A novel approach to incorporate graphene nanoplatelets to Cr_2O_3 for low-wear coatings

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Abstract

Cr_2O_3 (chromia) coatings have been widely used in wear and corrosion resistant applications thanks to their good tribomechanical properties, and graphene nanoplatelets (GNPs) have been employed as nanofillers to further improve these properties. In this work, we propose a process to deposit chromia/GNPs composite coatings on stainless steel substrates using Suspension High Velocity Oxy-Fuel (S-HVOF) thermal spray. The coating showed good microhardness, with successful incorporation of GNPs showing no or minor spray-induced degradation. Compared to a chromia-only coating, the tribological performance improved: both coating and alumina counterbody specific wear rates lowered by 20 and 70% respectively and coefficient of friction decreased by 15%. This study shows a non-expensive and simple method to incorporate GNPs to improve material performance in large scale.

Keywords

Nanocomposites; Graphene nanoplatelets; Ceramics; Wear; Chromia; Tribology.

1 – Introduction

Chromium oxide Cr_2O_3 (chromia) coatings have found a wide range of applications in protection against corrosion and wear thanks to their chemical inertness and high mechanical strength [1]. Also, they exhibit high microhardness when compared with other thermally sprayed ceramic oxide coatings [2]. Chromia can be deposited with different techniques including thermal spray (atmospheric plasma spray, high velocity oxy-fuel (HVOF) spray and detonation spray) [3] for coatings and field assisted sintering [4] for bulk samples. Chromia coatings deposition using High Velocity Oxy-Fuel (HVOF) thermal spray yields higher elastic modulus and toughness [5] and is widely used for paper and pulp industry.

Suspension HVOF (S-HVOF) thermal spray emerges as a convenient way to handle fine particles (< 1 µm), including chromia [6], allowing them to reach higher melting rate leading to improved deposition efficiency and mechanical properties. Also, the remarkable mechanical properties of graphene [7,8], are harnessed for enhancing mechanical properties of ceramic coatings [9]. Considering a stack of graphene layers, such as graphene nanoplatelets (GNPs), there is a dual beneficial effect in terms of lowering the coefficient of friction (CoF) due to the inertness of the single graphene layer [10] and to the ease of gliding between layers, as typical of lamellar solids [11]. The applicability of S-HVOF thermal spray to deposit GNPs has been presented in our recent work [12]. When GNPs undergo structural degradation they lose their good mechanical and tribological properties [13], therefore the deposition must be carried out carefully to preserve their unique structure.

In this work, we exploit the ability of S-HVOF thermal spray to handle fine, dissimilar particles in suspension, to deposit chromia/GNPs coatings for low-wear applications. The structural integrity of GNPs was analysed, and the mechanical and tribology properties of the coatings were studied.

2 – Material and methods

A commercial water-based chromia suspension (Millidyne, Finland) was diluted and merged with GNPs (abcr, Germany) suspension to a final solid load of 20 wt.% Cr_2O_3+0.2 wt.% GNP. The feedstock was sprayed on grit blasted AISI304 (19-9) stainless steel by S-HVOF thermal spray using a TopGun SS (GTV, Germany) operated with 462 slpm and 198 slpm flowrates of hydrogen and oxygen, to provide a reducing environment hindering GNPs degradation through oxidation and combustion [13]. This choice of particle size and spray parameters aimed at allowing enough chromia melting to obtain a suitable coating, while preventing GNP thermal degradation. The substrates surface velocity was 1.4 m/s for 26 spray passes in total. A chromia-only coating was sprayed under the same conditions for comparison. Raman spectroscopy measurements were carried out with a LabRam (Horiba, Japan) Raman spectroscope (532 nm laser). Scanning Electron Microscopy (SEM) was carried out using an XL30 SEM (Philips, The Netherlands), and microhardness and fracture toughness with a Vickers indenter (Buehler, USA) averaging 10 indents. Dry sliding wear tests were carried out with a rotary ball-on-flat tribometer (Ducom, The Netherlands) against 6 mm alumina counterbody balls. The tests had a 12 mm diameter circular path and a tangential velocity of 37.7 mm/s. The load was 10 N and the duration 30 minutes, corresponding to 67.86 m or 1800 cycles. The wear volume loss was measured by contact profilometry

(Taylor Hobson, United Kingdom). Each wear test was repeated twice, and the presented results are averaged.

3 – Results and discussion

3.1 - Coating deposition and characterisation

SEM images of the two feedstock materials are presented in Figure 1a,b, showing dissimilarities in the shape and size of the two materials. A schematic of the process is presented in Figure 1c. During spray, the small size of chromia particles allows efficient melting despite their spheroidal shape. GNPs, however very thin, can withstand the high temperature for the short time they reside in the spray jet. At the substrate, a dense chromia coating is deposited, with incorporated GNPs in forming a composite. Figure 1d,e show the cross-sections of the chromia-only and chromia/GNPs coatings, exhibiting similar microstructures. The GNPs are not visible in the cross-section as their thickness is below resolution. The Chromia/GNP coating had a low surface roughness R_a = 0.9 ± 0.3 µm, a low porosity (1.8 ± 0.3%), a Vickers microhardness of (1047 ± 46) $HV_{0.025}$, and a fracture toughness of (0.9 ± 0.2) MPa·$m^{0.5}$. Similar values within the experimental error were measured on the chromia-only coating (1077 ± 49 $HV_{0.025}$ and 1.2 ± 0.3 MPa·$m^{0.5}$). Compared to other chromia coatings from S-HVOF, this microhardness is not as high as the state-of-the-art (1400HV) [6], but still suitable for high-hardness materials applications.
Further insight is provided by Figure 1f, where it can be seen how the dark areas in Figure 1e are characterised by a submicrometric granular structure. This morphology suggests that the darker contrast is linked to non-melted or partially melted chromia particles, whereas the brighter contrast can be attributed to melted chromia. Our S- HVOF parameters choice is suitable for survival and preservation of GNPs, but not for an optimal spray of chromia. A higher-temperature S-HVOF flame would have fully melted the chromia particles, but damaged GNPs. Overall, the addition of GNPs to chromia appears not to significantly improve mechanical properties, conversely to what reported for other ceramic composites [9]. A different concentration of GNPs could be advisable for this purpose, as well as other forms of graphene e.g. stacks of fewer graphene layers.

3.2 - GNPs dispersion, morphology and structural integrity

The presence of GNPs in the coating was studied by top-surface SEM. A SEM-BSE image in Figure 2a shows dispersed GNPs appearing black with the overlaid red colour from carbon EDX. A high magnification SEM-SE image Figure 2b shows GNP particles exhibiting their typical sharp edges. Raman spectroscopy measurements were done to assess structural integrity of GNPs after spray. The average spectrum is shown in Figure 2c, containing all the main features expected from a GNP: the main D, G and 2D bands. A degraded GNP would have a spectrum characterised by a very high D band and a very low and broad 2D band, compared to the G band [13]. This average spectrum proves GNPs have undergone none or very minimal spray-induced degradation.

3.3 - Wear tests

Wear tests were carried out on the polished chromia/GNP and chromia-only coating for comparison; the results are shown in Table 1.

Sample	Specific wear rate (mm^3/Nm)		Average CoF
	Coating	Counterbody	
Chromia/GNP	**$(1.9 \pm 0.1) \times 10^{-8}$**	**$(1.1 \pm 0.1) \times 10^{-6}$**	**0.51 ± 0.03**
Chromia-only	**$(2.4 \pm 0.3) \times 10^{-8}$**	**$(3.7 \pm 0.3) \times 10^{-6}$**	**0.60 ± 0.05**

Table 1 – Wear test results. Specific wear rate of chromia/GNP and chromia-only coatings and alumina counterbodies, with average CoF.

A lower specific wear rate of both coating and countebody was measured in the chromia/GNP case compared to the chromia-only case; the values dropped by 20% and 70%, respectively. In addition, the average CoF is also reduced by 15%, suggesting solid lubrication is offered by GNPs, effectively reducing wear volume loss of both coating and counterbody.

Considering the CoF values over distance shown in Figure 3a, the behaviour of the two coatings follows the same trend. There is an initial bedding-in spike, then a sudden drop to around 0.5. Then, the two coatings behave differently: the chromia-only coating CoF increases and stabilises at around 0.6, whereas the chromia/GNP CoF stays at around 0.5. In both cases sudden small spikes originated by typical ceramics brittle fractures are visible. In Figure 3b,c, chromia-only and chromia/GNP coatings show similar wear behaviours, with delamination and cracking of some areas, and a wider, more evident wear track for the chromia-only coating. In addition, a network of smaller cracked areas can be seen throughout the darker contrast region. No GNPs residue could be found at this stage inside the wear track. GNPs possibly play a role in retarding these wear mechanisms [13] and, as the wear track deepens, fresh GNPs are exposed and favourably lower friction and wear [12].

5 – Conclusion

- A process has been established to deposit Chromia/GNP nanocomposite coatings through S-HVOF thermal spray. GNPs show no or minimal degradation upon spray as assessed by Raman spectroscopy.
- The composite coatings show good mechanical properties, with no delamination at the coating/substrate interface due to GNP addition.
- The addition of GNP improves tribological properties, lowering CoF by 15% and specific wear rate by 20% (coating) and 70% (counterbody).

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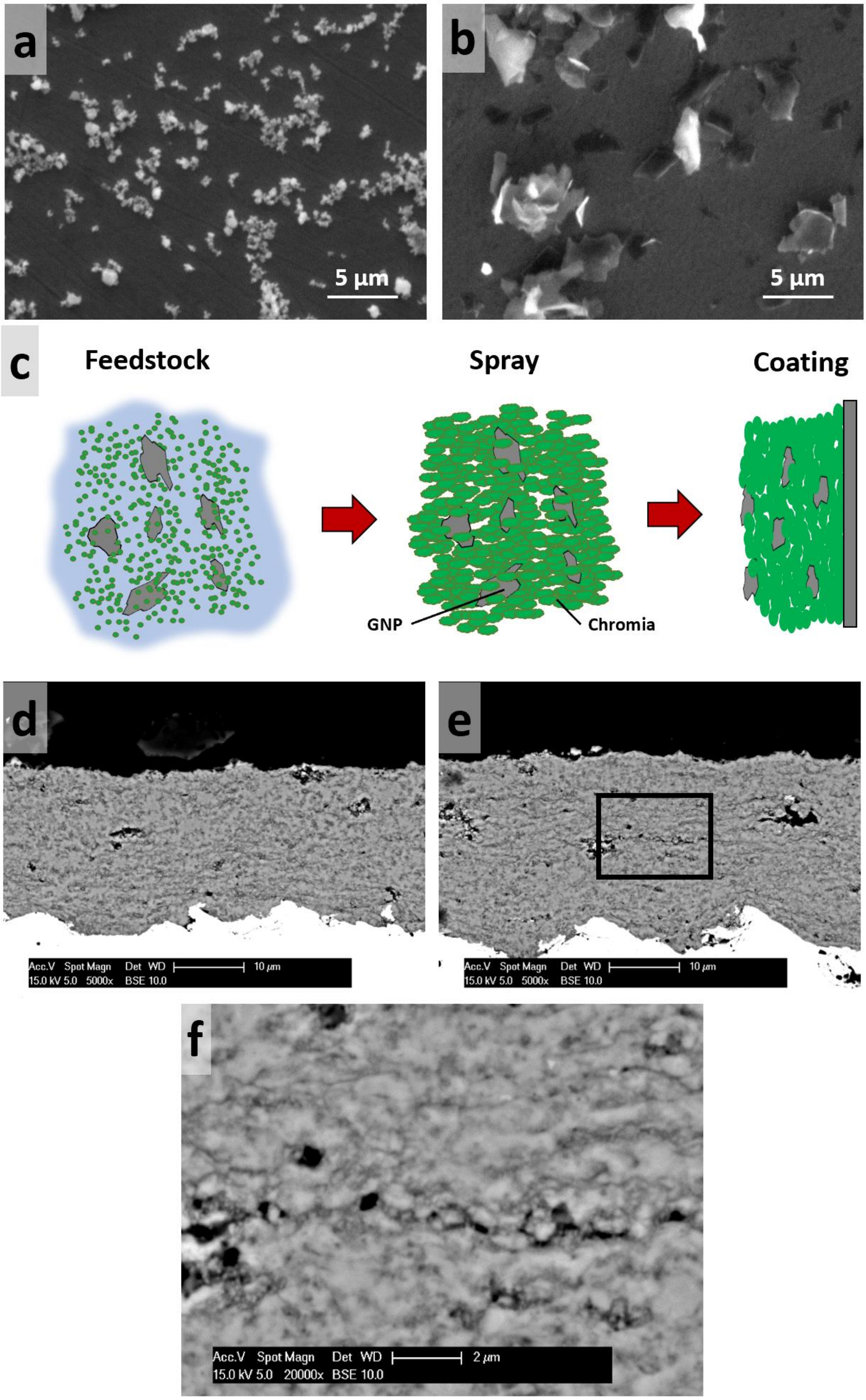
Figure 1: Feedstock morphology and coating microstructure. SEM micrograph showing submicrometric granular chromia (a) and flat sharp GNP (b) feedstock particles. (c) Schematic of the coating process. SEM-BSE cross-section of chromia coating (d) and chromia/GNP coating (e) and (f) from the marked area in (e). From (d) emerges no delamination at the coating/substrate interface and some localised porosity. In (e) a smooth brighter contrast corresponds to areas of melted chromia and darker granular areas to non-melted or partially melted chromia particles.

Figure 2: Chromia/GNPs sample top surface morphology and spectroscopy. (a) Overview BSE image showing scattered GNPs on the sample top surface in black with overlaid EDX showing carbon in red. (b) High magnification SE image of GNPs particles showing sharp morphology. (c) Raman spectroscopy average spectrum from five GNPs on top surface showing characteristic D, G and 2D bands.

Figure 3: Wear tests. (a) CoF over distance of wear test of chromia-only and chromia/GNP coatings. SEM-BSE micrographs of Chromia (b) and Chromia/GNP (c) wear tracks. Delamination can be seen, and the arrows indicate cracks.

Figures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5 µm
b
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Feedstock
Spray
Coating
GNP
Chromia
d
Acc.V Spot Magn Det WD 10 µm
15.0 kV 5.0 5000x BSE 10.0
e
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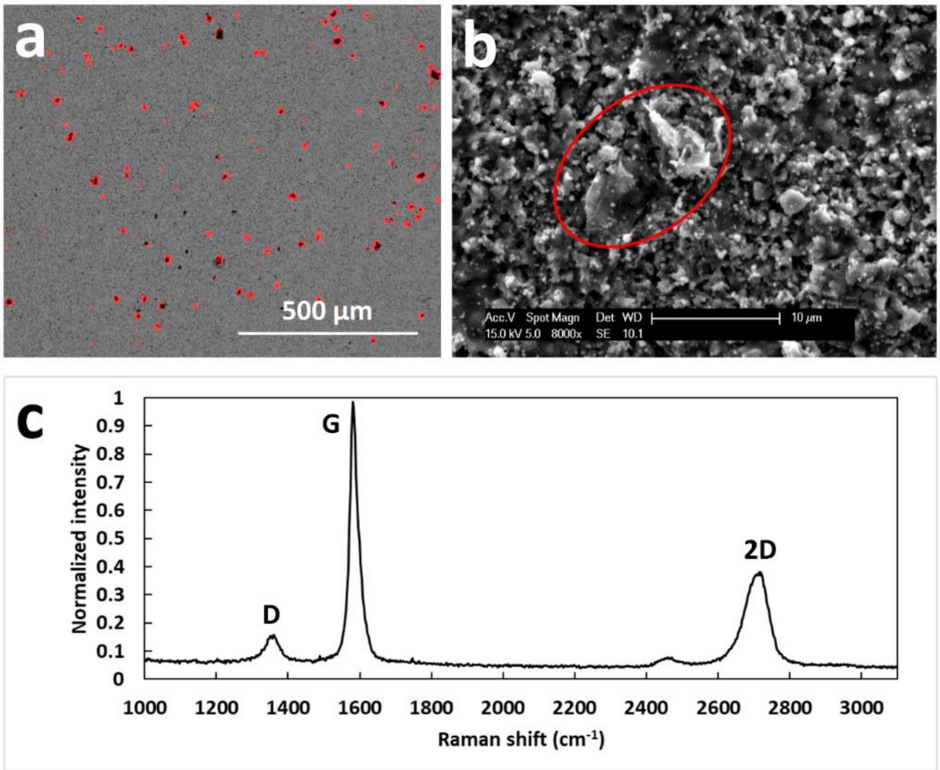
1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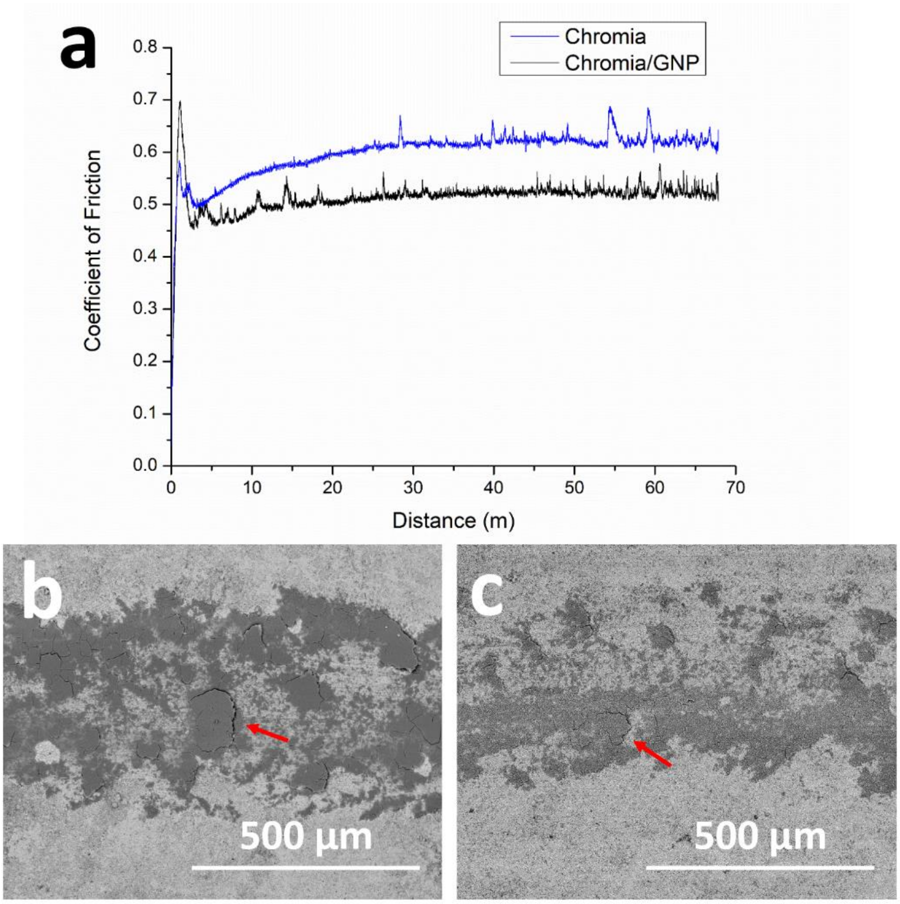
a
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3