Electrochemical and passivation behavior of a corrosion-resistant WC-Ni (W) cemented carbide in synthetic mine water

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1. Introduction

Cemented carbides are a family of powder metallurgical composite materials consisting of fine carbide grains in a metal binder phase. Due to their unique combination of high hardness and toughness, they are frequently used in systems working under severe tribological contact conditions, e.g., rock drilling, metal cutting, metal forming, etc. Traditionally, Co has been the most common metal binder in WC-based cemented carbides due to its excellent wettability and adhesion to WC. By adjusting the WC grain size and the Co content, the mechanical and tribological properties of the composite can be tailored to meet the requirements for specific applications and today cemented carbide has a unique position in the industry [1]. WC-Co cemented carbides are commonly used for rock drilling due to their high hardness, strength, toughness, and high wear resistance [2]. However, in applications such as rock drilling, the WC-Co cemented carbides are not only exposed to mechanical wear but also degradation caused by corrosion, i.e., selective removal of the Co binder, and tribo-corrosion, i.e., combined effects of mechanical wear and corrosion [2-5].

Further, due to the toxicity [6], health hazard concerns of Co [7], and the wish to improve the corrosion resistance of cemented carbides, research towards finding alternative binder metals/alloys is quite active. For example, Fe-Ni-Co alloy [8], Ni-Cr-Mo alloy [9], stainless steel grade 304 L [10], and multi-component Al0.5CrCoCuFeNi high entropy alloys [11], were successfully synthesized as binder alloys with better corrosion resistance than the conventional WC-Co. On the other hand, rather than binder alloys, pure metal binders of Fe and Ni are considered promising to replace Co due to their relatively low price, low toxicity, and good wettability with WC [12]. Mechanical and wear studies indicate the feasibility of using WC-Co and WC-Ni cemented carbides for rock drilling applications [12,13]. However, understanding the corrosion behavior of these cemented carbides in mine water conditions is important. In literature information about the corrosion behavior of WC-Co are available concerning the effect of binder fraction of Co [14], the effect of WC grain size [15], the presence of different carbides such as TiC [16], VC [17,18], Cr7C2 [18]. Further, the corrosion behavior of the
WC-Co with alternate composite binders was studied in various electrolytes, including H₂SO₄ [15,17–20], HCl [17,21], NaCl [18,22,23], NaOH [15,16,21,24], CaOH₂ [24], Na₂SO₄ [15], simulated mine water [3,4,22], simulated concrete [22], and simulated soil solutions [22]. In contrast to the relatively large number of corrosion studies of conventional WC-Co and alternate composite binders for WC-Co, very few studies focusing on the corrosion behavior of WC-Ni and WC-Fe grades can be found in the open literature [19,20].

Thus, this work aims to perform a systematic investigation on the microstructural, electrochemical, and passivation behavior of WC-20 vol.% Ni cemented carbide in synthetic mine water (SMW), aiming for application in rock drilling. For comparison, WC-20 vol.% Co cemented carbide was considered. Scanning electron microscopy and Auger electron spectroscopy were used to characterize the microstructural and elemental compositions of the cemented carbides. Electrochemical impedance spectroscopy, potentiodynamic polarisation, and potentiostatic polarization techniques are employed to investigate the effect of binders on the passivation and corrosion mechanisms of these grades. X-ray photoelectron spectroscopy was used to understand the passivation behavior of the WC-20 vol.% Ni.

2. Materials and methods

2.1. Materials

In this work, two plain WC-metal grade cemented carbides supplied by Sandvik Mining and Rock Technology, Sweden, were evaluated. The two grades have similar WC grain sizes but differ concerning the metal binder, i.e., Ni and Co, respectively. The nominal content of the binder phase and the WC grains of the cemented carbide samples were analyzed using Auger Electron Spectroscopy (AES). A PHI Quantera II XPS instrument was used for the angle-resolved X-ray Photoelectron spectroscopy (AR-XPS), to study the “passive condition” of the WC-20 vol% Ni sample, i.e., the sample exposed to SMW for 120 h of OCP. The instrument is equipped with a monochromatic aluminum X-ray beam, and the analysis spot size was approximately 100 μm in diameter. The detector was set to pass energy of 55 eV, time per step of 20 ms, and step size of 0.1 eV. To compensate for different atomic sensitivity factors and atomic concentration of the elements, the peaks were scanned 20, 10, 3, and 2 times respectively for C, O, Ni, and W. The analysis was run at six different take-off angles, from 15° to 90° in steps 15°. To compensate for the smaller analysis volume, the two lowest angles i.e., 15° and 30°, were measured 4 and 2 times, respectively.

3. Results and discussion

3.1. Microstructural and compositional analysis of cemented carbides

Fig. 1a and 1b show the EBSP orientation maps for the WC-20 vol% Ni and WC-20 vol% Co cemented carbides, respectively. The legend in the EBSP maps shows the inverse pole figure coloring and the colors represent the crystallographic orientation of the WC grains. The grain size analysis from the EBSP data confirmed that the average WC grain sizes are 1.1 and 0.9 μm, respectively for the WC-Ni and WC-Co grades. Fig. 2a and 2b are the microstructure of the WC-Ni and WC-Co samples, respectively. In both images, the WC grains and binder phases are observed as light grey and dark grey in contrast, respectively. AES point analysis (marked in Fig. 2a and 2b) were carried out on the WC grains and the binder phases and the obtained differentiated AES spectra are shown in Fig. 2c. For the as-polished condition, i.e., without any sputter cleaning of the surface, see spectrum (i) in Fig. 2c, an O peak was observed both in the WC phase and the metal binder phase (not shown). In general, the presence of an O peak shall be attributed to the air-formed native oxide film on the cemented carbide samples. However, to accurately estimate the composition of the WC and metal binder phases, it is important to remove the native oxide film, and thus Ar⁺ ion sputtering was carried out. After sputtering for 0.2 min, the O peak was not observed in the WC grains and nor in the Ni-, Co-binder phases (see
spectra (ii)-(iv) of Fig. 2 c). Even after sputtering, it is interesting to note the presence of W and C peaks along with the Ni and the Co peak, in the two spectra obtained from the binder phases, respectively. Fig. 3 a shows the C, W, Ni, and Co Auger peaks obtained (after sputtering) from the WC grains and the binder phases. For the WC grains, the C KLL Auger peaks revealed carbidic carbon peaks, indicating the binding of C with W \[26, 27\]. However, for Ni and Co binder phases, the carbidic carbon peak pattern was not observed, indicating the presence of C in a carbonaceous form probably due to contamination \[26, 27\]. Further, the intensity of the C KLL peak in the binder phases is negligible and thus it was not included in the compositional analysis of the binder phases. Previous studies by atom probe analysis also have confirmed that the binder phases of commercial (80WC-20Co wt%) cemented carbide has a carbon concentration <0.1 at. % \[28\] or free from carbon \[29\]. For binder phases and the WC grains, the W MNN Auger peaks ~1741 eV are consistent \[26\]. The Ni LMM (~852 eV) and Co LMM (~779 eV) peaks are corresponding to the metallic state of the respective binder phases \[26\]. For both grades, the WC phase shows the expected stoichiometric ratio of 50:50 for W:C already after a short sputtering time of 0.1 min (see Fig. 3b). Similarly, the compositions of Ni binder (Ni, W), and Co binder (Co, W), were quite constant after the sputtering time of 0.1 min (see Fig. 3b). Thus, the average composition of the binder phases is 79Ni-21 W (at. %) and 90Co-10 W (at. %), respectively for the WC-20 vol% Ni and WC-20 vol% samples. These AES results have confirmed that the binder phases of the studied cemented carbides are not pure metals but rather alloys of Ni—W and Co-W; hereafter referred to as Ni (W) and Co(W). For different WC-Co-based cemented carbides and cermetts, the presence of W in the binder phase was confirmed by atom probe \[28, 29\] and wavelength-dispersive electron-probe microanalysis techniques \[30\]. Similarly, for three different WC-Ni-based cemented carbides (WC-20 wt% Ni, WC-20 wt% Ni15Cr, and WC-20 wt% Ni11Cr6Mo), the presence of W in the binder phase was confirmed by energy dispersive X-ray spectroscopy technique and supported by thermodynamic computation \[31\]. The amount of solubility of W in the binder phase and its final composition depends on the initial elements of the binder (Co and Ni), initial carbon activity, binder thickness (mean free path), and cooling rate after sintering \[31, 32\]. The significantly higher concentration of W in the Ni binder, as compared with the Co binder, is in line with the experimental and computational studies related to cemented carbides \[31, 32\].

3.2. EIS analysis of the WC-Ni(W) and WC-Co(W) cemented carbides at OCP conditions

The OCP versus time behavior of the WC-Ni(W), and WC-Co(W), cemented carbides in SMW are shown in Fig. 4. For the WC-Ni(W), the initial OCP value was ~0.126 V which decreased to lower values for a short time but quickly increased to a final value of ~0.064 V. For the WC-Co(W), the OCP trend and the final OCP value (~0.399 V) indicate a more active behavior. It is also reported that the Co-containing binders exhibited active OCP values and dissolution behavior when compared to the Ni-containing binders, in different electrolytes such as H2SO4 \[20\], NaCl \[23\], and simulated mine water \[4\]. The enhancement of OCP indicates the passive behavior of the tested WC-Ni (W) in SMW.

EIS studies were carried out in detail to understand the passivation and corrosion behavior of cemented carbides at the OCP condition. The EIS data of the WC-Ni(W) sample is shown as a Nyquist plot (Fig. 5a) that revealed a single, incomplete, depressed semi-circle representing a capacitance loop. To analyze and fit the EIS data of WC-Ni(W), two
Fig. 3. AES analysis of cemented carbide samples (a) C KLL, W MNN, Ni LMM and Co LMM Augers peaks (b) Atomic concentration of WC grain and binder phases.
electrochemical equivalent circuit models as shown in Figs. 5b and 5c are considered. Model-1 is a simple \([R_S(QR)]\) circuit and model-2 is a \([R_S(Q[RW])]\) circuit. In these circuits, \(R_S\) is the solution resistance; \(Q\) is the constant phase element, \(R\) is the resistance and \(W\) is Warburg impedance. Circuit elements between () are in parallel, and circuit elements between [] are in series. The impedance of \(Q\) and \(W\) is given in eqs. (1) and (2).

\[
Z_Q = Y_0^{-1}(j\omega)^{-n}
\]

(1)

\[
Z_W = Y_0^{-1}(j\omega)^{-0.5}
\]

(2)

where, \(Y_0\) is a constant having a unit \(\Omega^{-1}s^n\) for \(Q\) and \(\Omega^{-1}s^{0.5}\) for \(W\), \(n\) is the power of \(Q\), \(\omega\) is the angular frequency, and the \(j\) is the imaginary number equal to \(\sqrt{-1}\). \(Q\) was used to obtain a better fit for the experimental data, and it could be treated as capacitance, resistance, and inductance when \(n = 1, n = 0,\) and \(n = -1,\) respectively. The fitted values of \(R_S, R, n,\) and \(Y_0\) values were shown in Table 1. From the % error of the fit parameters and the \(\chi^2\) value, it is evident that model 2 has resulted in a better fitting, see Table 1. The key process involved in the EIS studies is the charge transfer at the electrode-electrolyte interface which is related to the surface film property of the samples in the electrolyte [33]. For both the models, the \(n\) value is about 0.856–0.868, which indicates the electrode-electrolyte interface is not an ideal capacitor and thus the choice of \(Q\) is better than \(C\) for the EIS fitting. Model-1 \([R_S(QR)]\) estimates the polarization resistance, \(R_p\), and model-2 \([R_S(Q[RW])]\) estimates the charge transfer resistance, \(R_{ct}\), as shown in equations using (3) and (4).

\[
R_p = R
\]

(3)

\[
R_{ct} = R
\]

(4)

For simple reactions, either \(R_p\) or \(R_{ct}\) can be modeled by single resistance and result in a similar value which is quite often used interchangeably for high corrosion-resistant materials. The high \(R_p\) and \(R_{ct}\) values, see Table 1, indicated that the passive film formed on the WC-Ni(W) exhibits high stability in the SMW. The stability of the passive film is attributed to less charge transfer and their accumulation across the film-solution interface [33]. Further, the stability of the passive film formed on the WC-Ni(W) sample is studied for prolonged exposure periods of 1, 4, 8, 24, 72, and 120 h, and the EIS data was fitted using model-2, see Fig. 6a. The fitting parameters obtained using model-2 are shown in Table 2. Though the WC-Ni(W) sample was exposed for 120 h, the OCP values did not change significantly, however slightly ennobled, see Table 2. From the results, it is evident that for all the exposure periods the \(R_S\) value is in the range of 10.5–11.2 \(\Omega\) cm\(^2\) which is several orders lower than the \(R_{ct}\) values. Similarly, the EIS data for the different exposure periods were also fitted using model-1 (not shown). However, the obtained \(R_p\) (model-1) and \(R_{ct}\) (model-2) values are shown in Fig. 6b, which indicates that the resistance values increase as the exposure time.
On the other hand, the EIS data for WC-Co(W) in SMW at OCP for 1 and 24 h, has two incomplete semi-circles, and it is fitted by model-3 $[R_s(Q(R_1(CR_2)))]$, see Fig. 7. For complex reactions, $R_p$ and $R_{ct}$ are not the same. In such case, the $R_p$ is the limit of the faradaic impedance ($Z_F$) at low frequency, i.e., $\lim_{\omega \to \infty} Z_F$ and $R_{ct}$ is the limit of the faradaic impedance at high frequencies, i.e., $\lim_{\omega \to 0} Z_F$ which is explained elsewhere by Harington et al. [34]. For the WC-Co(W), this is the definition employed and the $R_p$ and $R_{ct}$ values are estimated using eqs. (5) and (6), and the corresponding values are given in Table 3.

$$R_p = R_1 + R_2$$  \hspace{1cm} (5)

$$R_{ct} = R_1$$  \hspace{1cm} (6)

As the exposure time is increased from 1 to 24 h, the $R_p$ and $R_{ct}$ values for the WC-Co(W) samples have decreased considerably, see Table 3. Further, the obtained $R_p$ and $R_{ct}$ values for the WC-Co(W) are several orders lower indicating its poor corrosion resistance in comparison to the $R_p$ and $R_{ct}$ values for the WC-Ni(W), see Tables 1-3. The obtained Q-Y and C values for the WC-Co(W) are higher when compared to the WC-Ni(W). The main reaction is the dissolution of the Co(W) binder phase. Pure metal dissolution is itself a complex process that shall undergo intermediate steps [35]. Certainly, the dissolution of Co(W) alloy proceeds via intermediates, and this can give rise to capacitor or inductor behaviors during EIS studies [15,21,35]. Thus, C is required to model the obtained WC-Co(W) EIS data, without C, it would be difficult to fit. Normally, the C value corresponding to dissolution as

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**Table 1**

EIS parameters for WC-Ni(W) cemented carbide exposed to synthetic mine water for 1 h. Models 1 and 2 are used for fitting and the values in the parentheses give the % error of the fit parameters. $\chi^2$ values indicate the better fit of the chosen model.

<table>
<thead>
<tr>
<th>Sample Condition: WC-Ni(W)</th>
<th>$R_s$</th>
<th>$R$</th>
<th>n</th>
<th>(Q) $Y_0$</th>
<th>(W) $Y_0$</th>
<th>$R_p - R$</th>
<th>$R_{ct} - R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCP-1 h</td>
<td></td>
<td></td>
<td></td>
<td>$\mu\Omega^{-1} \cdot \text{cm}^{-2}$</td>
<td>$\mu\Omega^{-1} \cdot \text{cm}^{-2}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model:1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi^2 0.24$</td>
<td>11.0</td>
<td>57,641</td>
<td>0.856</td>
<td>175.4</td>
<td>–</td>
<td>57,641</td>
<td>–</td>
</tr>
<tr>
<td>Model:2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi^2 0.15$</td>
<td>11.1</td>
<td>39,033</td>
<td>0.868</td>
<td>164.4</td>
<td>175.1</td>
<td>–</td>
<td>39,033</td>
</tr>
</tbody>
</table>

**Table 2**

EIS parameters for WC-Ni(W) cemented carbide exposed to synthetic mine water for different periods. Model 2 was used for fitting and the % error of the fit parameter “n” is <1% and for $R_s$, $R$, $Q$, and $W$ are in the range of 1 to 5%.

<table>
<thead>
<tr>
<th>Exposure period</th>
<th>OCP</th>
<th>$R_s$</th>
<th>$R_{ct} - R$</th>
<th>n</th>
<th>(Q) $Y_0$</th>
<th>(W) $Y_0$</th>
<th>C $\mu\text{F/cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>h</td>
<td>V</td>
<td>$\Omega^{-1} \cdot \text{cm}^2$</td>
<td>$\Omega^{-1} \cdot \text{cm}^2$</td>
<td></td>
<td>$\mu\Omega^{-1} \cdot \text{cm}^{-2}$</td>
<td>$\mu\Omega^{-1} \cdot \text{cm}^{-2}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-0.064</td>
<td>11.0</td>
<td>39,033</td>
<td>0.868</td>
<td>164.4</td>
<td>169.7</td>
<td>63.0</td>
</tr>
<tr>
<td>4</td>
<td>0.009</td>
<td>11.1</td>
<td>40,662</td>
<td>0.872</td>
<td>157.2</td>
<td>127.4</td>
<td>61.9</td>
</tr>
<tr>
<td>8</td>
<td>0.014</td>
<td>11.2</td>
<td>45,809</td>
<td>0.876</td>
<td>151.8</td>
<td>109.1</td>
<td>61.5</td>
</tr>
<tr>
<td>24</td>
<td>0.024</td>
<td>11.0</td>
<td>61,526</td>
<td>0.880</td>
<td>148.9</td>
<td>109.5</td>
<td>62.3</td>
</tr>
<tr>
<td>72</td>
<td>0.032</td>
<td>10.8</td>
<td>91,595</td>
<td>0.886</td>
<td>150.3</td>
<td>141.9</td>
<td>65.8</td>
</tr>
<tr>
<td>120</td>
<td>0.035</td>
<td>10.5</td>
<td>96,829</td>
<td>0.887</td>
<td>151.0</td>
<td>147.9</td>
<td>66.4</td>
</tr>
</tbody>
</table>

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Fig. 6. a) Nyquist plot of WC-Ni(W) when exposed to synthetic mine water for a different period; b) Evolution of $R_p$, $R_{ct}$, and C values for different periods obtained by fitting using model-1 and model-2, refer to the circuit model in Fig. 5.
Table 3

<table>
<thead>
<tr>
<th>Exposure period</th>
<th>OCP</th>
<th>R_4</th>
<th>R_1</th>
<th>R_2</th>
<th>(Q)</th>
<th>n</th>
<th>C</th>
<th>R_p = R_1 + R_2</th>
<th>R_1 = R_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>h</td>
<td>V</td>
<td>Ωcm^2</td>
<td>Ωcm^2</td>
<td>Ωcm^2</td>
<td>µΩ·cm^2·s^n</td>
<td>mF/cm^2</td>
<td>Ωcm^2</td>
<td>Ωcm^2</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-0.399</td>
<td>11.5</td>
<td>505</td>
<td>322</td>
<td>237</td>
<td>0.855</td>
<td>18.9</td>
<td>827</td>
<td>505</td>
</tr>
<tr>
<td>24</td>
<td>-0.413</td>
<td>8.9</td>
<td>369</td>
<td>159</td>
<td>397</td>
<td>0.785</td>
<td>49.6</td>
<td>528</td>
<td>369</td>
</tr>
</tbody>
</table>
(W), indicates a passive-like behavior in SMW. Further to confirm the passivation behavior of WC-Ni(W), potentiostatic polarization was performed.

The potentiostatic polarization curves of both the cemented carbides are shown in Fig. 9a, and 9b as semi-log and double-log plots, respectively. For the WC-Ni(W), at the initial time, the current value was relatively higher and decreased to a constant value, see Fig. 9a, which corresponds to passivation. For the WC-Co-based cemented carbides during the potentiostatic polarization, several authors have reported the current decay behavior in linear plots or semi-log plots and correlated to passivation [16,17,24]. In this study, for the WC-Co(W) sample, current decay behavior was not observed, rather the current value is high and further increased to higher values, and reached a constant steady-state value, see Fig. 9a. Moreover, the total charge density, q, during the potentiostatic polarization corresponds to the area under the curve of the semi-log plot. The calculated q value for the WC-Ni(W) is several orders lower than the WC-Co(W), see Table 4. The obtained q values and the current transient behavior discussed above clearly indicated that the WC-Ni(W) and WC-Co(W) exhibit passivation and corrosion behavior, respectively.

Under potentiostatic conditions, the current density (i), and time (t) are described as 
\[ i \propto t^m \]
and if plotted as a double logarithmic plot, the power of t is obtained from the slope, m, which helps in identifying the dominating layer growth processes [43,44]. For m = 1 high field mechanism, m = 0.5 diffusion-related, m ≥ 0 corrosion-related processes were discussed elsewhere [43,44]. For m = −1, typically for valve metals, the anodic oxide film is by the high field mechanism this means that both the anion and cation transport within the oxide depends strongly on the field strength. Thus, for a constant polarization time, the oxide film thickness on valve metal increases linearly with increasing electrode potentials. Apart from valve metals and other pure metals [43,44], the slope values obtained from potentiostatic tests were used to describe the oxide layer growth mechanism for different materials like

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_{corr} ) (vs.Ag/AgCl) (V)</th>
<th>( i_{corr} ) (µA/cm²)</th>
<th>q (C/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-Ni(W)</td>
<td>−0.063 ± 0.004</td>
<td>0.57 ± 0.05</td>
<td>0.006 ± 0.001</td>
</tr>
<tr>
<td>WC-Co(W)</td>
<td>−0.399 ± 0.005</td>
<td>78.1 ± 2</td>
<td>2.8 ± 0.1</td>
</tr>
</tbody>
</table>

Fig. 8. Potentiodynamic polarization behavior of WC-Ni(W), and WC-Co(W) cemented carbide samples in synthetic mine water; a) semi-log plot; b) linear plot.

Fig. 9. Potentiostatic polarization curves for WC-Ni(W), and WC-Co(W) cemented carbide samples in synthetic mine water; a) semi-log plot of current density–time; b) log-log plot of current density–time. A potential of +0.2 V vs. OCP, was applied for 1 h.
commercial Ni-Cr-Mo alloys [45], novel Zr/Ti-based nano-structured dendrite composites [46], and Ni-, Mg-based amorphous alloys [47, 48]. On the other hand, no effort was made to obtain the slope value and interpret the potentiostatic results of cemented carbides as a log(i)-log(t) plot [16, 17, 24]. From Fig. 9b, for the WC-Co(W), the slope of the current transient, \( m \geq 0 \), implies the corrosion process, and for the WC-Ni(W), \( m = -0.5 \), indicating the formation of the passive film could be associated with the diffusion-controlled process [44]. This indicates that for the WC-Ni(W) sample, at the applied lower anodic potential the growth of oxide film is mainly due to the migration or diffusion of oxide ions through the film. Also, the thickness of the passive film would mainly be dependent on the polarization time and not the electrode potential. Further, regarding anodic oxide growth, this result has confirmed that the studied WC-Ni(W) composites do not behave like valve metal.

3.4. SEM analysis of the WC-Ni(W) and WC-Co(W) cemented carbides after the electrochemical studies

SEM analysis of the WC-Ni(W) samples before and after the electrochemical studies are shown in Fig. 10. The as-polished microstructure (Figs. 10a, and 10b) shows the WC grains and the Ni(W) binder pockets. SEM analysis of the WC-Ni(W) after the EIS, i.e., after exposure to SMW for 120 h at OCP (Fig. 10a’), and potentiostatic polarization (Fig. 10b’) confirmed that the samples show no significant changes in microstructure. The SEM results corroborated the high \( R_p \) and \( R_{ct} \) from the EIS fitting (Fig. 6, Table 2) and the low charge density value (Table 4) from the potentiostatic polarization. These SEM results confirm the high corrosion resistance of WC-Ni(W) at these conditions, and it could be due to the formation of a protective passive film.

On the other hand, the potentiodynamically polarized WC-Ni(W) up to 1.0 V vs. Ag/AgCl, exhibited a corroded morphology, in comparison to the as-polished condition, see Fig. 11a and 11a’. After the corrosion study, the binder phase appears smoother (see green color arrows in Fig. 11a’), i.e., the polishing scratches in the Ni(W) binders have decreased, (except for some deep scratches). Also, the corroded WC grains seem like protruded out of the Ni(W) binder matrix, and thus it is reasonable to expect that the Ni(W) binders have undergone dissolution at the studied anodic transpassive condition. Further, the dissolution of the Ni(W) binder seems to be uniform but slightly enhanced at the interface of the WC grains, (see red color arrows in Fig. 11a’). Several features, such as cracks, porous, and removal of a top surface of the WC grain, as indicated by yellow arrows of Fig. 11a’ were observed on the corroded WC grains. A recent study has shown that, for a WC-NiCrMo binder sample, when potentiostatically polarized at anodic potentials for 47 h in synthetic seawater (pH 7), the WC grains were corroded, and it appeared like an eroded morphology [31]. This SEM result confirms that the protective nature of the passive film that has formed over the Ni (W) binder and WC has been lost. At the transpassive condition, the

![Fig. 10. SEM analyses of the WC-Ni(W) cemented carbides: a-b) as-polished; and a’-b’) after electrochemical studies in synthetic mine water (SMW); a’) after EIS at OCP for 120 h; b’) after potentiostatic polarization at +0.2 V vs. OCP for 1 h; *-marked as an indicator to show and compare the same microstructural area before and after the electrochemical studies.](image-url)
increase in anodic dissolution and the corrosion morphology of WC grains could be attributed to the electro-oxidation of WC due to the formation of soluble W-complexes as explained elsewhere [49].

Similarly, SEM analysis of the WC-Co(W) samples before and after the electrochemical studies is shown in Fig. 12. The as-polished microstructure (Fig. 12a) shows the WC grains and the Co(W) binder. The lower R_p and R_τ values from EIS studies at OCP, high q value from the potentiostatic test, and high current density values after potentiodynamic polarization, all correlate to the selective dissolution of the Co(W) binder phase, respectively, see Figs.12(c’-d’). Figs. 12a-12a’ and Fig. 12b show the WC-Co(W) surface after EIS for 1 and 24 h, respectively, and illustrate that corrosion products are re-deposited on the WC grains. These corrosion products are poorly adhered, if cleaned or wiped with tissue paper shall be removed, see the absence of corrosion products in Fig. 12c and 12d. These SEM results confirmed that WC grains are unaffected in OCP and in anodic conditions, indicating that the presence of W in the Co binders does not contribute to the passivation of the WC-Co(W) samples. The WC grains shall be protected by the formation of a passive film. On the surface of WC-Co after cyclic polarization tests in several corrosive environments (including SMW) formation of hydrated WO_3 was confirmed by the Raman spectroscopy technique [22]. At OCP conditions, the galvanic corrosion reactions proposed for the WC-Co cemented carbides [50] are still valid for the WC-Co(W), where the Co (W) binder and WC grains act as an anode and cathode, respectively.

3.5. Passive film analysis of WC-Ni(W) cemented carbide by AR-XPS

To our knowledge, the passive film composition and thickness formed on the WC-Ni(W) when exposed to SMW at OCP condition are not available in the literature. Thus, AR-XPS studies were carried out to characterize the same. The obtained high-resolution spectra of Ni 2p, O 1s, C 1s, and W 4f measured at the different take-off angles (α) of 15, 30, 45, 60, 75, and 90° are shown in Fig. 15. The measured peaks were compared to reference positions for pure elements [51], nickel oxide [52], tungsten oxide [53], and tungsten carbide [54]. The Ni 2p spectra confirm that the observed Ni is in the metallic state as opposed to NiO_2 oxide. The O1s spectra indicate that the peak position is close to WO_3 rather than NiO_2. Most of the W is bound to C as WC as observed from both the C1s and W 4f spectra. WC peaks also have the highest intensity indicating that oxide is much thinner than the inelastic mean free path. The composition and thickness of the passive film of the cemented carbides shall depend on the environments it was exposed to. For instance, XPS analysis of the WC-(8Co2Ni) sample when exposed to HCl solution confirmed the formation of WO_3 film [21]. However, no passive film was formed on the binder due to the dissolution of the 8Co2Ni in the HCl medium. On the other hand, for the same sample when exposed to NaOH, the film composed of WO_3, Co (OH)_2, CO_3O_4, NiO_2, and Ni (OH)_2 was confirmed, and no attempts were made to estimate the film thickness [21]. Thus, for the WC-Ni(W) sample when exposed to SMW, it is reasonable that the WO_3 uniformly formed over both the Ni(W) binder and the WC grains.

The atomic concentration of O, C, and W concerning relative depth, is shown in Fig. 14. For all the conditions, the signal from WC was observed predominantly along with the presence of a thin oxide film. However, as expected, when analyzing smaller depths, there is an increase in the observed oxygen content and a decrease in the carbon content, see Fig. 14. It is difficult to calculate the exact thickness of the oxide, especially due to relatively low signal-to-noise ratios for most of the peaks [55]. Ignoring effects due to different electron energies and estimating that the origin of the signal is evenly spread to the probed depth, a purely geometric calculation can be made by observing the ratio of carbon concentration between the smallest and largest relative depth is 0.85. An oxide film of about 0.05 relative depth could explain this difference. The measured concentration of carbon is related to the fraction of the sample consisting of WC and not WO_3. The relative signal from carbon would then be 0.21/0.26 divided by 0.95/1, equaling 0.85. The inelastic mean free path in the material was estimated to be 5 nm by calculating a value for pure tungsten carbide using NIST Database 71 [56]. This finding holds, independent of the take-off angle correlating to the depth sensitivity. With an estimated inelastic mean free path of 5 nm, this would indicate a WO_3 oxide film of only 0.25 nm in thickness. The uncertainty in this passive film thickness estimation is large, but it at least suggests that the oxide is extremely thin and complements the thickness results obtained from the capacitance values of EIS studies.

4. Conclusion

A systematic investigation on the microstructural and electrochemical behavior of WC-20 vol% Ni cemented carbide was carried out and the results were compared with WC-20 vol% Co and the following conclusion shall be drawn.

- SEM-EBSD analysis verified that the WC grain size is quite similar (0.9–1.1 μm) for both grades. AES analysis has established that the binder phase of the cemented carbides is not pure metal, but rather
alloyed with W. The concentration of W present in the Ni-binder is at least twice as high as that in the Co-binder.

- Concerning the corrosion resistance in SMW, the electrochemical parameters obtained from EIS, potentiodynamic, and potentiostatic polarization studies indicate that the WC-Ni(W) cemented carbide shall exhibit far better performance than the WC-Co(W).

- SEM studies have confirmed that the WC grains and the Ni(W) binder phase did not show any sign of corrosion even for a prolonged exposure period of 120 h in SMW. The high charge transfer resistance ($R_{ct}$) values for the WC-Ni(W) obtained from the EIS studies have supported these findings. AR-XPS confirmed the extremely thin 0.25
nm passive film of WO$_3$ responsible for its high corrosion resistance in SMW.

CRediT authorship contribution statement

J. Jayaraj: Conceptualization, Investigation, Validation, Formal analysis, Writing – original draft, Writing – review & editing, Visualization. Robin Elo: Investigation, Visualization. Kumar Babu Surreddi: Investigation, Visualization. Mikael Olsson: Resources, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they are aware of the content of the manuscript and approve its submission and assure that no conflict of interest exists.

Data availability

Data will be made available on request.

References
