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EFFECT OF CORROSION-INDUCED DAMAGE ON MICROSTRUCTURE AND RESIDUAL STRENGTH OF WC-Co,Ni CEMENTED CARBIDES

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Abstract

In this work the corrosion behavior of cemented carbides with two different binders, Co and Ni, and carbide mean grain size, ultrafine and coarse, was studied. Immersion tests in acidic, neutral and alkaline solution were performed to induce corrosion damage in a controlled way and to determine corrosion rates. Electrochemical parameters were measured together with a microstructural characterization of the corroded surfaces. The influence of microstructure on the tolerance to corrosion damage was carried out by using residual strength as the critical parameter. Results revealed that corrosion rates were lower in alkaline solution. In contrast, acidic solution led to a higher corrosion rates especially for cemented carbides with Co regardless the influence of carbide mean grain size. Corrosion damage resulted in strength degradation due to the formation of surface corrosion pits in acidic solution. In neutral and alkaline solutions, higher strength losses were determined for the ultrafine grade.

Keywords: Corrosion, Cemented carbides, Binder, Grain size, Damage tolerance

1. Introduction

Cemented carbides, often simply called as hardmetals, belong to a group of ceramic-metal composite materials that exhibit an extraordinary combination of hardness, strength, toughness and wear resistance [1,2]. They are widely used in a large number of industrial applications demanding high performance under severe working environment, such as cutting and forming tools, mechanical seals and mining bits [3]. These applications often expose them to chemically aggressive media including a large variety of corrosive environments, such as lubricants, chemical and petrochemical products as well as mine- and sea-water.

Corrosion mechanisms in cemented carbides are really complex and depend on a large numbers of factors, such as surface state, corrosive medium, hardmetal microstructure and binder chemical nature. It has been found that nickel, nickel-chromium and nickel-cobalt binder have generally exhibited higher corrosion resistance compared to cobalt binder phase, especially in acidic and neutral media [4]. In these conditions, metallic binders are preferentially attacked while ceramic phase is easily corroded in alkaline solution [5,6]. Regarding the influence of grain size, no clear picture can be found in the literature: Human and Exner found almost no influence of the grain size on the corrosion behavior in acids [7], while Tomlinson and Ayerst reported an increase of the passive current densities by rising grain size in acidic solutions [8]. As neither the materials, nor the electrolytes are identical in these studies, it is difficult to draw conclusions from the results reported in the literature.

In-service performance of hardmetals is not only dependent on their intrinsic mechanical properties but also is highly influenced by their resistance to the aggressive medium to which they are exposed. Therefore, it is of crucial importance to improve the corrosion resistance of cemented carbides in order to increase their service life and to prevent premature failure of tools and components. Accordingly, several studies have been done focused on studying the synergic effects between erosion/abrasion and corrosion on the wear rates of cemented carbides [9,10]. Cemented carbides exhibit brittle fracture behavior related to the propagation of pre-existing flaws which may be processing-, shaping-, or service induced defects. Therefore, corrosion damage may also induce a detrimental effect on the strength and fatigue resistance of hardmetals. However, the correlation between strength reduction and corrosion damage in cemented carbides has been scarcely reported [11-14].

Following the above ideas, cemented carbides with two different binders, Co and Ni, and carbides mean grain sizes, ultrafine and coarse, were studied in order to: (1) evaluate the corrosion behavior under acid, neutral and alkaline conditions and (2) correlate the corrosion-induced damage on the microstructure and the residual strength.

2. Experimental procedure

Four hardmetal grades with different binder and carbide mean grain size were studied. All materials were supplied by Sandvik Hyperion. Main microstructural characteristics, including specimen designations, binder content ($\%_{wt.}$), mean grain size (d_{WC}), contiguity (C_{WC}) and binder mean free path (λ_{binder}) are listed in **Table 1**. Mean grain size was measured following the linear intercept method, using field emission scanning electron microscopy (FESEM) micrographs. On the other hand, carbide contiguity and binder mean free path were deduced according to empirical relationships given in the literature [15]. A small amount of Cr_3C_2 (i.e. < $1\%_{wt.}$) was added to the composition of 10CoUF and 9NiF grades as grain growth inhibitor.

Table 1. Microstructural parameters for the investigated cemented carbides.

Specimen code	wt.% Co	wt.% Ni	d_{WC} (µm)	C_{WC}	λ_{binder} (µm)
10CoUF	10	--	0.39 ± 0.19	0.46 ± 0.06	0.16±0.06
10CoC	10	--	2.33±1.38	0.31±0.11	0.68±0.48
10CoNiC	8	2	1.44±0.86	0.38±0.08	0.47±0.30
9NiF	--	9	0.83±0.49	0.44±0.08	0.29±0.18

Corrosion behavior was studied on the basis of the electrochemical response of the studied grades in three different solutions: acidic (0.1M HCl), neutral (0.1M NaCl), and alkaline (0.1M NaOH). The electrochemical tests were carried out using a standard three-electrode system in which the test specimen was the working electrode, a platinum wire was the counter electrode and a silver/silver chloride electrode was used as the reference electrode. After immersion in the electrolyte, the open circuit potential was stabilized for 30 min. Subsequently, the samples were polarized into the cathodic region at -500 mV. Then, the potential was increased towards the anodic region with a scan rate of 600 mV/h in the positive direction up to 500 mV.

Immersion tests were performed to induce corrosion damage in a controlled way and to determine corrosion rates. These tests were done at room temperature in the same three solutions (stirred) as mentioned above. Weight loss was measured after immersion tests performed from 1 h to 240 h. Before and after immersion tests, the specimens were hand-cleaned using soapy water, then ultrasonically cleaned for 15 min in ethanol, and subsequently dried in air. The specimens were weighted using an electronic balance having a resolution of ±0.1 mg, and the corrosion rates were determined using Equation 1:

$$Corrosion(mm/year) = 87.6\left(\frac{w}{A\rho t}\right) \qquad \text{Eq.1}$$

where w is the weight loss in mg; A is the surface area of the specimen in cm^2; ρ is the density of the material in g/cm^3; and t is the corrosion time in hours.

After immersion tests, retained flexural strength (σ_r) was determined by subjecting 4 mm × 3 mm × 45 mm specimens to failure using a four-point bending fully articulated test with inner and outer spans of 20 and 40 mm, respectively. Subsequently, a detailed FESEM fractographic inspection was conducted with the purpose of characterizing corrosion damage as well as to identify critical failure sites.

3. Results and discussion

3.1. Potentiodynamic polarization behavior

Figure 1 shows the obtained potentiodynamic polarization curves for the studied grades in the acidic, neutral and alkaline solutions. The electrochemical parameters measured for the studied cemented carbides are listed in Table 2. They which include corrosion potential (E_{corr}), corrosion current density (i_{corr}), measured using the Tafel method, and critical current density (i_c), which refers to the current density necessary to reach the passive or pseudo-passive potential. As it can be observed, the grade with nickel as a binder, 9NiF, displayed the most noble corrosion potential in acidic and neutral solution while cobalt grades with a coarse mean grain size, 10CoC, presented the most negative values. For this type of microstructure, the corrosion potential was shifted to more positive values with the presence of 2 $_{wt\%}$ of nickel as a binder, 10CoNiC. It is important to point out that although i_{corr} is higher in either acidic or neutral solutions for 9NiF, i_c was at least one order of magnitude lower than the rest of the cobalt grades. The addition of chromium in cobalt grades, 10CoUF, did not contribute to a better corrosion response in acidic solution. As can be seen in the Table 2, the E_{corr} is moved in the noble direction. Likely, the apparent transpassive region is shifted to higher potentials and lower i_c, compared to the other grades. However, at about +100 mV, the self-passivating layer, undergo pitting corrosion and the surface response became similar to the other cobalt grades. This phenomenon is supposed to be related to the fracture of the protective oxide film as mention in previous studies [16]. Nevertheless, future works are needed to corroborate it. Regarding alkaline solution, no significant differences were observed for cobalt grades. In this media where the ceramic phase is easily corroded [5,6], the nickel grade showed the highest current densities.

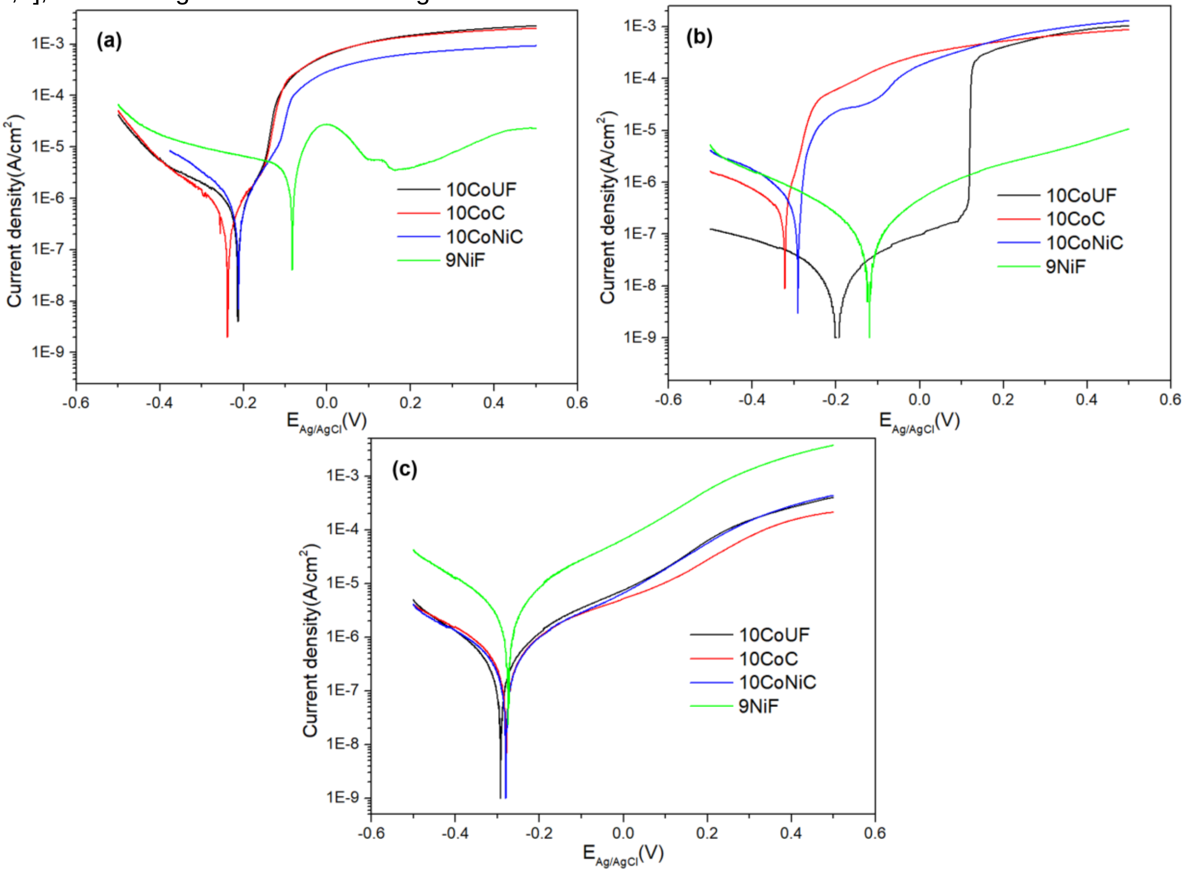

Figure 1. Potentiodynamic polarization curves of studied cemented carbide grades in: (a) 0.1M HCl, (b) 0.1M NaCl and (c) 0.1M NaOH.

Table 2. Electrochemical corrosion parameters of studied cemented carbide grades in acidic, neutral and alkaline solutions.

Corrosive Media	Specimen Code	E_{corr}(V)	i_{corr}(A/cm^2)	i_c (A/cm^2)
0.1M HCl	10CoUF	-0.213	1.05×10^{-6}	1.90×10^{-3}
	10CoC	-0.237	9.27×10^{-7}	1.90×10^{-3}
	10CoNiC	-0.212	1.30×10^{-6}	8.92×10^{-4}
	9NiF	-0.084	1.54×10^{-5}	2.11×10^{-4}
0.1M NaCl	10CoUF	-0.196	7.38×10^{-8}	2.21×10^{-7}
	10CoC	-0.322	5.05×10^{-6}	3.67×10^{-4}
	10CoNiC	-0.291	5.22×10^{-6}	2.07×10^{-4}
	9NiF	-0.124	5.20×10^{-7}	--
0.1M NaOH	10CoUF	-0.292	1.19×10^{-6}	--
	10CoC	-0.278	1.12×10^{-6}	--
	10CoNiC	-0.279	1.02×10^{-6}	--
	9NiF	-0.274	1.20×10^{-6}	--

3.2. Immersion tests

In immersion, the corrosion rates were higher for all studied cemented carbides grades in acidic solution compared to neutral and alkaline ones, where lower values were measured. Coarse carbide mean grain size cobalt grade, 10CoC, displayed in each solution the highest values while 9NiF showed the best corrosion resistance. The presence of small amount of chromium in 10CoUF grade together with the ultrafine microstructure was proved to be more effective than the presence of 2%$_{wt.}$ of nickel in a coarse microstructure of a cobalt grade, 10CoNiC. This result is in agreement with previous studies which pointed out that during sintering chromium dissolves into the binder, resulting in a beneficial effect against corrosion [8,17]. TEM analysis performed by Suttihiruangwong et al. demonstrated the formation of a passivating Co-based chromium oxide layer film at the binder surface, which strongly decreased the rate dissolution of the binder, and hence improved the corrosion resistance of Cr-containing cemented carbides [17].

For all studied grades and solutions, the corrosion rates decreased with increasing immersion time. In acidic and alkaline solutions, the corrosion rates sharply decreased after the first 6-8 hours of immersion, remaining constant beyond 24 h. For these two solutions, no layer of corrosion products was observed at the surface. In neutral solution, the reduction of the corrosion rate as a function of immersion time was observed to be more gradual for the coarse cobalt grades,10CoC and 10CoNiC. In this case, the presence of chloride ions enhanced the formation of a corrosion product layer which slowed down the dissolution of cobalt. The presence of such layer was demonstrated with AFM measurements for samples immersed in synthetic mine water [16]. This layer does not protect the material from corrosion, as chromium, but hinders the dissolution process of cobalt.

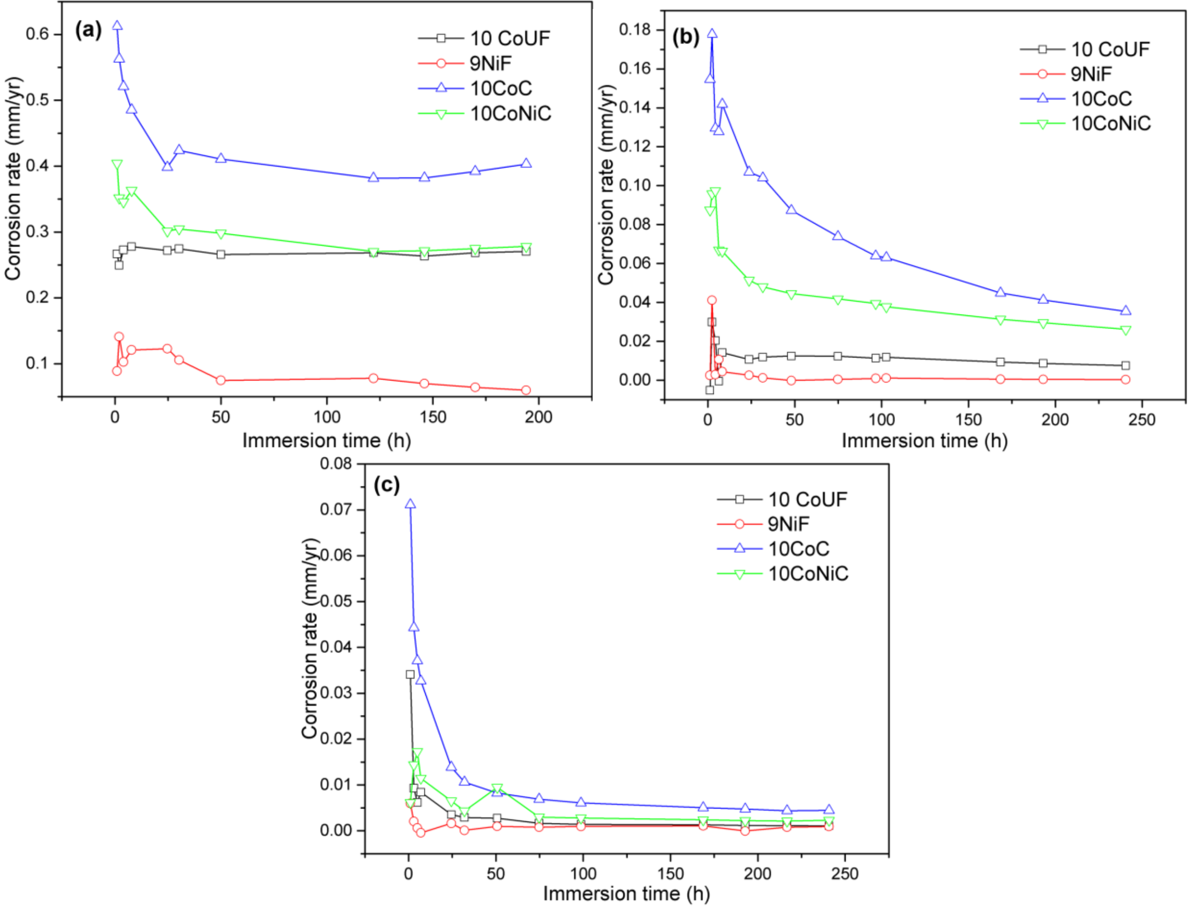

Figure 2. Corrosion rates as a function of immersion time for the studied cemented carbides in different solutions: (a) 0.1M HCl, (b) 0.1M NaCl and (c) 0.1M NaOH.

3.3. Flexural strength

Retained strength was measured using samples subjected to immersion tests of 240 h in acidic, neutral and alkaline solutions respectively, Figure 3. Values are plotted as normalized strength loss, using as reference baseline the strength exhibited by uncorroded specimens. As it can be observed, each studied corrosive media may cause different strength loss, most likely related to significant differences in the size and geometry of corrosion-induced damage acting as critical flaws for fracture. HCl solution was the most aggressive media which significantly deteriorated the flexural strength for all studied grades, including the one with nickel as a binder. The highest strength loss, 60% approximately, was observed for 10CoC. For neutral and alkaline solutions, retained strength was at least 80% in the worst-case scenario. Aiming to analyze corrosion-induced damage promoting failure, a detailed inspection of fractured surfaces was conducted by means of FESEM. The observations revealed clear differences between the corrosion induced damage as a function of the pH solution. In this sense, the affected depth from the surface for 10CoC in acidic media was 146 μm, Figure 4a, while in alkaline media the affected depth was maximum 20 μm, Figure 4b.

Taking into account the effect of carbide grain size, in the neutral and alkaline solutions, the ultrafine-sized studied grade was much more affected by corrosion-induced damage than coarse-sized one. As reported in the previous investigation, sharp corrosion pits are formed in ultrafine-sized cemented carbides as immersion time increases, which have a much more pronounced stress rising effect. Consequently, higher strength loss were determined for ultrafine grades [13].

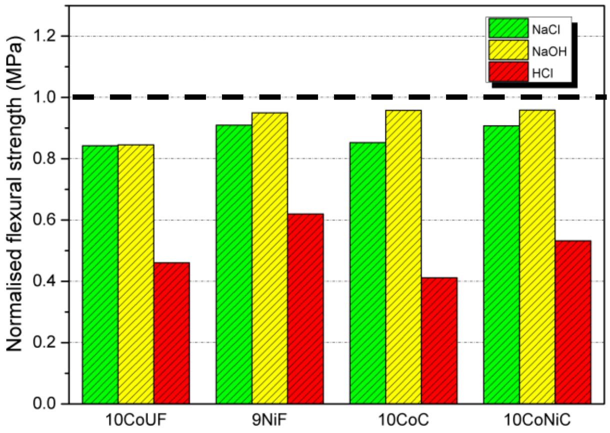

Figure 3. Normalized retained strength for the studied materials in different corrosive medias. Strength of uncorroded specimens is used as reference baseline.

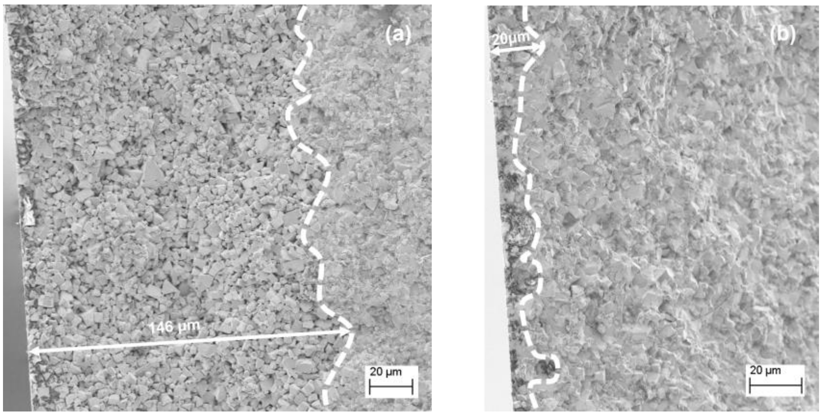

Figure 4. Critical corrosion damage promoting failure in different corrosive solutions for 10 days for studied cemented carbides: (a) 10CoC in HCl, (b) 10CoC in NaOH,

4. Conclusions

In this study, corrosion behavior was studied together with the effect of the corrosion induced damage on residual strength of cemented carbides with different binders and carbide grain size by immersing them in acidic, neutral and alkaline solutions. The main conclusions are drawn as follows:

- Electrochemical and immersion tests test revealed that nickel binder displays more noble corrosion potential and critical current density compared to cobalt grades in acidic and neutral solutions. In these conditions, the presence of small amounts of chromium improves more the corrosion resistance of the materials than mixing nickel and cobalt as a binder. No significant differences among studied grades where observed at alkaline solution.

- Corrosion damage resulted in strength degradation on the basis of stress rising effects associated with the formation of surface corrosion pits in acidic solution for all studied grades. In neutral and alkaline solutions, much more pronounced stress rising effects and consequently higher strength losses were determined for the ultrafine grade.

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