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**A critical comparison of the tribocorrosive performance in highly-alkaline
wet medium of ultrafine-grained WC cemented carbides
with Co, Co+Ni, or Co+Ni+Cr binders**

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Abstract

The tribocorrosion (resistance, mode, and mechanism) of ultrafine-grained cemented carbides of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) was evaluated and compared critically under the typical conditions of use in highly-alkaline wet medium by means of detailed studies of wet-sliding wear at pH~13.65, complemented by separate detailed studies of both corrosion at pH~13.65 and dry-sliding wear. It is shown that: (i) WC-Co undergoes the most severe tribocorrosion, and separately the most intense corrosion and little mechanical wear; (ii) WC-(Co+Ni) undergoes moderate tribocorrosion, and separately modest corrosion and little mechanical wear; and (iii) WC-(Co+Ni+Cr) undergoes only slight tribocorrosion, and separately almost negligible corrosion and very little mechanical wear. These observations were explicable

in the framework of a conceptual model based on the different severities of the leaching of the binder pools and weakening of the WC/binder interfaces induced by corrosion, followed by material pullout (of both individual WC grains and large chunks of WC grains and binder) caused by frictional mechanical contact. It was also demonstrated that any of these three cemented carbides would be very useful for tribological applications because, despite their differences in performance, they all undergo just mild tribocorrosion and very mild dry-sliding wear. Nonetheless, WC-(Co+Ni+Cr) is to be recommended over both WC-Co and WC-(Co+Ni) for tribological applications in dry conditions, and is doubtless the cemented carbide of choice for tribological applications in alkaline corrosive media.

Keywords: cemented carbides; WC; metal binder; tribocorrosion; corrosion; dry-sliding wear.

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1. Introduction

Cemented carbides [1-3], also termed hardmetals, are an outstanding subfamily of cermets [4] whose microstructure is specifically constituted by grains of an interstitial carbide of the transition metals embedded in a metal matrix that acts as binder [1-3,5,6]. The carbide grains provide high stiffness and hardness, and the metal binder high ductility and toughness [1-2], so that the cemented carbides possess a synergic combination of mechanical properties that makes them the materials of choice for a myriad of engineering applications requiring high tribo-mechanical performance, reliability, and durability. WC with Co is by far the best exponent of the cemented carbides [2], and since its "invention" about a century ago is being widely used worldwide as tribomaterial in many industrial sectors [3].

Very often, WC-Co cemented carbides operate in very harsh working conditions involving frictional contact in corrosive media. This is the case for example when water-based lubricants are used, an extremely common situation since water is cheap, abundant, and environmentally friendly and also has high cooling capacity. Of such lubricants, alkaline water is generally preferred because WC-Co is less prone to tribocorrosion in an alkaline medium than in acidic or neutral media (since in the latter cases Co forms less stable and adherent oxide layers) [7-10]. A representative example is that of the downhole tools used in geo-engineering (rock drilling, mineral cutting, gas and oil drilling, and tunnel) [11-13]. Here, the WC-Co drill bits operate assisted by a drilling fluid that normally is a highly-alkaline aqueous solution of NaOH (together with a number of other additives). The same is the case in other typical applications of the cemented carbides, such as when they are used (*i*) as tools for manufacturing (i.e., machining and finishing operations by cutting, milling, and turning, to name just a few) with coolant [14], (*ii*) as mechanical seals and valves in tap water and sea water pumps [15], (*iii*) as nozzles in

water-coal slurry boilers and high-pressure water jet cutting [16], and (iv) many other uses too numerous to mention explicitly. Unfortunately however, even under these conditions WC-Co is more vulnerable to tribocorrosion than desirable, which is a serious drawback because this significantly reduces its service lifetime.

To delay the premature tribocorrosion failure of WC-Co, the Co binder has to be replaced partially, not totally, with other nobler metals [2]. This has led to soaring interest in more complex binders containing Ni and/or Cr because they are cheaper and safer than Co, and form more stable and adherent passivating layers (i.e., more protective oxide layers) [2]. This is especially true for Cr, which is also preferable over Ni because the superior hardness that it provides is an additional plus in terms of wear resistance [1,17,18]. Binders of Co+Ni+Cr are particularly appealing [19-22] because with this combination Co offers the needed sinterability, Ni provides the desired ductility and oxidation/corrosion resistance, and Cr gives the sought-for greater hardness and even more improved oxidation/corrosion resistance. As is the case for other materials [23], refining the microstructure of the cemented carbides has also been proven to be an effective strategy to improve their wear resistance [2], which has attracted much attention to ultrafine-grained cemented carbides too. Interestingly, Cr binders are very useful in attempts to achieve these desired microstructures because they act as grain-growth inhibitors during the liquid-phase sintering of WC [1,2,24,25]. It therefore seems that ultrafine-grained cemented carbides of WC with Co+Ni+Cr binders would be very appealing for applications demanding high tribocorrosion resistance.

Given the above, the present study is a model investigation aimed at evaluating and comparing critically, within the same common experimental platform **and identical processing/testing conditions**, the tribocorrosion (resistance, mode, and mechanism) under wet-

sliding wear in highly-alkaline medium of ultrafine-grained WC cemented carbides with Co, Co+Ni, or Co+Ni+Cr binders, fabricated by spark plasma sintering (SPS). WC-Co and WC-(Co+Ni) are today's typical cemented carbides, and will therefore serve as referents for comparison with the promising WC-(Co+Ni+Cr) cemented carbide. The relevance of the present work is that there is a paucity of comparative studies of this type, which nonetheless are especially needed because studies in the available literature are so variable¹ that comparison of their results would be meaningless. Moreover, the study was designed to clarify the relative importance of the separate effects of corrosion and mechanical wear on the tribocorrosion of each of these cemented carbides, and to offer a direct comparison between their sliding-wear resistances in highly-alkaline wet conditions and in dry conditions.

2. Experimental Procedure

Three types of cemented carbides were fabricated as described in detail elsewhere [26]. They had the same nominal composition of 83.307 vol.% WC plus 16.693 vol.% metal binder, which are equivalent to the WC and Co proportions of the typical WC-10wt.%Co cemented carbides: (i) WC-Co, with binder of only Co; (ii) WC-(Co+Ni), with binder of 80 vol.% Co and 20 vol.% Ni; and (iii) WC-(Co+Ni+Cr), with binder of 40 vol.% Co, 20 vol.% Ni, and 40 vol.% Cr. The nominal carbon content is the stoichiometric one. Very briefly, commercially available (Alfa Aesar, Germany) powders of WC (Ref. 12482; $d_{50} < 1 \mu\text{m}$), Co (Ref. 10455; $d_{50} \sim 1.6 \mu\text{m}$),

¹ For example, there are wide variations in the raw materials (purity and features of the WC and metal powders) and sources of Cr (metal Cr or Cr₃C₂) or other metals, pre-processing (dry or wet mixing, ball milling, etc.) and densification methods (pressureless sintering, hot-pressing, hot-isostatic pressing, or spark plasma sintering), microstructures of the cemented carbides prepared (density, proportion of metal binder, etc.), methods/conditions for the tribological characterization (loads, speeds, wet medium, type of test, etc.).

Ni (Ref. 10255; $d_{50} \sim 2.2\text{-}3.0 \mu\text{m}$), and Cr (Ref. 41797; $d_{50} < 10 \mu\text{m}$)ⁱⁱ were first wet mixed in appropriate amounts in abundant methanol for 24 h, and the resulting powder mixtures, once completely dried at $\sim 70^\circ\text{C}$, were densified within graphite dies by SPS in dynamic-vacuum atmosphere at 1250°C (heating ramp of $100^\circ\text{C}/\text{min}$) for 5 min under 50 MPa pressure. The cemented carbides thus obtained were ground and polished to a $0.25 \mu\text{m}$ finish (in the same batch to ensure the same surface finish), and characterized microstructurally by X-ray diffractometry (XRD; D8 Advance, Bruker AXS, Germany) and field-emission scanning electron microscopy (FE-SEM; S4800, Hitachi, Japan or Quanta 3D, FEI, The Netherlands), as well as mechanically (hardness and toughness) by Vickers indentation tests (MV-1, Matsuzawa, Japan) at 30 kgf (i.e., at $\sim 294.2 \text{ N}$).

Most importantly for the purposes of the present study, these cemented carbides were also characterized tribologically by pin-on-disk tests (THT1000, Anton Paar, Switzerland) at room temperature, both in wet corrosive conditions and in dry conditions. The former constitute the main focus of this study, while the latter are needed for comparison purposes. In both cases the pins were superhard diamond-coated SiC balls (Dball G10, Nova Diamant, UK) of 3 mm diameter, which ensures wear of the cemented carbides onlyⁱⁱⁱ, the normal contact load 20 N, the linear sliding speed 10 cm/s, the track radius 2 mm, and the total sliding distance 1000 m. The counterballs, which are commercially available, have a $10 \mu\text{m}$ thick diamond layer deposited onto the SiC ball by chemical vapour deposition and are polished to a shiny and specular reflection with a surface roughness of $\sim 20 \text{ nm}$. The wear tests in wet corrosive conditions (i.e., tribocorrosion tests) were performed with the cemented carbides fully immersed in fresh highly-

ⁱⁱ See Ref. [26] for a detailed characterization of the starting WC, Co, Ni, and Cr powders.

ⁱⁱⁱ Examination of the counterballs by optical microscopy revealed no appreciable evidence of wear.

alkaline 0.5 M NaOH aqueous suspensions (with pH~13.65). The wear tests in dry conditions (i.e., tribological tests) were performed without external lubricant, simply with the cemented carbides exposed to air. The coefficient of friction (CoF) was continuously logged during the wet and dry wear tests (both performed in duplicate), at the conclusion of which the worn surface of the cemented carbides was characterized in detail. Specifically, the wear tracks were imaged by optical profilometry (OP; Profilm 3D, Filmetric, USA) to measure the worn volumes and thence to compute the specific wear rates (SWRs) and the attendant wear resistances. To accurately measure the worn volumes, two-dimensional cross-sectional profiles of the residual wear track were carefully extracted from the corresponding three-dimensional images acquired by OP and corrected by their baselines, after which their areas were multiplied by the length of the wear tracks. The SWRs were computed by dividing the worn volumes (mm^3) thus calculated by the load applied (20 N) and the total distance slid (1000 m). The wear resistances are simply the inverse of the SWRs. Moreover, the wear tracks were also observed by optical microscopy (OM; Epiphot 300, Nikon, Japan) and FE-SEM to examine the damage at the macro- and micro-scales, respectively. Energy-dispersive X-ray spectrometry (EDS) analyses were also conducted in selected cases. Finally, the microstructure of the non-worn surface of the cemented carbides subjected to tribocorrosion was also characterized by FE-SEM and glazing-incidence XRD (GI-XRD) at an incidence angle of 0.5° . Note that these microstructures are equivalent to those of the same cemented carbides exposed only to chemical corrosion for the same time as the tribocorrosion tests. All this was done intentionally so because the comparisons (i) between the dry and wet wear tests and (ii) between the non-worn microstructures before and after tribocorrosion will be used to shed light on the respective individual contributions of the mechanical wear and the corrosion to the tribocorrosion.

3. Results and Discussion

3.1. Microstructural and mechanical characterizations of the cemented carbides

Fig. 1 shows representative FE-SEM micrographs of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr). As was to be expected for cemented carbides fabricated by liquid-phase assisted SPS, all three have dense, ultrafine-grained microstructures constituted by a homogeneous distribution of submicrometre WC grains embedded in a binder matrix. This is because the ultrafast sintering (only ~20 min in total) with pressure (50 MPa) promoted the densification of these cemented carbides with little coarsening (i.e., grain growth) by solution-precipitation (Ostwald ripening). In addition, the microstructures of these cemented carbides are observed to be free of defects (such as microcracks or fragmented WC grains). Nonetheless, comparatively it seems that the WC grains are larger and faceted in both WC-Co (Fig. 1A) and WC-(Co+Ni) (Fig. 1B), and smaller and rounded in WC-(Co+Ni+Cr) (Fig. 1C). Interestingly, the smallest WC grains in the microstructure of WC-(Co+Ni+Cr) correspond to the smallest particles in the starting WC powders [26]. This could indicate that the rate-controlling mechanism for coarsening is different in WC-Co and WC-(Co+Ni) from the case in WC-(Co+Ni+Cr) because the general rule is that faceted grains are characteristic of interface-reaction-controlled coarsening, and rounded grains of diffusion-controlled coarsening [27]. This is also consistent with the expectation that the Co+Ni+Cr molten phase would be more viscous than the Co and Co+Ni molten phases [1,19], which would slow down the diffusion of W and C through the liquid phase, thus resulting in smaller WC grains, as was observed experimentally here. Investigating these aspects was beyond the scope of the present tribocorrosion study, but is certainly something deserving more attention in future work.

Fig. 2 shows the XRD patterns of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr). Depending on their chemical composition, the three are formed by α -WC as major phase plus β -M(W,C) as minor phase (M=Co; Co,Ni; Co,Ni,Cr). In fact, β -M(W,C) is a solid solution formed during SPS due to the W and C dissolving into the β -M host. Moreover, WC-(Co+Ni) and WC-(Co+Ni+Cr) also contain traces of M_3W_3C (M_6C), which is a metastable sub-stoichiometric ternary carbide, known as the η -phase, also formed during SPS. It was not formed in WC-Co because in that case the two-phase WC+liquid region occurs at a lower temperature (because the eutectic temperatures are higher when Co is partially replaced with Ni or with Ni+Cr) [19,26]. In any case, WC-(Co+Ni+Cr) does not contain binary chromium carbides (such as Cr_3C_2 or Cr_7C_3).

As for the mechanical properties determined by Vickers indentation, the hardnesses ($H_{V,30}$) of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) are 17.8 ± 0.8 , 17.3 ± 1.3 , and 20.9 ± 0.8 GPa, respectively, while the corresponding fracture toughness (K_{IC}) values are 12.8 ± 1.1 , 11.8 ± 1.1 , and 9.2 ± 0.7 $MPa\cdot m^{1/2}$. Thus, WC-(Co+Ni+Cr) is much harder and brittle than WC-Co (i.e., ~17.5% and 28%, respectively) and WC-(Co+Ni) (i.e., ~21% and 22%, respectively), which is because (i) Cr is harder and less ductile than both Co and Ni, (ii) the WC grains are smaller, and (iii) of the presence of M_6C . Essentially, WC-Co and WC-(Co+Ni) are equally hard and tough despite Ni being softer and more ductile than Co because, while their WC grain sizes are similar, the latter contains some M_6C .

3.2. Tribocorrosion in highly-alkaline medium

Fig. 3 shows the friction curves logged during the tribocorrosion tests on WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) in highly-alkaline water. It can be seen that the three cemented

carbides exhibited very low friction, with the same steady-state CoF of only ~ 0.12 . This value of CoF is typical for lubricated sliding contacts [28]. In principle, given that the low friction attests to ease of sliding, the expectation would then be that the three cemented carbides should undergo little wear. However, it can also be seen that both WC-(Co+Ni) and especially WC-Co displayed much noisier friction curves than WC-(Co+Ni+Cr), whose friction curve is strikingly smooth. These friction instabilities suggest changing conditions in the contact region for WC-(Co+Ni) and especially WC-Co, but not for WC-(Co+Ni+Cr), and are therefore attributable to the occurrence of greater tribocorrosion damage in the first two.

Fig. 4 compares representative OM images of the residual wear tracks in WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) at the conclusion of the tribocorrosion tests. As can be seen, the differences are certainly striking. Thus, WC-Co exhibits by far the widest wear track, and also the roughest worn surface (Fig. 4A). On the contrary, WC-(Co+Ni+Cr) exhibits the narrowest wear track, and also the smoothest worn surface (Fig. 4C). Indeed, the worn surface in WC-(Co+Ni+Cr) remains intact overall and seems simply polished, and the tribocorrosion damage is definitively very shallow. The situation for WC-(Co+Ni) (Fig. 4B) is intermediate between those of WC-Co and WC-(Co+Ni+Cr). Interestingly, abundant accumulation of wear debris is seen over a wide area in the vicinity outside the wear track in WC-Co (Fig. 4D), and the non-worn surface is very corroded. All this occurs to a much lesser extent in WC-(Co+Ni) (Fig. 4B), and does not occur in WC-(Co+Ni+Cr) whose non-worn surface is essentially "clean" with only some corrosion pits (Fig. 4C) which is nonetheless typical for the Cr-containing materials. Therefore, these observations already indicate, at least qualitatively, that WC-(Co+Ni+Cr) is doubtlessly much more resistant to alkaline tribocorrosion than WC-(Co+Ni), and this in turn

more so than WC-Co. The differences in tribocorrosion resistance thus do not correlate with the similarity in CoF, but do so with the differences in "smoothness" of the friction curve.

Fig. 5 shows representative two-dimensional cross-sectional profiles of the residual wear track in WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) measured by OP at the conclusion of the tribocorrosion tests. The magnitude of the difference in tribocorrosion resistance is now quantitatively evident. In particular, the wear track in WC-Co is the widest ($\sim 320 \mu\text{m}$) and deepest ($\sim 7 \mu\text{m}$) of all, and the worn volume is $\sim 1.68 \cdot 10^{-2} \text{ mm}^3$. On the contrary, the wear track in WC-(Co+Ni+Cr) is the narrowest ($\sim 145 \mu\text{m}$) and shallowest ($\sim 0.75 \mu\text{m}$) of all, and the worn volume is only $\sim 8.28 \cdot 10^{-4} \text{ mm}^3$. The wear track in WC-(Co+Ni) is intermediate ($\sim 215 \mu\text{m}$ width and $\sim 3.5 \mu\text{m}$ depth) between those in WC-Co and WC-(Co+Ni+Cr), as is also the case for the worn volume ($\sim 5.94 \cdot 10^{-3} \text{ mm}^3$). Thus, the worn volume in WC-(Co+Ni+Cr) is one order of magnitude less than in WC-(Co+Ni), and as much as two orders of magnitude less than in WC-Co. The SWRs of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) are $\sim 8.42 \cdot 10^{-7}$, $2.97 \cdot 10^{-7}$, and $4.14 \cdot 10^{-8} \text{ mm}^3/(\text{N} \cdot \text{m})$, respectively, and the corresponding values of tribocorrosion resistance are $\sim 1.19 \cdot 10^6$, $3.37 \cdot 10^6$, and $2.42 \cdot 10^7 \text{ (N} \cdot \text{m)/mm}^3$. Hence, the tribocorrosive wear undergone by the three cemented carbides is classified as mild [28,29], attesting as to why they are in such wide demand in industry. Notwithstanding the above, it is also true that WC-(Co+Ni+Cr) was found to be ~ 7 times more resistant to tribocorrosion than WC-(Co+Ni) and ~ 20 times more so than WC-Co, and that WC-(Co+Ni) was in turn ~ 3 times more resistant to tribocorrosion than WC-Co. Thus, these figures support the established axiom that, among the cemented carbides, those with Cr in the binder are the most adequate for applications where tribocorrosion resistance is a primary concern.

Fig. 6-8 show representative FE-SEM images of the worn surfaces of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) at the conclusion of the tribocorrosion tests. It can be seen that the tribocorrosion damage is markedly different at both the qualitative and the quantitative levels. Thus, WC-Co is by far the most damaged of the three cemented carbides, with a very rough wear track and a distinctive wholesale accumulation of wear debris outside the wear track (Fig. 6A). The wear debris, which is formed of both small and large chunks of material (Fig. 6B), is not adhered to the surface but simply deposited on top because it can easily be removed by gentle surface cleaning (Fig. 6C). This wear debris is direct evidence of significant material removal during tribocorrosion. The observations within the wear track show that at the macroscale there is formation of a brittle, non-coherent tribocorrosion layer (Fig. 6D), and that at the microscale there are shallow scratches running in parallel to the sliding direction (Fig. 6E), pullout of material (mostly binder) (Figs. 6E-F), and attacked WC/ β -Co(W,C) interfaces (Fig. 6F). Taken together, all these observations indicate that tribocorrosion of WC-Co proceeded with both marked corrosion and much mechanical wear by severe two- and three-body abrasion dominated by fracture [28]. Two-body abrasion is more relevant than three-body abrasion because, as explained above, the wear debris is expelled out of the contact area.

Comparatively, WC-(Co+Ni) underwent much less tribocorrosion damage than WC-Co. Indeed, there is hardly any evidence of wear debris outside the wear track (Fig. 7A), which indicates that there was much less material removal during tribocorrosion. This is consistent with the observations of the damage within the wear tracks at the microscale, which show multiple shallow scratches running in parallel to the sliding direction and locally a little material removal (Fig. 7B) in the form of pullout of individual or just a few grains. There are some regions within the wear track where a tribocorrosion layer can be seen, but not like those observed in WC-Co.

Consequently, it can be concluded that tribocorrosion of WC-(Co+Ni) proceeded with little corrosion and with little mechanical wear by slight two-body abrasion dominated by plastic deformation (ploughing) plus localized fracture [28].

Lastly, the wear track in WC-(Co+Ni+Cr) is hardly distinguishable (Fig. 8A), and there is no wear debris at all. Indeed, the worn surface of WC-(Co+Ni+Cr) is almost free of damage, and the little damage existing is in the form of shallow scratches running in parallel to the sliding direction, with negligible pullout of WC grains or binder. Again, neither is there any evidence of formation of the thick tribocorrosion layers observed in WC-Co. Basically, the worn surface of WC-(Co+Ni+Cr) simply looks as if it has been polished, and indeed resembles its microstructure in the as-SPSed condition. With this set of observations, it seems evident that tribocorrosion of WC-(Co+Ni+Cr) proceeded with negligible corrosion and with just a very little mechanical wear by a moderate two-body abrasion dominated by plastic deformation in the form of ploughing [28].

The differences in tribocorrosion resistance between WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) can be understood within the framework of a common conceptual model [13] as described in the following. Driven by the difference of electrode potentials in contact with the highly-alkaline medium, corrosion of WC-Co takes place due to the formation of micro-galvanic couples in which the β -Co(W,C) binder acts as sacrificial anode and the WC grains as cathode. Unfortunately however, WC-Co does not present passivating corrosion behaviour with formation of an entirely-protective oxide layer [30-32]. Instead, its corrosion behaviour is pseudo-passivating [30-32] with formation of an incoherent non-protective oxide layer. This results in the continuous and extensive solution of the β -Co(W,C) binder from both the binder pools and WC/binder interfaces. The leaching of the binder pools leaves WC grains unsupported, or at least

loosely bound, due to the lack of surrounding matrix, whereas the corroded, and therefore weakened, WC/binder interfaces provide easy paths for the propagation of the lateral and vertical cracks generated during the frictional contact. All this causes extensive material removal by pullout of individual WC grains, detachment of large chunks of WC grains and binder, and spalling/delamination of the incoherent non-adhered oxide layers. Most of the wear debris thus generated does not remain trapped under the contact however. Instead, due to the rotary movement in the presence of liquid, it is expelled to progressively accumulate outside of the wear track. This, together with the lubrication given by the aqueous solution, is why the friction remains so low (CoF of only ~ 0.12) despite the great microstructural damage.

Interestingly, as a consequence of the wholesale material removal and of the continued immersion in the highly-alkaline medium, the just-worn surface of WC-Co is exposed again to corrosion. This is especially relevant for the present tribocorrosion tests under the pin-on-disk geometry because the cemented-carbide disks are subjected to intermittent mechanical contact since the counterball slides without rotating on itself, and this favours the interaction of the worn surface of the cemented carbide with the corrosive liquid medium. The result is a negative synergy in which corrosion accelerates wear and wear accelerates corrosion, making tribocorrosion of the WC-Co cemented carbide very deleterious. This intermittent coupling of corrosion and wear and the rougher surface would explain the instabilities observed in the WC-Co friction curve.

The situation is different, however, when Ni, and even more so Ni+Cr, are used to partially replace Co. Both Ni and Cr are nobler than Co, and, unlike WC-Co, WC-(Co+Ni) and WC-(Co+Ni+Cr) do present passivating corrosion behaviour in alkaline solutions due to their ability to form protective oxide layers [32-34]. This is especially so for WC-(Co+Ni+Cr) because

(i) the binder contains half of the amount of Co (i.e., only 40 vol.% instead of 80 vol.%), which is inherently non-protective, and (ii) Cr is itself much more resistant to corrosion than Ni. Hence, replacing Co with Ni, and especially Co with Ni+Cr, reduced the leaching rate of the binder in the corrosive medium and also delayed the degradation of the WC/binder interfaces. Consequently, the WC grains lost less (WC-Co+Ni), or much less (WC-(Co+Ni+Cr)), bond integrity by corrosion, and therefore remained more strongly cohesive during tribocorrosion, resulting in much more limited damage by mechanical wear. There is thus a positive synergy in which the only slight corrosion generates only slight mechanical wear, and vice versa. This synergy is more pronounced when there is Cr in the binder, and therefore WC-(Co+Ni+Cr) exhibits much less (indeed negligible) corrosion and mechanical wear than WC-(Co+Ni). This is also why the friction curve is much smoother for the former than for the latter.

Lastly, it should be mentioned that, while the chemical composition of the binder was the major factor ultimately responsible for the greater tribocorrosion resistance of both WC-(Co+Ni) and especially WC-(Co+Ni+Cr), there were other minor factors that contributed positively. In both cases one was the formation of M_6C , which, because it consumed some metal, slightly reduced the proportion of binder in the microstructure. Corrosion was then less severe, and therefore affected mechanical wear less negatively. In the case of WC-(Co+Ni+Cr), another was its superior hardness (~21 GPa vs ~17-18 GPa), which provided much greater resistance to the mechanical wear by abrasion dominated by plastic deformation.

Whichever the case, from the practical point of view, the most relevant is that the experimental results and analyses indicate that the resistance to alkaline tribocorrosion follows the order $WC-(Co+Ni+Cr) > WC-(Co+Ni) \gg WC-Co$.

3.3. Separate effects of corrosion and mechanical wear

Let us start first by considering the effect of corrosion alone. Fig. 9 compares optical photographs of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) before and after the tribocorrosion tests. The visual differences speak for themselves. Indeed, it is evident that: (i) WC-Co was severely corroded; (ii) WC-(Co+Ni) only underwent slight corrosion; and (iii) WC-(Co+Ni+Cr) stayed essentially as it was without corroding. Fig. 10 shows representative FE-SEM images of the non-worn surfaces of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) at the conclusion of the tribocorrosion tests. Because they were taken very far from the wear tracks, they shed light on the separate effect of the corrosion. It can be seen that the surface of WC-Co is completely covered by a thick layer of corrosion products (Fig. 10A), which, being both cracked and not dense, is not protective. If the corrosion layer is partially removed by gentle surface cleaning (Fig. 10B), then it becomes clear that the microstructure underneath is comprised of a skeleton of corroded WC grains and leached binder pools (Fig. 10C). In sum therefore, corrosion substantially altered the microstructure of WC-Co. In particular, these observations indicate that the β -Co(W,C) binder initially protected the WC grains from corrosion by acting as a sacrificial anode until it was completely leached, at which moment the WC grains were no longer protected galvanically, and started to be attacked chemically by the alkaline solution. The microstructure of WC-(Co+Ni), however, changed little with the corrosion (Fig. 10D), with no formation of the thick corrosion layers observed in WC-Co and exhibiting a much less severe leaching of the binder pools. This was even more the case for WC-(Co+Ni+Cr), whose microstructure after corrosion (Fig. 10E) showed no signs of degradation, being essentially indistinguishable from the original microstructure.

Fig. 11 shows the GI-XRD patterns of the non-worn outermost surface of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) at the conclusion of the tribocorrosion tests. It can be seen that in WC-Co no α -WC is detected, only corrosion products which are mostly crystalline cobalt oxides and hydroxides (i.e., Co(OH)_2 , Co_3O_4 , and CoO) and perhaps some crystalline WO_3 or other crystalline mixed oxides (all of them hard to distinguish). GI-XRD cannot confirm whether or not any amorphous oxides are present. On the contrary, in both WC-(Co+Ni) and WC-(Co+Ni+Cr) only α -WC is detected, but no corrosion products. Hence, GI-XRD confirms that, while WC-Co was severely corroded, there was little or essentially no corrosion in the cases of WC-(Co+Ni) and WC-(Co+Ni+Cr).

Again, whichever the case, from the practical point of view, the most relevant is that the experimental results and analyses indicate that the resistance to alkaline corrosion also follows the order $\text{WC-(Co+Ni+Cr)} > \text{WC-(Co+Ni)} \gg \text{WC-Co}$.

Let us now consider the effect of mechanical wear alone. Fig. 12 shows the friction curves logged during the dry tribological tests on WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr). It can be seen that the three cemented carbides exhibited the same friction curve. Unlike tribocorrosion, the friction is now extremely smooth in all three cases, not only for WC-(Co+Ni+Cr). Also, the friction is strikingly low, with a steady-state CoF of only ~ 0.06 that is just half that in the highly-alkaline wet condition (Fig. 1). This indicates that there must have been a very efficient lubrication process operating during the dry tribological tests [28], and that the consequent wear damage must have been very low.

Fig. 13 shows representative OM images of the residual wear tracks in WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) at the conclusion of the dry tribological tests. It can be seen that the wear tracks are all very narrow and very similar in size, with a width of $\sim 130 \mu\text{m}$ that is even

less than that of the wear track of WC-(Co+Ni+Cr) subjected to tribocorrosion (the most favourable case of tribocorrosion). It is therefore clear that WC-Co wore comparatively much less in dry (Fig. 13A) than in wet (Fig. 4A), WC-(Co+Ni) somewhat less in dry (Fig. 13B) than in wet (Fig. 4B), and WC-(Co+Ni+Cr) nearly the same, although a little less, in dry (Fig. 13C) than in wet (Fig. 4C). Interestingly, the wear tracks are also similar to each other in appearance, with smooth worn surfaces that appear polished and that exhibit **thin** oxide tribolayers, without any accumulation of wear debris at their exteriors. **These tribolayers form in situ during the tribological tests due to the frictional heating generated under air atmosphere, and are thinner in the inner region of the wear track because there the greater cumulative wear results in greater “polishing”.** All this is even more evident in Fig. 14, which shows by way of example a low-magnification FE-SEM image of the wear track in WC-Co and the attendant EDS spectra collected outside and inside its worn surface. These oxide tribolayers did not form in the tribocorrosion tests because the aqueous suspension (*i*) dissipates the frictional heating and (*ii*) avoids direct exposure of the cemented carbides to air. With their low shear strengths [28], the oxide tribolayers observed by OM and FE-SEM/EDS lubricated the contact, and are therefore the cause of the very low friction registered experimentally during the dry tribological tests (Fig. 12).

Fig. 15 shows representative two-dimensional cross-sectional profiles of the residual wear track in WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) measured by OP at the conclusion of the dry tribological tests. Again, the similarity between the three wear tracks is evident. Quantitatively, the worn volumes of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) are only $\sim 2.29 \cdot 10^{-4}$, $2.50 \cdot 10^{-4}$, and $1.90 \cdot 10^{-4}$ mm³, respectively. The corresponding SWRs are then $\sim 1.14 \cdot 10^{-8}$, $1.25 \cdot 10^{-8}$, and $9.48 \cdot 10^{-9}$ mm³/(N·m), and the wear resistances are $\sim 8.75 \cdot 10^7$, $7.99 \cdot 10^7$, and $1.05 \cdot 10^8$ (N·m)/mm³. With these orders of magnitude, dry wear of the three

cemented carbides is classified as very mild [28,29]. Therefore, while already being very useful tribocomponents for applications under alkaline corrosive conditions, they are much more so for applications without lubrication. There are two interesting comparisons to be made. First, of the three cemented carbides, WC-(Co+Ni+Cr) was also the one that wore the least under dry wear, but its wear resistance is only ~1.2-1.3 times that of WC-Co and WC-(Co+Ni), and not ~20 and 7 times, respectively, as were the cases under tribocorrosion. Moreover, WC-(Co+Ni) and WC-Co are essentially equally resistant under dry wear, whereas the former was ~3 times more resistant to tribocorrosion than the latter. And second, relative to dry wear, all three cemented carbides wore faster under tribocorrosion, but WC-(Co+Ni+Cr) did so only ~4.5 times faster, WC-(Co+Ni) ~24 times faster, and WC-(Co+Ni+Cr) as much as ~74 times faster. Indeed, all three cemented carbides wore more slowly under dry wear ($<1.3 \cdot 10^{-8} \text{ mm}^3/(\text{N} \cdot \text{m})$) than the best of them (i.e., WC-(Co+Ni+Cr)) did under tribocorrosion ($\sim 4.14 \cdot 10^{-8} \text{ mm}^3/(\text{N} \cdot \text{m})$). The differences are clearly impressive.

Finally, Fig. 16 shows representative FE-SEM images of the worn surfaces of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) at the conclusion of the dry tribological tests. It can be seen that these surfaces have remained intact overall and seem simply polished, and that the little damage existing (underneath the thin oxide tribolayers) is mostly in the form of shallow scratches running in parallel to the sliding direction (Fig. 16A-C). There is almost no pullout of WC grains, and only limited pullout of binder (Fig. 16D). Hence, these observations indicate that dry wear of the three cemented carbides essentially occurred by a slight two-body abrasion dominated by plastic deformation in the form of ploughing [28], **with the abrasive being the asperities of the counterball**. Since the mechanism and mode of dry wear is the same for the three cemented carbides, it can then be easily understood that WC-(Co+Ni+Cr) wore less simply

because its greater hardness (~21 GPa vs 17-18 GPa) made it more resistant to plasticity, and also that WC-Co and WC-(Co+Ni) wore similarly because they are equally hard and the oxidative wear played either just a secondary role or none at all.

Once again, whichever the case, from the practical point of view, the most relevant is that the experimental results and analyses indicate that the resistance to dry-sliding wear follows the order WC-(Co+Ni+Cr) > WC-(Co+Ni) \cong WC-Co.

3.4. Final considerations

With all the above, it is then feasible to elucidate the relative importance of the contributions of corrosion and mechanical wear to the tribocorrosion of each of these three cemented carbides. In particular, it has been shown that WC-Co underwent the most severe tribocorrosion, and separately the most intense corrosion while little mechanical wear. Therefore, corrosion played the determining role and mechanical wear a secondary role in the tribocorrosion of WC-Co, which could therefore be defined essentially as a pernicious corrosion notably accelerated by mechanical wear. In contrast, WC-(Co+Ni+Cr) underwent only slight tribocorrosion, and separately almost negligible corrosion and very little mechanical wear. Hence, corrosion played a secondary role and mechanical wear the limiting role in the tribocorrosion of WC-(Co+Ni+Cr), which could therefore be defined fundamentally as a placid mechanical wear minimally assisted by corrosion. As for WC-(Co+Ni), it underwent intermediate tribocorrosion, and separately modest corrosion and little mechanical wear. Thus, corrosion played the predominant role and mechanical wear an accompanying role in the tribocorrosion of WC-(Co+Ni), which could therefore be classified basically as a moderate corrosion with a contribution from mechanical wear.

Lastly, it emerges from the above results and analyses that any of these three cemented carbides would be very useful for tribological applications because they all undergo just mild tribocorrosion and very mild dry wear. That said, it is also evident, however, that WC-(Co+Ni+Cr) is somewhat more recommendable than its typical WC-Co and WC-(Co+Ni) counterparts for use in tribological applications under dry conditions, and that it is without doubt the cemented carbide of choice for use in tribological applications under alkaline corrosive media conditions.

4. Conclusions

Ultrafine-grained cemented carbides of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) were fabricated by SPS, and their tribocorrosive performance in highly-alkaline wet medium (pH~13.65) was evaluated and compared critically. Based on the experimental results and analyses, the following conclusions can be drawn:

1. Owing to its much lower SWR and microstructural damage, WC-(Co+Ni+Cr) is the cemented carbide of choice for tribological applications under alkaline corrosive media conditions. In turn, WC-(Co+Ni) is preferable over WC-Co.
2. WC-(Co+Ni+Cr) has greater resistance to both alkaline corrosion and dry wear than WC-(Co+Ni) and WC-Co. Therefore, it is also preferable over the other two for applications involving these phenomena. In turn, in terms of corrosion WC-(Co+Ni) is preferable over WC-Co, but in terms of dry wear both are equally recommendable.
3. In conceptual terms, the tribocorrosion, corrosion, and dry wear of these three cemented carbides occur similarly, but with varying severity depending on the binder composition

(i.e., severity decreasing with the partial replacement of Co with Ni and especially with Ni+Cr).

4. Even with these differences in performance, tribocorrosion in alkaline medium of these three cemented carbides is in any case mild, attesting as to why they are in such wide demand in industry. This is even more the case for dry-sliding wear, which is very mild.

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Figure Captions

Figure 1. FE-SEM micrographs of the cemented carbides of (A) WC-Co, (B) WC-(Co+Ni), and (C) WC-(Co+Ni+Cr).

Figure 2. XRD patterns of the cemented carbides of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr), as indicated. Peak assignments with the phase identification are included.

Figure 3. Friction curves (CoF vs sliding distance) of the cemented carbides of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) measured during the tribocorrosion tests in highly-alkaline wet medium (pH~13.65).

Figure 4. OM micrographs of the residual wear tracks at the conclusion of the tribocorrosion tests in highly-alkaline wet medium (pH~13.65) in the cemented carbides of (A) WC-Co, (B) WC-(Co+Ni), and (C) WC-(Co+Ni+Cr), as well as of (D) WC-Co at lower magnification.

Figure 5. Representative two-dimensional cross-sectional profiles (i.e., depth vs width) obtained by OP of the residual wear tracks at the conclusion of the tribocorrosion tests in highly-alkaline wet medium (pH~13.65) in the cemented carbides of WC-Co, WC-(Co+Ni), and (C) WC-(Co+Ni+Cr), as indicated. These profiles are corrected by their baselines to avoid an inaccurate calculation of the worn volumes.

Figure 6. FE-SEM micrographs of the residual wear track at the conclusion of the tribocorrosion tests in highly-alkaline wet medium (pH~13.65) in the cemented carbide of WC-Co, taken (A) at

low magnification, (B) outside in the vicinity of the worn surface, (C) at low magnification once gently cleaned, and (D)-(E)-(F) at different magnifications within the worn surface. The inset in (B) is a magnified image showing details.

Figure 7. FE-SEM micrographs of the residual wear track at the conclusion of the tribocorrosion tests in highly-alkaline wet medium (pH~13.65) in the cemented carbide of WC-(Co+Ni), taken (A) at low magnification, and (B)-(C) at different magnifications within the worn surface.

Figure 8. FE-SEM micrographs of the residual wear track at the conclusion of the tribocorrosion tests in highly-alkaline wet medium (pH~13.65) in the cemented carbide of WC-(Co+Ni+Cr), taken (A) at low magnification, and (B)-(C) at different magnifications within the worn surface. The arrows mark the wear track.

Figure 9. Optical photograph of the cemented carbides of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) taken both before and after the tribocorrosion tests in highly-alkaline wet medium (pH~13.65). The circle visible at the surface after the tribocorrosion tests is the corresponding residual wear track. The disks are 2 cm in diameter.

Figure 10. FE-SEM micrographs of the non-worn surface at the conclusion of the tribocorrosion tests in highly-alkaline wet medium (pH~13.65) in the cemented carbides of (A) WC-Co at the outermost surface, (B) WC-Co once gently cleaned, (C) WC-Co at the inner surface, (D) WC-(Co+Ni) at the outermost surface, and (E) WC-(Co+Ni+Cr) at the outermost surface. The inset in (C) is a magnified image showing details.

Figure 11. GI-XRD patterns taken at the conclusion of the tribocorrosion tests in highly-alkaline wet medium (pH~13.65) at the non-worn outermost surface of the cemented carbides of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr), as indicated. The GI-XRD pattern of the blank sample holder is also shown. Peak assignments with the phase identification are included.

Figure 12. Friction curves (CoF vs sliding distance) of the cemented carbides of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) measured during the dry tribological tests.

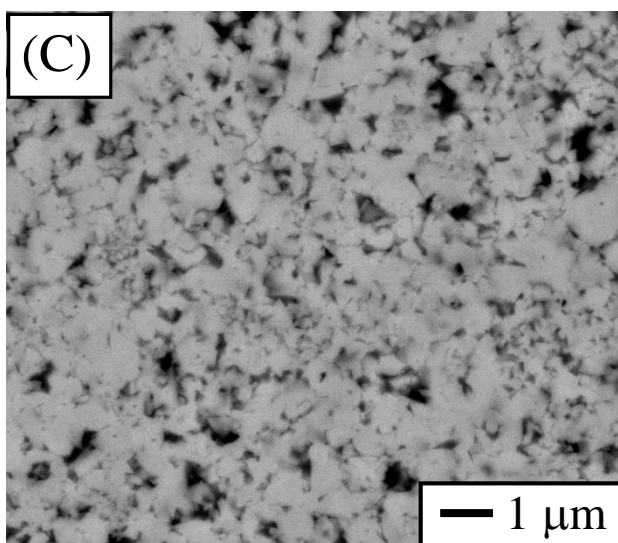
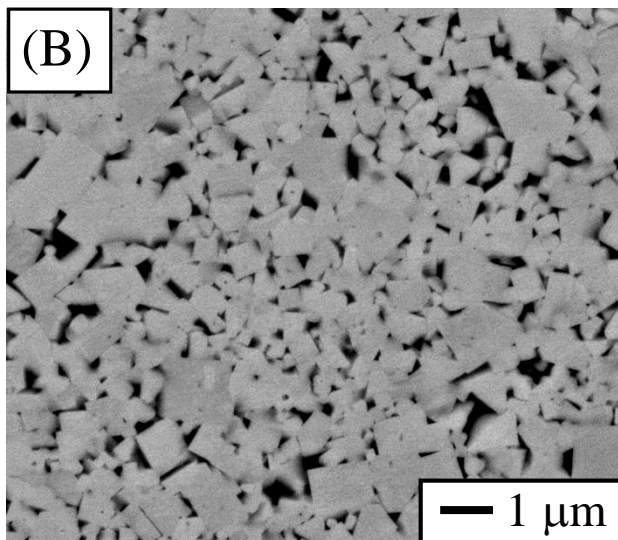
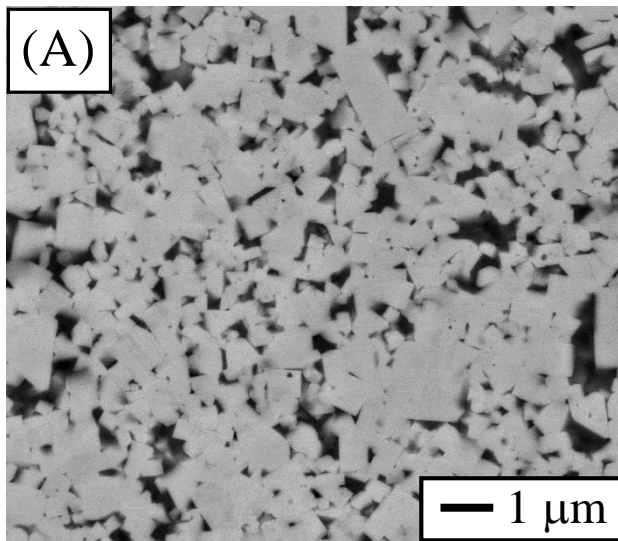
Figure 13. OM micrographs of the residual wear tracks at the conclusion of the dry tribological tests in the cemented carbides of (A) WC-Co, (B) WC-(Co+Ni), and (C) WC-(Co+Ni+Cr).

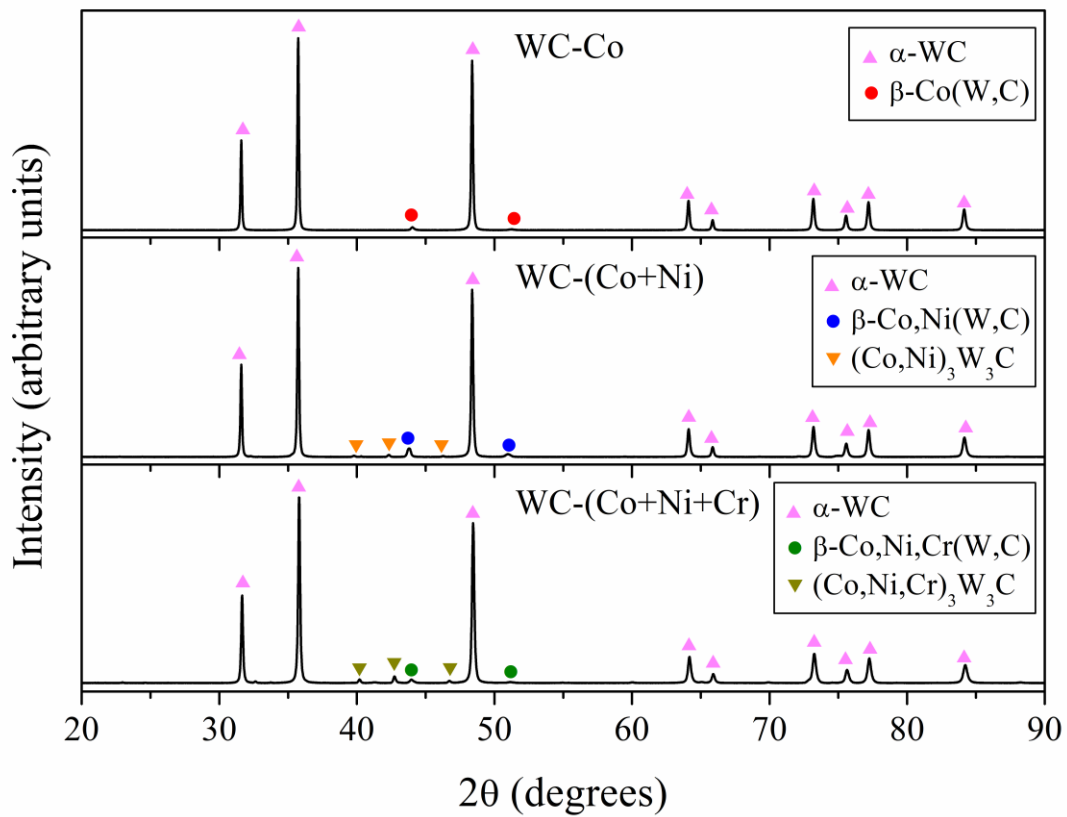
Figure 14. (A) Low-magnification FE-SEM micrograph of the residual wear tracks at the conclusion of the dry tribological tests in the cemented carbide of WC-Co, and (B) EDS spectra taken both outside (labeled as 1) and inside (labeled as 2) the worn surface, with the corresponding peak assignments included.

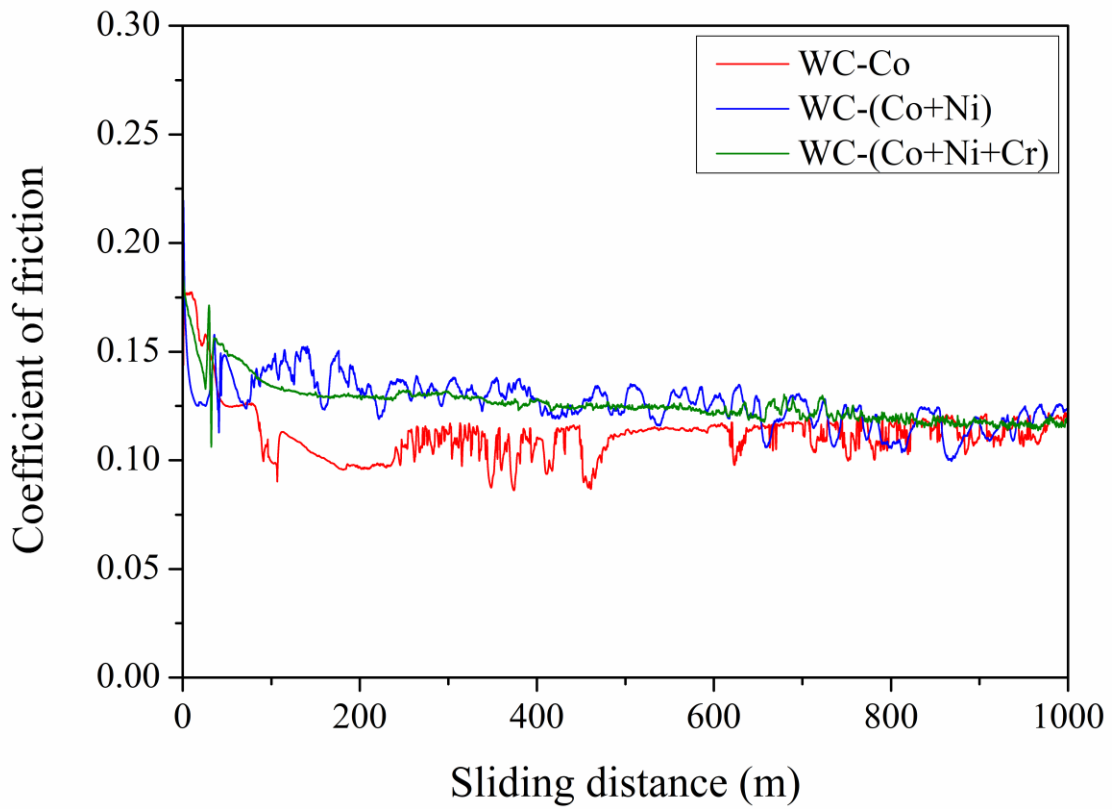
Figure 15. Representative two-dimensional cross-sectional profile (i.e., depth vs width) obtained by OP of the residual wear tracks at the conclusion of the dry tribological tests in the cemented carbides of WC-Co, WC-(Co+Ni), and (C) WC-(Co+Ni+Cr), as indicated. **These profiles are corrected by their baselines to avoid an inaccurate calculation of the worn volumes.**

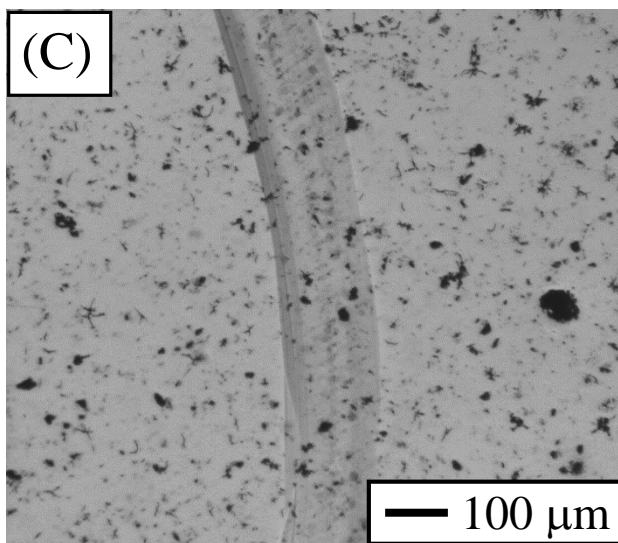
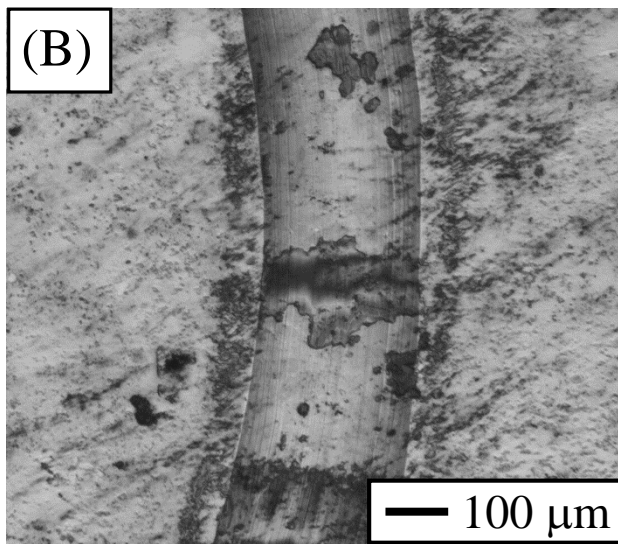
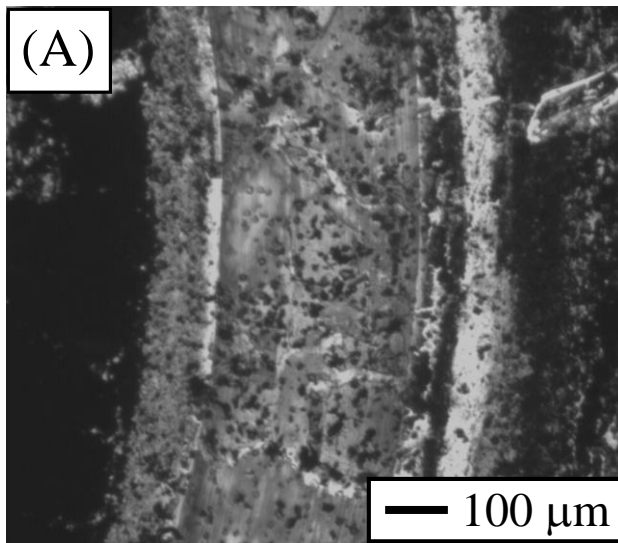
Figure 16. FE-SEM micrographs of the worn surface within the residual wear track at the conclusion of the dry tribological tests in the cemented carbides of (A) WC-Co, (B) WC-

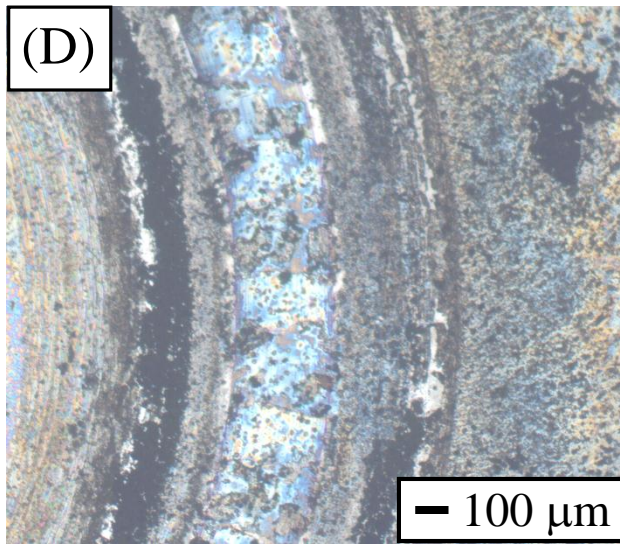
(Co+Ni), and (C) WC-(Co+Ni+Cr), as well as of (D) WC-(Co+Ni) at higher magnification.

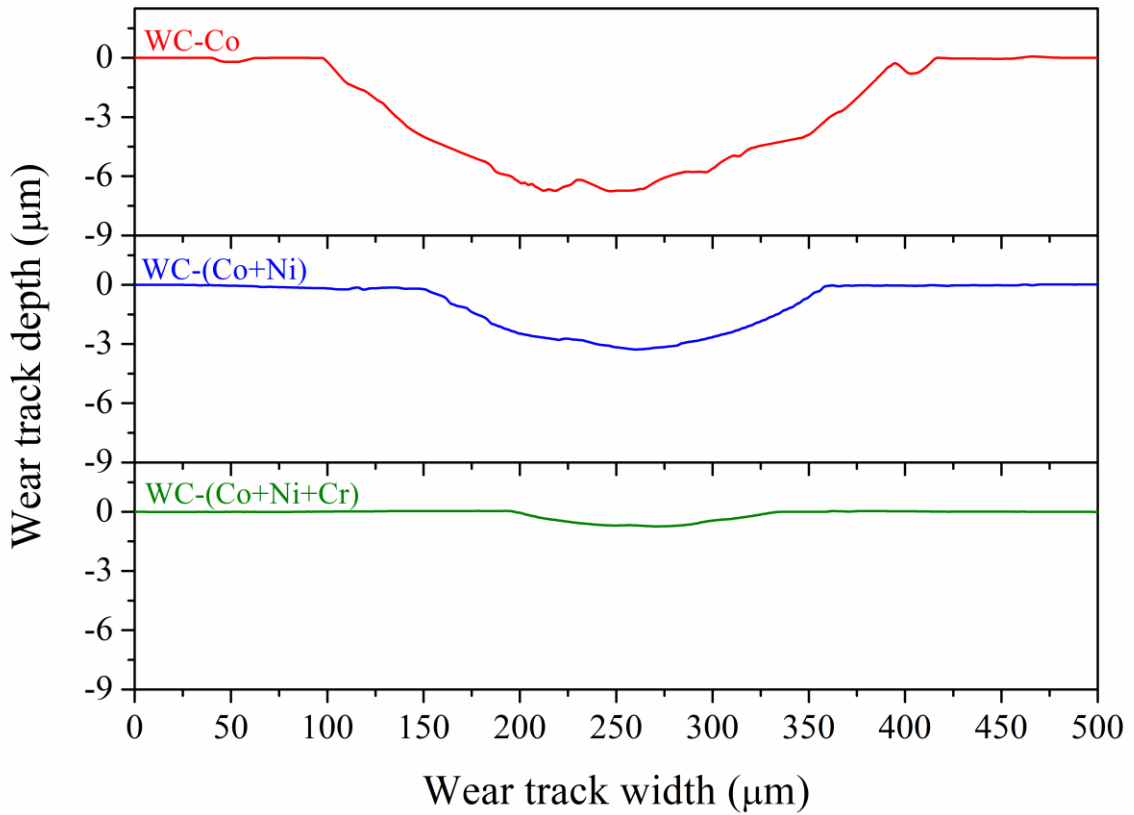


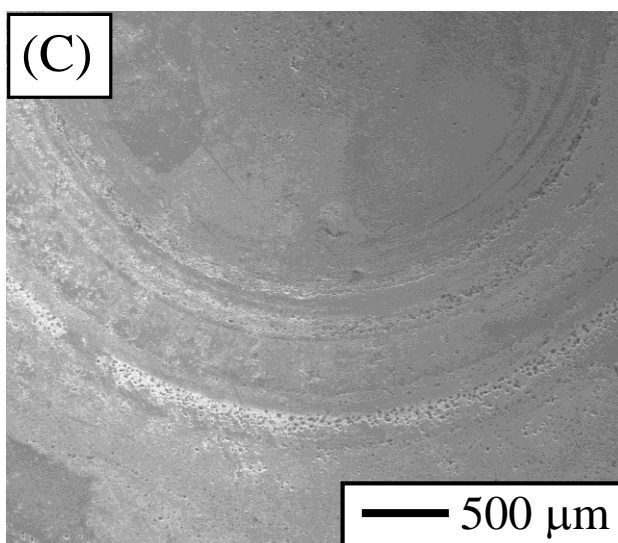
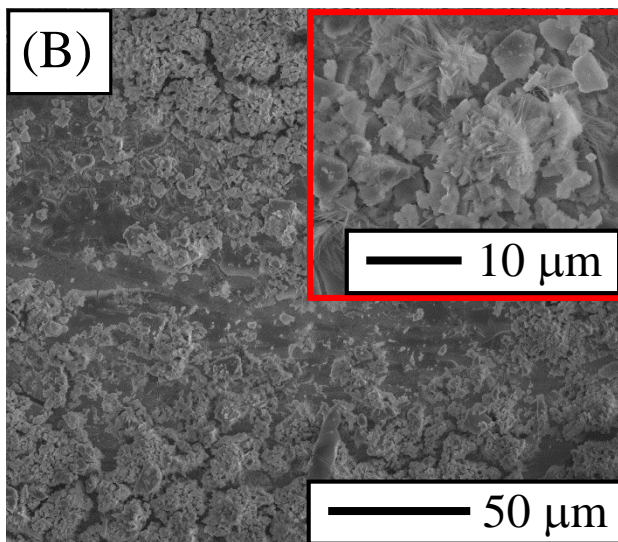
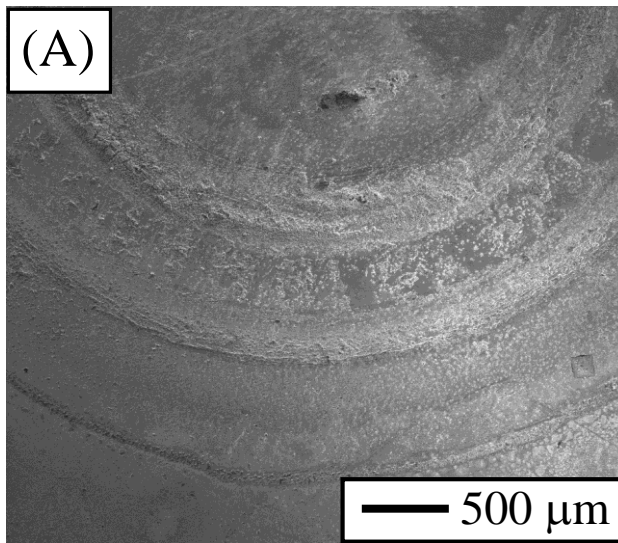


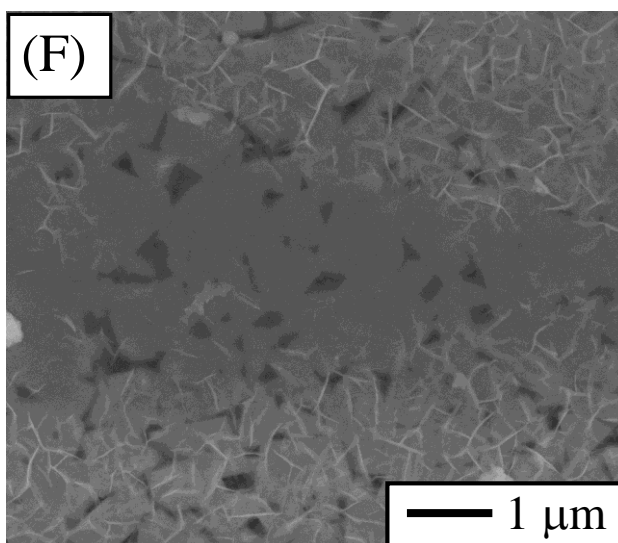
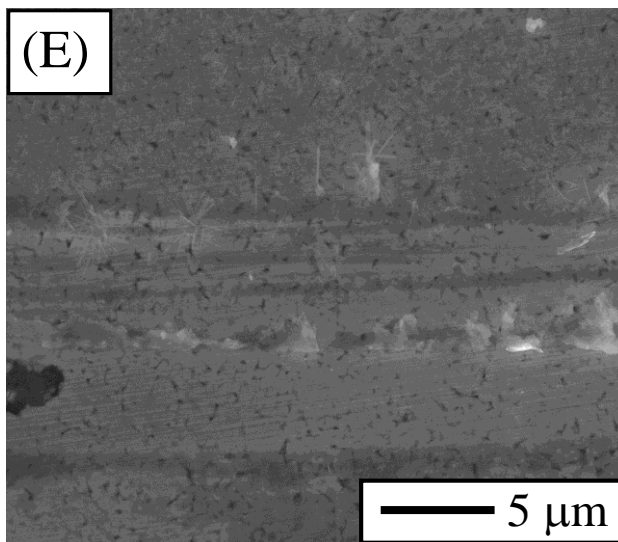
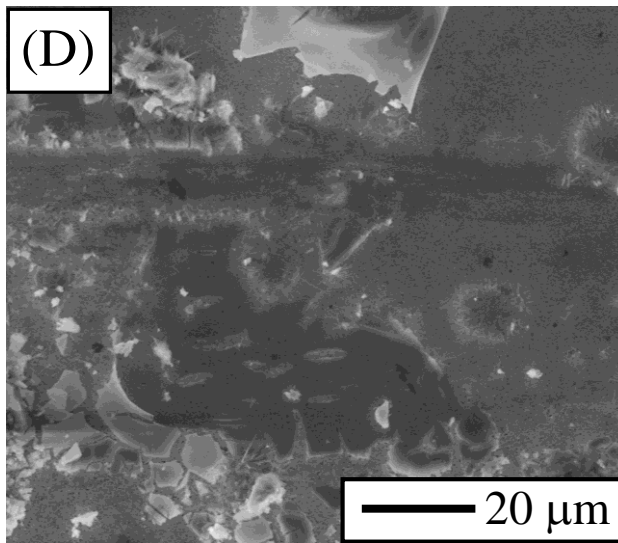


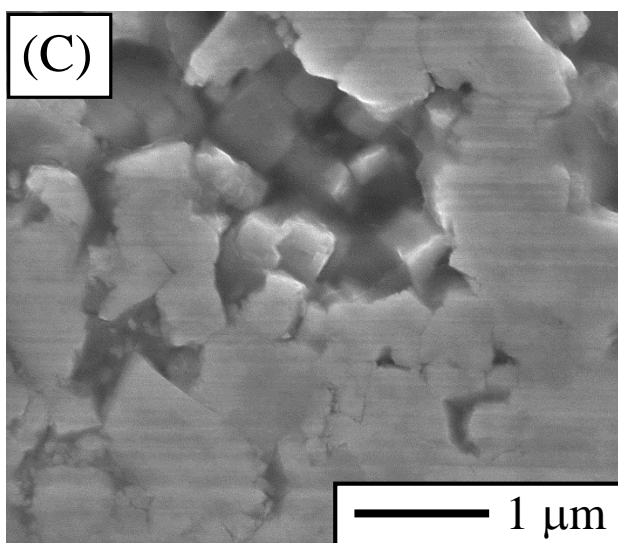
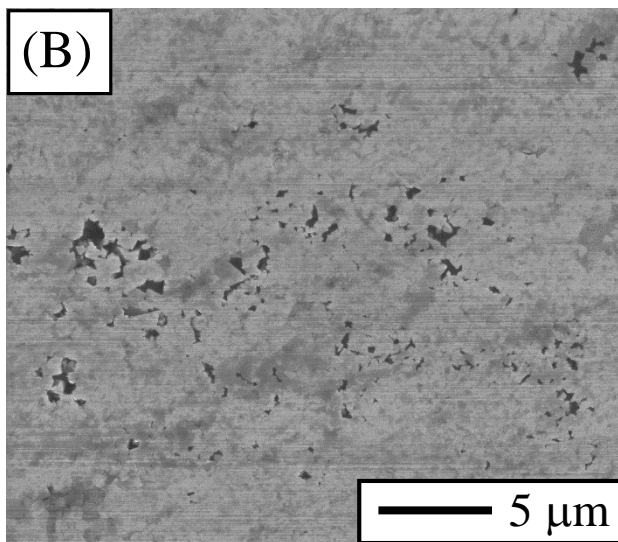
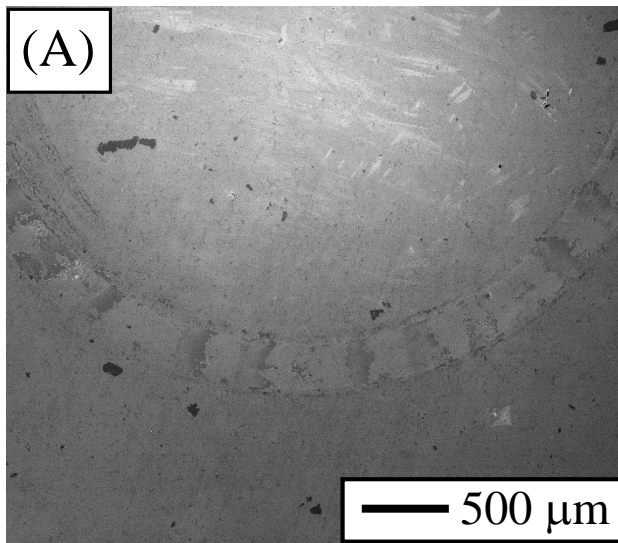


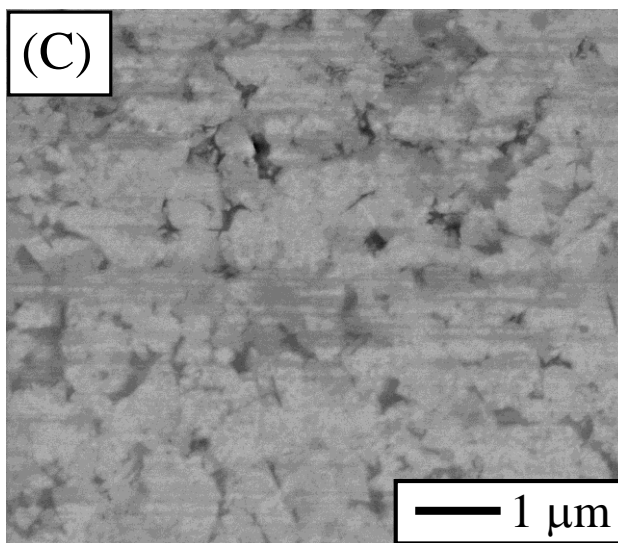
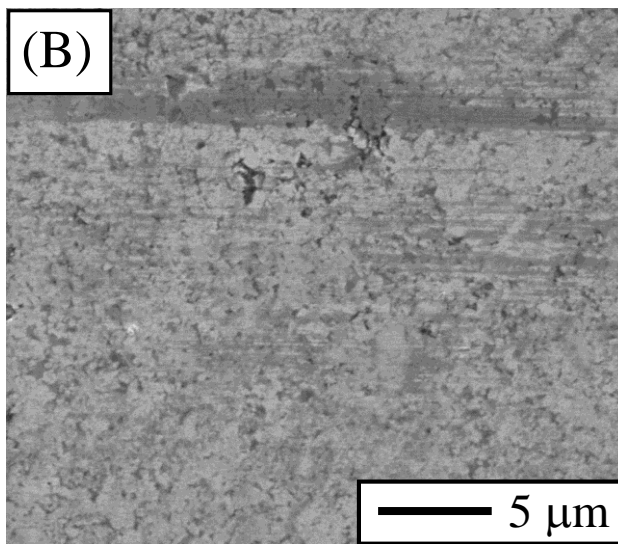
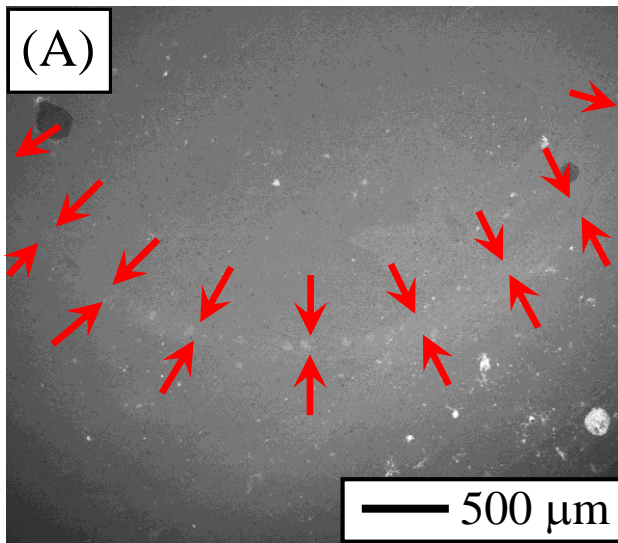




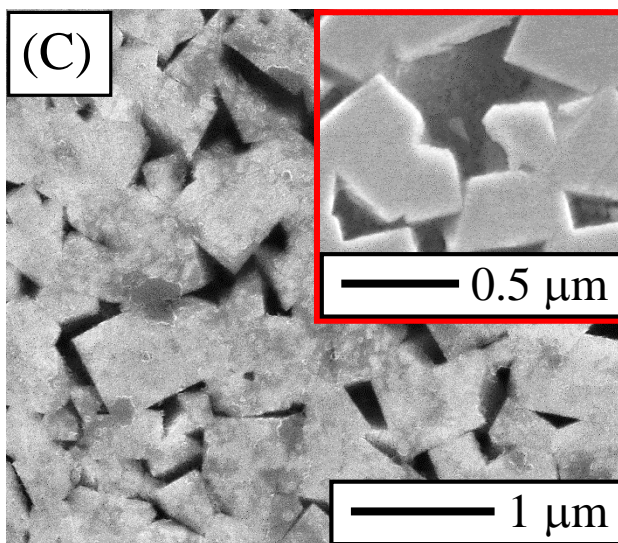
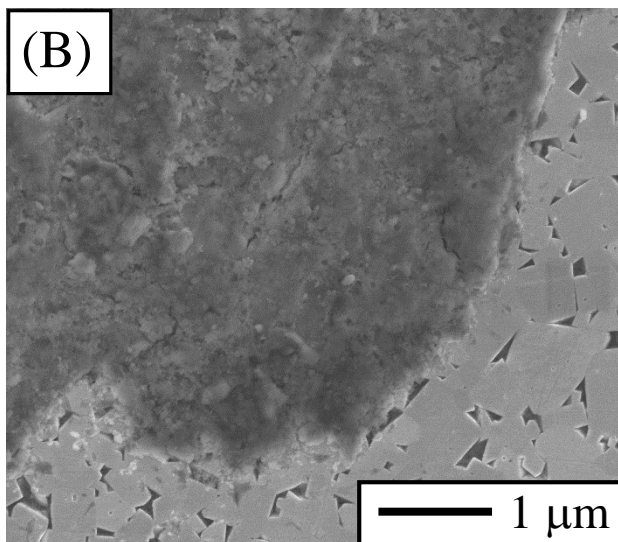
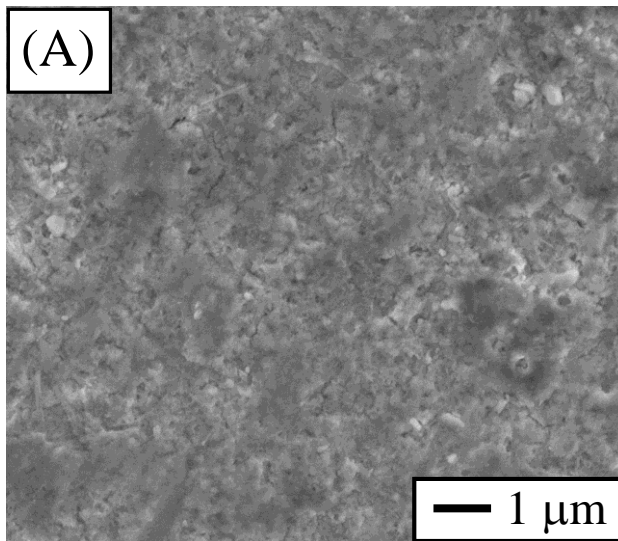


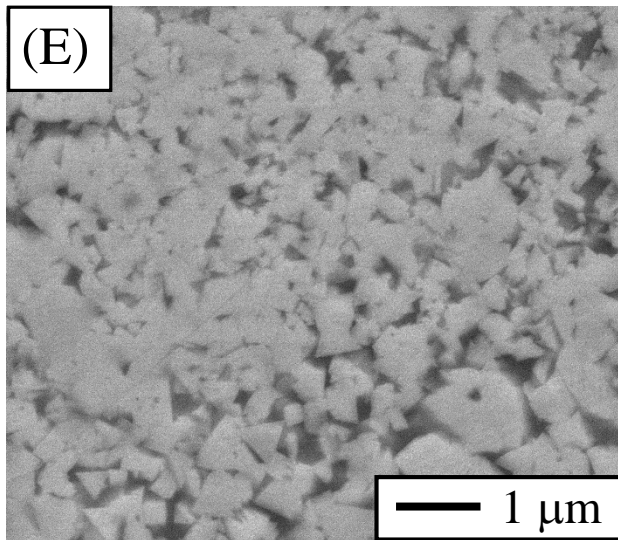
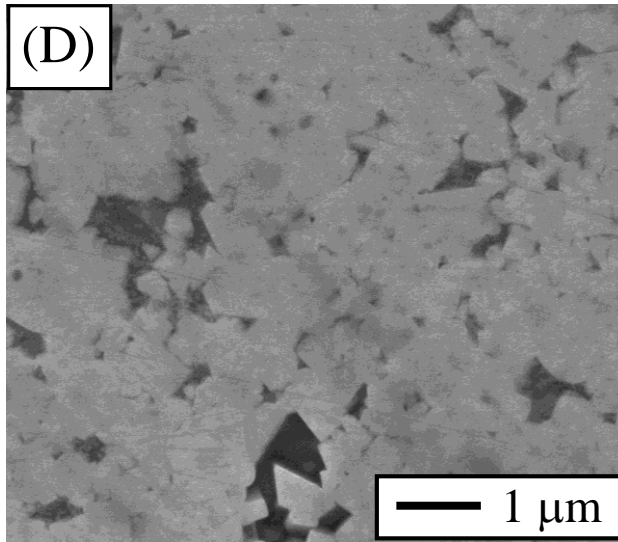


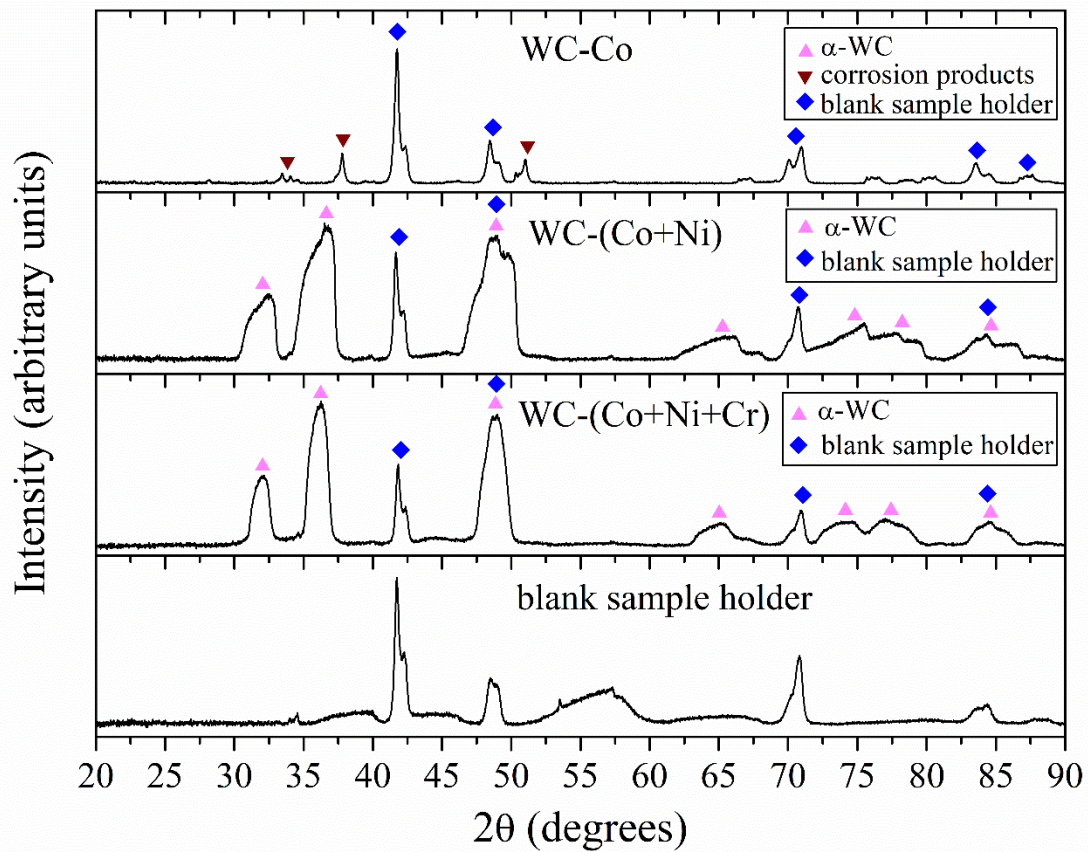


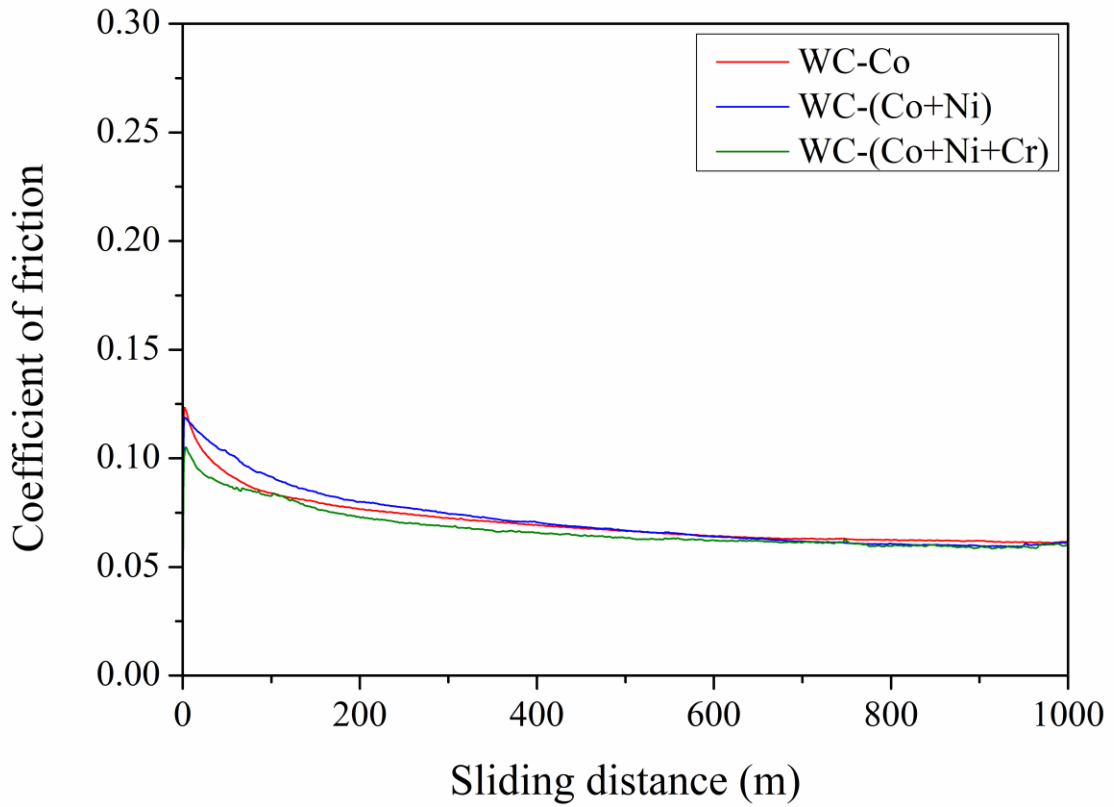


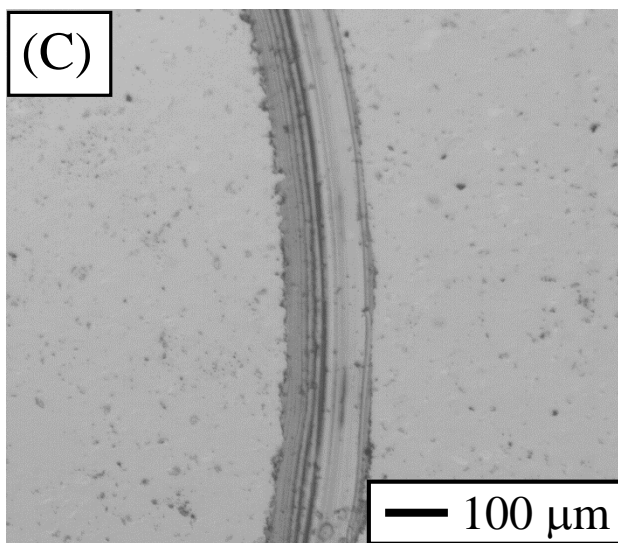
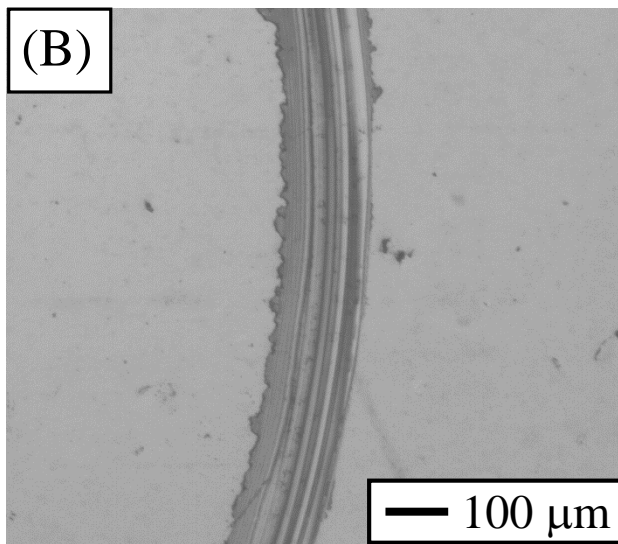
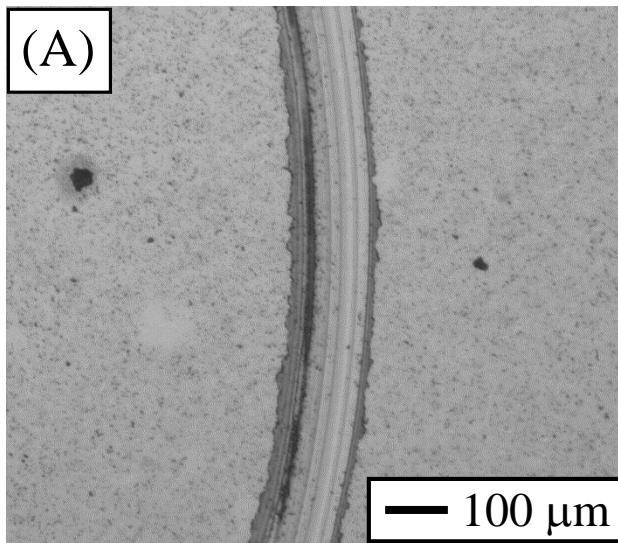


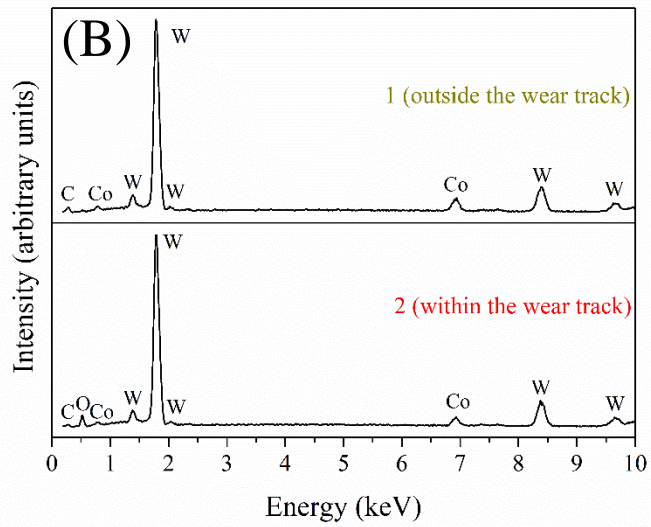
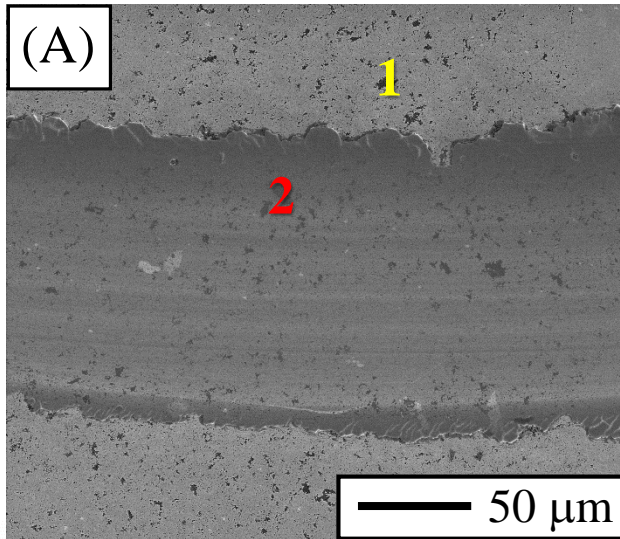


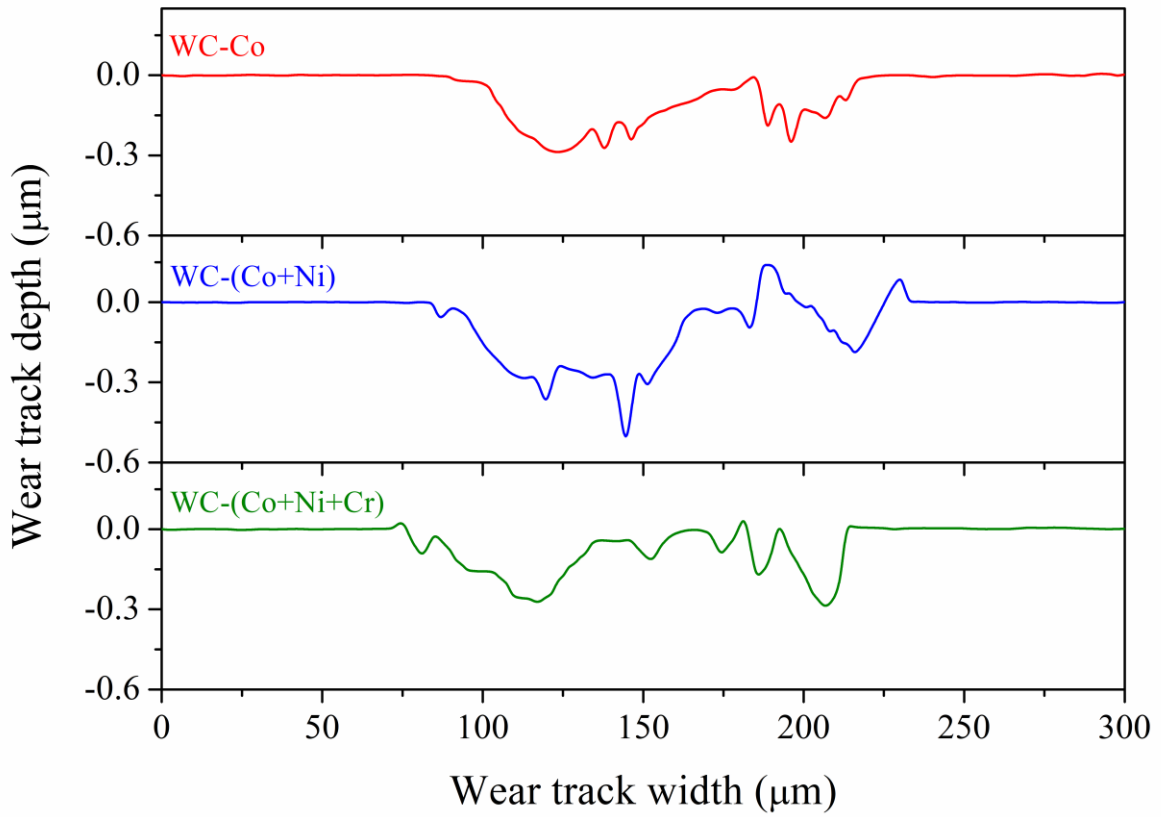


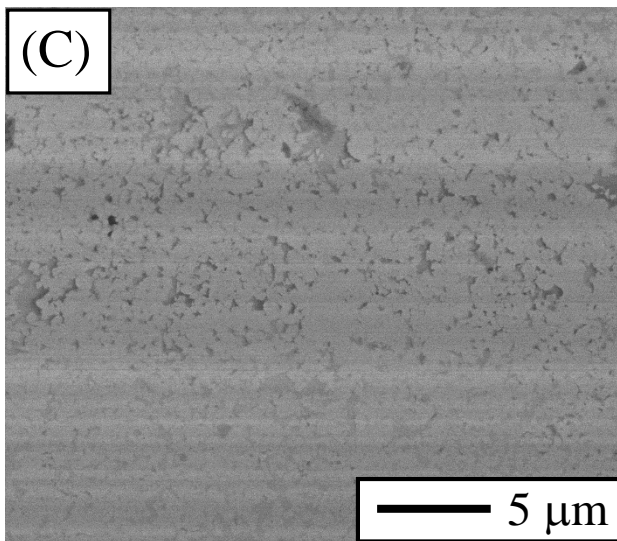
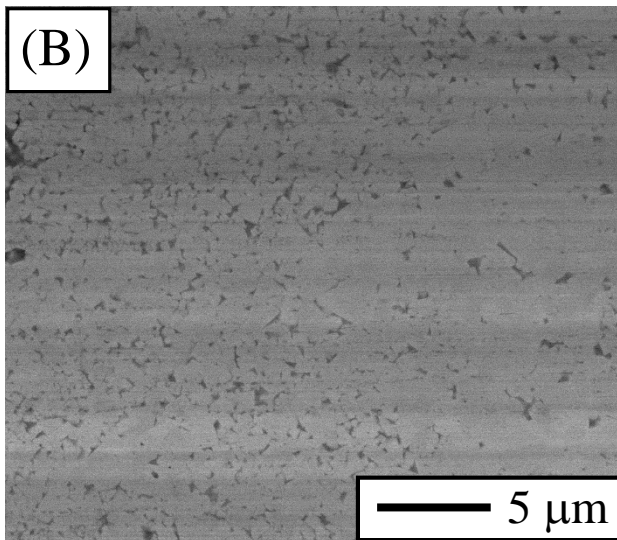
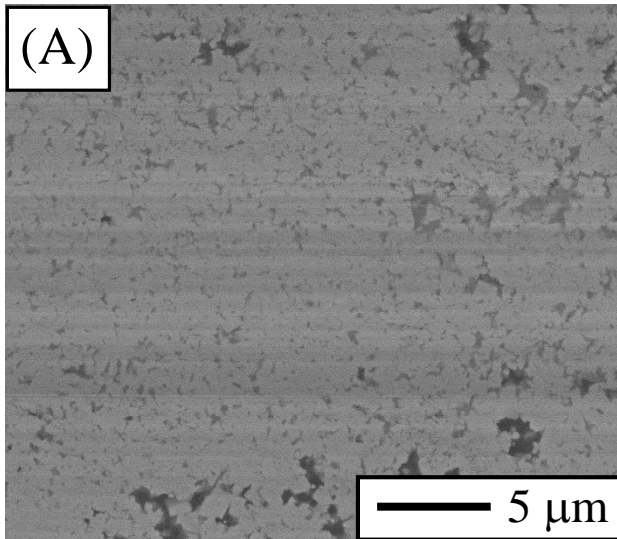


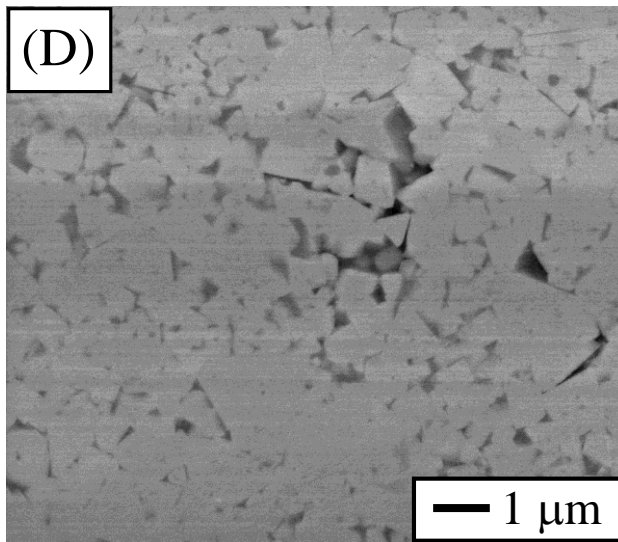












Aniss-Rabah Boukantar decided the research topic, discussed the research plan, collected relevant bibliography, performed most experiments, debated the results, and revised the manuscript. Boubekeur Djerdjare decided the research topic, discussed the research plan, and revised the manuscript. Fernando Guiberteau discussed the research plan, debated the results, and revised the manuscript. Angel L. Ortiz discussed the research plan, designed the study, assisted in some experiments, analysed the results, and wrote the manuscript.

- Tribocorrosion in highly-alkaline wet medium of WC-Co, WC-(Co+Ni), and WC-(Co+Ni+Cr) is evaluated and compared critically.
- WC-(Co+Ni+Cr) is shown to be the material of choice for tribological applications in alkaline media. In turn, WC-(Co+Ni) is preferable over WC-Co.
- WC-(Co+Ni+Cr) has greater resistance to both alkaline corrosion and dry wear than WC-(Co+Ni) and WC-Co. In turn, in terms of corrosion WC-(Co+Ni) is preferable over WC-Co, but in terms of dry wear both are equally recommendable.
- Conceptually, the tribocorrosion, corrosion, and dry wear of these cemented carbides occur similarly, but with varying severity depending on the binder composition.
- Tribocorrosion in alkaline medium of these materials is mild, attesting as to why they are in such wide demand in industry. Dry-sliding wear is indeed very mild.