A study on WC-Ni cemented carbides: Constitution, alloy compositions and properties, including corrosion behaviour

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ABSTRACT
The manuscript presents a systematic study on three groups of Ni-based cemented carbides (WC-20 wt% Ni, WC-20 wt% Ni15Cr and WC-20 wt% Ni11Cr6Mo) based on thermodynamic calculations and experimental studies. Samples were prepared with different gross carbon contents (carbon activities) with the aim to provide a comprehensive overview on: constitution and phase formation, solubility of elements in the binder phase, binder and composite hardness, as well as their corrosion behaviour. A WC-20 wt% Co8Cr was used as standard binder system for comparison.

The results show that the amount of alloying elements that can be dissolved in the binder phase is significantly higher in the Ni binder as compared to the Co binder (e.g., the solubility of W in WC-Ni is about double of that observed in conventional WC-Co). The degree of alloying is primarily affected by the carbon content. The lower the gross carbon content within the processing window, the higher is the degree of binder alloying. In WC-Ni, up to 12 at% W is observed in solution in low carbon alloys, as compared to 4 at% W in high carbon grades. Additions of Cr are limited to 9–11 at% Cr, depending on the gross carbon content. When exceeding this value, Cr3C2 is formed in high carbon Ni alloys. The solubility of Mo in WC-NiCrMo cemented carbides is limited to about 2 at%, at higher additions a carbide is formed, most likely (W,Mo)C.

The high hardness values observed in NiCr and NiCrMo alloys when compared to plain Ni alloys can be attributed to the effect of Cr and Mo as WC grain growth inhibitors, and not to a significant enhancement of the intrinsic binder hardness. In contrast, our standard Co grade demonstrated a significantly higher binder and composite hardness than all of the nickel variants studied.

Finally, high-alloyed materials (low carbon NiCr- and NiCrMo alloys) did present a superior corrosion resistance compared to the CoCr grade even in the most severe corrosion environments. Higher degree of alloying (i.e., higher amounts of Cr, W, and Mo present in solid solution in the binder) is indicative of superior corrosion behaviour due to the nature of the protective layers formed under corrosive environments.

1. Introduction
Nickel bonded cemented carbides, as described in the original patent of Karl Schröter in 1923 [1], have almost entirely remained within the research and development stages until the 1980’s [2]. The first iterations using plain WC-Ni alloys have shown inferior hardness and strength when compared to cobalt bonded grades while demonstrating superior corrosion resistance [3]. At that time, it was also known that the corrosion resistance of nickel can be further improved by additions of chromium and tungsten (i.e. forming a NiCrW alloy), because the group of corrosion resistant nickel chromium tungsten Stellites® were already known and patented in 1907 [4].

In the monograph of Richard Kieffer (Hartmetalle; 1964; [5]) we can read about the first nickel grades, with alloy compositions ranging from Ni/Cr 80/20 to 70/30, similar to the composition described in the Stellite® patent [4]. The alloys exhibited excellent corrosion resistance in acidic and alkaline media, however the strength values were reported to be comparatively low [2,6]. This low observed strength was the result of precipitations of very fine chromium carbides which formed at such high chromium additions to nickel in the presence of WC.

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Based on this knowledge and further industrial research new nickel alloy systems were offered by the industry in the 1980’s, focused on applications and wear parts where corrosion resistance played a crucial role in improving the lifetime of tools [2,6,7]. Around the same time, very fine-grained WC-(CoCr) grades were developed in the industry, which demonstrated very high hardness and strength combined with a much better corrosion resistance than plain WC-Co grades. These WC-CoCr alloys have gained importance in corrosive applications where tribocorrosion is dominating.

To date, two nickel grades have become state-of-the-art in the industry: WC-NiCr(Mo) and WC-CoNiCr. A number of studies are published on these alloy systems, but most of the work is devoted to the corrosion behaviour. Little information is available on the constitution of the systems, in particular on alloy compositions, which govern the corrosion behaviour of the respective materials (i.e., the chemical nature of protective films which form during the corrosion process).

The work presented here is divided into two parts:

First, three different alloy systems, (1) WC-20 wt% Ni (plain grade), (2) WC-20 wt% Ni15Cr and (3) WC-20 wt% NiCr11Mo6 are presented to the reader. The authors focus on the alloy preparation, phase formation, solubilities, (Cr,W,Mo) and the alloy hardness (macro, micro and nano). This part demonstrates the broad variations in alloy compositions that can be found in Ni based systems. Thermodynamic software tools (CALPHAD methodology) are used to support the experiments and further reveal where thermodynamic data are still missing to correctly describe the phase equilibria in the studied system.

In the second part, we report the results of corrosion investigations based on selected compositions (demonstrating both high carbon and low carbon variants of the systems). These alloys are tested in different corrosive media and are compared to each other as well as to a WC-20Co8Cr and an industrial WC-20CoNiCr grade. The two latter grades were selected based on their competitive performance to nickel alloys from the viewpoint of tribocorrosion, based on their higher wear resistance and hot properties. In addition, the corrosion behaviour of pure nickel metal and pure WC was studied.

1.1. WC-Ni

1.1.1. Constitution, solubilities, hardness, strength and WC grain growth

As early as 1936, Takeda compared the C-Ni-W system with the C-Co-W system and concluded that the two systems have similar overall characteristics, however show differences in the invariant temperatures, widths of the two-phase field (carbon window) and solubilities of tungsten and carbon [8,9].

Invariant temperatures of the C-Ni-W system (fcc + WC + C + liq.) and (fcc + WC + MoC + liq.) are significantly higher than those of the C-Co-W system (1298 °C resp. 1368 °C), and vary significantly depending on the respective source. In equilibrium with graphite, temperatures between 1336 °C and 1348 °C are reported in the Ni system [2,10–14], whereas in equilibrium with eta-phase (Ni4W3C) the values range between 1433 °C [13] and 1445 °C [11].

There is still ongoing disagreement on the solid solubilities of tungsten in nickel in high carbon alloys (High Carbon (HC)-presence of graphite– 7 to 15 wt% W), but there is a sound agreement on solubilities of about 30 wt% W in Low Carbon (LC) alloys (with presence of Ni2W3); see Table 1. It is striking, that calculated values for HC alloys result in significantly higher W values when compared to experimental investigations. The lattice parameter of the fcc NiW solid solutions varies from 0.3542 nm (HC) to 0.3580 nm (LC) [3].

Sintering temperatures for plain WC-Ni alloys are higher than those used for WC-Co materials, due to the higher liquidus temperatures. Temperatures range from 1420° to 1500 °C, and depend on the processing parameters (WC particle size, amount of binder, carbon content).

Table 1: Solubility values of tungsten in nickel obtained by different authors [3,15–17] both in HC and LC alloys. Data obtained in experiments (exp.) resp. through thermodynamic calculations (calc.). Note that the experimental values are affected by the cooling rate, WC grain size and binder volume.

<table>
<thead>
<tr>
<th>Method</th>
<th>HC [wt% W]</th>
<th>LC [wt% W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drake &amp; Krawitz [16]</td>
<td>7</td>
<td>29</td>
</tr>
<tr>
<td>Danielsson [17]</td>
<td>15.4</td>
<td>31.4</td>
</tr>
</tbody>
</table>

The hardness and transverse-rupture strength of WC-Ni alloys was shown to be higher than that of comparable WC-Co grades [3,18]. The superior mechanical properties of WC-Co alloys are explained by the strain-induced transformation of the cobalt binder phase [18]. A complete replacement of cobalt by nickel lowers the hardness between 100 HV to 200 HV [9]. However, upon decreasing the particle size of the WC to about 0.5 μm hardness and transverse-rupture strength became almost the same as those of WC-Co [19]. Alloy gross carbon content turned out to be a crucial factor for WC grain growth in Ni alloys, and consequently on hardness [20], even with additions of grain growth inhibitors (VC, Cr3C2, TaC). WC coarsening was more pronounce in HC alloys, compared to LC grades, resulting in a significantly lower hardness [3,20]. VC proved to be the most effective grain growth inhibitor, followed by TaC, Cr3C2, TiC and ZrC [20].

1.1.2. Corrosion resistance

Suzuki et al. [3] obtained a superior corrosion resistance of WC-Ni alloys compared to WC-Co using a weight loss corrosion test in 10% HNO3 and 35 wt% HCl. Due to the higher amount of tungsten in solid solution, LC nickel alloys exhibited a significantly better corrosion resistance against the two acids than HC alloys. A nickel binder was more corrosion resistant in a solution of 0.01 M H2SO4 + 0.99 M Na2SO4 than a cobalt binder, but its performance was lower than that expected by comparison to pure nickel metal [21]. Seawater corrosion was significantly improved in low carbon WC-15 wt% Ni alloys as compared to high carbon variants, in particular at higher oxidizing potential [22]. A WC-9 wt% Ni alloy showed superior corrosion resistance in seawater when compared to WC-6 wt% Co at temperatures up to 80 °C. No pitting occurred in the nickel alloys [23]. The corrosion resistance of nickel alloys was superior to cobalt alloys in acetic acid solution, and self-passivation was noticed [24].

1.2. WC-NiCr

1.2.1. Constitution, solubilities, hardness, strength and WC grain growth

Despite the wide use of WC-NiCr alloys for corrosion resisting and non-magnetic parts, only a few systematic investigations have been published on this system [22,25–27]. Tsuchiya et al. [25] were the first to study the influence of chromium additions to WC-15 wt% Ni alloys. Up to 8 wt% Cr2C2 were added. The only chromium carbide formed in the system was Cr7C3. It was found that the solubility of Cr in the solid binder phase varied according to the carbon content and showed a maximum of 16 wt% Cr at the LC side. In the presence of graphite about 9 wt% Cr was obtained in solid solution. Similar results were obtained by Imasato et al. [26]; (see comparison in Table 2).

R. de Oro Calderon et al. [27] report on WC-Ni15Cr cemented carbides. Alloys were prepared with different carbon content, and CALPHAD methodology was used to describe the phase equilibria in the form of an isopleth (Fig. 1). From this isopleth one would expect the presence of chromium carbides (Cr7C3 or Cr2C2) over the whole carbon window, and the occurrence of an eta carbide (Ni4W3C) on the low carbon side. However, only Cr3C2 was observed experimentally on the high carbon side, and no Cr7C3 on the low carbon side was found within the carbon window. In contrast to the work of Tsuchiya [25], a kappa
3

Table 2
Solubility values of tungsten and chromium in nickel obtained by different authors [22,25–27] both in HC and LC alloys. Values obtained in experiments (exp.) resp. by thermodynamic calculations (calc.).

<table>
<thead>
<tr>
<th>Method</th>
<th>HC [wt% W]</th>
<th>HC [wt% Cr]</th>
<th>LC [wt% W]</th>
<th>LC [wt% Cr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tsuchiya et al. [25]</td>
<td>10</td>
<td>18.8</td>
<td>exp.</td>
<td></td>
</tr>
<tr>
<td>Imasato et al. [22]</td>
<td>9</td>
<td>16</td>
<td>exp.</td>
<td></td>
</tr>
<tr>
<td>De Oro Calderon [27]</td>
<td>10</td>
<td>17</td>
<td>11</td>
<td>exp.</td>
</tr>
<tr>
<td>De Oro Calderon [27]</td>
<td>9.5</td>
<td>6</td>
<td>22</td>
<td>9–10 cal.</td>
</tr>
<tr>
<td>Li et al. [26]</td>
<td>3.15</td>
<td>8.9</td>
<td>18.3</td>
<td>11 exp.</td>
</tr>
<tr>
<td>Li et al. [26]</td>
<td>5.0</td>
<td>8.8</td>
<td>18.4</td>
<td>10.65 cal.</td>
</tr>
</tbody>
</table>

Carbide (NiW4C3) was observed instead of a M6C carbide. These contradictory results emphasize that to-date inaccuracies emerge when calculated diagrams are used to predict all the details in the four-component system. However, the diagram captures the width of the carbon window and can be used for selecting proper carbon contents for the experiments. The diagram indicates the strong decrease of the liquidus temperatures, as a result of the addition of Cr. Calculated solubilities resulted in 9.5 wt% W and 6 wt% Cr in the HC alloy and 22 wt% W and 9–10 wt% Cr on the LC side (Table 2).

Recently, Li et al. [26] presented a study on WC-Ni-Cr3C2 model alloys with high Ni content (79 to 87 wt% Ni) based on electron-probe microanalysis and thermodynamic calculations. At 1100 °C, solubility values of 3.15 wt% W and 8.9% Cr in HC alloys were measured and 18.3 wt% W and 11 wt% Cr in LC alloys, respectively. Calculations resulted in 5 wt% W and 8.8 wt% Cr (HC), and 18.4 wt% W and 10.65 wt% Cr in LC alloys (for comparison with other work see Table 2).

The authors also report on WC-9 wt% Ni cemented carbides prepared with varying Cr additions (0.0 up to 0.9 wt% Cr). The hardness increased with increasing addition of Cr but reached a maximum at 0.75 wt% Cr. With increasing hardness, the fracture toughness decreased.

WC-NiCr cemented carbides are non-magnetic and are therefore used for the manufacturing of non-magnetic dies for pressing magnets. To-date, there are no published studies describing the phase equilibria and phases formed at such composition. Roebuck et al. [31] report that on adding higher amounts of Mo to the alloy, as in case of 20 wt% of the binder phase, electron probe microanalysis indicated that the maximum solid solubility of the molybdenum in the NiCrMo binder phase was not more than 3 to 5 wt%.

The corrosion behaviour of WC-15 wt% Ni-2 wt% Cr alloy (close to the saturation limit of Cr in Ni) was discussed by Imasato et al. [29] in solutions containing 0.03, 0.3, 3 and 10 wt% NaCl. They demonstrated that the highest corrosion resistance was obtained with low carbon alloys. The corrosion resistance declined with increasing NaCl concentration owing to the destruction of the surface passivation film with dissolution of Cr, which was influenced by the composition of the binder phase. The results were confirmed by immersion tests. Dissolution measurements obtained from solutions after potentiostatic polarization at 500 mV demonstrated a strong difference between HC and LC alloys. While the former mainly contained Ni besides Cr in aqueous solution, the solution from the corroding LC alloy contained very little Ni.

Three different WC-10 wt% NiCrMo alloys were investigated by Santos et al. [32] with different additions of Mo (0.1, 0.4 and 0.6 wt%). A Mo content of 0.6 wt% (besides 1.1 wt% Cr) was said to be effective in inhibiting WC grain growth and increasing hardness by 5%. Therefore, NiCrMo alloys are a promising candidate to replace Co as a binder for WC-based grades. Interestingly, the presence of W as an important alloying element in nickel is said to vary between 8 and 10 wt%.

1.3. WC-NiCrMo

1.3.1. Constitution, solubilities, hardness
WC-NiCrMo cemented carbides are considered the most corrosion resistant nickel alloys. Cr improves the corrosion resistance at low pH conditions and Mo is required to improve the pitting resistance in chloride environments. A typical composition used for corrosion-resistant applications would be WC-8Ni-0.7Cr-0.3Mo [9].

Fig. 1. Isovalue T vs wt% of the system WC-20 wt% Ni15Cr at carbon contents between 4.0 and 6.0 wt% C. Calculated with the software Thermocalc using the database TCFE 9 (HCP phase rejected).
that Ni as binder has a higher solubility than Co. Ni demonstrated higher solubility for Mo and Cr with higher carbon content, opposite to the cobalt binder. This is unexpected due to the usually observed influence of carbon activity on solubility of carbide forming metals. However, no concrete solubility data are presented to substantiate the findings. With addition of Mo, hardness and abrasion resistance increased, whereas fracture toughness decreased. In spite of the WC grain size, the Co grades exhibited higher hardness than all of the Ni-base alloys.

1.3.2. Corrosion resistance

The corrosion resistance of WC-NiCrMo alloys was investigated by several authors under different chemical environments. Human and Exner [35] observed a reduced active corrosion rate for the NiCrMo binder and the ability to passivate in 1 M H₂SO₄ as compared to WC-Co grades. In synthetic mine water the measured current densities -indicating corrosion- were steadily increasing with increasing electrochemical potential. Ekemar [2] describes a series of applications where WC-NiCrMo parts have performed superior compared to WC-Co wear parts: seal rings operating in sea water, bearings used in crude oil flow meters, nozzles in hydrocyclone used in the production of fertilizers or plungers and cylinders in high pressure equipment for polymer synthesizing.

Santos [32] describes the passivation of WC-NiCrMo alloys in acidic Na₂SO₄ solution (pH 1.5) and the enhancement of the active-passive transition in chloride medium NaCl/HCl (pH 2). The alloy with 0.6 wt % Mo exhibited a higher corrosion resistance than the alloy with 0.1 wt %. Intermediate additions of 0.4 wt% appeared to be detrimental. Rocha et al. [33] compared the corrosion resistance of a WC-10 wt% Ni11Cr6Mo alloy exposed to a 0.5 M NaCl solution with the corrosion resistance of several alloys with alternative binder compositions (WC-FcCoNi, WC-NiCrCoMo, WC-Co). They concluded that both NiCrMo and NiCrCoMo binders are good replacements for WC-Co in neutral and near neutral chloride environments.

On comparing the corrosion behaviour of Mo-containing CoCr-, NiCr- and CoNiCr-hardmetals in aerated 35 g/l NaCl solution [34] the authors observed an improvement of the corrosion resistance, provided the solubility limit is not exceeded, in particular in Ni- and CoNi-base grades. Mo additions demonstrated higher effectiveness in the nickel binder, while they were shown to be detrimental to the performance of Co-base systems:

In this context it is interesting to note, that on investigating the passivity of Fe-29 ferritic stainless steels it was demonstrated that the effects of tungsten on the passivation of the steels in a chloride or an acid solution were almost equivalent to those of molybdenum when compared on the basis of atomic percent, “a result of the similarities in chemical and electrical properties between the two elements” [36].

2. Experimental procedure

Three different alloy systems were investigated in the present study. All alloys were formulated as WC-20 wt% binder materials. For two alloy systems, WC-Ni and WC-Ni15Cr, four nominal carbon contents were prepared to provide information on phase formation and composition in low carbon (LC), intermediate carbon (two alloys) and high carbon variants (HC). LC refers to the occurrence of sub-stoichiometric phases during sintering, such as eta or kappa carbides, whereas HC refers to the presence of graphite within the microstructure. The nominal carbon contents were selected from calculated isopleths of the systems as presented thereafter. In case of the WC-NiCrMo system the nominal composition of the binder was adapted to the composition of Santos [32], resulting in a WC-20wt%Ni11Cr6Mo cemented carbide. For this alloy, two variants were prepared with C contents within the carbon window towards the low carbon side. In addition, two sub-stoichiometric WC-20 wt%Co8Cr grades were prepared to offer a comparison between corrosion resistant nickel/chromium and cobalt/chromium grades.

Powder metallurgical (PM) standard grade powders (Ni, Cr₂N, Cr₃C₂, Mo₂C, Co) were used for the preparation of WC-20wt%Ni, WC-20wt% Ni15Cr, WC-20wt%Ni11Mo6 and WC-20wt%Co8Cr cemented carbides. WC powder with a mean particle size of 6.75 µm was used (provided by Wolfram Bergbau- und Hütten AG, Austria).

For the preparation of the powder batches, the respective powders were mixed for 2 h in a Turbula mixer without wax. Mixing was used instead of ball milling in order to avoid any contamination in the Ni alloys by cobalt and iron. The coarse and rounded morphology of the WC provided a good mixing quality and homogeneous microstructures after sintering. Cylindrical green samples with a diameter of 14.7 mm (diameter of the punch) and a height of approximately 10 mm were produced by pressing at 200 MPa. The parts were then sintered in a semi-industrial GCA vacuum sintering furnace on yttria or zirconia supports to prevent uncontrolled carbon pick up. The heating rate was 10 ºC/min up to 1250 ºC, and then 3 ºC/min to the final hold. Soak time at the isothermal hold was 1 h at 1450 ºC for most of the alloys. Only the alloys WC-Ni with carbon contents 4.3 wt% (LC) and 4.5 wt% were sintered at a higher temperature (i.e. 1480 ºC). The cooling rate was about 15 ºC/min down to 1200 ºC. Temperature measurement was performed by a Pt/Pt13Rh thermostate. The total pressure was <0.01 mbar throughout sintering. To minimize vapor losses of nickel, the samples were sintered in a graphite box (used for WC-Ni alloys only) together with WC-Ni sintering dummy, obtained from industry. Metallographic preparation was carried out in different steps using a prolonged polishing time at 9 µm (120 µm- 40 N, 5 µm- 35 N- 30 min, 3 µm- 30 N – 10 min, 1 µm – 25 N – 5 min) in order to reduce internal stresses in the microstructure.

For the sake of comparison an industrial corrosion resistant grade based on the system WC-20CoNiCr was also included in the study.

2.1. Characterisation of the alloys

Sample cross sections were characterized using a Scanning Electron Microscope (SEM) FEI QUANTA 200 ESEM. Energy-Dispersive X-ray Spectrometry (EDS) was used as a qualitative and semi-quantitative method to measure the chemical composition in different regions of the microstructure. Both point analysis and element mapping identification in selected areas were taken for this purpose. An acceleration voltage of 20 kV was used in all measurements, and carbon was always excluded from the quantification when measuring the composition of the binder phase. Point analyses were made in the center of large binder pools (∼10 µm in diameter) located in the core part of the samples, as possible surface decarburization/carburization might slightly alter the carbon content and therefore the solubility of the elements in the binder regions located in the outer rim part of the sample. At least 10 different binder pools were measured on each sample in order to give an average value with a scatter below 1 wt%. However, giving a confidence interval for these data is not possible as the values can be affected by the particular chemical composition of the phase, the possible co-detection of other phases, the instrument used, the software and method used for quantification, etc. For this study, EDS measurements on the same samples were additionally carried out with a different instrument at Wolfram Bergbau- und Hütten AG (Austria) using an EDX Bruker X-Flash 6, under the same measuring conditions. In any case, the values provided should only be taken as semi-quantitative.

X-Ray Diffraction (XRD) was used to identify the phases present in the “as-sintered” alloy, using a PANalytical XPert PRO diffractometer (Cu Kα1 radiation), as well as for lattice parameter measurements of the fcc nickel binder. For the lattice parameter measurements, the WC peaks were used as internal standard. For some selected samples selective etching of phases on the sample cross section was performed by using different reactants (as described in earlier works [27,37]). WC grain size and size distribution was estimated with the linear-peak technique following the standard ISO 4499.

The hardness of the different alloys was determined with Vickers...
hardness measurements on the cross section of the samples, following the norm ISO 3878. Indentations were made with a hardness tester M4U 025 by Emco (Austria) applying a load of 30 kgf. Measurements were taken on each sample at a distance of more than 1–2 mm from sample edge and distributed all over the sample. At least 5 macro-hardness were used to calculate an average value with a deviation below 10 HV30.

The hardness of the binder was estimated by micro-hardness measurements as well as with nanoindentation measurements. In both cases, large binder pools (at least 10 μm in diameter) were selected for these measurements (see example in Fig. 2-left). A minimum of 15 micro-hardness measurements were selected to obtain an average value for each sample with a deviation below 10 HV0.01. Micro-hardness measurements were carried out using an Ahotec ecoHARD XM1270A equipment and a load of 0.01 kgf. Nanoindentation measurements were carried out with a nanoindenter Hysitron TI 750 L Ubi equipped with a Berkovich Pyramide. Before the measurement and afterwards, the surface was scanned using the piezo scanner of the device (topography image) with the indenter tip and a load of 2 μN. The image size was 40 × 40 μm with 0.5 s per line and a total of 256 lines. Positioning of the indenter was done using this image. A new image was taken after the measurement to re-check the position (see example in Fig. 2-right). For each sample, 25 similar measurements were taken.

2.2. Thermodynamic calculations

Thermodynamic calculations based on the CALPHAD methodology were performed in order to evaluate the predictive power of the simulation tool for phase equilibria in the above-described alloys. The in-silico results were compared to experimental data. Thermodynamic calculations were carried out using the software Thermocalc, and the commercially available database TCFE9. For the calculations in the systems WC-NiCr and WC-NiCrMo the HCP phase was rejected, as our commercially available database TCFE9. Phase formation and solubilities were also determined experimentally by combining the results from metallographic examinations, SEM-EDS and X-Ray diffraction patterns, according to the methodology described in previous publications [27,37]. A summary of the results are summarized in Table 4.

2.3. Corrosion experiments

Potentiodynamic measurements were carried out in a three-electrode set up. The analysed sample was the working electrode, a Pt wire served as the counter electrode, and a saturated silver-silver chloride reference electrode (SSE) was used. The composition and acidity of used electrolytes are provided in Table 3. During the measurement the electrolyte was not stirred. Upon immersion, the working electrode was allowed to equilibrate for 10 min at open circuit potential. Then, the working electrode was polarised to −500 mV_{SSE} for 30 s and subsequently scanned in the anodic direction at a rate of 1 mV/s. The measured current was normalized to the geometrical area of the sample, yielding the current densities. The analysed area had a surface of ~28 mm² (circle of 6 mm diameter) and was located in the center of the sample. The analysed sample was the working electrode, a highly alloyed stainless-steel mesh acted as counter electrode and a SSE was used as reference electrode.

Potentiostatic measurements were performed on polished samples with defined surfaces, of approximately 1 cm², submerged in synthetic seawater, as defined in DIN 50905-4 [38]. The samples were immersed in approx. 1.5 l of electrolyte and set to the desired potential, −100 mV_{SSE} or +500 mV_{SSE}. These potentials were selected from the results of the potentiodynamic experiments. Measured currents were sampled once per minute. Depending on the observed current level, the experiments were aborted at different times.

3. Results

3.1. Constitution, solubilities and hardness of the alloys studied

Phase formation in the alloys studied was predicted with the software ThermoCalc. The stable phases as well as the calculated solubility of different elements in the binder at 1000 °C are summarized in Table 4. Phase formation and solubilities were also determined experimentally by combining the results from metallographic examinations, SEM-EDS and X-Ray diffraction patterns, according to the methodology described in previous publications [27,37]. A summary of the results are summarized in Table 4.

Table 3 Composition and acidity of electrolytes used for corrosion experiment.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Composition</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.025 M H₂SO₄</td>
<td>−1.5</td>
</tr>
<tr>
<td>2</td>
<td>0.01 M H₂SO₄ + 0.99 M Na₂SO₄</td>
<td>−2.5</td>
</tr>
<tr>
<td>3</td>
<td>Phosphate-Citrate buffer: 0.1 M Na₂HPO₄ + 0.1 M citric acid</td>
<td>−4.0</td>
</tr>
<tr>
<td>4</td>
<td>Synthetic seawater [38]:</td>
<td>−7.0</td>
</tr>
<tr>
<td>5</td>
<td>28 g NaCl</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5 g MgCl₂ · 6 H₂O</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.4 g CaCl₂ · 6 H₂O</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>7 g MgSO₄ · 7 H₂O</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.20 g NaHCO₃</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Example of the regions selected for measurements. Left) A binderpool where EDS point analysis was carried out to estimate the composition of the binder phase. Such binderpools were also used for measuring microhardness (HV0.01). Right) Image of a binderpool after nanoindentation. The image was taken right after the measurement using the piezo scanner of the nanoindentation device. The depth of the indent mark is around 300 nm.
obtained experimentally is provided in Table 4. The most relevant microstructural features of each specific family of samples will be presented in the discussions chapter. An aspect to be remarked here is that the information presented in Tables 4 and 5 corresponds to samples with no remarkable macroscopic heterogeneities. This applies in particular to the information presented in Tables 4 and 5 corresponds to samples with temperature had to be increased to 1480 °C in order to avoid heterogeneities in the binder distribution. A detailed explanation of this effect will be presented in the discussion section.

When comparing experimental and theoretical values it must be considered that a carbon loss of approximately 0.05 wt% has to be expected during sintering (compared to the nominal composition). However, as the compositions are selected to cover the whole carbon window, they provide a good basis for understanding phase formation and maximum/minimun solubilities in the binders. Different features of the alloys (hardness HV30 and WC average grain size) as well as of the binder phase (microhardness HV0.01, hardness measured by nanoindentation, and Ni lattice parameter) are presented in Table 5 (missing values correspond to measurements that could not be carried out, often due to the absence of a sufficient number of large binder pools). Regarding the differences between microhardness values and nanoindentation values, and the conversion of nano-hardness to data from other length scales the reader is referred to the work of Walbühr et al. [39] where an in-depth explanation of the different phenomena involved is provided. In the present work the values are treated in a qualitative manner, with the main aim of providing a basis for comparison of the different binder chemistries.

Two Co8Cr alloys were prepared (4.8 and 4.9 wt% C), with compositions selected to remain a two-phase alloy after sintering, following the predictions of ThermoCalc calculations and the work of Kaplan et al. [40]. However, the lower carbon variant was shifted towards the formation of eta-carbides in our experiments, in contrast to what was predicted from the calculated phase diagram (Table 4).

The alloy WC-CoNiCr was provided by an industrial partner and was investigated as a competitive material for our corrosion experiments. The material was selected due to its high binder content (20 wt%) which makes it appropriate as a comparative sample to our materials. Compositional analyses presented in Table 4 suggest that this material is based most likely on a 50:50 Co:Ni alloy, with about 7 to 8 wt% chromium. The low tungsten content as measured in the binder phase implies a two-phase high carbon material. The alloy is finer grained, however exhibits about the same composite hardness as the WC-Ni11Cr6Mo alloy.

### 3.2. Corrosion experiments

Table 6 depicts the results of the electrochemical study. Figs. 3, 4 and 5 depict potentiodynamic measurements as comparative insight into the corrosion behaviour of the materials studied, under varying corrosion conditions.

From the potentiodynamic measurements, the corrosion potential \( E_{corr} \) was determined at zero current and the corrosion current \( I_{corr} \) was estimated from the cathodic Tafel-line extrapolated to \( E_{corr} \). These results are summarized in Table 6 for all tested material systems and described below in subsections corresponding to the different corrosive media. Since the investigated materials are composites, a galvanic couple exists between WC and the binder. The cathodic influence of WC diminishes with increasing pH and the corrosion potentials of WC and the binder converge at \( pH = 7 \). Due to the composite nature of all samples, a mixed potential was measured.

#### 3.2.1. Electrolyte 1: 0.025 M H₂SO₄ \( \cdot \) pH ~ 1.5

At pH 1.5 (0.025 M H₂SO₄) all investigated composites follow similar trends (Fig. 3-a). Initially, the corrosion current on the anodic branch increases exponentially with increasing polarization, until it reaches the maximum of the active region, which is the critical passive current density. After that maximum, the materials passivate, as evidenced in the subsequent drop and plateau of the current levels. Passivation of the CoCr system is rather weak, the minimum current level remains high (260 \( \mu \)A/cm²) and the current increases monotonically with increasing potential. For all other systems, the current level of the plateau in the passive range differs significantly between binder compositions (7–60 \( \mu \)A/cm²). Under these conditions, the corrosion resistance is increasing in the following order following the observed trend in current density: Ni(W), CoNiCr, NiCr and NiCrMo. Particularly NiCr and NiCrMo show low corrosion currents, 7 \( \mu \)A/cm² and 10 \( \mu \)A/cm² respectively, highlighting the important role of chromium content in the binder for corrosion resistance in acidic conditions. The passive plateau is limited to higher potentials and above ~700 mV, all investigated composites are corroding rapidly. This upper limit of the passive range towards higher potentials coincides for all composites with the anodic
Table 5
Properties of the binder and the composite material.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Binder</th>
<th>Carbon (wt %)</th>
<th>Ni-FCC Lat. Param. (Å)</th>
<th>Hardness Vickers (HV 0.01)</th>
<th>Binder hardness nanoindentation (GPa)</th>
<th>Composite: WC-20 wt% Binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-20</td>
<td>WC-20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>4.3</td>
<td>3.5823</td>
<td>–</td>
<td>5.15 ± 0.27</td>
<td>694</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>3.5695</td>
<td>230</td>
<td>4.53 ± 0.29</td>
<td>680</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>4.7</td>
<td>3.5530</td>
<td>184</td>
<td>4.29 ± 0.36</td>
<td>672</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>4.9</td>
<td>3.5468</td>
<td>193</td>
<td>3.99 ± 0.16</td>
<td>642</td>
<td>3.8</td>
</tr>
<tr>
<td>Ni15Cr</td>
<td>4.6</td>
<td>3.5685</td>
<td>225</td>
<td>–</td>
<td>787</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td>3.5611</td>
<td>174</td>
<td>5.20 ± 0.30</td>
<td>762</td>
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</tr>
<tr>
<td></td>
<td>5.0</td>
<td>3.5485</td>
<td>–</td>
<td>4.38 ± 0.33</td>
<td>769</td>
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<td>3.5712</td>
<td>221</td>
<td>–</td>
<td>803</td>
<td>2.6</td>
</tr>
<tr>
<td>6Mo</td>
<td>4.9</td>
<td>3.5615</td>
<td>180</td>
<td>–</td>
<td>794</td>
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<td>4.8</td>
<td>–</td>
<td>311</td>
<td>–</td>
<td>976</td>
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<tr>
<td></td>
<td>4.9</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>902</td>
<td>3.4</td>
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<tr>
<td>CoNiCr</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.97 ± 0.34</td>
<td>796</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 6
Results for corrosion potentials and corrosion currents (all potentials vs. Ag/AgCl).

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>E_{corr} [mV_SSE]</th>
<th>I_{corr} [A/cm^2]</th>
<th>Electrolyte</th>
<th>E_{corr} [mV_SSE]</th>
<th>I_{corr} [A/cm^2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 M H_2SO_4</td>
<td></td>
<td></td>
<td>H_2SO_4 + Na_2SO_4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-4.3%C</td>
<td>−151</td>
<td>4 × 10^{-6}</td>
<td>Ni-4.3%C</td>
<td>−151</td>
<td>4 × 10^{-6}</td>
</tr>
<tr>
<td>Ni-4.5%C</td>
<td>−139</td>
<td>5 × 10^{-6}</td>
<td>Ni-4.5%C</td>
<td>−139</td>
<td>5 × 10^{-6}</td>
</tr>
<tr>
<td>Ni-4.7%C</td>
<td>−131</td>
<td>7 × 10^{-6}</td>
<td>Ni-4.7%C</td>
<td>−131</td>
<td>7 × 10^{-6}</td>
</tr>
<tr>
<td>Ni-4.9%C</td>
<td>−132</td>
<td>1 × 10^{-5}</td>
<td>Ni-4.9%C</td>
<td>−132</td>
<td>1 × 10^{-5}</td>
</tr>
<tr>
<td>Ni-15Cr-4.6%C</td>
<td>−110</td>
<td>6.5 × 10^{-6}</td>
<td>Ni-15Cr-4.6%C</td>
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<td>−148</td>
<td>3 × 10^{-6}</td>
<td>Ni-15Cr-5.0%C</td>
<td>−148</td>
<td>3 × 10^{-6}</td>
</tr>
<tr>
<td>Ni-11Cr-6Mo-4.8%C</td>
<td>−213</td>
<td>2 × 10^{-5}</td>
<td>Ni-11Cr-6Mo-4.8%C</td>
<td>−213</td>
<td>2 × 10^{-5}</td>
</tr>
<tr>
<td>CoCr-4.8%C</td>
<td>−153</td>
<td>10 × 10^{-5}</td>
<td>CoCr-4.8%C</td>
<td>−153</td>
<td>10 × 10^{-5}</td>
</tr>
<tr>
<td>CoNiCr</td>
<td>−114</td>
<td>2 × 10^{-6}</td>
<td>CoNiCr</td>
<td>−114</td>
<td>2 × 10^{-6}</td>
</tr>
<tr>
<td>Pure Ni</td>
<td>+114</td>
<td>+56</td>
<td>Pure Ni</td>
<td>+114</td>
<td>+56</td>
</tr>
<tr>
<td>WC</td>
<td>+114</td>
<td>+56</td>
<td>WC</td>
<td>+114</td>
<td>+56</td>
</tr>
</tbody>
</table>

Fig. 3. Potentiodynamic measurements of hardmetal samples with various binder compositions and pure WC in a) electrolyte 1 and b) electrolyte 2.
dissolution of WC. This indicates that no conclusions about the trans-passive dissolution behaviour of the binders can be drawn from the experiments presented here.

3.2.2. Electrolyte 2: 0.01 M H$_2$SO$_4$ + 0.99 M Na$_2$SO$_4$ - pH ~ 2.5

All investigated composites exhibit an almost identical behaviour in the electrolyte of higher pH (Fig. 3-b) when compared to the data at pH 1.5 (Fig. 3-a)). None of the systems depict improved corrosion resistance subject to the more moderate acidic conditions.

3.2.3. Electrolyte 3: citrate-phosphate buffer - pH ~ 4

A different corrosion behaviour was observed in citrate-phosphate buffer of pH 4 (Fig. 4-a). WC-CoCr is more stable in this medium than the Ni(W), up to a potential of +230 mV$_{SSE}$. With the exception of Ni(W), the characteristic peak of the critical passive current density is almost diminished and there is a smooth transition from the corrosion potential to the current plateau in the passive region. At pH 4, WC-NiCrMo and WC-NiCr are the most corrosion resistant alloys followed by WC-CoNiCr, WC-CoCr and WC-Ni(W). The upper potential limit of the passive region coincides for all composites with the anodic dissolution of WC.

3.2.4. Electrolyte 4: synthetic seawater - pH ~ 7.0

Exposed to synthetic seawater, the composites perform significantly different compared to acidic media (Fig. 4-b). At low potentials up to +150 mV$_{SSE}$, all investigated compositions behave in a similar way. At potentials above +150 mV$_{SSE}$, the corrosion current of WC-CoCr increases by 4 orders of magnitude in a very short interval of raising potential. Such behaviour is typically related to a breakdown of passivity and the initiation of localized corrosion. The other grades remain at low current level indicating passive state. The dissolution current for WC-Ni(W) increases steadily with increasing potential. In contrast, the current raises sharply for WC-CoNiCr above +400 mV$_{SSE}$. NiCr and NiCrMo depict higher corrosion resistance, with the respective corrosion current increasing relatively slowly and without indication for localized attack.

Fig. 5 compares potentiodynamic measurements for different carbon contents in alloys WC-Ni and WC-NiCr. A clear trend can be observed. Composites with lower carbon content of 4.5 and 4.8 wt% C, for WC-Ni and WC-NiCr respectively, exhibit lower, almost identical corrosion current in the full potential range compared to the higher carbon samples with 4.7 and 5.0 wt% C. For comparison, a wire of pure nickel was measured as reference. It exhibits a short range of passivity and high corrosion rates at potentials above breakdown at ca. +100 mV$_{SSE}$.

4. Discussion

We present a systematic study of three different groups of Ni alloys -Ni(W), Ni15Cr(W) and Ni11Cr6Mo(W)- used as binders in hardmetals. The aim is to provide a clear overview on the characteristics of these alloys in terms of: constitution and phase formation, solubility of elements in the binder phase, binder hardness and composite hardness as well as corrosion behaviour.
4.1. Phase formation, solubility and correlation with thermodynamic calculations

a) WC-Ni

The gross carbon content of the four WC-20 wt% Ni alloys covers a range of 0.6 wt% ΔC. This range was selected from the calculated isopleth (Fig. 6). As shown in Fig. 6 and in Table 4, there is an agreement between predicted phases and experimentally observed phases in the WC-Ni system. However, considering the two carbon extremes (4.3 and 4.9 wt% C) one would expect the presence of significant eta-phases or graphite under such conditions, while metallographic examination revealed only minor amounts of eta phase and graphite in the respective microstructures (Fig. 6). Furthermore, the presence of coarse, dendritically grown eta phases indicates that the carbides were most likely formed upon cooling, due to the “roofing” of the two-phase region on the left side of the carbon window. These observations suggest that the processing window is experimentally wider than the calculated one, the difference being from approximately 0.6 wt% C. The processing window is, however, no influence on the results of the study discussed thereafter.

Regarding the solubility in the binder phase, the solubility of tungsten in the solidified nickel binder is about double compared to a cobalt binder. At the presence of eta carbides (Ni2W4C) about 30 wt% W (12 at % W) is in solid solution in Ni binders compared to about 5.5 to 6 at% W in Co binders [15]. In presence of graphite about 30 wt% W (11 wt% W) in solution was obtained in this study in WC-Ni as compared to about 1.5 at% W obtained in coarse grained WC-Co [15]. (Note that these values are also affected by cooling rates, the WC grain size and the binder volume). The results of this study are in excellent agreement with the experimental values obtained by Suzuki et al. [3] and Drake & Krawitz [16]. However, there is a notable discrepancy in the high carbon alloys with the calculated solubilities (see results in Table 4) and with published solubility data calculated by thermodynamic assessment [15,17].

b) WC-Ni15Cr

As the amount of Cr added to the WC-Ni system exceeds the maximum solubility in the binder, the carbon window (processing window) decreases progressively due to the formation of Cr carbides (see Fig. 7). This limit is set by the nominal composition, and, according...
to the calculations, should result in the formation of either Cr$_3$C$_2$ or Cr$_7$C$_3$ in the WC-20 wt% Ni15Cr alloy, depending on the gross carbon content (see Fig. 1). Whereas the result was confirmed experimentally at the high carbon side (i.e., formation of Cr$_3$C$_2$), the occurrence of Cr$_7$C$_3$ at lower carbon contents was not observed (see Table 4). This discrepancy at low carbon contents was already discussed in an earlier investigation [27].

The maximum Cr solubility obtained in alloys with presence of graphite (and Cr$_3$C$_2$) was measured to be about 9 wt% Cr in solid solution, not considering the presence of C in solution (Table 4). This data matches reasonably well with the data published by Li et al. [26] (8.9 wt % Cr) who did consider the carbon in solid solution in the binder. With decreasing gross carbon content, an increase in Cr solubility up to ~11 wt% is observed in 2-phase samples. At lower carbon contents (i.e. outside the carbon window) the amount of Cr dropped to about 7 wt% Cr with the occurrence of a Cr-containing kappa carbide Ni(W,Cr)$_3$C. In the work of Li et al. [26] a maximum solubility of 10.65 wt% Cr was observed experimentally in the substoichiometric region, but this value was measured in a binder-rich Ni model alloy with presence of eta phases and M$_7$C$_3$.

The tungsten content dissolved in the binder decreases as the carbon content increases (Table 4). In the 4.6 wt% C alloy (substoichiometric) 25 wt% W is measured in the binder phase and significantly decreases to 15 wt% in the 4.8 wt% C alloy (2-phase), ultimately down to 6 wt% W in the samples with graphite. The tungsten content in the substoichiometric sample (25 wt%) is close to the predicted value (22.4 wt % W), but at higher carbon contents the W measured in our samples (6 wt%) is considerably below the value expected from the calculations (9.5 wt%). In the case of Cr, the highest concentration dissolved in the binder is reached in a sample in the 2-phase region close to the precipitation of kappa carbide (i.e., in the 4.8 wt% alloy), and is around 11 wt% Cr. This result agrees well with our earlier investigation on high chromium nickel alloys [27].

Experimental investigations therefore suggest that in order to avoid
the presence of chromium carbides a maximum of 9–11 wt% Cr should not be exceeded. Additionally, the gross carbon content in the alloy has to be considered, since it influences both the amount of Cr and W in solid solution as well as the occurrence of (Cr,W)2C6 at high carbon potentials significantly.

c) WC-Ni11Cr6Mo

An isopleth of the system WC-20 wt% (Ni11Cr6Mo) calculated using ThermoCalc is presented in Fig. 8. This calculation was used to select the targeted carbon contents for obtaining samples without graphite or substoichiometric carbides. Calculations of the WC-20(Ni11Cr6Mo) system predict the occurrence of chromium carbides at both carbon contents selected (i.e., 4.8 and 4.9 wt% C) either as M2C3 or as M23C6 (see Fig. 8 and Table 4). However, no chromium carbides were found experimentally, and both of our selected compositions (4.8 and 4.9 wt% C) turned out to be two-phase alloys. Predicted solid solubilities of the metallic elements (W, Cr, Mo) in fcc-nickel indicated that only minor amounts of Mo can be dissolved in the binder phase. Part of the molybdenum added should be present as (W,Mo)C carbide, due to its strong carbon affinity. This was confirmed by our experimental measurements. Mo contents were below 2 wt% in both alloys, i.e., considerably lower than the nominal 6 wt% Mo. Elemental mapping reveals a Mo-enrichment on the surface of the WC particles (Fig. 9), most likely due to the formation of a (W,Mo)C layer.

Comparing the Mo solubility predicted by the software (0.3–0.5 wt %) and the solubility measured in the experiment (~2 wt%) is complicated by the fact that the software considers a homogeneous dissolution of Mo in the WC, which does not appear to happen in practice (i.e., under non-equilibrium conditions).

Additions of Mo in WC-Ni alloys are common in corrosion resistant grades. However, if the solubility of Mo in the Ni(W, Cr) binder is exceeded, the formation of Mo carbides is observed [31,41,42]. The alloys studied in this work demonstrate that this limit is rather low, in the order of 2 wt% Mo. Above this limit, an hexagonal (Mo,W)C is formed upon sintering and/ or cooling by precipitating on the surface of the already present WC grains. This (W, Mo) carbide can increase the contiguity of the WC grains, in particular in fine-grained and low binder alloys, thus increasing the hardness but most likely at the expense of toughness.

d) Overview on the solubility of alloying elements in different Ni binders

Fig. 10 provides a comparison of the solubility of W, Cr and Mo in the Ni alloys studied in this work, expressed in atomic percent. It is evident that the amount of W dissolved in the Ni binder is considerably affected by the gross carbon content. In WC-Ni alloys, it is clear that at low carbon additions, significantly more W is present in solution as compared to high carbon conditions. In WC-Ni15Cr systems the trend in W remains the same, but at an overall lower level, indicating that Cr additions decrease the solubility of W in the binder. In terms of at% the amount of Cr is always higher than the amount of W dissolved, irrespectively of the carbon content. This also holds for the WC-NiCrMo alloys where the amount of Cr is lower than in WC-NiCr because there is less Cr in the original nominal composition (11 wt% in NiCrMo and 15 wt% Cr in NiCr alloys).

Importantly, when comparing the samples in the 2-phase region, the solubility of W in WC-NiCrMo alloys is considerably higher than in WC-NiCr alloys. In fact, in the WC-NiCrMo alloys with the lowest carbon content (4.8 wt% C) the sum of alloying elements reached about 18 at% (7 at% W, 9 at% Cr and 2 at% Mo), being the highest of all alloys investigated in this study. This high degree of alloying is also reflected in the strong lattice expansion observed in this material, as shown in Table 5.

Compositional differences provide an important basis for the interpretation of binder hardness and corrosion properties. The type and amount (in at%) of alloying elements dissolved in the binder will affect the composition and the properties of the passive layers that may be formed during corrosion experiments. As it is clearly evidenced in Fig. 10, the two materials WC-Ni15Cr and WC-Ni11Cr6Mo with low carbon contents present particularly high amounts of alloying elements. The two-phase WC-Ni15Cr with lower carbon (i.e., 4.8 wt%) is the most Cr-rich binder of all samples investigated in our study. On the other hand, the WC-Ni11Cr6Mo alloy with 4.8 wt% C (which was produced as a LC variant) exhibits a lower Cr content than the LC WC-15Cr alloy but a higher amount of W in solid solution (7.3 at% compared to 4.9 at% W – obviously a result of the lower Cr addition). In addition, 1.7 at% of Mo adds to the solid solution. Both of these two LC variants exhibited superior performance compared to all other materials in our corrosion experiments.

The binder hardness is also affected by the amount and type of elements dissolved, since the solute atoms provide a strengthening effect as a result of the lattice distortion and the interaction between solute atoms and dislocations. Strengthening constants for solution strengthening in nickel (with the unit of MPa at. fraction 1/2), published by Roth et al. [43], demonstrate a much higher strengthening (hardening) constant for W, Mo and C as compared to Cr.

4.2 Sintering conditions in WC-Ni and WC-NiCr(Mo) alloys

Sintering temperatures for straight WC-Ni alloys are higher than those used for WC-Co grades, due to their higher liquidus temperatures. Beyond that, the formation of liquid phase is strongly related to the gross carbon content, as demonstrated in Fig. 6. In this study, 1450 °C was used for most of the samples, with the exception of WC-Ni alloys with low carbon contents. Sintering of low carbon (4.5 and 4.3 wt% C) WC-Ni alloys at 1450 °C resulted in dense samples but exhibited a core-shell microstructure with significantly less binder in the outer part and significantly more binder in the inner part of the specimen (see Fig. 11).

A distinct difference in hardness is found between core (570 HV10) and rim (910 HV10) regions. This observation indicates an insufficient sintering temperature for such grades and a binder migration during
sintering. In contrast, liquid phase sintering at 1480 °C (i.e., about 50 °C above the invariant temperature of 1434 °C for the fcc + WC + MoC + liq. equilibrium) resulted in uniform microstructures without any core-shell formation. The temperature of liquid phase sintering of WC-Ni grades must therefore be carefully adjusted to their respective gross carbon content.

Additions of chromium (Fig. 1) and chromium/molybdenum (Fig. 8) to WC-Ni systems significantly lower the liquidus temperatures and thus allow for lower sintering temperatures, even in the case of low carbon variants. Subsequently, 1450 °C provided an optimum temperature for our comparative study.

4.3. WC grain growth in WC-Ni and WC-NiCr

With the exception of the two samples with core-shell structures all alloys showed uniform, coarse-grained microstructures with a bimodal WC grain size distribution, resulting from the bimodal particle size distribution of the starting WC powder. Since the powders were mixed and not milled prior to sintering, no changes in WC particle size occurred due to particle comminution. Changes in WC grain size and size distribution are therefore a result of the different growth conditions during sintering prevailing in the different binder phases.

Similar to cobalt alloys, high carbon contents result in higher mean WC grain sizes (measured by intercept lengths, see Table 5 and Fig. 12) because the carbon in solution is acting as a grain growth promoter. Under such high carbon conditions, the resulting shape of the WC grains is faceted as compared to the more nodular shape of the WC grains at low gross carbon contents (see Fig. 12). Also, the finer fraction of WC particles shows significant growth in the high carbon variants.

Additions of Cr and Cr+Mo have a grain growth inhibition effect, and
reduce significantly the final mean particle size of the WC (see NiCr alloys in Fig. 12, and NiCrMo and CoCr alloys in Fig. 13). However, the influence of the gross carbon content is still evident in the NiCr alloys, when comparing the low and high carbon variants in Fig. 12. The strongest WC growth inhibition is observed in the WC-Ni11Cr6Mo cemented carbide (Fig. 13). We emphasize that in WC-NiCrMo alloys with low carbon, most of the WC grains have a nodular shape (Fig. 13-left).

4.4. Solid solution hardening, binder hardness and composite hardness

Fig. 14 compares the binder hardness (HV0.01) and the composite hardness (HV30) of all alloys studied (summarized in Table 5). At first glance, one can recognize the higher composite hardness of WC-20 wt% Co8Cr as compared to the hardest nickel grade, i.e., WC-NiCrMo. About 970–900 HV30 is measured in WC-CoCr alloys compared to about 800 HV30 in WC-NiCrMo alloys. This higher composite hardness of the cobalt alloy is observed in conjunction with a significantly higher binder micro-hardness of 311 HV0.01 compared to about 220 HV0.01 in WC-NiCrMo. This significantly higher micro-hardness is confirmed by nano-indentation where 7.0 GPa were measured for the Co grade in comparison to 4.0 to 5.2 GPa for the nickel alloys.

In WC-Ni alloys, the incorporation of W into the fcc nickel lattice leads to a significant lattice expansion from 3.547 Å in the sample with graphite, to 3.582 Å at presence of eta-phase (see Table 5). A prominent solid-solution strengthening effect is demonstrated by both micro and nano hardness measurements of the metallic binder (Table 5 and Fig. 14). The micro-hardness of the binder in WC-Ni alloys varies within the range of 180–230 HV0.01. The higher the amount W in solid solution, the higher the binder hardness. The composite hardness values (HV30) are also increasing with increasing tungsten in solid solution (i.e. at lower carbon contents). This observation is also influenced by the lower average WC grain size, i.e. a slightly finer-grained cemented carbide.

The hardness of the WC-Ni15Cr cemented carbides is significantly higher than the hardness of the WC-Ni alloys, by approximately 80–90 HV30 (see Table 5 and Fig. 14). It is evident that this increase in hardness in the WC-NiCr alloy is mainly related to the finer-grained microstructure in Cr-containing binders, rather than a higher binder hardness. In fact, the amount of Cr in solid solution -although present in higher amounts as compared to W - seems to contribute less to alloy strengthening as compared with the remarkable effect of W in solution observed in Ni alloys. This is in agreement with the highest lattice distortion observed in WC-Ni alloys due to the presence of more W atoms in the lattice as compared to WC-NiCr alloys (see Table 5).

The hardness of the two Mo-containing alloys was slightly higher than those observed in the WC-Ni15Cr alloys, accompanied by a stronger lattice distortion in case of the lower carbon variant. As compared to the Ni15Cr variant, the amount of Cr dissolved in the binder is lower in the Ni11Cr6Mo alloys, however the amount of W is higher (this applies to the WC-NiCr samples with a 2-phase microstructure). As one would expect from earlier investigations, the composite hardness of the nickel alloys increases with additions of Cr and Mo, due to a significant WC grain refinement by the additives (Table 5). The WC-NiCr and WC-NiCrMo grades are about 100 Vickers units harder than the hardest WC-Ni straight grade.

The results clearly depict the lower hardness of the nickel alloy binder when compared to the cobalt alloy binders despite the fact that more W and Cr is soluble in nickel. In addition, the data suggest that it is not reasonable to compare hardness or wear performance between WC-NiCr(Mo) alloys and WC-Co alloys (with no additions of Cr or other grain
growth inhibitor) - as sometimes found in the literature - because the differences observed will be significantly influenced by the differences in WC grain size.

4.5. Corrosion resistance

4.5.1. pH range: 1.5 - 2.5

In this pH range WC-CoCr alloys exhibit significantly higher passive current densities (i.e., dissolution rates) as compared to the Cr-containing Ni grades. Both WC-NiCr and WC-NiCrMo demonstrate the highest corrosion resistance followed by WC-CoNiCr and plain WC-Ni (W) alloys.

Subjected to strong acidic conditions, straight WC-Co grades (not considered in our work) are rapidly corroding, a behaviour which is even utilized industrially for recycling of Co-based cemented carbides [44].

The higher corrosion resistance of WC-NiCr and WC-NiCrMo can be attributed to the formation of a protecting Cr/Ni oxide layer in acidic media. The addition of Cr and Mo is not solely responsible for this effect as W, which is always present in quite large amounts in the alloy binder (as shown in Table 4) also contributes. Lloyd et al. [45] have demonstrated the ability of the alloy components in Ni-based alloys to segregate Cr/Ni to the alloy-oxide interface and Mo/W to the oxide-solution interface, contributing to an increase in oxide thickness with applied potential.

The corrosion current comprises almost exclusively the oxidation of the binder phase for a wide potential range, however above a threshold potential WC itself starts contributing in a significant portion to the observed current, and the exact role of binder corrosion cannot be determined in this potential region. In Fig. 15 this is demonstrated by comparing the current densities of WC at pH of 1.5 with two corrosion resistant metallic alloys (a Co-based high Cr-stellite and a Ni-based Cr-Mo-superalloy), both with comparable alloying characteristics. At oxidation potentials above ca. +500 mV_{SSE}, WC exhibits a significantly higher anodic dissolution current than the Co-based and Ni-based alloy which remained passive up to ca. +1000 mV when transpassive.

Fig. 13. Microstructures of the lower carbon variants in the systems WC-20 (Ni11Cr6Mo) (left) and WC-20 (Co8Cr) (right). In the WC-Ni11Cr6Mo-4.8C (left) a 2-phase microstructure was obtained, while in the WC-Co8Cr-4.8C (right) a small amount of η-carbides were found. The WC-Ni11Cr6Mo-4.8C sample presents a fine and uniform microstructure with nodular shaped grains.

Fig. 14. Hardness of different WC-20wt%Binder alloys (HV30), and micro hardness (HV0.01) of the corresponding binder measured in large binder pools.
4.5.3. pH = 7 (sea water)

In synthetic seawater the mode of corrosion changes. In Fig. 5, the corrosion behaviour of pure nickel is depicted. The formation of a protective nickel hydroxide surface layer can be observed at lower anodic potentials [46]. Successively, the layer breaks down and rapid dissolution of the metal begins, resulting in complete disintegration of the nickel wire used in this experiment. Chloride ions are being incorporated into the surface layer, which impairs its stability with increasing chloride concentration [47]. Similarly, the corrosion current of the investigated composites is initially low, but with increasing potential the abrupt breakdown of the protective layer causes an observed jump in current density and rapid dissolution of the binder. Nickel based binders seem to be more resistant to this breakdown of the protective layer (as compared to pure Ni), as their corrosion rate increases only gradually. WC-NiCr and WC-NiCrMo again depict the best performance, omitting a breakdown of the surface layer even at high potentials. It is important to note that this is only true for the LC variants of the respective binder alloys. With increasing carbon content, less chromium and tungsten are dissolved in the binder (Table 4). As a result, the corrosion current of WC-NiCr-LC is found to be ten times lower compared to the HC variant, while WC-NiCrMo remains at lower currents (<4×10^{-6} and <2×10^{-5} A/cm² for +100 and +500 mV_sse, respectively), which do not change much over time but some reaction of binder material is indicated by minimal fluctuation of the current. This is indicative of a more localized attack.

4.6. Tribocorrosion

Although not considered in our study as a topic, a few remarks can be made on tribocorrosion of cemented carbides based on nickel alloy binders. Two important alloy parameters can be identified in tribocorrosive studies that govern the performance of a part during use: composition and microstructure [48]. As the hardness of the WC is superior to that of the alloy binder, wear resistance is enhanced by both decreasing binder volume and the grain size of the WC. In this case it is possible that the softer but more corrosion resistant nickel grades can become increasingly competitive for uses in tribocorrosive systems, up to now low carbon variants. They also demonstrated the breakdown of the passive layers in HC alloys at +500 mV_sse. Analysis of the dissolved elements in solution (Ni, Cr, W) under these stronger oxidizing conditions depicted that in LC alloys, in contrast to the HC alloy, the concentration of Ni in solution was significantly lower than that of chromium and the rate of dissolution was strongly retarded under the same corrosion conditions [29].

This suggests that the low carbon alloys are indeed able to build thicker and stronger passivating oxides with a layered structure consisting of an inner Cr/Ni oxide layer and an outer W/Cr/Mo oxide layer (most likely in the form of insoluble tungstates), as proposed by Lloyd et al. for the corrosion of Ni-based superalloys [45]. Molybdenum additions further increase the stability of the outer protecting layer (forming molytungstates). Lloyd et al. also concluded that chromium in the Ni-based alloy contributes mainly to the reduction of passive current at low potentials (~200 mV_sse), while tungsten and molybdenum are mainly important in keeping the passive current low at higher potentials (+500 mV) [45]. Obviously, no such layer is formed in (less alloyed) HC WC-NiCr alloys at higher oxidizing potentials.

4.5.4. Potentiostatic investigations (+100 mV, +500 mV)

Based on the potentiodynamic measurements the best performing material in this study (i.e WC-NiCrMo, selecting the lower carbon alloys located inside the 2-phase region) was chosen for supplementary potentiostatic testing to evaluate longer term corrosion resistance. In addition, WC-NiCr 5.0 (HC) was chosen to further investigate the influence of carbon content, and WC-CoNiCr serves as comparison to a commercial grade sample. As depicted in Fig. 16, WC-NiCr-5.0 and WC-CoNiCr exhibit much higher corrosion rate with a tendency to further increase with time. This is the case at both selected potentials of +100 and +500 mV_sse, respectively. WC-NiCrMo remains at lower currents (<4×10^{-6} and <2×10^{-5} A/cm² for +100 and +500 mV_sse, respectively), which do not change much over time but some reaction of binder material is indicated by minimal fluctuation of the current. This is indicative of a more localized attack.

Two distinct features of the corrosion mechanism of NiCr binder in synthetic seawater can be observed. The interface between WC-grains and the binder are preferential sites of attack (Fig. 17-a). Corrosive attack might start here due to higher defect density compared to the bulk. Secondly, not the entire binder material is attacked to the same extent (Fig. 17-b). Areas where the binder has completely dissolved are found close to areas without visible damage. This suggests a corrosion mechanism similar to pitting where localized acidification by the anodic process leads to high corrosion rates in crevices or pits.

Considering WC-NiCrMo, a completely different pattern of attack is found after potentiostatic testing (Fig. 18-a). Here, the binder alloy does not seem to be attacked at all, whereas the WC-grains appear eroded. This can be attributed to the longer exposure time to the corroding medium (47 h) at a potential, where the binder exhibits stable passivity while WC dissolves slowly. In contrast, under the same test conditions but after much shorter time (2.5 h), the binder of the the WC-CoNiCr specimen was found completely etched with WC remaining virtually unaffected, see Fig. 18-b.
dominated by CoCr- and CoNiCr-grades, simply by adapting the microstructure of the grade. Ultrafine and even near-nano WC-NiCr(Mo) low-binder cemented carbides (2–4 wt% binder) with a hardness of up to >2300 HV are now offered by the industry for the use in oil and gas exploitation, woodcutting, food processing, and others [49].

5. Conclusions

This paper presents a study on Ni-based binders for the use in WC-based cemented carbides. Phase formation and alloy constitution was systematically analysed for WC-Ni, WC-NiCr and WC-NiCrMo alloys with different gross carbon contents, and the influence on binder and composite properties, including corrosion resistance, was evaluated. We present the following conclusions:

- Significant amounts of W can be dissolved in Ni-based binders and therefore it is important to remember that the binder phase will always be an alloy, i.e., Ni(W), Ni(Cr, W) or Ni(Cr, Mo, W). Furthermore, the exact composition of such alloy can be changed by simply modifying the gross carbon content in the material. The carbon content dramatically affects the solubility of alloying elements in the binder phase. Thus, the amount of elements dissolved in the binder (in this case W, Cr and Mo) increases upon decreasing the carbon content, and reaches a maximum at the limiting carbon concentration resulting in eta- or kappa-carbide formation.
- In WC-Ni(W) cemented carbides, up to 30 wt% (12 at%) W can be present in solid solution in the binder, i.e., about double the amount of W observed in comparable WC-Co(W) cemented carbides. In addition, the experimentally observed carbon window in plain WC-Ni(W) alloys is significantly broader than in WC-Co(W).
- As a consequence of the formation of Cr-rich carbides, additions of Cr to the Ni-based binders may reduce the carbon window width if the maximum solubility of Cr in the binder is exceeded. Experimental results show that such solubility limit is around 11 wt% Cr (13 at%) at the lowest carbon contents, and around 9 wt% Cr (11 at%) at the highest carbon contents. For a given carbon content, the amount of
Cr that can be dissolved in the binder is always higher than the amount of W (in at%). We highlight that, for the same carbon activity, the addition of Cr to the Ni binder reduces the solubility of W in the binder phase.

- The maximum amount of Mo that can be added to the binder phase is limited by the solubility limit. Experimentally this limit was observed around 2 wt% Mo (2 at%) for the alloys considered in this study. Additions of Mo above this limit result in the precipitation of a (W, Mo)C carbide on the surface of the surrounding WC grains. As the amount of Mo further increases above this limit, the degree of carbide intergrowth is expected to increase, therefore increasing the carbide contiguity.

- The hardness of the cemented carbide is influenced by the binder hardness and the WC grain size. The addition of alloying elements in solid solution in the binder phase increases the binder hardness and the lattice distortion of the fcc crystal. The effect of W on lattice distortion, and thus presumably on solid solution strengthening, is more prominent than that of Cr. However, even in alloys with a higher degree of binder alloying, the binder hardness (micro and nano) is significantly lower than the hardness observed in CoCr(W) binders. This results in a decrease in composite hardness of about 100 HV30 in Ni-based binders when compared to CoCr binders. Within the different Ni-based binders, the superior composite hardness observed in WC-Ni(Cr, Mo, W) as compared to WC-Ni(W) is attributed to the superior grain refinement caused by both Cr and Mo.

- Under all corrosion conditions tested (pH 1.5–7), cemented carbides based on low carbon WC-Ni(Cr,W) and WC-Ni(Cr,Mo,W) demonstrated a superior corrosion resistance as compared to WC-Ni (W), WC-Co(Cr,W) and WC-CoNiCr(W), as well as the high carbon grades (lower degree of alloying). This behaviour is due to the formation of passivation layers rich in Cr and W (resp. Mo) which withstand a layer breakthrough even under strongly corroding conditions (e.g., sea water corrosion with strong oxidizing potential).

- Thermodynamic software tools were successfully used to select the carbon contents to be used in this study, and to obtain a prediction of the phase formation and solubilities in the binder phases. We find some disagreement between calculations and experiments: In WC-Ni systems, the processing window was experimentally shown to be significantly broader (0.6 wt% C) than the window predicted by the calculation (0.4 wt% C). Furthermore, at high carbon contents the predicted amount of W dissolved in the binder phase is significantly higher than the experimentally observed concentration. For WC-Ni15Cr systems, the main differences are found in the low carbon region. Experimentally, kappa carbides are found instead of eta carbides (as predicted). Finally, the M7C3 carbides predicted by thermodynamic calculations for WC-Ni15Cr alloys with low carbon contents were not observed experimentally.

Authors contribution

All authors contributed to the study, either in its conception and design, in the scientific discussions, writing/reviewing parts of the manuscript, or performing measurements. All authors read and approved the final manuscript.

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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