



Corrosion and tribocorrosion behaviour of WC/C coating on beryllium-copper mould alloy

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ABSTRACT

In this study, WC/C coating was applied on beryllium (Be)-copper (Cu) mould alloy by arc physical vapor deposition (PVD) as a corrosion and wear protection barrier against alumina ball in a 3.5 wt% NaCl solution. Tribocorrosion tests were carried out in a triboelectrochemical cell using a ball-on-plate tribometer integrated with a potentiostat for electrochemical control. The results showed a clear improvement of wear resistance on the WC/C coating without reducing the corrosion behavior in a 3.5 wt% NaCl solution. © 2020 Elsevier Ltd. All rights reserved.

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1. Introduction

Beryllium Copper (Be-Cu) alloy is most extensively used copper alloy and prominent for its strength and hardness compared with other trade copper alloys [1]. Among the Be-Cu alloys, Be-Cu alloy with 1.6–2.1% wt. (Be) is preferred for making industrial mold inserts because of its relatively good strength and high thermal conductivity [2,3]. Be-Cu alloy moulds without any coating might not meet high requirements for both wear and corrosion resistance which brings certain restrictions in polymeric material processing [4,5]. To address these problems, one of the most effective approaches is to employ hard coatings such as physical vapour deposited (PVD) coatings to meet all the requirements. The combination of thin PVD coatings (usually having thicknesses of a few micrometres) with the negligible dimensional changes in mould tolerances allied to low friction, high wear and corrosion resistance makes these coatings excellent candidates for plastic injection moulds [6].

A well-established coating with the commercial brand Balinit C (WC/C) is assumed to obey a lower friction as compared to uncoated moulds [6]. Unfortunately, up to now, there is no information available in the literature related to the tribocorrosion behaviour of this coating. It is worth to emphasize that in many cases, the industrial components (e.g. moulds) are required to be operated in the presence of aggressive additives in polymeric

formulations (i.e. corrosive media) [6]. Since WC/C coatings have been considered as a wear resistant coating [7–10], tribocorrosion behaviour of this coating used to modify the surface state of commercially Be-Cu alloy without significantly affecting its high thermal conductivity properties is also needed to be studied, especially before considering them as an alternative material for specific applications that are being exposed to a tribocorrosion environment during their service life. Thus, the present study aims to investigate the corrosion and tribocorrosion behaviour of WC/C coated Be-Cu alloy in comparison with its base alloy in 3.5 wt% NaCl solution.

2. Material method

The alloy used as substrate material was a commercial Be-Cu alloy of chemical composition Cu – 1.9 Be – 0.25 Co + Ni (wt%) containing other trace elements. The Be-Cu sample with a hardness of 414 HV_{0.025} was polished with alumina paste and the roughness was measured at around 0.12 μm (R_a). The Be-Cu alloy plate was then coated by Balinit C, a low-friction metal carbide rich carbon coating (WC/C), deposited by Oerlikon Balzers. Prior to the coating, the Be-Cu alloy plates were cleaned by an industrial cleaning procedure.

Microstructural characterization was made by microscopic examinations and microhardness measurements. Cross-section of the WC/C coated sample was prepared by using SiC papers and alumina suspension down to 1 μm grain size. The surface morphology

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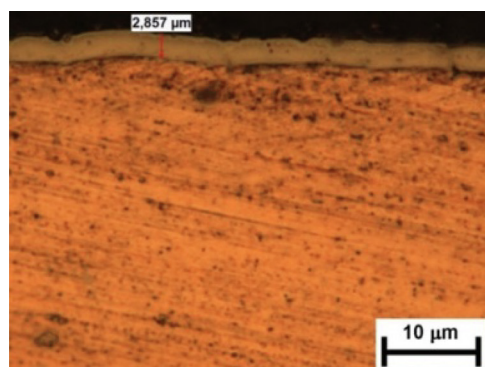
and cross-section of the coating were studied by a Zeiss Supra Field Emission Gun Scanning Electron Microscope (FEG-SEM) equipped with Energy Dispersive X-Ray (EDX) spectroscopy and a Nikon Eclipse LV150 Light Optic Microscope (LOM), respectively. The cross-sectional microhardness measurements were carried out using a Vickers microhardness tester (Shimadzu) with a load 25 g and a dwell time of 15 s.

The electrochemical tests were carried out using a Gamry model PC4/300 mA potentiostat/galvanostat controlled by a computer with DC 105 Corrosion analysis software in the corroding media of aerated solution of 3.5 wt% NaCl at room temperature. Before potentiodynamic polarization measurements, a stabilization period of 30 min was employed in order to measure the open circuit potential (OCP) between working and reference electrodes. Potentiodynamic polarization curves were generated by sweeping the potential from cathodic to anodic direction at a scan rate of 1 mV s^{-1} , starting from -0.6 up to $+0.2$ V. The corrosion tests were evaluated from the Potentiodynamic polarization. Finally, the surface images of the corroded samples were examined using a LOM and FEG-SEM in order to determine the morphology of the developed corrosion.

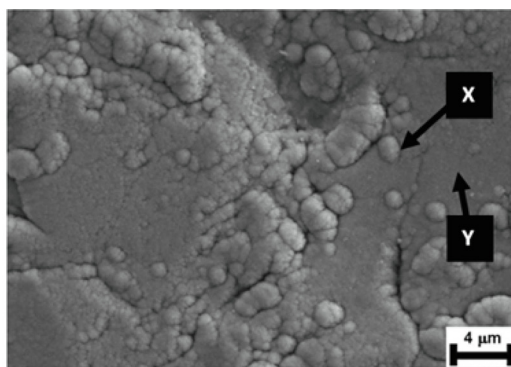
The tribocorrosion tests of the polished Be-Cu alloy substrate and WC/C coated sample were conducted in a triboelectrochemical cell containing 25 ml of 3.5 wt% NaCl solution by using a homemade tribometer with linear reciprocating system coupled with a three electrode electrochemical cell previously described [11]. Reciprocating sliding wear tests were performed in a reciprocating mode with a 1.7 cm s^{-1} sliding rate under 10 N applied load at open circuit potential (OCP) conditions. The sliding tests were run for 45 min corresponding to a sliding distance of 50 m and during testing the coefficient of friction (COF) was continuously recorded. The OCP was measured before, during and after sliding where the sliding action started after reaching the stable OCP values for each test. The counter body was an Al_2O_3 ball with 10 mm diameter. The ball holder was made of a polymeric material to prevent the corrosion effects. During the test, surface with an area of 2.4 cm^2 was exposed to the corrosive electrolyte. After tribocorrosion tests, the worn surfaces of the wear tracks that formed on the examined samples were investigated by the FEG-SEM. The depth profiles of wear tracks and the roughness of the coating were examined using a surface profilometer (Mitutoyo SurfTest SJ-400) by taking average measurements along the wear tracks.

3. Results and discussion

Fig. 1 depicts cross-sectional micrograph and surface morphology of the WC/C coated sample. From the LOM image in Fig. 1a, it is evident that the WC/C coated surface had remarkably uniform



(a)



(b)

Element (wt. %)	X	Y
W	4.41	1.19
C	6.86	3.3
Cr	88.73	95.51

thickness. The thickness of the coating was approximately $2.8 \mu\text{m}$ and showed a relatively good adherence to the Be-Cu alloy substrate. Small cluster defects, $\sim 1 \mu\text{m}$ in diameter, were dispersed over the surface of WC/C coated sample, as illustrated in Fig. 1b. The analysis using EDX showed the existence of the W, C and Cr in the defects (marked as X) and flat (marked as Y) zones. However, the defects (marked as X) were rich in W and C content. Because of the high amount of defects on the WC/C coated sample (Fig. 1b), it seems that the WC/C coated surface had a high roughness value $R_a = 0.54 \mu\text{m}$. After WC/C coating, a 2.4 fold increase in hardness ($\geq 1000 \text{ HV}_{0.025}$) was achieved compared to the uncoated Be-Cu alloy not subjected to PVD deposition ($\sim 414 \text{ HV}_{0.025}$).

In the present study, the WC/C coated sample showed relatively good resistance to corrosion in 3.5 wt% NaCl solution as witnessed from Fig. 2. Zhang et al. [7] reported that the good corrosion resistance of Balinit C coating protected the substrate from destructive attack. The corrosion potential of the WC/C coated sample shifted to more positive potential value (-170 mV) and lower current density value ($342 \times 10^{-9} \text{ A/cm}^2$) than those of the uncoated Be-Cu alloy (-316 mV and $633 \times 10^{-9} \text{ A/cm}^2$). After the corrosion tests, the samples were examined using a LOM and FEG-SEM, and the typical morphology of the corroded samples is presented in Fig. 3. As seen in Fig. 3a, a degradation of the surface of the uncoated Be-Cu alloy can be observed, which has led to the penetration of the corrosive solution and to a localised selective dissolution of the uncoated Be-Cu alloy to some degree. Experiments on

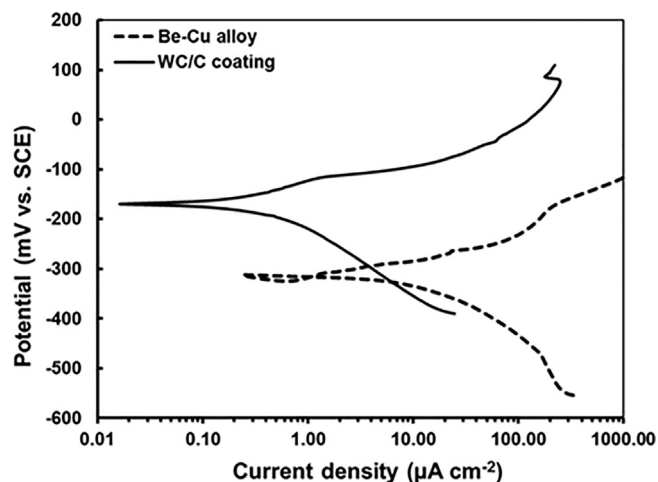


Fig. 2. Potentiodynamic polarization curves of the uncoated Be-Cu alloy and WC/C coated sample in 3.5 wt% NaCl solution.

Fig. 1. (a) Cross-section micrograph and (b) surface morphology with EDX analysis results of WC/C coated sample. Arrows indicate the location of EDX analyses.

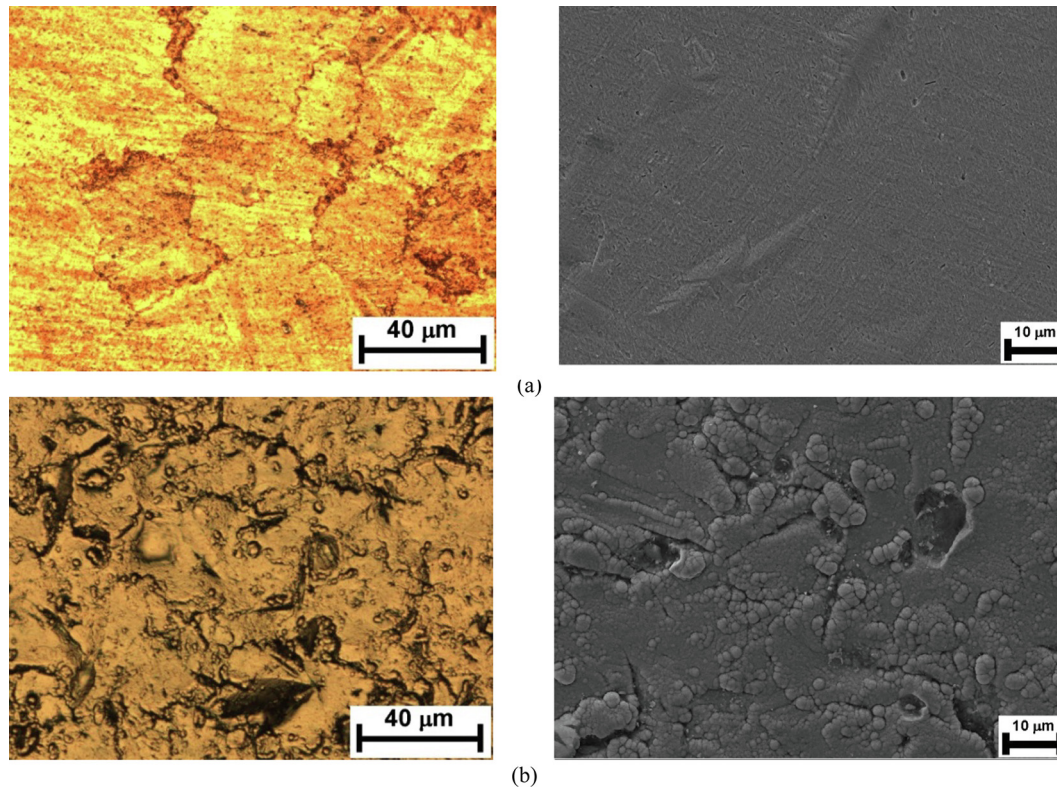


Fig. 3. Surface morphologies after polarization tests of the (a) uncoated Be-Cu alloy and (b) WC/C coated sample (low and high magnifications).

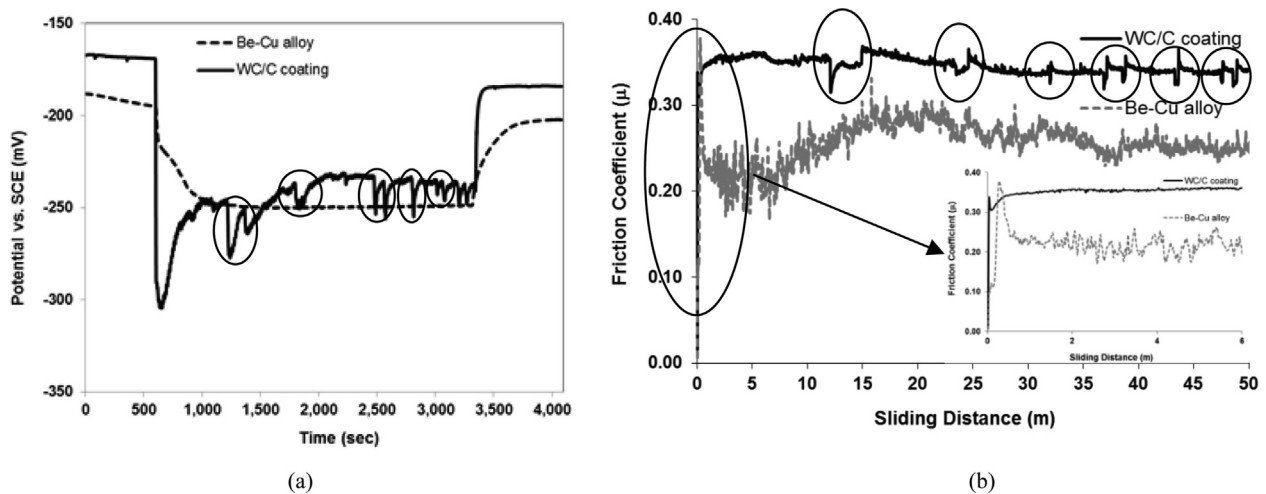


Fig. 4. Evolution of the (a) OCP and (b) COF during the OCP tribocorrosion tests.

Be-Cu alloy showed that at chloride concentrations lower than 1 M (5.8 wt%), copper dissolution occurs through the formation of CuCl , which is not protective enough and is converted to soluble CuCl_2 by reacting with excess chloride [12]. In contrast, no significant severe corrosion was observed on the surface of the WC/C coated sample (Fig. 3b). These results corresponded well with the results of the polarization measurement.

The evolution of the OCP with time before, during, and after the sliding is presented in Fig. 4 for the uncoated Be-Cu alloy and WC/C coated sample, together with the COF values obtained during the

sliding. Before starting of the sliding, OCP of uncoated Be-Cu alloy was slightly lower than the WC/C coated sample. This indicates that the applied surface treatment imparted a more noble potential in case of the coated sample with respect to the uncoated Be-Cu alloy, pointing out a higher protection of the surface against corrosion [13]. When sliding started, it can be clearly seen that the WC/C coated sample exhibited a totally different behavior, where the OCP immediately dropped down to the values around -300 mV. After about 19 m sliding distance, WC/C coated sample presented a cathodic shift, having values around -240 mV with small

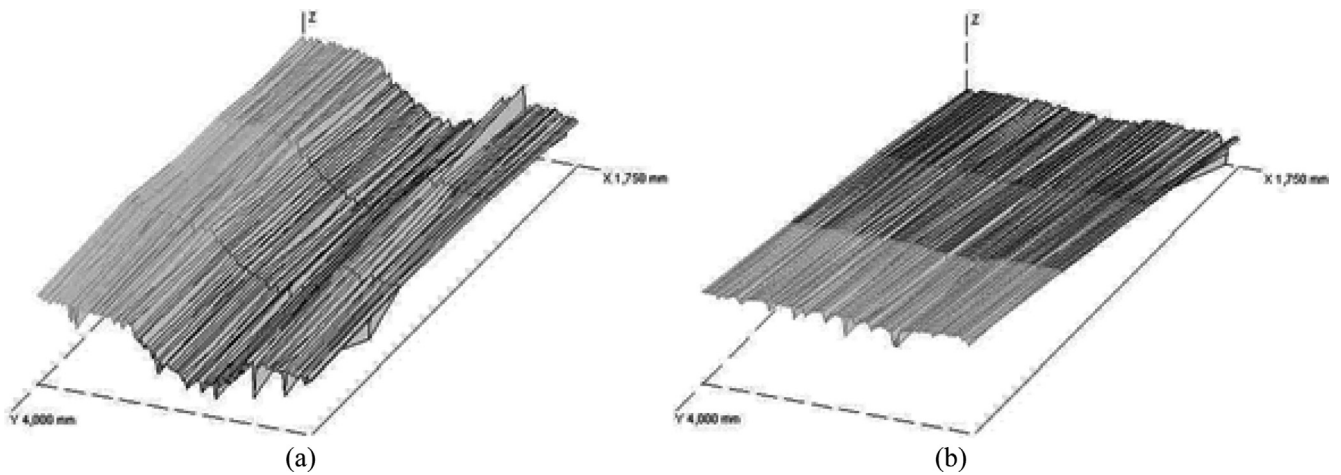


Fig. 5. Wear track profiles of the (a) uncoated Be-Cu alloy and (b) WC/C coated sample.

oscillations, indicating that the WC/C coating was effective in protecting the Be-Cu alloy from corrosion during the sliding. The potential oscillations may be related with the small defects on the surface of WC/C coated sample (Fig. 1b). It is known that corrosion products and/or thin tungsten oxide layer on the WC/C coated sample could contribute to the surface passivation [14,15], thus, the cathodic shift observed on WC/C coated sample can be related to depassivation due to the sliding action. The wear depth of the WC/C coated sample was approximately $1.2 \mu\text{m}$ (Fig. 5b), a value much lower than the thickness of the WC/C coating layer ($\sim 2.8 \mu\text{m}$) (Fig. 1a). Therefore, the Be-Cu alloy was neither exposed to the corrosive environment nor affected by

plastic deformation along the sliding direction. On the other hand, in case of the uncoated Be-Cu alloy, when sliding started, OCP values gradually started to decrease, and after a certain point, the values ($\sim -250 \text{ mV}$) stayed relatively stable till the end of the sliding. The OCP drop indicated a partial removal of the passive film caused by the mechanical action [11,16] confirming an increase in susceptibility of the fresh active Be-Cu alloy for corrosion, and thus a need for surface protection. In this case, the depth of the wear track for the uncoated Be-Cu alloy was found to be approximately $1.6 \mu\text{m}$ (Fig. 5a). As can be seen, there was an initial increase in the COF ($\mu = 0.36$) for the uncoated Be-Cu alloy (Fig. 4b). After a friction displacement of 5 m, it dropped to ~ 0.2

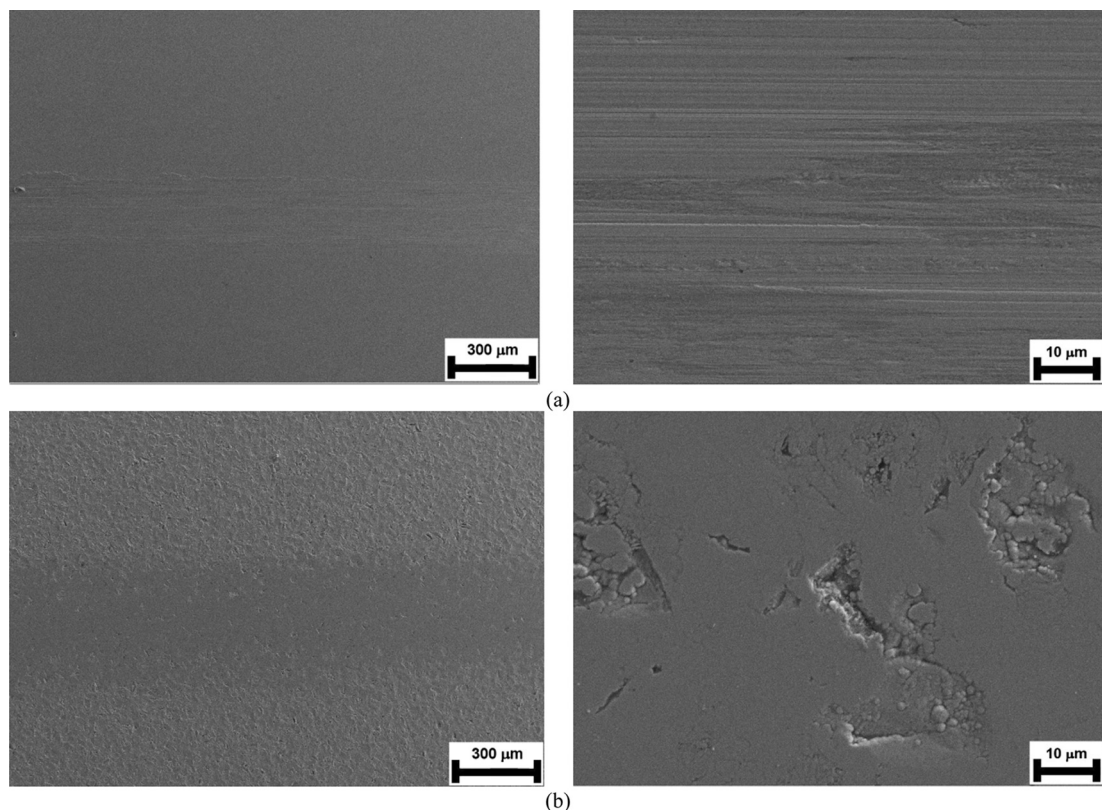


Fig. 6. Worn surface FEG-SEM micrographs of the (a) uncoated Be-Cu alloy and (b) WC/C coated sample against Al_2O_3 balls (low and high magnifications).

and the COF rose again to ~ 0.29 and its values decreased to 0.26 ± 0.024 , along a displacement of 35–50 m. On the other hand, it can be clearly seen that the WC/C coated sample showed a significantly high stabilized COF of about 0.34 ± 0.011 when compared with the uncoated Be-Cu alloy. Such interruptions shown in circles in the OCP and COF measurements (Fig. 4) have been attributed to the existence and ejection of small cluster defects from the contact area of WC/C coated sample (Fig. 1 b). When the sliding motion was stopped, the potential of both the uncoated Be-Cu alloy and WC/C coated sample exhibited a shift in the noble direction with respect to the OCP, suggesting the repassivation of the active area in the rubbed zone. Furthermore, the repassivation time was higher for the uncoated Be-Cu alloy when compared to the WC/C coated sample and this could be attributed to a relatively higher damaged area of the rubbed zone on the uncoated Be-Cu alloy that increased the time required for repassivation.

A detailed investigation of the morphology of the worn surface on the uncoated Be-Cu alloy and WC/C coated sample obtained after identical sliding tests is shown in Fig. 6. Characterisation of the worn samples using FEG-SEM revealed that the Be-Cu alloy/ Al_2O_3 ball contact yielded a rough wear track in the formation of grooves in the wear track along the sliding direction (Fig. 6a). On the contrary, the WC/C coated alloy/ Al_2O_3 ball contact yielded a smooth and compact morphology almost unaffected by the tribological contact as shown in Fig. 6b. Previously, Zhang et al. [7] pointed out that the WC/C coating showed a superior protection against abrasion, tribooxidation and adhesion (scuffing).

4. Conclusions

The corrosion and tribocorrosion behaviour of uncoated Be-Cu alloy and WC/C coated sample have been systematically investigated. The following conclusions can be derived from the research;

- The corrosion resistance of the WC/C coating on the Be-Cu alloy was higher than that of the Be-Cu alloy, as shown by the potentiodynamic polarization curves.
- Under OCP conditions, the WC/C coated sample exhibited better tribocorrosion performance when compared to the uncoated Be-Cu alloy. This was attributed to their improved corrosion resistance, and high hardness and therefore high resistance to wear.

- The surface morphology after the sliding revealed a smooth and polished appearance of the WC/C coating, highlighting the outstanding wear and corrosion performance of this coating in a 3.5 wt% NaCl solution under OCP conditions.

CRediT authorship contribution statement

Harun Mindivan: Methodology, Investigation, Writing - original draft, Writing - review & editing.

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.

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