% TiO_2, and Al_2O_3 + 40 wt% ZrO_2 coatings were deposited by atmospheric plasma spraying (APS) and detonation gun spraying (DGS). The coatings were evaluated by optical microscopy, microhardness measurements, and X-ray diffraction. Wear resistance of the coatings was evaluated by rubber wheel sand abrasion and particle erosion test methods. Detonation gun-sprayed coatings exhibited more homogeneous microstructures and somewhat higher microhardness than corresponding plasma-sprayed coatings. Small additions of TiO_2 (3 wt%) improved both the abrasion and erosion wear resistance, whereas 40 wt% TiO_2 significantly decreased the erosion wear resistance of both APS and DGS coatings. Alumina + 40% ZrO_2 coatings exhibited the best abrasion wear resistance of both APS and DGS coatings, but the erosion wear resistance of these coatings was lower than that of the Al_2O_3 and Al_2O_3 + 3 wt% TiO_2 coatings. The best abrasion wear resistance of the coatings studied was obtained with DGS Al_2O_3 + 40 wt% ZrO_2 and Al_2O_3 + 3 to 40 wt% TiO_2 coatings. These coatings exhibited lower wear rates than bulk Al_2O_3. The best erosion wear resistance was obtained with the DGS Al_2O_3 + 3 wt% TiO_2 coating; however, it exhibited a higher wear rate than bulk Al_2O_3. In general, detonation gun-sprayed coatings showed significantly enhanced abrasion and erosion wear resistance than the corresponding plasma-sprayed coatings.

1. Introduction

THERMALLY sprayed alumina-based coatings are widely used in various applications. Atmospheric plasma spraying (APS) is an economical way to deposit these coatings and is satisfactory in many cases. The properties of alumina-based coatings can be influenced by alloying. For example, an addition of TiO_2 to Al_2O_3 increases toughness and decreases porosity of coatings deposited by plasma spraying (Ref 1). In the case of plasma-sprayed alumina-titania coatings, the abrasion wear resistance tested using the SiC-paper grinding method has been found to increase with small additions of TiO_2 (3 wt%), whereas addition of 40 wt% TiO_2 decreased wear resistance (Ref 2). Zirconia has also been reported to increase the toughness of Al_2O_3 based coatings (Ref 3). In addition, the characteristics, e.g., abrasion wear resistance, of alumina-based coatings can be significantly higher when these coatings are deposited by high-velocity combustion processes (HVOF). Detonation gun spraying (DGS) is a promising HVOF technique used to deposit high-quality oxide ceramic coatings, because under detonation conditions the flame temperature is about 1000 °C higher than in a free burning gas mixture of acetylene and oxygen gas. Thus, it is possible to spray high-melting-point ceramics, e.g., Cr_2O_3 and ZrO_2 by DGS methods, and ceramic coatings with extremely good wear characteristics (Ref 4-7) have been produced.

In the present study Al_2O_3, Al_2O_3 + 3 to 40 wt% TiO_2 and Al_2O_3 + 40 wt% ZrO_2 coatings were deposited by APS and DGS on low-carbon steel substrates. The microstructure, microhardness, and phase structures of the coatings were studied, and wear resistance was evaluated by the dry sand rubber wheel abrasion and particle erosion tests. The wear characteristics of the deposited APS and DGS coatings were compared to those of bulk alumina.

Key Words: Alumina materials, atmospheric pressure plasma spraying, detonation gun spraying, wear and erosion

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2. Experimental Procedure

Alumina and Al_2O_3 + TiO_2 powders selected for this study were supplied by Hermann C. Starck (Germany) and L + 40 wt% ZrO_2 powders by Plasma-Technik AG (Switzerland). Powder details are presented in Table 1. The coarser powders were used for APS and finer powders for DGS. The coatings were deposited onto low-carbon steel substrates without bond coatings.

Deposition of the coatings was performed at the Institute of Materials Science in Tampere University of Technology (Finland), except for plasma spraying of Al_2O_3 + 40 wt% ZrO_2 coatings, which were deposited in Plasma-Technik AG (Swit-

Table 1 Spray Powder Details

Powder composition	Commercial designation	Particle size, μm
Al_2O_3 (fused)	Amperit 740.0	5.6-22.5
	Amperit 740.1	22.5-45
Al_2O_3 + 3% TiO_2 (fused)	Amperit 742.0	5.6-22.5
	Amperit 742.1	22.5-45
Al_2O_3 + 40% TiO_2 (agglomerated)	Amperit 746.0	5.6-22.5
	Amperit 746.3	5.6-45
Al_2O_3 + 40% ZrO_2 (fused)	Plasmatex F0036	5.6-22.5
	Plasmatex PT 12	10.0-40.0

zerland). Plasma spraying was performed with Plasma-Technik A3000S 4/2 equipment using argon and hydrogen as plasma gases. The specimens were grit blasted with coarse alumina just before the coating process.

Detonation gun spraying was performed with Perun P equipment (Ref 8) developed in the Institute for Superhard Materials of Ukrainian Academy of Sciences and E.O. Paton Electric Welding Institute in Kiev. Technical data for the Perun P detonation unit are given in Table 2. The spraying conditions and parameters were optimized at the Institute of Materials Science in Tampere University of Technology. The explosive gas mixture used in this study was acetylene + oxygen, and spraying was carried out with a short barrel. The coating thickness was about 300 μm for both coating methods.

Microstructural evaluation of the coatings was carried out using optical microscopy. Microhardness values (average of ten tests) were measured with the Vickers pyramid method using a weight of 0.2 kg. Phase analysis of the alumina-zirconia coatings was performed by X-ray diffraction (XRD).

Abrasion wear resistance of the coatings was evaluated using rubber wheel abrasion test equipment (Fig. 1). The specimen for abrasion testing was 20 × 20 × 50 mm, and the coating, 300 μm in thickness, was deposited on one long side of the specimen. Dry quartz sand with a grain size of 0.1 to 0.6 m was used as an abrasive. Five samples were tested simultaneously over a test time of 60 min. Each sample was tested 12 min in each of the test positions to eliminate differences in wear characteristics that might arise from different positions of the sample holders. Weight losses were measured after each 12 min to a precision of 0.001 g. The surface speed of the rubber wheel was 1.64 m s^{-1}, which resulted in a total wear length of 5904 m in each 1-h run. Samples were pressed against the rubber wheel with a force of 13 N.

Table 2 Technical Data of Perun P Detonation Gun Unit

Firing rate	6.6 or 3.3 s^{-1}
Barrel length	660 or 1100 mm
Bore diameter	21 mm
Powder feeders	2
Coating thickness/cycle	3 to 10 μm
Working gases:	
fuel	propane-butane, acetylene or hydrogen
oxidizer	oxygen
diluent	air or nitrogen
Powder carrier gas	air or nitrogen

The erosion wear resistance of the coatings was studied with a centrifugal accelerator in which 15 samples could be tested simultaneously. The samples were 15 × 20 × 4 mm. Quartz sand (see the abrasion test above) was used as an erosive. Weight losses were measured to a precision of 0.0001 g. The velocity of the erosive particles was 80 m s^{-1}, and the wear loss of the coatings was studied at impact angles of 30 and 90°.

3. Results and Discussion

Optical microscopy studies of the coatings revealed that the porosity level in the DGS coatings was significantly lower than

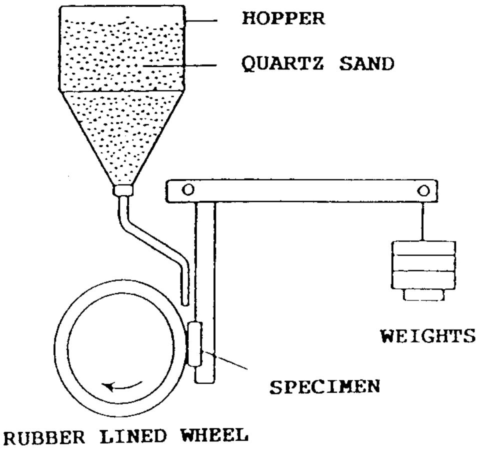

Fig. 1 Schematic of abrasion wear test apparatus (Ref 9)

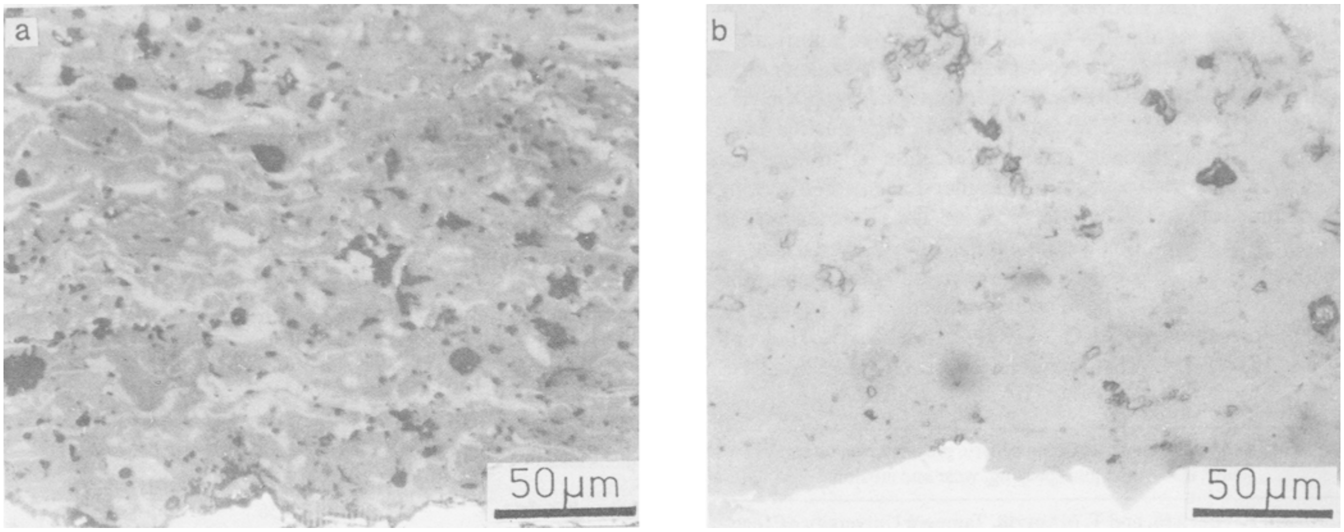

Fig. 2 Optical micrograph of Al_2O_3 coating deposited by (a) atmospheric plasma spraying and (b) detonation gun spraying

that in the coatings prepared by APS. Examples of the microstructures of the coatings are presented in Fig. 2 and 3.

The average microhardness values of the coatings are presented in Table 3. The microhardness values of the DGS coatings are about 100 to 200 HV (0.2 kg) units higher than those of the corresponding APS coatings.

The XRD analysis results of Al_2O_3 + 40 wt% ZrO_2 powders and coatings are presented in Table 4. The Al_2O_3 + 40 wt% ZrO_2 powder consists of α-Al_2O_3 and monoclinic ZrO_2 (*m*-ZrO_2) phases. The α and γ phases of alumina are present in the coatings, and part of the *m*-ZrO_2 phase has transformed into the tetragonal-ZrO_2 (*t*-ZrO_2) phase. The amount of *t*-ZrO_2 is higher in the DGS coating than in the APS coating. Therefore, the DGS coating is favored for wear applications, because *t*-ZrO_2 is assumed to have better abrasion wear resistance than the *m*-ZrO_2 phase.

Table 3 Mean Microhardness Values of Plasma Sprayed and DGS Alumina, Alumina-Titania, and Alumina-Zirconia Coatings

Coating composition	Average microhardness, HV(a) Plasma sprayed	 Detonation gun sprayed
Al_2O_3	780 ± 98	1023 ± 52
Al_2O_3 + 3 wt% TiO_2	881 ± 125	990 ± 70
Al_2O_3 + 40 wt% TiO_2	827 ± 72	896 ± 62
Al_2O_3 + 40 wt% ZrO_2	967 ± 93	1030 ± 57

(a) 0.2 kg

Rubber wheel abrasion test results of the coatings are presented in Fig. 4. The abrasion wear resistance of the plasma-sprayed Al_2O_3 + TiO_2 coatings is improved as the TiO_2 content increases. The Al_2O_3 + 40 wt% ZrO_2 coating exhibited the best abrasion wear resistance of the tested APS coatings. Also, in the case of DGS coatings, the abrasion wear resistance of the Al_2O_3 + TiO_2 and Al_2O_3 + 40 wt% ZrO_2 coatings was better than that of the pure Al_2O_3 coating. The best abrasion wear resistance was obtained with the DGS Al_2O_3 + 40 wt% ZrO_2 coating, but Al_2O + 3 wt% TiO_2 and Al_2O_3 + 40 wt% TiO_2 coatings exhibited similar high wear resistance.

A significant difference between APS and DGS coatings was observed by comparing the rubber wheel abrasion wear test results. The weight losses of the APS coatings were about sixfold greater than the corresponding DGS coatings. Moreover, the abrasion wear resistance of DGS Al_2O_3 + 40 wt% ZrO_2, Al_2O_3 + 3 wt% TiO_2 and Al_2O_3 + 40 wt% TiO_2 coatings is improved over that of bulk alumina (97.5% Al_2O_3) (Fig. 5).

Particle erosion test results of the coatings are presented in Fig. 6. The wear loss of both APS and DGS coatings decreases with small additions of TiO_2 (3 wt%), but increases with 40 wt% TiO_2 additions at both impact angles (90 and 30°). Erosion wear losses of the APS and DGS Al_2O_3 + 40 wt% ZrO_2 coatings (Samples 3 and 7) were higher than with Al_2O_3 and Al_2O_3 + 3 wt% TiO_2 (samples 1, 2, 5, and 6) at both impact angles. In general, erosion wear losses were higher with the impact angle of

Table 4 Summary of XRD Analysis of Al_2O_3 + 40 wt.% ZrO_2 Powder andCoatings

Powder/coating	Phases $\alpha-Al_2O_3$	 $\gamma-Al_2O_3$	 *t*-ZrO_2	 *m*-ZrO_2
Feedstock powder	*****	...	...	*****
APS processed	**	***	**	***
DGS processed	**	***	***	**

***** ≥ high. ** ≥ low

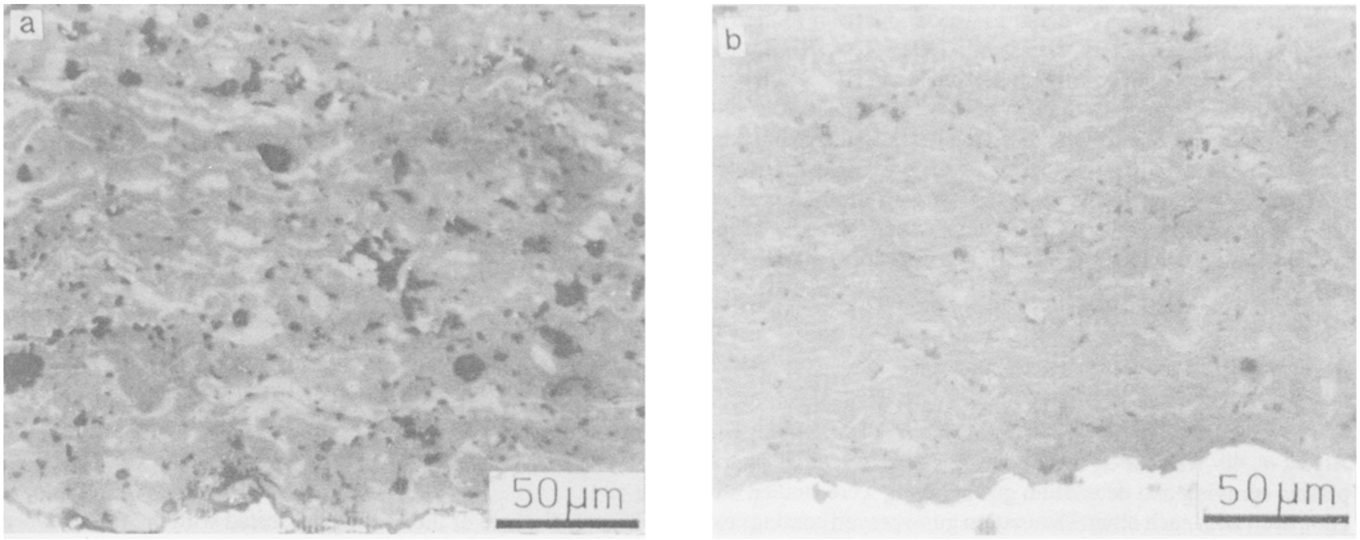

Fig. 3 Optical micrograph of Al_2O_3 + 40 wt% ZrO_2 coating deposited by (a) atmospheric plasma spraying and (b) detonation gun spraying

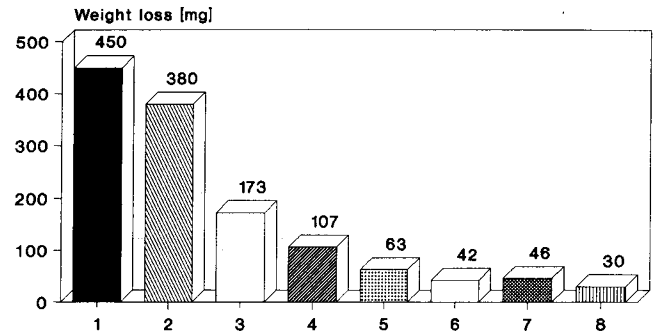

Fig. 4 Rubber wheel abrasion test results of atmospheric plasma sprayed (APS) and detonation gun sprayed (DGS) alumina, alumina-titania and alumina-zirconia coatings. The weight loss was obtained after 1 h test, which equals wear length of 5904 m. Samples 1 to 4 were manufactured by APS and samples 5 to 8 by DGS methods. (1) Al_2O_3, APS. (2) Al_2O_3 + 3% TiO_2, APS. (3) Al_2O_3 + 40% TiO_2, APS. (4) Al_2O_3 + 40% ZrO_2, APS. (5) Al_2O, DGS. (6) Al_2O + 3% TiO_2, DGS. (7) Al_2O_3 + 40% TiO_2, DGS. (8) Al_2O_3 + 40% ZrO_2, DGS

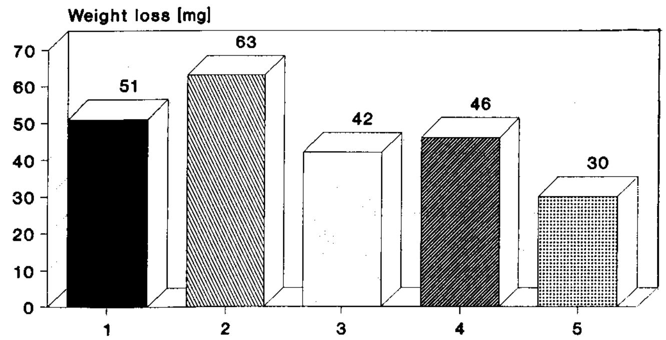

Fig. 5 Comparison of abrasion wear resistance of bulk alumina (97.5% Al_2O_3) to that of DGS alumina-based coatings. The weight loss was obtained after 1 h test, which equals wear length of 5904 m. (1) Bulk Al_2O_3. (2) DGS Al_2O_3. (3) DGS Al_2O_3 + 3% TiO_2. (4) DGS Al_2O_3 + 40% TiO_2. (5) DGS Al_2O_3 + 40% ZrO_2

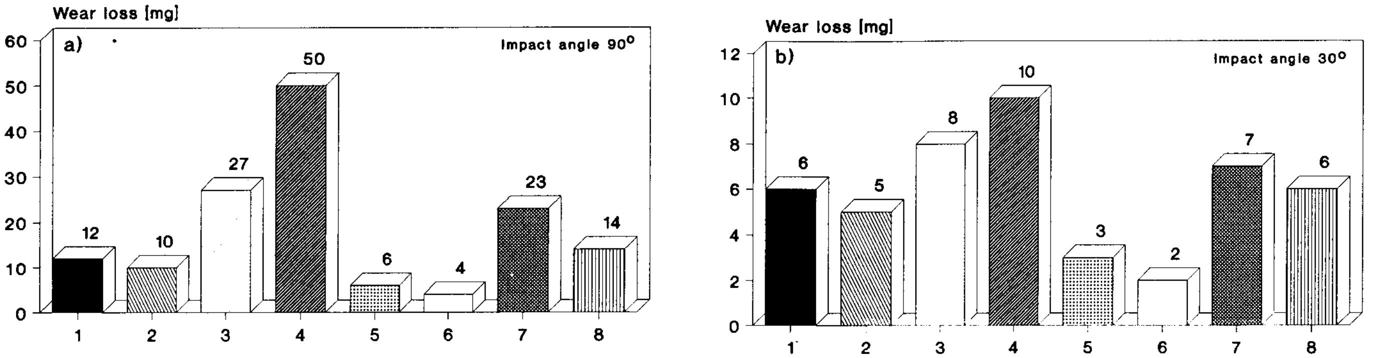

Fig. 6 Particle erosion test results of APS and DGS alumina, alumina-titania, and alumina-zirconia coatings. The weight loss was obtained after using 1 kg of quartz sand as an erosive with a velocity of 80 m s^{-1} at impact angles of (a) 90°, and (b) 30°. Samples 1 to 4 were manufactured by APS and Samples 5 to 8 by DGS methods. (1) Al_2O_3, APS. (2) Al_2O_3 + 3% TiO_2, APS. (3) Al_2O_3 + 40% TiO_2, APS. (4) Al_2O_3 + 40% ZrO_2, APS. (5) Al_2O_3, DGS. (6) Al_2O_3 + 3% TiO_2, DGS. (7) Al_2O_3 + 40% TiO_2, DGS. (8) Al_2O_3 + 40% ZrO_2, DGS

90° than with 30°, as could be expected in the case of ceramic materials. With Al_2O_3 and Al_2O_3 + 3 wt% TiO_2 coatings, the erosion wear losses of the APS coatings were about twice as high as with DGS coatings, but in the case of Al_2O_3 + 40 wt% TiO_2 the wear losses were significantly higher and about equal with both coating methods used. As in the rubber wheel abrasion test, the DGS Al_2O_3 + 3 wt% TiO_2 indicated the best erosion wear resistance of the studied coatings. The erosion wear resistance of bulk Al_2O_3 is compared to the coatings with the best erosion wear resistance in Fig. 7. The erosion wear resistance of the studied coatings is lower (i.e., a higher wear loss) than that of bulk Al_2O_3.

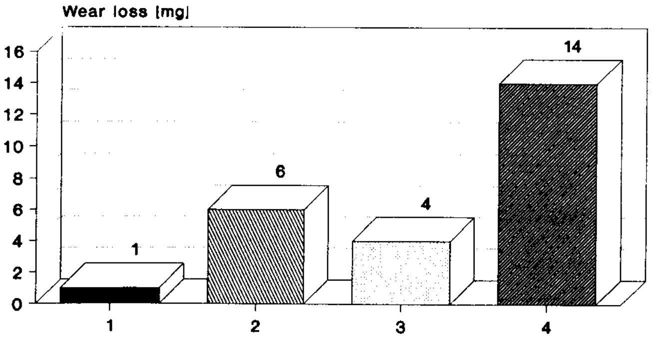

Fig. 7 Comparison of erosion wear resistance of bulk alumina (97.5% Al_2O_3) to DGS alumina-based coatings. (1) Bulk Al_2O_3. (2) DGS Al_2O_3. (3) DGS Al_2O_3 + 3% TiO_2. (4) DGS Al_2O_3 + 40% ZrO_2. The weight loss was obtained after using 1 kg of quartz sand as an erosive with a velocity of 80 m s^{-1} at the impact angle of 90°.

4. Conclusion

Alumina, Al_2O_3 + 3 wt% TiO_2, Al_2O_3 + 40 wt% TiO_2 and Al_2O_3 + 40 wt% ZrO_2 coatings deposited by atmospheric plasma spraying and detonation gun spraying were studied and compared with each other. Detonation gun-sprayed coatings exhibited low-porosity microstructures and higher microhardness values than corresponding plasma-sprayed coatings. Abrasion wear resistance of the coatings as tested with the rubber wheel abrasion test and particle erosion tests showed that the wear resistance of the plasma-sprayed and detonation gun-sprayed coatings is improved with small additions of TiO_2, whereas 40 wt% TiO_2 significantly decreases the erosion wear resistance. Alumina + 40 wt% ZrO_2 coatings showed the best abrasion wear resistance among both APS and DGS coatings. On the other hand, erosion wear resistance of these coatings was lower than with Al_2O_3 and Al_2O_3 + 3 wt% TiO_2 coatings.

Detonation gun-sprayed Al_2O_3 + 40 wt% ZrO_2, Al_2O_3 + 3 wt% TiO_2 and Al_2O_3 + 40 wt% TiO_2 coatings exhibited the best abrasion wear resistance of the coatings examined and were also more wear resistant than bulk Al_2O_3.

Detonation gun-sprayed Al_2O_3 + 3 wt% TiO_2, Al_2O_3 and Al_2O_3 + 40 wt% ZrO_2 coatings exhibited the best erosion wear resistance of the studied coatings; however, these coatings exhibited a higher wear rate than bulk Al_2O_3.

The detonation gun-sprayed coatings tested in this program were significantly better in abrasion and erosion wear resistance than the corresponding plasma sprayed coatings. Detonation gun sprayed alumina-based coatings, therefore, have benefits over atmospheric plasma sprayed coatings in applications that demand high abrasion and erosion wear resistance.

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