

A comparative study of the wear performance of hard coatings for nuclear applications

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ARTICLE INFO

Keywords:

Sliding wear
Ceramics
Thermal spray coatings
Electron microscopy
Surface analysis
Nuclear power

ABSTRACT

Hard chromium plate (HCP) has been the wear resistant coating of choice in the nuclear industry for decades, but new protective coatings are required as a result of the hazardous nature of Cr(VI) compounds used in electroplating. This study compares the wear performance of candidate replacements materials, Cr₂O₃ and Cr₃C₂-NiCr. These two coatings are also compared with HCP and a WC-(W,Cr)₂C-Ni coating assessed in an earlier publication.

The Cr₂O₃ and Cr₃C₂-NiCr coatings were supplied having been applied to Inconel 625 substrates using high velocity oxy fuel (HVOF) and thermal detonation gun spray techniques, respectively. A ball-on-flat sliding wear configuration was used with three environments: dry, deionised water, and borated water to partially simulate nuclear reactor water chemistry. Wear rates were measured using both volume and mass standard metrics. The wear surface samples were characterised using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) in order to establish the operative wear mechanisms.

All three candidate coating materials exhibited similar wear performance to HCP in the three test environments. There was, however, enough of a difference between performance in deionised and borated water, to merit the use of borated water in future testing. The data gathered using SEM and XPS provided insight into the wear mechanisms. These include both particle pull-out and tribolayer formation. The XPS data revealed that Cr₃C₂ is preferentially removed from the Cr₃C₂-NiCr coating during wear testing in a borated water environment.

1. Introduction

A variety of ceramic and cermet coatings are available for deposition by thermal spraying methods [1,2]. They perform well in arduous conditions due to a range of properties in many applications such as thermal barrier coatings on turbine engines, mining drill bits, and electrical insulation in engine components [3–5]. In general, thermal spray coatings have high adhesion strengths to various substrates, low corrosion rates, and high performance wear resistance [6–8]. They are typically applied to weaker underlying materials in demanding wear applications to increase component lifetime. In the nuclear industry, there are many applications where high material performance is required at high loads and in a corrosive nuclear reactor water environment [9].

Hard chromium plate, deposited by electrodeposition, has traditionally been used to provide both excellent wear and corrosion resistance. Nuclear reactors contain many applications for hard chromium plate, such as bearings, which experience high levels of wear. In the future, hard chromium plate will be heavily controlled and restricted due to the extremely harmful Cr(VI), produced during the deposition process. The European Union regulation REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) commenced the first phase of restrictions to Cr(VI) in 2017 [10].

There have been only a few studies that have conducted large-scale testing regimes of multiple hard chromium plate replacement materials. In one such study, a variety of metallic coating materials were evaluated for their corrosion performance and compared with a reference sample of hard chromium plate; they were found to offer some

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<https://doi.org/10.1016/j.wear.2021.204124>

Received 23 March 2021; Accepted 21 September 2021

Available online 23 September 2021

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Table 1
Surface roughness measurements of coatings under investigation.

Coating Material	Cr ₂ O ₃	WC-(W,Cr) ₂ C-Ni	Cr ₃ C ₂ -NiCr
Ra Surface Roughness (μm)	0.29 ± 0.04	0.18 ± 0.06	0.20 ± 0.05

Table 2
Hard chromium plate deposition parameters.

Deposition Parameter	Bath Temperature (°C)	Deposition Current (A)	Deposition Period (hours)
Value	55	50	20

comparable performance [11]. For cermet coatings, a previous study, by the authors of this paper, compared WC-(W,Cr)₂C-Ni with hard chromium plate in a simulated nuclear reactor coolant water environment [12]. This coating was found to have comparable sliding wear performance to the hard chromium plate when it was tested against an Inconel 625 counterpart. For Cr₂O₃ and Cr₃C₂-NiCr coatings there is currently no literature assessing these coatings in a simulated nuclear borated water environment. Previous research has, however, individually assessed the wear performance of HVOF Cr₂O₃ and Cr₃C₂-NiCr coatings compared with hard chromium plate [13,14]. Both studies suggested superior wear performance compared with hard chromium plate, with the Cr₂O₃ coating tested against itself under engine oil lubrication and the Cr₃C₂-NiCr coating tested in dry conditions against a WC-6%Co pin.

The lack of previous studies means that there is value in comparing a

number of candidate materials. As in the previous investigation, testing in pure water must still be evaluated as this has caused varying wear performance when compared with borated water (simulated nuclear reactor coolant) [12]. Dry testing was also evaluated to observe and emphasise any potential wear mechanisms.

2. Experimental

2.1. Materials

Commercial powders of Cr₂O₃, WC-(W,Cr)₂C-Ni and Cr₃C₂-NiCr were deposited on Inconel 625 (25 × 25 × 5 mm) substrates using thermal spray techniques. The Cr₂O₃ powder was deposited using HVOF spraying and the WC-(W,Cr)₂C-Ni and Cr₃C₂-NiCr powders deposited using detonation gun. The deposition was performed by Praxair Surface Technologies Ltd. using optimised proprietary deposition parameters. Typical powder morphologies for these coatings and spray parameters from this supplier have been explored previously [15–17].

The sprayed coatings were found to have a thickness of around 100 ± 25 μm. A broadly comparable surface roughness was achieved by post-deposition grinding, see Table 1 (measured by supplier).

To compare with the sprayed coatings, hard chromium plate was also deposited on Inconel 625 plate supplied by Phoenix Electroplate Ltd. using electrodeposition with the parameters shown in Table 2. Other parameters cannot be disclosed due to their proprietary nature. The plated samples were ground to achieve a comparable surface roughness to the as-sprayed samples.

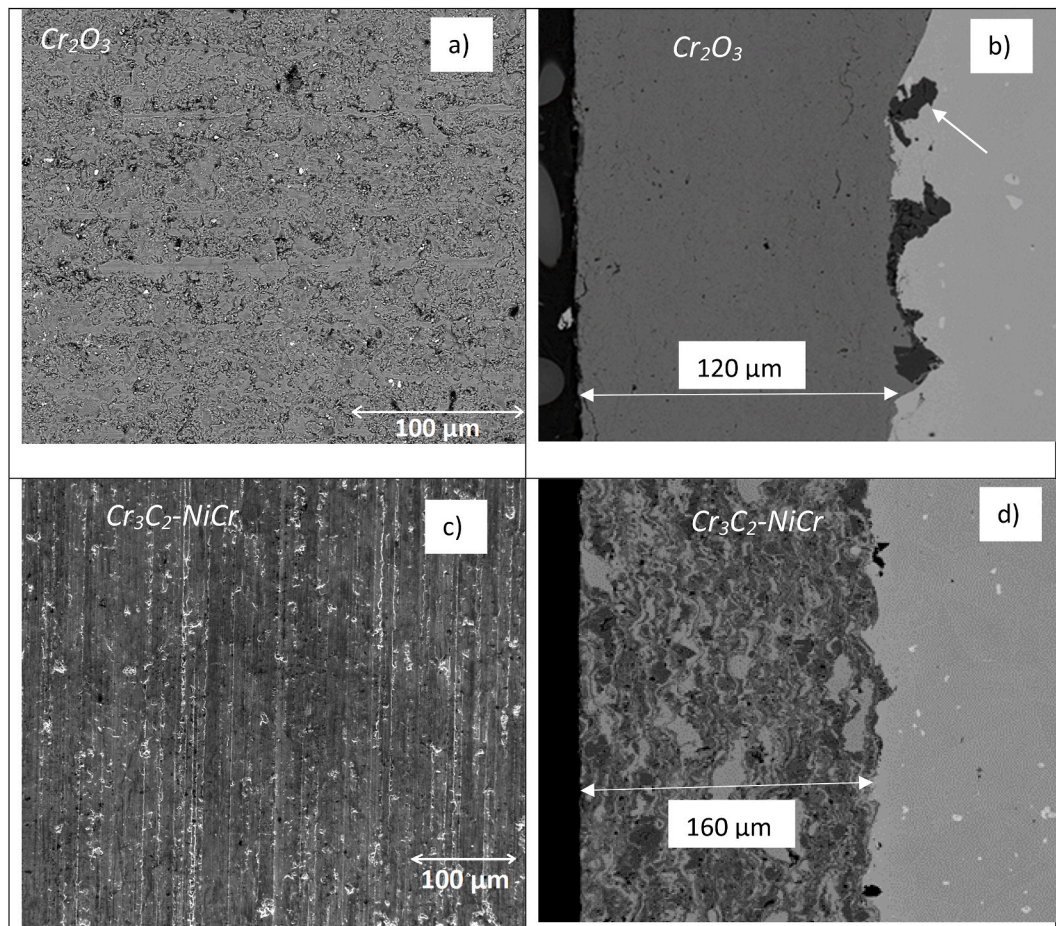


Fig. 1. SEM images of the as received Cr₂O₃ and Cr₃C₂-NiCr coatings. Fig. 1a and c shows secondary electron images of the plan view of Cr₂O₃ and Cr₃C₂-NiCr coatings. Fig. 1b and d shows back scattered electron images of the cross-sections of the coatings. Fig. 1b shows a particle of alumina (white arrow), which is most likely residue remaining from substrate pre-treatment.

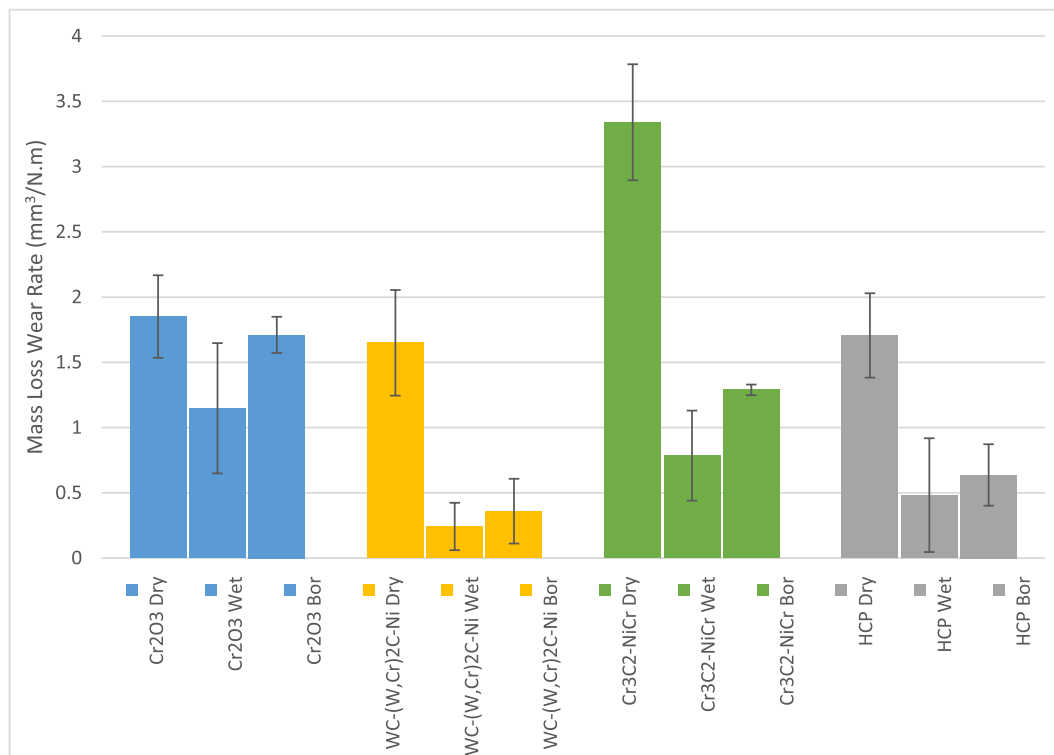


Fig. 2. Coating wear rates determined using a mass loss method.

2.2. Microstructural characterisation

Scanning electron microscopy was used to analyse the samples before and after wear testing (JEOL JSM7100F). Both secondary electron and back scattered electron imaging was used at an accelerating voltage of 15 kV. Assay purity acetone was used to clean samples before and after wear testing, in an ultrasonic cleaner for a duration of 5 min. For cross-sectional analysis, Bakelite was used for mounting and samples were polished with standard metallographic methods. A Thermo Scientific UltraDry Energy dispersive X-ray spectroscopy system was used to quantify material compositions and that of any discrete phases.

2.3. Wear testing

A sliding wear tribometer (Phoenix Tribology TE 77) was used for the wear testing. Inconel 625 ball counterparts (6 mm diameter) were selected for the testing to closely emulate a typical superalloy used in nuclear reactors. These counterparts were high precision, with a diameter tolerance of better than $\pm 2.5 \mu\text{m}$, maximum sphericity tolerances of $2.5 \mu\text{m}$ and maximum surface roughness values of $0.125 \mu\text{m}$ (Atlas Ball and Bearing Co. Ltd). A test frequency of 5 Hz was used, together with a load of 5 N and a slide length of 15 mm. Testing was at room temperature ($21 \pm 0.5^\circ\text{C}$) over 2×10^5 cycles. The above values were chosen to closely replicate typical nuclear reactor conditions whilst also producing a sensible level of wear. The enclosure system developed in Ref. [12] was used for tests using aqueous solutions, and this ensured that limited losses were encountered during testing. Fresh solutions were continuously pumped at 0.1 ml/s. The deionised water had a resistivity of $>1 \text{ M}\Omega \text{ cm}$, conductivity of $<1 \mu\text{S/cm}$ and $<50 \text{ ppb}$ of total organic carbon. The borated water comprised deionised water solution, 650 ppm soluble boron and 2.2 ppm lithium. This was achieved using standard H_3BO_3 and LiOH solutions, to emulate actual reactor water chemistry [18]. Previous results have found that separate tests are needed in borated and deionised water, as these environments produce varying wear performance [12]. Three repeats per tests were performed. The wear testing setup is shown in Ref. [12].

2.4. Assessment of wear rate

The previous study demonstrated that volume loss can be calculated using two techniques, and so they are only briefly described here [12]. For the first method, mass loss and therefore volume loss (using manufacturer evaluated densities, ASTM B328-73) was calculated by measuring mass before and after wear testing (Mettler Toledo Balance XS105, readability 0.01 mg, repeatability 0.02 mg). The second technique calculates the volume lost from the wear testing by measuring the volume of wear scars using a quantified reconstruction of the wear volume, using an Alicona G5 InfiniteFocus 3D microscope. By reconstructing the original surface, using reference points adjacent to the wear scar, both the wear volume and maximum wear depth were calculated.

Both techniques measured volume losses. Eq. (1) was used to calculate wear rates;

$$K = V / W.L \quad (1)$$

Here, K is the wear rate ($\text{mm}^3/\text{N.m}$), V is volume loss, W is the load normal to wear surface, and L is the sliding distance. By weighing the Inconel 625 balls before and after the wear tests, mass losses for the wear counterpart could also be calculated. The mass loss from the Inconel 625 balls was also established via a reconstruction of the ball's surface.

2.5. Surface analysis

X-ray photoelectron spectroscopy (XPS) was used to examine surface films formed following the wear testing (Thermo Scientific K-Alpha⁺). Full operating conditions can be found in Ref. [12].

3. Results and discussion

3.1. As-received coatings

SEM images of the plan views and cross sections of Cr_2O_3 and

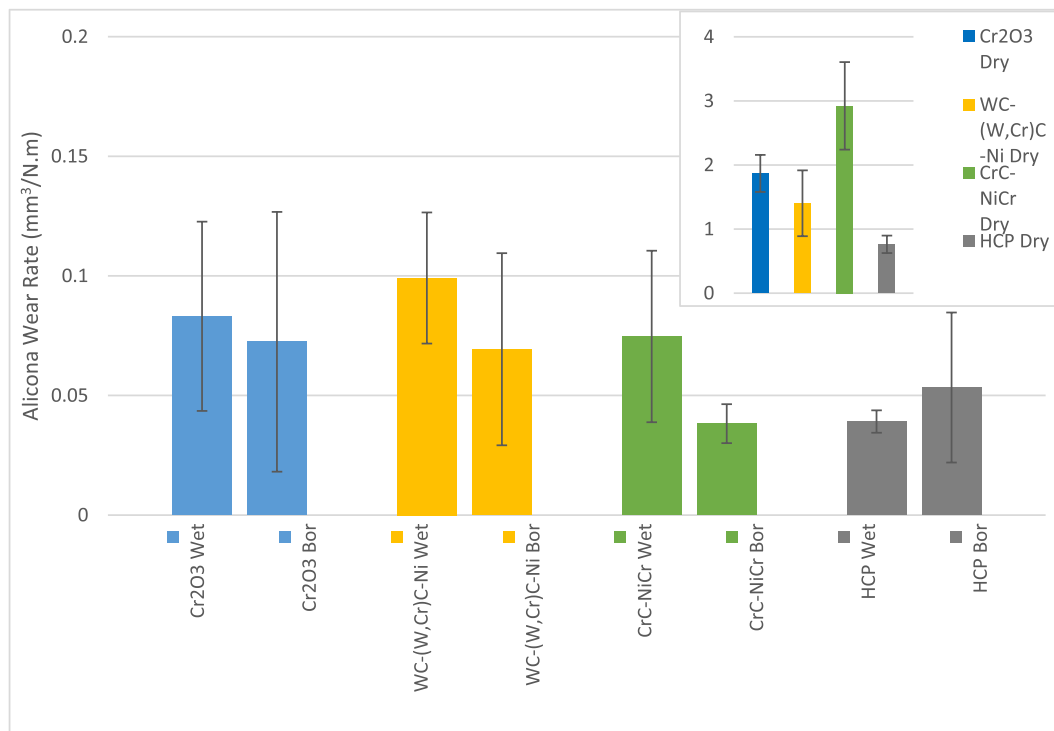


Fig. 3. Coating wear rates determined using microscopy. The inset shows the results from the dry testing regime.

Cr₃C₂-NiCr coatings are shown in Fig. 1.

Initial microstructural analysis has shown that the Cr₂O₃ coating has a uniform structure and is a single phase with some limited levels of surface contamination (Fig. 1b). Visible porosity can also be seen for this coating. The Cr₃C₂-NiCr coating has a more typical thermal spray microstructure, see Fig. 1d showing the lamella-shapes that are evidence of the splats created during deposition [19]. This also shows the multiphase nature of this coating. The darker regions are the Cr₃C₂ phase whereas the lighter regions are similar in composition to the substrate and are therefore the NiCr phase. The darker particles embedded in the substrate and coating interface have been identified as alumina (shown by the white arrow in Fig. 1b) and are most likely be remnants of 'grit' blasting from substrate pre-treatment prior to coating.

Further examination of the coatings revealed visible regions of porosity when examined in a cross-sectional view. Image analysis of one hundred 1 × 50 × 50 μm slices in cross-section, made by plasma focused ion beam milling, using a TESCAN Fera 3 with a Xe source, revealed coating densities of 99.6 ± 0.1% (Cr₂O₃) and 98.6 ± 0.1% (Cr₃C₂-NiCr).

3.2. Wear rates

Wear rates have been analysed using two techniques; a mass loss and an optical microscopy method. Cr₂O₃ and Cr₃C₂-NiCr coatings have been tested in dry, deionised water and borated water environments. The data obtained are shown in Figs. 2 and 3, which also compares the data for a WC-(W,Cr)₂C-Ni coating and hard chromium plate from previous research [12].

Previous research has indicated that both the mass loss and 3D microscopy method should both be used in parallel to evaluate wear performance as they provide complementary information [12]. The two techniques both show that the wear rate tends to be higher during dry testing compared with the wet testing. This work continues to confirm that testing is required in borated water and that the deionised water testing is not an appropriate analogue. Interestingly, the mass loss testing showed that the borated water testing had a detrimental impact on wear performance compared with deionised water testing whereas

Table 3

Maximum penetrations in each testing regime.

Test Regime	Max Depth (μm)			
	Cr ₂ O ₃	WC-(W,Cr) ₂ C-Ni	Cr ₃ C ₂ -NiCr	Hard Chromium Plate
Dry Testing	7.0 ± 1.0	10.9 ± 0.9	11.8 ± 0.8	7.9 ± 0.6
Water Testing	4.1 ± 0.2	7.3 ± 3.3	5.2 ± 0.6	2.5 ± 0.7
Borated Testing	3.1 ± 1.3	5.3 ± 1.0	4.1 ± 0.7	2.4 ± 0.5

the 3D microscopy technique typically showed the opposite with the exception of hard chromium plate, although the associated errors suggest they are similar for both techniques.

On the basis of the mass loss results alone, the WC-(W,Cr)₂C-Ni coating is the best replacement for hard chromium plate in water with a simulated reactor chemistry (with an Inconel 625 counterface). However, the 3D microscopy method suggests that the Cr₃C₂-NiCr coating is the most suitable replacement (again in a system with an Inconel 625 counterface). Both methods for wear rate determination gave data with a significant degree of uncertainty. In both approaches, the mass transfer from the counter face to the coating was not accounted for. For both water environments, optical metrology is expected to have greater reliability. This is because it assesses the volume of the wear scar, whereas mass loss methods are additionally affected by corrosion mechanisms. This may explain why the two techniques offer similar results for the tests performed under dry conditions, but the results vary significantly for the wet tests.

The maximum penetration depths after wear testing were also analysed as described previously (Table 3). This was to understand how quickly the coatings might expose the substrate, which would be considered a failure.

The maximum penetration depths for the three potential replacement materials follow the trends of the wear rates obtained from volume measurements. The Cr₂O₃ coating typically had the lowest maximum

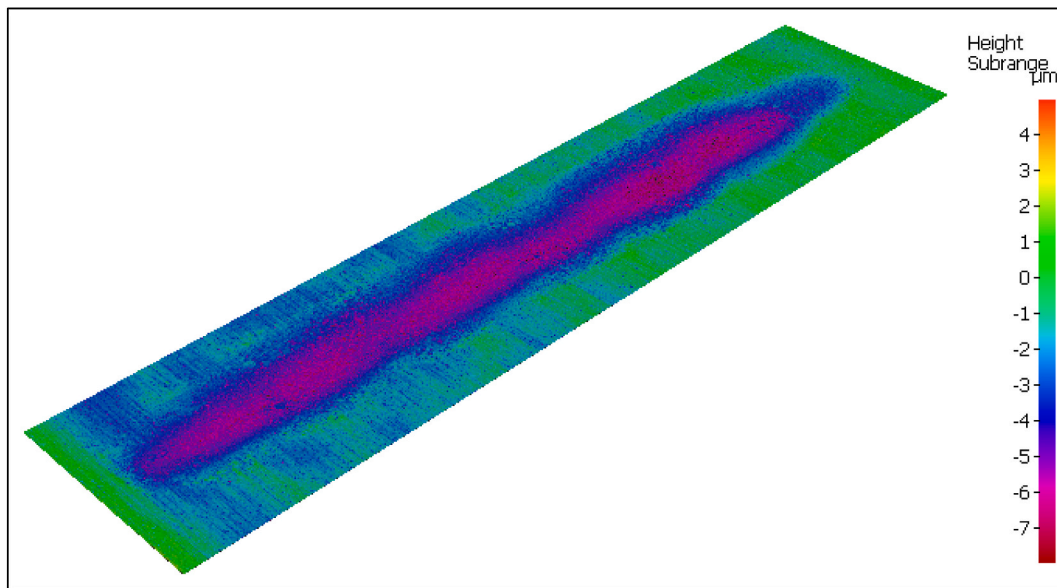


Fig. 4. 3D profile (Alicona G5) for a Cr_2O_3 coating wear tested in dry conditions [COLOUR]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

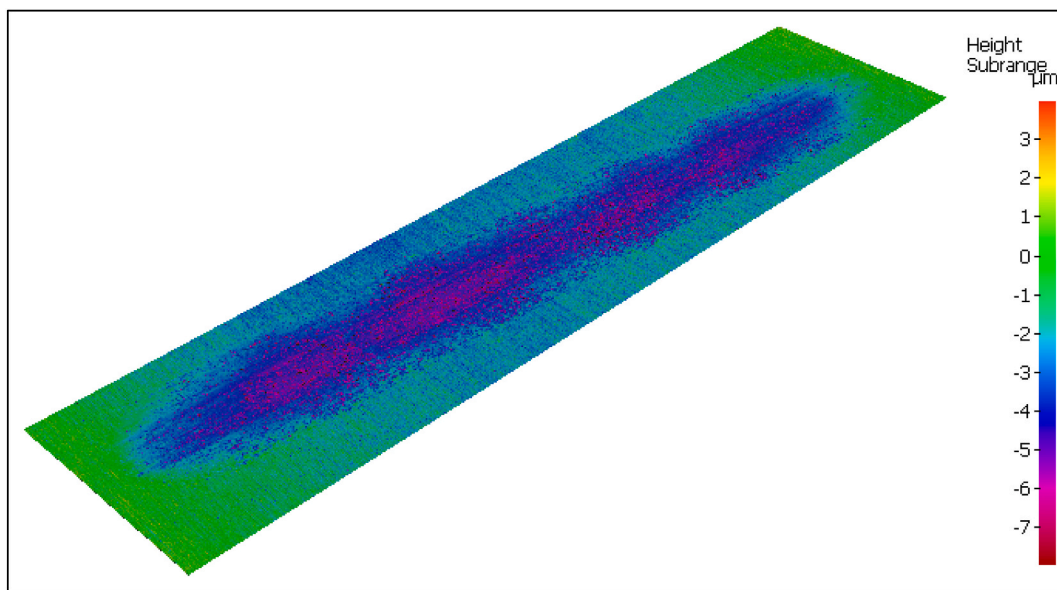


Fig. 5. 3D profile (Alicona G5) for a $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating wear tested in dry conditions [COLOUR]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

penetration depth, suggesting this is performing comparably to hard chromium plate. The $\text{Cr}_3\text{C}_2\text{-NiCr}$ and $\text{WC-(W,Cr)}_2\text{C-Ni}$ coatings had much larger penetrations. This might be the result of particle pull-out or localised microcracking. This shows that in high wear applications, despite the higher wear rates, hard chromium plate and the Cr_2O_3 coating could offer longer protection to the underlying substrate. It is, however, possible that more significant penetrations through the coatings are present but they may not have been detected due to the resolution limit.

Example surface profiles of the Cr_2O_3 and $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings are shown in Figs. 4 and 5 for dry testing. The 3D microscopy analysis in Figs. 4 and 5 indicates that the materials have worn differently. The $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating has a wear scar with visible isolated regions of more extreme wear, whereas the Cr_2O_3 coating shows a more uniform penetration depth, suggesting material at a more even rate.

The mass losses calculated by the two methods described above are shown in Table 4 for all testing regimes.

The results in Table 4 show that the average mass loss from the counterpart varies depending on the testing regime and to a lesser extent on method of measurement, although the trends in mass loss data measured using both methods are the same. When tested in deionised or borated water, the mass loss is reduced. The ceramic and cermet alternatives cause significant mass losses by comparison with the HCP. This has implications for the final application. The average worn radii appear to correlate well with the average wear scar widths. The values in Table 4 also give an upper limit to the mass of the amount of material that could have been transferred to the coating surfaces. It is therefore vital to evaluate the any tribolayer presence on the sample surfaces.

Table 4

Mass losses for the Inconel ball counterpart.

	Cr ₂ O ₃	WC-(W, Cr) ₂ C-Ni	Cr ₃ C ₂ -NiCr	HCP
Dry Worn Radius (mm)	3.03 ± 0.23	3.42 ± 0.15	2.98 ± 0.26	1.50 ± 0.03
Radius Mass Loss (mg)	12.4 ± 2.8	20.7 ± 2.8	11.7 ± 3.0	0.69 ± 0.04
Weighed Mass Loss (mg)	13.6 ± 3.4	21.0 ± 4.9	11.9 ± 4.8	0.75 ± 0.25
Water Worn Radius (mm)	1.05 ± 0.11	1.59 ± 0.01	1.67 ± 0.09	0.49 ± 0.30
Radius Mass Loss (mg)	0.16 ± 0.05	0.88 ± 0.02	1.08 ± 0.18	0.008 ± 0.014
Weighed Mass Loss (mg)	0.14 ± 0.10	0.74 ± 0.19	0.97 ± 0.20	0
Borated Worn Radius (mm)	0.97 ± 0.15	1.26 ± 0.04	1.02 ± 0.22	0.48 ± 0.08
Radius Mass Loss (mg)	0.12 ± 0.06	0.34 ± 0.03	0.15 ± 0.10	0.006 ± 0.003
Weighed Mass Loss (mg)	0.05 ± 0.04	0.24 ± 0.19	0.12 ± 0.19	0

3.3. Characterisation of the worn coatings

Examination of the coatings after wear testing in the three testing regimes has revealed evidence of particle, or material, pull-out for Cr₃C₂-NiCr but not for the Cr₂O₃ coating (Fig. 6). SEM analysis of the wear scar revealed significant grooves and brittle cracking, likely caused by abrasive wear. The three candidate coating materials, Cr₂O₃, WC-(W, Cr)₂C-Ni and Cr₃C₂-NiCr have all shown limited abrasive wear in the dry regime. This is in contrast to HCP, which shows high levels of abrasive wear when tested in a dry environment [12]. For the deionised and borated water testing, the opposite is observed, whereby Cr₂O₃, WC-(W, Cr)₂C-Ni and Cr₃C₂-NiCr coatings show high levels of abrasive

wear and HCP shows lower levels. This suggests that HCP is likely to perform better in a lubricated environment compared with Cr₂O₃, WC-(W, Cr)₂C-Ni and Cr₃C₂-NiCr coatings.

Particle pull-out and cracking has been observed for many of the materials under investigation, particularly when looking at samples tested in borated water conditions. Comparing materials, the Cr₂O₃ coating was the only coating material to show no particle pull-out and very limited cracking in the material matrix (Fig. 6a). This correlates with it having the lowest maximum depth in the wear scar of the three candidate materials.

The Cr₃C₂-NiCr coating showed very small (approximately 1 µm) particle pull-out underneath a suspected tribolayer and showed very limited cracking (Fig. 6c). The WC-(W, Cr)₂C-Ni coating is the only HCP replacement material to show significant particle pull-out. This is associated with cracking, leading to grooves within the wear track (Fig. 6b). HCP shows this pull-out effect much more severely, with increased material pull-out compared with the other materials under investigation (Fig. 6d). Large grooves, typically 50 µm long, were observed. The WC-(W, Cr)₂C-Ni coating had individual grooves on the surface but they were less severe than the grooves in hard chromium plate. This local material loss might have been unaccounted for by 3D microscopy, described above, and therefore the values in Table 4 may underestimate wear scar penetration depth.

The Cr₂O₃ and Cr₃C₂-NiCr coatings were evaluated in a plan view to analyse the tribolayer deposit, expected given the counterpart's mass loss. EDS analysis was performed to establish the presence of Inconel 625 constituents embedded in the coating. Nickel was used as the indicator for the Cr₂O₃ coating whereas molybdenum was analysed for the Cr₃C₂-NiCr coating due to the abundance of nickel in this material. The SEM imaging in Fig. 7 shows both coatings with Ni Kα and Mo L maps inset. The WC-(W, Cr)₂C-Ni coating and hard chromium plate have been examined in previous work [12]. Tribolayers, containing material from the counterface, were observed in all cases.

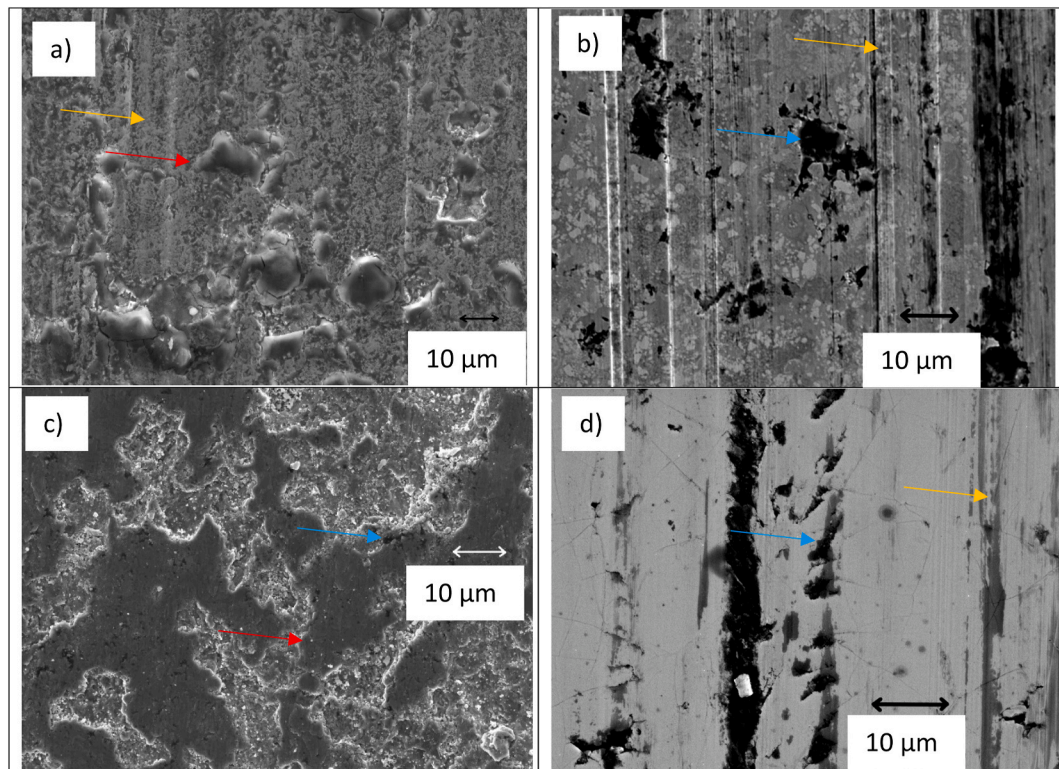


Fig. 6. Secondary electron micrograph showing worn grooves (yellow arrows), tribolayer deposits (red arrows) and particle pull-out (blue arrows) in the borated water tested coatings. a shows the micrograph for the Cr₂O₃ coating, b is WC-(W, Cr)₂C-Ni, c is Cr₃C₂-NiCr and d is hard chromium plate. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

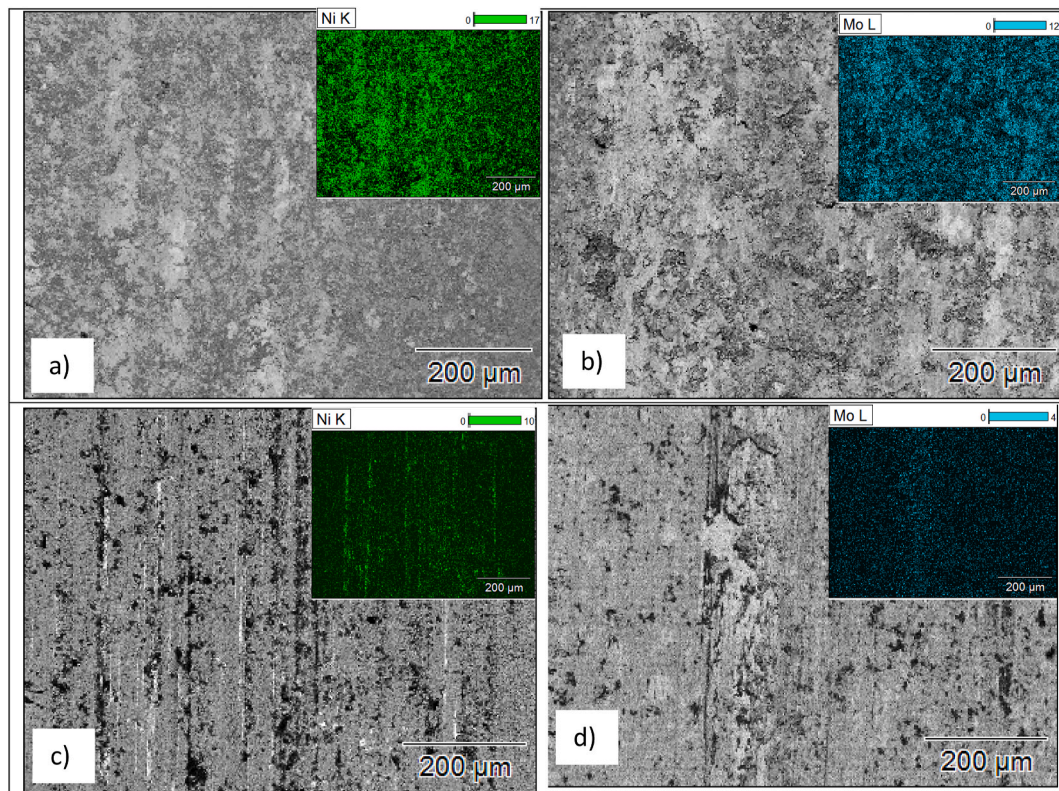


Fig. 7. SEM micrographs of wear scars (backscattered electron imaging) formed on coatings of Cr_2O_3 (a: dry testing, c: borated water testing) and $\text{Cr}_3\text{C}_2\text{-NiCr}$ (b: dry testing, d: borated water testing). The wear direction is vertical, in line with the wear scars. EDS maps are included inset to reveal nickel or molybdenum content [COLOUR]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

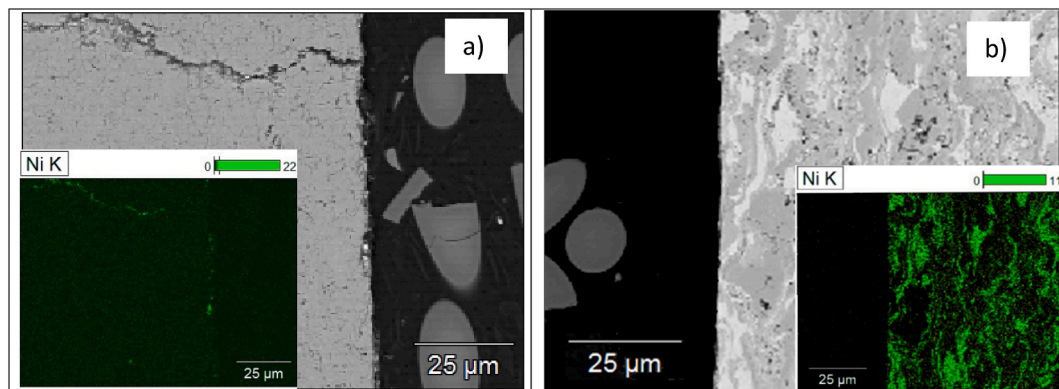


Fig. 8. Back scattered electron micrographs of cross-sections, wear tested in borated water for (a) Cr_2O_3 and (b) $\text{Cr}_3\text{C}_2\text{-NiCr}$. EDS maps inset to indicate any nickel present. No molybdenum was observed on the surface of the $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating.

Different test regimes appear to have a significant effect on the wear scar morphology. The ball counterface has created a visible wear scar, except for where the surface has suffered more significant damage (see Fig. 7b for example). Plan view analysis in Fig. 7 confirms material transfer from the ball to the coating for the Cr_2O_3 and $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings. The dry testing SEM analysis for these coatings has revealed the presence of significant tribolayers. These are large deposits which are embedded within the coating surface, in addition to dispersed smaller deposits. Testing in borated water shows a more consistent tribolayer, appearing as rows of deposits along the whole length of wear scar, parallel to the sliding wear. The EDS analysis, in Fig. 7, indicated that the tribolayers observed are of Inconel 625 in origin, through the observation of nickel and molybdenum.

Cross-sections of the wear scars were also examined using SEM.

Micrographs of the metallographically prepared cross-sections are shown in Fig. 9.

The cross-sections in Fig. 8 reveal a micrometre-scale tribolayer of Ni on the Cr_2O_3 coating, but this is not present in the $\text{Cr}_3\text{C}_2\text{-NiCr}$ (confirmed for multiple samples examined in cross-section for all regimes). Molybdenum was also not found on the $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating, further confirming that no tribolayer is present. The Cr_2O_3 coating also showed comparable tribolayers when tested in both dry and deionised water. The presence of a tribolayer corroborates the plan view SEM imaging for Cr_2O_3 , but the absence of a tribolayer is inconsistent with the EDS observations for $\text{Cr}_3\text{C}_2\text{-NiCr}$ in a plan view where a tribolayer was observed (Fig. 7d). This indicates that the formation of a tribolayer is a less prevalent and more localised phenomena for the Cr_2O_3 coating.

Tribolayer deposition varies significantly between the four materials

Table 5

Showing the nature of the tribolayer deposits for each coating material in each testing environment.

Material	Dry Testing	Deionised Water Testing	Borated Water Testing
Cr_2O_3	Dispersed deposits	Lines of deposits	Lines of deposits
WC-(W, Cr) ₂ C-Ni	Dispersed deposits	Lines of deposits	Lines of deposits
Cr_3C_2 -NiCr	Dispersed deposits	Dispersed deposits	Limited dispersed deposits
HCP	Lines of deposits	Lines of deposits	Limited dispersed deposits

investigated when analysed using SEM. This is summarised in Table 5.

In most cases, tribolayer formation was incomplete in that discrete areas or a line of deposits, in the direction of reciprocation, rather than a continuous layer were observed. The deposits are probably attaching to areas of the surface that either had pre-existing pores/cracks or had material pull-out during the wear process. Testing in deionised and borated water conditions reduces the tribolayer deposit (Table 5). This is probably the result of water reducing the amount of abrasive wear and hence creating less sites for preferential transfer of the counterface to the coating. Hard chromium plate has shown that it has reduced tribolayer deposits compared with other materials, perhaps an indication of its higher wear resistance when tested in this regime.

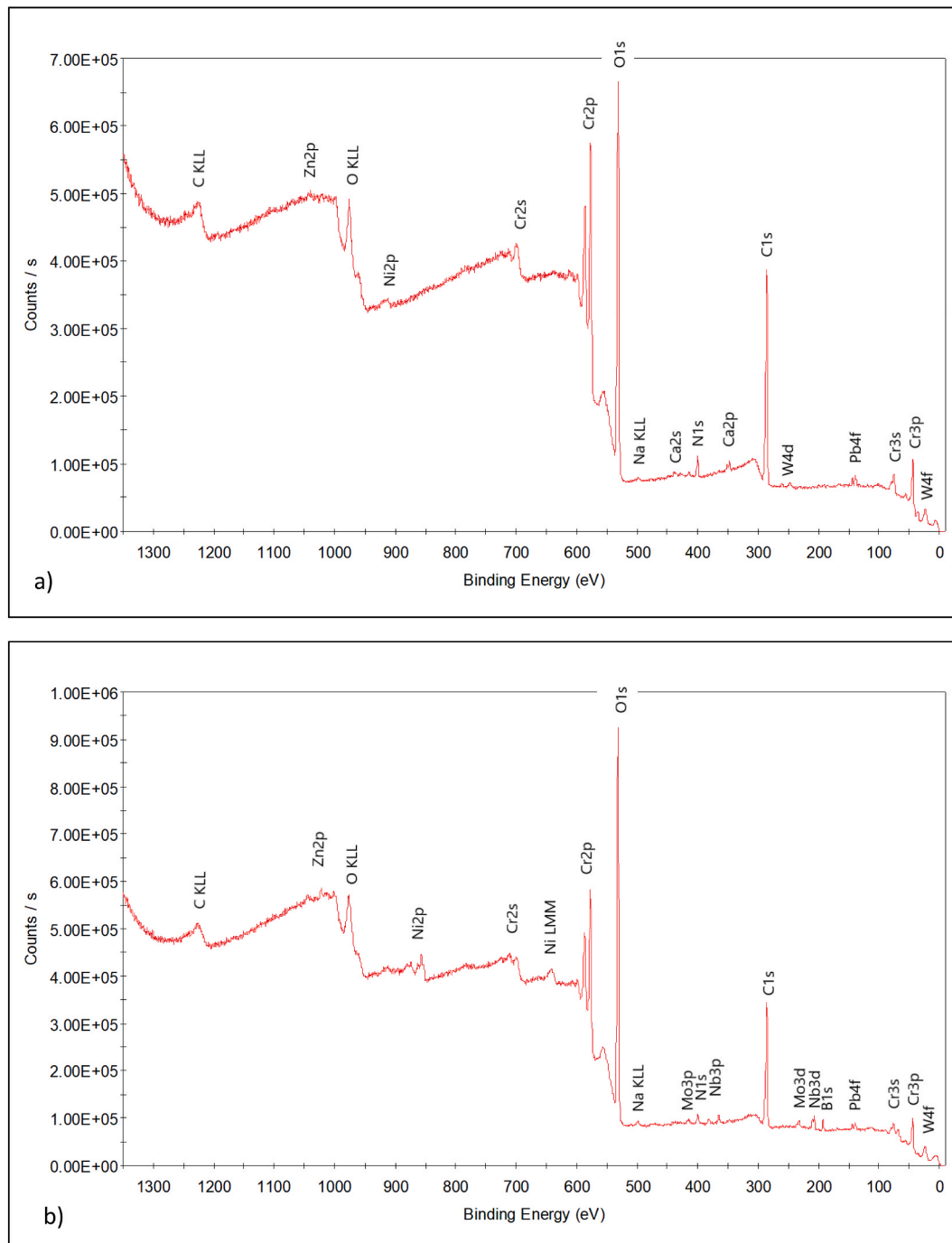


Fig. 9. XPS survey spectra for Cr_2O_3 (a) unworn and (b) wear track.

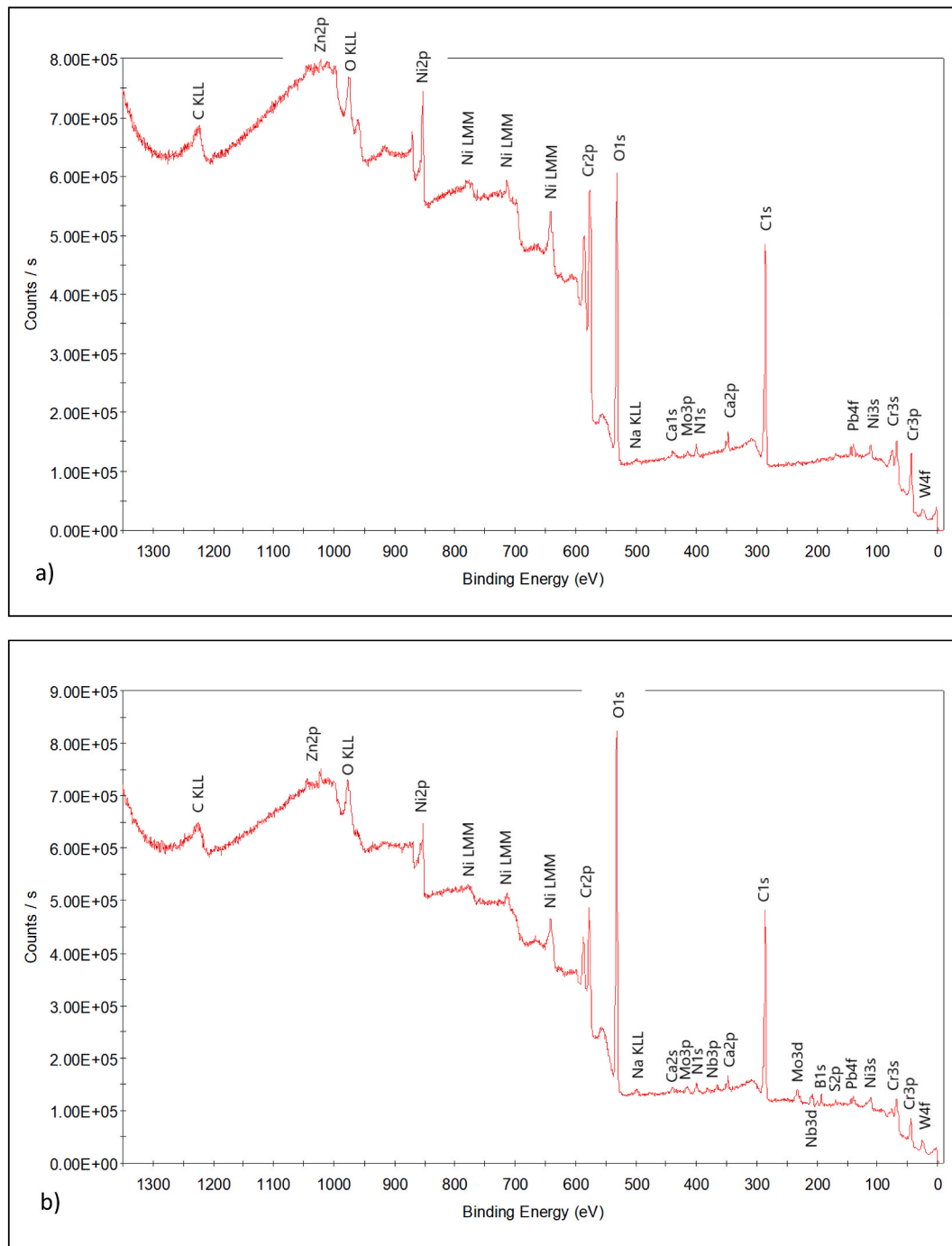


Fig. 10. XPS survey spectra for the $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating a) unworn and (b) wear track.

3.4. Surface analysis

Microstructural analysis has revealed numerous tribolayer deposits in addition to particle pull-out and abrasive wear. Surface analysis using XPS was performed to gather thin film surface compositions on the surface of the worn coatings in addition to chemical-state information data. This has given an improved understanding of the tribolayer and material pull-out composition. The pristine and worn surfaces of the Cr_2O_3 and $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings were analysed for all three regimes. Data for WC-(W,Cr) $_2\text{C-Ni}$ and hard chromium plate have been reported in previous research [12].

The borated water testing XPS spectra for the other two coating materials have been subjected to the most detailed examination, as this

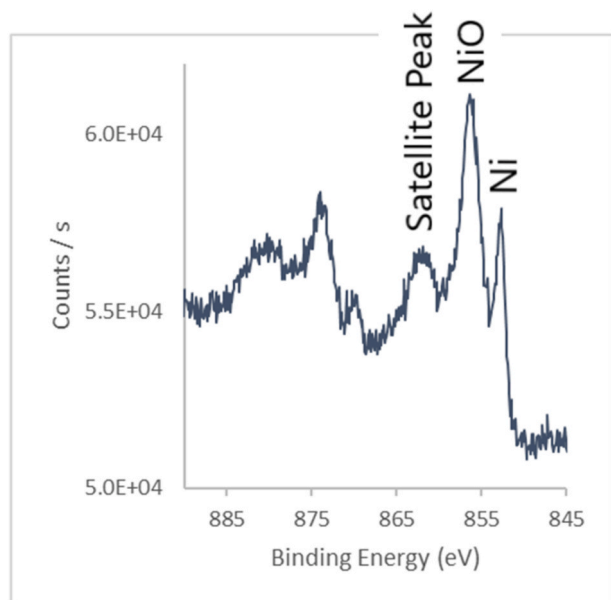
Table 6

XPS atomic composition for the Cr_2O_3 coating.

Element core level	Cr_2O_3 Surface Composition/atomic %	
	Away from wear scar	Wear scar
C1s	34.8	27.2
O1s	33.4	44.5
Cr2p	9.4	9.0
Ni2p		2.0
N1s	2.0	1.1
Mo3d		Trace
Nb3d		Trace
B1s	1.5	6.0

Table 7XPS atomic composition for the Cr₃C₂-NiCr coating.

Element core level	Cr ₃ C ₂ -NiCr Surface Composition/atomic %	
	Away from wear scar	Wear scar
C1s	45.5	41.2
O1s	29.6	37.2
Cr2p	12.2	6.4
Ni2p	3.7	3.6
N1s	1.5	1.2
Mo3d		Trace
Nb3d		Trace
B1s		5.2

**Fig. 11.** XPS Ni2p peak for a worn Cr₂O₃ coating tested in borated water showing metallic nickel and metal oxide peaks.

is the target environment for the coatings. The spectra are shown in Figs. 9 and 10. The spectra for dry and deionised water tests appeared largely comparable with the only significant difference of the presence

of a B1s peak for the tests in borated water. This is particularly significant due to the low cross section of the B1s peak when analysing using XPS.

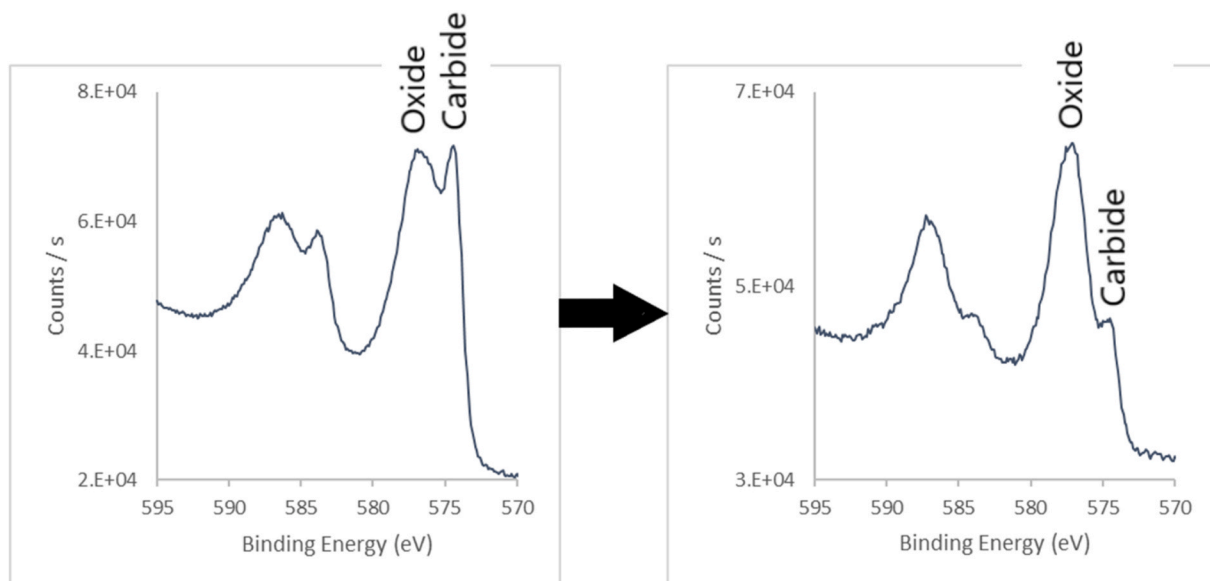
Compositional analysis is presented in Tables 6 and 7 for the Cr₂O₃ and Cr₃C₂-NiCr coatings respectively following testing in borated water. This is comparable to the compositions following testing in the other environments with the exception of a boron peak at 192.1 eV.

From the compositional analysis in Table 6, detailed information regarding the surface layers before and after wear testing can be obtained for the Cr₂O₃ coating. Across all regimes following wear testing, evidence of an Inconel 625 based tribolayer is present. This is apparent due to the presence of Ni, Mo, and Nb in the wear scar, as these elements are not present in the coating but are found in the counterface (Inconel 625 ball). The atomic percentage of oxygen increases, suggesting the deposition of oxidised forms of the constituents of Inconel 625 including nickel, molybdenum and niobium oxides. A relatively high level of boron has also been observed during the borated testing. On a region of the sample 1.5% atomic percentage of boron has been observed whereas within the wear scar 6% atomic percentage has been observed. This suggests that during testing, boron preferentially forms compounds such as borates or boron trioxide within the wear scar. Lithium borate may also form due to the presence of lithium within the borated water solution, although no lithium peak was observed in the spectra.

Further analysis of the nickel peak for a sample of the Cr₂O₃ coating tested in borated water is shown in Fig. 11.

The deposited nickel is in the form of metallic nickel and nickel oxide (Fig. 11). The shape of the peak suggests that more nickel oxide is present compared with metallic nickel. This is likely as a result of the wear testing allowing most of the metallic nickel from Inconel 625 to oxidise with the testing solution or air environment following testing.

From the compositional analysis in Table 7, information regarding the surface films for the Cr₃C₂-NiCr coating formed during wear testing in the three regimes can be interpreted. Following wear testing, the appearance of molybdenum and niobium in the wear tracks confirms that a tribolayer of Inconel 625 origin is formed. The levels of molybdenum and niobium deposited are very low compared with other materials tested suggesting a reduced deposition of Inconel 625 based tribolayer. This confirms observations from the cross-sectional SEM imaging (Fig. 8b) suggesting limited levels of tribolayer deposit. Plan view imaging did confirm some presence of Inconel 625 tribolayer and so some trace levels of detection by XPS was to be expected (Fig. 7b). A strong boron peak is also observed in the spectra (Fig. 10b). Again, as

**Fig. 12.** Evolution of the XPS Cr2p peak for the Cr₃C₂-NiCr coating before and after wear testing in the borated water solution.

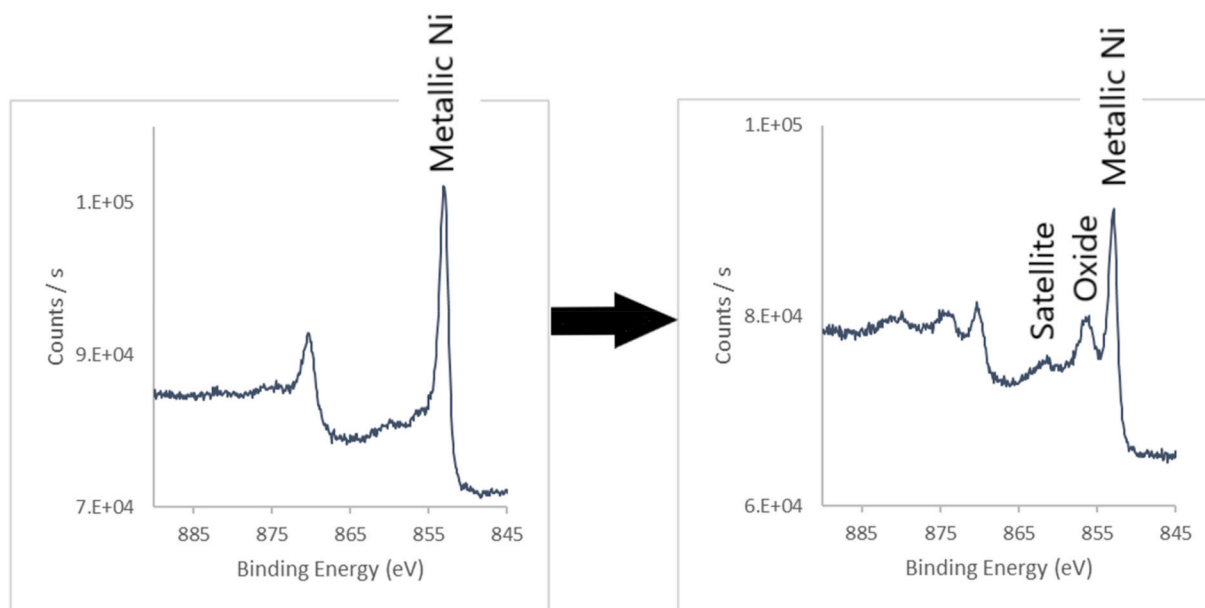


Fig. 13. Evolution of the XPS Ni2p peak for the Cr_3C_2 -NiCr coating before and after wear testing in borated water.

with the Cr_2O_3 coating this suggests the thin film formation of borates, boron trioxide or lithium borate within the wear scar.

As with the previously examined $\text{WC}-(\text{W,Cr})_2\text{C-Ni}$ coating [12], the Cr_3C_2 -NiCr coating also demonstrates a transition from a mixed chromium oxide and chromium carbide surface layer to a predominantly chromium oxide surface layer. This is demonstrated for the borated wear testing of the Cr_3C_2 -NiCr coating in Fig. 12.

When analysing the nickel peak for Cr_3C_2 -NiCr it is also clear that this elemental peak undergoes a transition following wear testing (Fig. 13). This shows a predominantly metallic nickel change to a mixed metallic nickel and nickel oxide following testing. This is likely a combination of nickel from both the Inconel 625 counterpart and nickel from the material matrix oxidising during the wear test or after when exposed to air. This effect has been seen for all three test regimes.

Using the method developed by Strohmeier [20], the oxide thickness on the worn Cr_3C_2 -NiCr sample was found to be approximately 3 nm.

3.5. Wear mechanisms

Following wear testing, Cr_2O_3 exhibited the characteristics of abrasive wear. From Fig. 6a shallow worn grooves can be seen, although these are without the presence of pronounced grooves and show limited surface cracking. This therefore suggests that material from this coating is removed relatively uniformly and not in isolated regions such as in particle pull-out. This is likely due to the single-phase nature of the coating meaning the material wears evenly in this testing method.

Significant tribolayer deposits have been observed for Cr_2O_3 in all three regimes using SEM imaging in a plan view (Fig. 7) and cross-sectional view (Fig. 8). EDS analysis has confirmed that the tribolayers are Inconel based due to the nickel EDS maps identifying high concentrations of the nickel on the surface of the worn samples. This indicates the preferential wear of the Inconel 625 counterpart that is then deposited on the coating surface. Fig. 6a also reveals that the tribolayer appears to deposit in the form of 'micro-splats'.

The surface analysis of the worn Cr_2O_3 coating seems to confirm the previous suggestion that chromium oxide layers are removed from the surface of the coating uniformly. This is shown by the reduction in the atomic percentage of chromium in the wear scar when compared with the as deposited sample (Table 4) as chromium oxide is lost through abrasive wear and replaced by the oxidised constituents of Inconel 625 including Ni, Mo and Nb. The formation of borates is also seen when the

Cr_2O_3 was tested in the borated water testing solution.

Cr_3C_2 -NiCr has shown limited visible abrasion when looking in a plan view SEM orientation (Fig. 7). Whilst the magnified view in Fig. 6c also shows limited visible abrasion in the form of grooves, it does show a high quantity of holes within the sample surface as a result of suspected particle pull-out. Visible surface cracking is also limited in this view, particularly when compared with other coating materials. When cracking is visible, this is typically localised to areas of particle pull-out. Particle pull-out appears to dominate wear of this material and the associated wear rate.

Some isolated regions of tribolayer can be seen on the surface of Cr_3C_2 -NiCr but only when analysing from a plan view (Fig. 7). However, this tribolayer was not visible when analysing in a cross-sectional view (Fig. 8b). This suggests that the tribolayer is intermittent and dispersed across the surface of the coating, with a much lower rate of tribolayer formation compared with Cr_2O_3 and $\text{WC}-(\text{W,Cr})_2\text{C-Ni}$ coatings. EDS analysis has confirmed that the tribolayer this is primarily Inconel 625 based when present.

The XPS compositional analysis suggests the possible particle pull-out is the Cr_3C_2 phase of the Cr_3C_2 -NiCr coating. This is likely due to the hard and brittle nature of this phase causing preferential pull-out compared with the NiCr phase. The XPS analysis also confirms a transition of a mixed chromium carbide and chromium oxide surface layer to a predominantly chromium oxide surface layer following wear testing (Fig. 12), indicating that the Cr_3C_2 phase is not only pulled out, but also oxidises during wear testing. The analysis has also revealed that borates form on the surface of the coating when wear tested in borated water. These formed products may influence the wear performance.

Fig. 14 visually demonstrates the proposed wear mechanisms for the Cr_2O_3 and Cr_3C_2 -NiCr coatings and indicates the layers present, indicated by XPS.

4. Conclusions

The sliding wear performance of some alternatives to hard chromium plate— Cr_2O_3 , $\text{WC}-(\text{W,Cr})_2\text{C-Ni}$ and Cr_3C_2 -NiCr—has been critically evaluated. The wear experiments were performed using dry testing and under both deionised and borated water. Although further consideration should be made for the fully representative conditions of a nuclear reactor, a number of conclusions can be drawn:

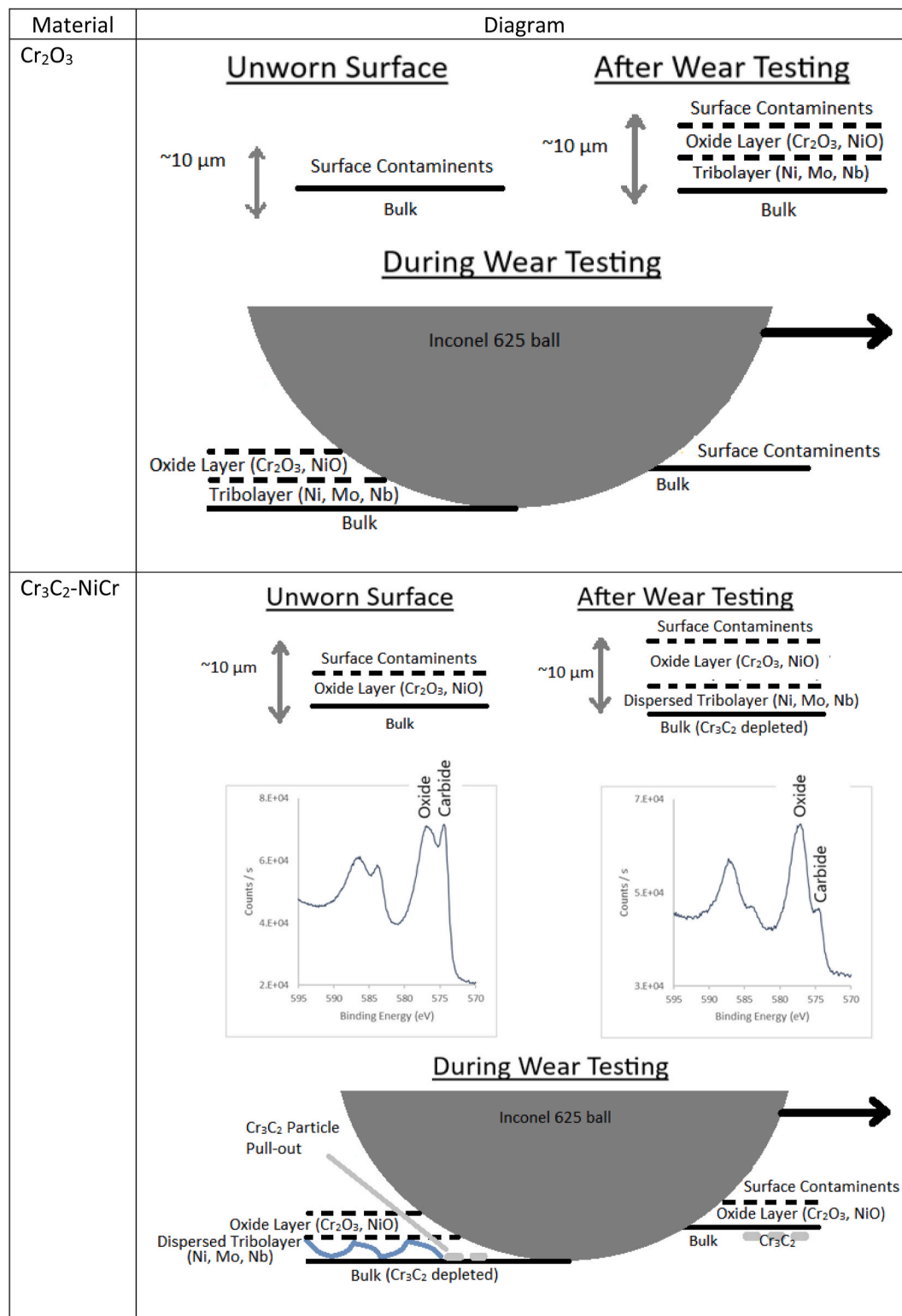


Fig. 14. Schematic diagrams highlighting the proposed wear mechanisms of Cr_2O_3 and $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings (diagrams not to scale). The XPS spectra for the $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating shows the changes of the form of chromium before, and after, testing. Cr_3C_2 particle pull-out is also shown in this figure for this coating. The Cr_2O_3 coating depicts material abrasion in this figure for comparison.

1. Cr_2O_3 , WC-(W,Cr)₂C-Ni and $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings deposited by thermal spray have provided similar wear rates to conventional hard chromium plate for system with an Inconel 625 counterface in three testing environments. The WC-(W,Cr)₂C-Ni and $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings were found to have significant levels of particle pull-out, increasing the maximum penetrations through these coatings. This suggests that

the Cr_2O_3 coating is arguably the best replacement for HCP for wear applications in this environment against an Inconel 625 counterface using the geometries explored in this study.

2. Hard chromium plate has shown marginally better wear performance than the ceramic alternatives when evaluating wear rate but there are some concerns with particle pull-out and microcracking.

- Testing the candidate materials and hard chromium plate in deionised and borated water reduces tribolayer formation in all cases compared with dry testing.
- This study has confirmed our previous observation [12] that significant differences exist between wear behaviour in deionised water and borated water. Deionised water is therefore not suitable substitute for reactor water chemistry in evaluating nuclear hard coatings.
- Analysing the wear scars for Cr₂O₃ and Cr₃C₂–NiCr coatings for all three environments showed evidence of surface abrasion and localised wear in the form of both particle and material pull-out. The presence of tribolayers comprising material from the Inconel 625 counter face was observed on all four materials, although this was found to be more dispersed for the Cr₃C₂–NiCr coating and hard chromium plate.
- XPS surface analysis for Cr₂O₃ has indicated that chromium oxide layers are worn away in a uniform manner with limited chemical changes on the sample surface after testing in borated water. XPS analysis of the Cr₃C₂–NiCr coating has confirmed Cr₃C₂ particle pull-out and an oxidation mechanism of chromium at the surface following testing.
- XPS has been further shown to provide vital extra information when elucidating the complexity of tribolayer formation.

Future studies in the following areas would be valuable:

- The use of other counterface materials to assess the performance of the coating materials in other tribological systems commensurate with nuclear environments.
- Identifying the precise nature of the boron-rich material found on the post-wear surfaces.
- Further tests to more closely emulate a nuclear reactor environment such as performing tests under typical pressures and temperatures with a neutron flux.

Declaration of competing interest

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.

Acknowledgements

The authors would like to acknowledge the EPSRC, National Physical Laboratory and Rolls-Royce plc for funding and supporting this study. It was carried out as part of an Engineering Doctorate Programme in Micro- and Nano-Materials and Technologies at the University of Surrey, Grant Numbers EP/L016788/1 and EP/P001521/1. The authors would like to express their gratitude to Dave Jones, Steve Hinder and Dave Cox at the University of Surrey for their invaluable technical assistance.

References

- G. Barbezat, A.R. Nicol, A. Sickinger, Abrasion, erosion and scuffing resistance of carbide and oxide ceramic thermal sprayed coatings for different applications, *Wear* 162–164 (1993) 529–537, [https://doi.org/10.1016/0043-1648\(93\)90538-W](https://doi.org/10.1016/0043-1648(93)90538-W). Part A.
- D. Toma, W. Brandl, G. Marginean, Wear and corrosion behaviour of thermally sprayed cermet coatings, *Surf. Coating. Technol.* 138 (2–3) (2001) 149–158, [https://doi.org/10.1016/S0257-8972\(00\)01141-5](https://doi.org/10.1016/S0257-8972(00)01141-5).
- X.Q. Cao, R. Vassen, D. Stoeber, Ceramic materials for thermal barrier coatings, *J. Eur. Ceram. Soc.* 24 (2004) 1–10, [https://doi.org/10.1016/S0955-2219\(03\)00129-8](https://doi.org/10.1016/S0955-2219(03)00129-8).
- K.T. Kembaiyan, K. Keshavan, Combating severe fluid erosion and corrosion of drill bits using thermal spray coatings, *Wear* 186–187 (1995) 487–492, [https://doi.org/10.1016/0043-1648\(95\)07142-3](https://doi.org/10.1016/0043-1648(95)07142-3).
- M. Onozuka, S. Tsujimura, M. Toyoda, M. Inoue, T. Abe, Y. Murakami, Electrical insulation and conduction coating for fusion experimental devices, *Fusion Technol.* 29 (1996) 73–82, <https://doi.org/10.13182/FST96-A30657>.
- T.S. Sidhu, S. Prakash, R.D. Agrawal, Studies on the properties of high-velocity oxy-fuel thermal spray coatings for higher temperature applications, *Mater. Sci.* 41 (2005) 805–823, <https://doi.org/10.1007/s11003-006-0047-z>.
- J.A. Cabral-Miramontes, R. Rocha Reséndez, C. Gaona Tiburcio, P. Zambrano-Robledo, C. Poblano Salas, F. Almeraya Calderon, Effects of heat treatments in corrosion behavior of HVOF-sprayed Ni-based alloy coatings, in: *Proceedings of the Symposium of Aeronautical and Aerospace Processes, Materials and Industrial Applications*, 2018, https://doi.org/10.1007/978-3-319-65611-3_5.
- A.S. Kang, J.S. Grewal, G.S. Cheema, Effect of thermal spray coatings on wear behavior of high tensile steel applicable for tiller blades, Part A, *Mater. Today: Proceedings* 4 (2) (2017) 95–103, <https://doi.org/10.1016/j.matpr.2017.01.001>. ISSN 2214-7853.
- T. Allen, J. Busby, M. Meyer, David Petti, Materials challenges for nuclear systems, *Mater. Today* 13 (Issue 12) (2010) 14–23, [https://doi.org/10.1016/S1369-7021\(10\)70220-0](https://doi.org/10.1016/S1369-7021(10)70220-0).
- European Parliament and Council, Regulation Concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency (REACH), 2006, pp. 1–849.
- G. Bolelli, L. Lusvardi, R. Giovanardi, A comparison between the corrosion resistances of some HVOF-sprayed metal alloy coatings, *Surf. Coating. Technol.* 202 (2008) 4793–4809, <https://doi.org/10.1016/j.surfcoat.2008.04.056>.
- E.H. Williamson, M. Gee, D. Robertson, J.F. Watts, M.J. Whiting, J.A. Yeomans, Wear performance and characterisation of coatings for nuclear applications: WC-(W,Cr)(2)C-Ni and hard chromium plate, *Wear* 430 (2019) 169–182, <https://doi.org/10.1016/j.wear.2019.05.001>.
- J.A. Picas, A. Forn, G. Matthäus, HVOF coatings as an alternative to hard chrome for pistons and valves, *Wear* 261 (2006) 477–484, <https://doi.org/10.1016/j.wear.2005.12.005>.
- F. Rastegar, A.E. Craft, Piston ring coatings for high horsepower diesel engines, *Surf. Coating. Technol.* 61 (1993) 36–42, [https://doi.org/10.1016/0257-8972\(93\)90199-X](https://doi.org/10.1016/0257-8972(93)90199-X).
- Y. Ding, Effects of Elevated Temperature Exposure on the Microstructural Evolution of Ni(Cr)-Cr₃C₂ Coated 304 Stainless Steel, PhD thesis, University of Nottingham, 2009.
- J. Zhang, Z. Wang, P. Lin, Effects of sealing on corrosion behaviour of plasma-sprayed Cr₂O₃–8TiO₂ coating, *Surf. Eng.* 29 (2013) 594–599, <https://doi.org/10.1179/1743294413Y.0000000161>.
- L. Berger, S. Saaro, T. Naumann, M. Kašparova, F. Zahálka, Influence of feedstock powder characteristics and spray processes on microstructure and properties of WC-(W,Cr)2C–Ni hardmetal coatings, *Surf. Coating. Technol.* 205 (2010) 1080–1087, <https://doi.org/10.1016/j.surfcoat.2010.07.032>.
- J. Park, I. Kim, Y. Jung, H. Kim, D. Park, W. Kim, Long-term corrosion behavior of CVD SiC in 360°C water and 400°C steam, *J. Nucl. Mater.* 443 (2013) 603–607, <https://doi.org/10.1016/j.jnucmat.2013.07.058>.
- V. Katranidis, S. Gu, D.C. Cox, et al., FIB-SEM sectioning study of decarburization products in the microstructure of HVOF-sprayed WC-Co coatings, *J. Therm. Spray Technol.* 27 (2018) 898–908, <https://doi.org/10.1007/s11666-018-0721-3>.
- B.R. Strohmeyer, An ESCA method for determining the oxide thickness on aluminum alloys, *Surf. Interface Anal.* 15 (1990) 51–56, <https://doi.org/10.1002/sia.740150109>.