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Short communication

Wear resistance of chromium oxide nanostructured coatings

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Abstract

Nanostructured plasma-sprayed chromium oxide ceramic coatings, with a higher wear resistance than coatings obtained using micrometric powder as starting material have been developed. The influence of the starting powder, i.e. Cr_2O_3 fused crushed powders and Cr_2O_3 nanopowders having grains size of 100 nm, has been investigated. The nanopowders are reconstituted into spherical micrometer sized granules by the spray-drying process before plasma spraying. It is shown that due to their specific microstructure the wear resistance of the nanostructured coatings is more than 20 times higher compared to the coatings obtained using micrometric powder.

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1. Introduction

Plasma-spray is a widespread technique to prepare coatings in a variety of applications, also including aerospace and automobile applications [1]. The solid particles introduced in the plasma jet are accelerated and melted or partially melted. At the time of the impact on the substrate, the droplets form splats which solidify in a few microseconds. The coating resulting from the layering of splats has a lamellar structure [2]. Wear is closely related to the adhesion of the coating to the substrate because if the adhesion is poor, the coating will wear off quite rapidly and deterioration of the substrate by environmental factors will be greatly accelerated [1,3].

The wear resistance improvement of the nanostructured coatings obtained from nanostructured powder could be ascribed to both the decrease of the defects size and the grains size [4–8]. Furthermore, the higher fracture resistance of nanostructured coatings is due to a unique microstructure generated under appropriate plasma spray conditions [9,10] and composed of a mixture of fully melted splats and partially melted particles [6]. The partially melted regions can provide a variety of cracks arrest and deflection mechanisms, thereby increasing the crack growth resistance of the coating [6].

Due to the very poor flowability and the low mass of the nanopowders [7,11], these cannot be directly introduced in the plasma jet and must be reconstituted by spray-drying into spherical micron-sized granules that can be thermally sprayed [7,11]. The size of the agglomerated powder must preferably be between 20 and 50 μm [12] in order to be efficiently introduced into the plasma jet.

Chromium oxide (Cr_2O_3, eskolaite) has a wide range of applications such as green pigments, coating materials for thermal protection and wear resistance, refractory applications due to the high melting temperature (about 2435 °C) [13]. Chromium oxide exhibits excellent wear and friction characteristics [14], therefore this material was selected to study the wear resistance of plasma-sprayed coatings.

The present paper deals with the wear-resistance of plasma-sprayed chromium oxide coatings achieved with two kinds of powders: Cr_2O_3 granulated nanopowders and conventional micrometer fused crushed Cr_2O_3 powders.

2. Experimental details

Cr_2O_3 nanopowders have been prepared by a sol–gel process (DGTec, Moirans, France). The mean particles diameter of the

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starting powder is about 100 nm. Pure eskolaite phase is observed by XRD. These nanopowders have been reconstituted by spray-drying into spherical micron-sized nanostructured granules suitable to be plasma-sprayed. Two different size distributions for the granules have been achieved: 20–63 and 63–100 μm [15]. The Cr_2O_3 conventional powders Amperit 704.1 (HcStarck) are obtained from a fused crushed process. These conventional powders have an angular and an irregular morphology with particles size ranging between 10 and 45 μm. Chromium oxide nanostructured coatings (obtained from granulated nanopowders) and conventional chromium oxide coatings (obtained from conventional fused crushed powders) have been deposited by Atmospheric Plasma Spraying (APS) at 2PS (Projection Plasma Système, Montbazens, France) with the following spray parameters: argon flow rate 70 l/min, hydrogen flow rate 15 l/min, current 600 A, voltage 75 V, powder flow rate 19 g/min, spray distance 100 mm. Tribological tests have been carried out on an oscillating tribotester, running in accordance with the ASTM G 133–95 standard. The coating surface is subjected to an oscillating movement (8 Hz frequency) on a counterpart of 6 mm diameter ruby ball. A normal load F_n of 20 N is applied on the coating surface with a sliding average velocity of 96 mm/s during 10 h. Two wear tests have been carried out on each type of coating. The standard deviation on experimental measurements is ±3%. The coatings have been deposited on a 304 L stainless steel substrate. Coatings morphology and microstructure were examined, after burnishing, by scanning electron microscopy (SEM) with a JEOL 840 ALGS and by environmental scanning electron microscopy (ESEM) with an ESEM-FEG FEI XL30. As trivalent chromium oxide Cr_2O_3 is conductive of electric current [16], there was no need to metallize samples.

3. Results and discussion

From SEM observations, the coatings thicknesses are about 200 μm whatever the samples. Roughness has been evaluated: the average roughness (Ra) is of the order of 5 μm for all the coatings, except for the coating 63–100 μm (NC) which shows a Ra of 10 μm.

The results of the wear tests realized on the different polished chromium oxide coatings are indicated in Fig. 1. Values obtained in the same conditions for other monolithic

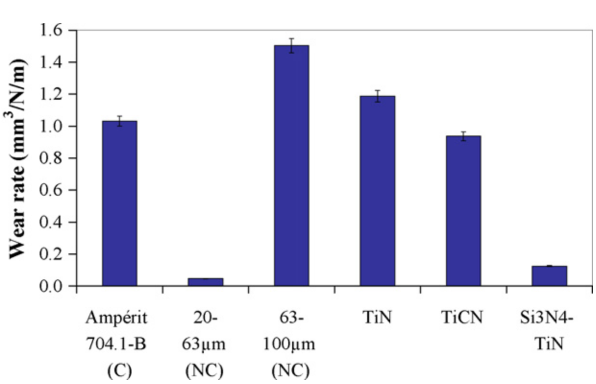

Fig. 1. Wear rate obtained for the different coatings.

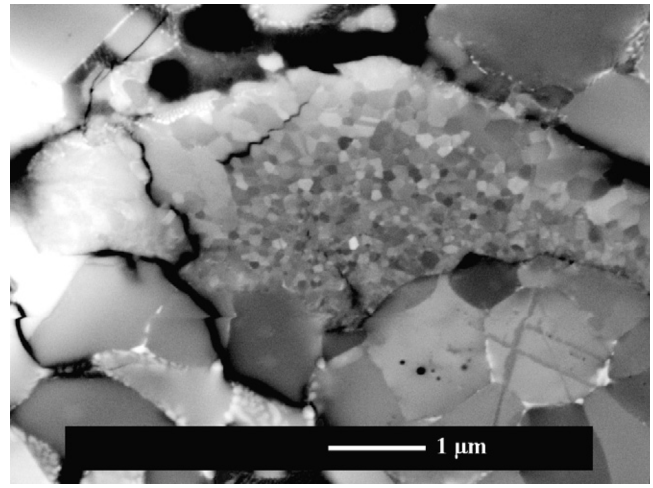

Fig. 2. ESEM micrograph cross-section of a specific area observed in both nanostructured coatings 20–63 μm (NC) and 63–100 μm (NC).

hard ceramics TiN, TiCN and Si_3N_4–TiN (laboratory experimental samples) are reported for comparison.

It appears that the wear resistance of nanostructured coatings (NC) 20–63 μm (achieved with chromium oxide nanopowders granulated under the granulometric distribution 20–63 μm) is better than for the others coatings with a very small wear rate of 0.048 ± 0.002 mm^3/Nm, 21–30 times lower than for the others chromium oxide coatings. The chromium oxide nanostructured coatings 63–100 μm (NC) have the weakest wear resistance with the highest wear rate of 1.50 ± 0.05 mm^3/Nm. This result could be explained by a larger granules size distribution and by plasma projection parameters not optimized for these nanostructured coatings, which leads to the presence of many cracks and a high porosity (16.8%). Conventional chromium oxide coatings have a wear resistance intermediate between 20–63 μm (NC) and 63–100 μm (NC) with a wear rate of 1.03 ± 0.03 mm^3/Nm. The friction coefficients obtained for the different chromium oxide Cr_2O_3 coatings lie between 0.5 and 0.6.

From ESEM observations, the nanostructured coatings 20–63 (NC) and 63–100 μm (NC) present particular areas with

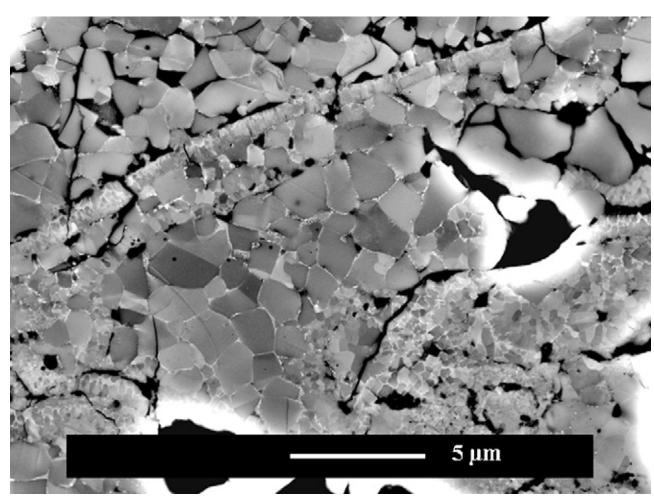

Fig. 3. ESEM micrograph cross-section of a general view of the nanostructured coating 63–100 μm (NC).

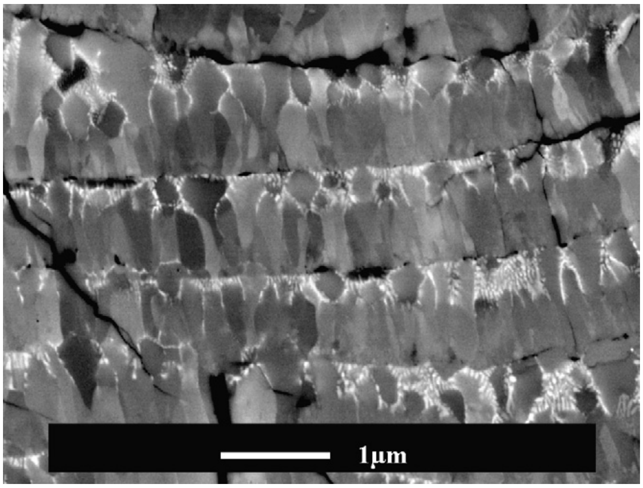

Fig. 4. ESEM micrograph cross-section of lamellas thickness inside the conventional coatings Amperit 704.1-B (C).

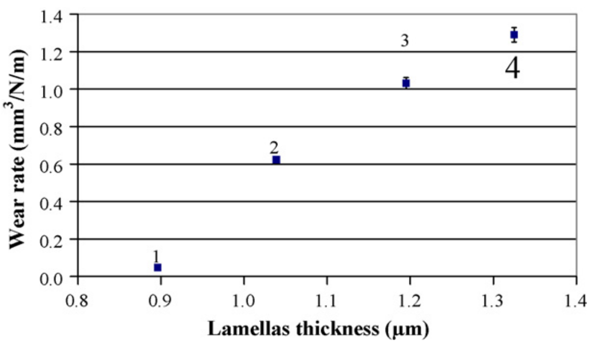

Fig. 5. Coatings wear rate as a function of the lamellas thickness inside the coatings. (1) 20–63 µm (NC) and (2, 3 and 4) different conventional coatings of Amperit with or without specific oxide doping (confidential composition).

many very small equiaxed grains (grains size lower than 100 nm) (Fig. 2). Furthermore, ESEM observations have also shown that the chromium oxide coatings 20–63 µm (NC) seem to have less areas with large equiaxed grains, unfavourable to

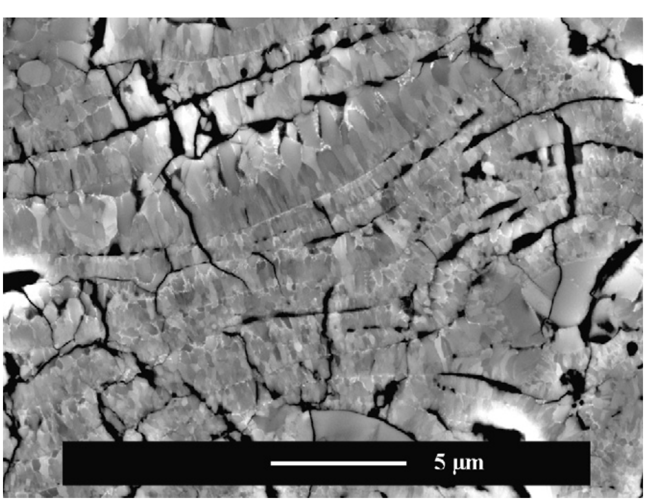

Fig. 6. ESEM micrograph cross-section of a general view of the nanostructured coating 20–63 µm (NC).

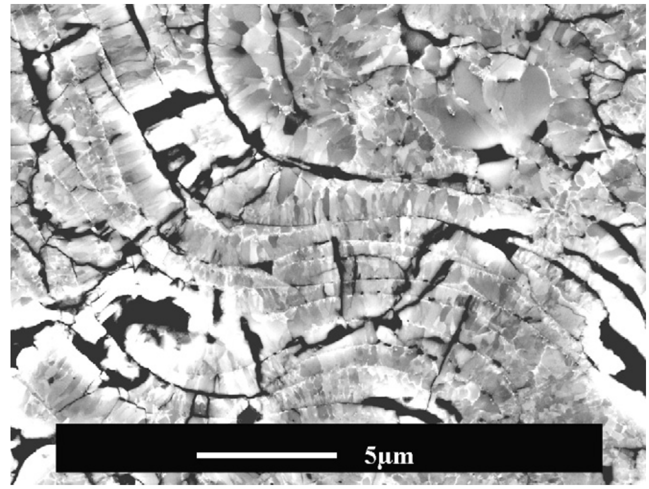

Fig. 7. ESEM micrograph cross-section of a general view of the conventional coating Amperit 704.1-B (C).

the wear resistance, compared to the coatings 63–100 µm (NC) which seem to have much more large equiaxed grains (Fig. 3). These observations confirm the bibliographic results [3,4] about the grains size effect which must be the smallest as possible to improve the coatings wear resistance.

Fig. 4 shows an ESEM micrograph of lamellas thickness inside the conventional coatings Amperit 704.1-B (C). From Fig. 5, the smaller the lamellas thickness inside the coatings, the better is the wear resistance.

Fig. 6 shows a general view of the nanostructured coatings 20–63 µm (NC) which exhibits the highest wear resistance and the smallest lamellas thickness. For comparison, Fig. 7 shows a general view of the conventional coating Amperit 704.1-B (C).

4. Conclusions

Granulated Cr_2O_3 nanopowders with the granulometric distribution 20–63 µm have been found to improve chromium oxide coatings wear resistance. However, many microstructural parameters (grains size, porosity and interlamellar cracking rates, lamellas thickness, presence of unmelted and partially melted particles) simultaneously interfere on the coatings wear resistance and the mechanisms leading to a wear resistance improvement remain complex. Complementary studies on optimization of plasma spray projection parameters for each granules size distribution and for others granules size granulometric distributions are needed to specify these mechanisms.

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