See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/272169715

Effect of nanostructuring and alloying element on electrochemical behaviour of HVOF sprayed WC-Co coatings

Article in Journal of The Electrochemical Society · January 2009



Some of the authors of this publication are also working on these related projects:

Project Looking for Post Doctoral Position View project

BIOTIP View project

All content following this page was uploaded by Michail Vardavoulias on 12 February 2015.

Effect of nanostructuring and alloying element on electrochemical behaviour of HVOF sprayed WC-Co coatings

A. K. Basak*^{, 1}, J.-P. Celis¹, P. Ponthiaux², F. Wenger², P. Matteazzi³, M. Vardavoulias⁴

¹Katholieke Universiteit Leuven, Dept. MTM, B-3001 Leuven (Belgium)
 ² Ecole Centrale Paris, LGPM, F-92295 Châtenay-Malabry (France)
 ³CSGI, via Della Lastruccia, 3, I-50100 SestoFiorentino (Italy)
 ⁴PyroGenesis SA, Technological Park of Lavrion, Gr-19500, Lavrion (Greece)

Abstract

HVOF sprayed WC-Co nanostructured coatings deposited on low carbon steel and alumina substrates were investigated in artificial sea water. The objective is to get a better insight into anodic/cathodic behaviour of such nanostructured materials in comparison to common micro-structured ones. Impedance spectroscopic data were recorded and fitted with equivalent electrical circuits. A good fitting is obtained between experimental data and a proposed equivalent electrochemical model over a wide range of frequencies. The nanostructuring as well as the coating composition greatly influence the electrochemical response of such materials. The EIS-investigation revealed that the polarization resistance of nanostructured WC-Co coatings is slightly reduced compared to micron-sized WC-Co coatings. Moreover nanostructuring reduce corrosion potential and enhance Co dissolution. It was also shown that 'through coating pores' are most unlikely in the tested samples notwithstanding a not yet minimized coating porosity.

Keywords: nanostructure, cermets, thermal spraying, electrochemistry, impedance spectroscopy, corrosion.

E-mail address: <u>Animesh.Basak@mtm.kuleuven.be</u>

^{*} Corresponding author:

Tel.: +32 16 321238

Fax: +32 16 321991

1. Introduction

The demand for hard coatings to combat wear and corrosion is still large and the prime requirement is to ensure that the coating system does not deteriorate the mechanical properties of the substrate. To meet the industrial requirements on wear and corrosion resistance, WC-Co hard coatings are frequently used. However, these types of WC-Co coatings generally contain certain amount of pores. If the coating is free from 'through coating pores' then the corrosion resistance of coated materials depends on the corrosion resistance of the coating itself. Additionally, a corrosion process similar to crevice corrosion may take place at pores in which the electrolyte can penetrate [1].

Recently nanostructured WC-Co coatings were deposited by HVOF (high velocity oxyfuel) thermal spraying to get the optimum benefit from the high wear resistance of WC-Co and the improved mechanical and/or electrochemical properties due to nanostructuring. Nanostructuring can significantly improve the engineering properties resulting from the fact that some 30 to 50% of the atoms reside at grain boundaries. A crystallite or grain size below 100 nm can be achieved. Such grain sizes are 100 to 1000 times smaller than the grain size of current engineering materials [2]. In thermal sprayed coatings pores, grain/particle boundaries or pores between the deposited powders are generally inevitable because the coating results from a splashing of powders. In the case of sprayed WC-Co coatings, the pore walls consist of WC particles and Co matrix. As a result, the pore walls are electrically conductive in nature and participate in the electrochemical reactions. Saenger *et al.* has classified this type of conductive pore walls as 'active pores' [3].

It has already been proven that electrochemical impedance spectroscopy (EIS) is very efficient to study the electrochemical kinetics of porous materials, and the corrosion behaviour of coatings [4-13]. The EIS technique shows promise in assessing the corrosion performance of materials, coating quality, and corrosion reactions at the coating/substrate interfaces (especially at pores or pinholes). EIS provides much more information than routine d.c. electrochemical methods like open circuit potential measurement, poitentiostatic and potentiodynamic polarization measurements etc. [10]. One of the main advantages of EIS is that the measured data can be described analytically using equivalent electrochemical circuits [14]. The elements of an equivalent circuit model represent the microscopic processes involved in the transport of mass and/or electrical charge.

In this paper, the corrosion mechanism of nanostructured WC-Co coatings deposited by HVOF on different substrates is investigated. Electrochemical impedance spectroscopy was performed with complementary d.c. electrochemical techniques. HVOF sprayed micron-sized WC-Co coatings of common industrial quality (producer: Pyrogenesis, Lavrion, Greece) and low carbon steel are used as reference materials. The novelty of this work is that, for the first time, effect of the nanostructuring on the electrochemical behaviour of HVOF sprayed WC-Co based coatings was investigated by EIS as well as the effect of small amount Al addition as alloying element in such coatings.

2. Experimental methods

2.1. Materials

Three types of coatings deposited starting from nanostructured powders by HVOF were investigated namely (i) a micron-sized WC-12Co coating (referred as μ WC-Co), (ii) a nanostructured WC-12Co coating (referred as nWC-Co) and (iii) a nanostructured WC-12Co-2Al coating (referred as nWC-Co-Al). To evaluate the effect of substrate as well as porosity on the electrochemical responses, each type of coating was deposited on two different flat substrates, (i) a chemically inert alumina substrate, and (ii) a corrosion sensitive low carbon steel (LCS) substrate. Uncoated low carbon steel (referred as LCS) was also investigated as reference material. The coatings were deposited on 50 mm x 50 mm x 5 mm substrates.

Nanostructured powders (crystal size 11-13 nm) were produced by the Mechanomade® process (MBN, San Vendemiano TV, Italy). In that technique, mechanical agitation and chemical reaction simultaneously take place in a reactor to produce nano-phased powders [15]. Thermal spraying of agglomerated nanostructured powders (~ 50 μ m) was performed by HVOF (Pyrogenesis, Lavrion, Greece) by using a Sulzer Metco DJ 2700 spraying gun with propane as fuel gas. The spraying gun was adjusted on a fully automated and robotized spray system in order to ensure repeatability.

All the electrochemical experiments except potentiostatic polarization measurements were carried out on as-received samples. Prior to potentiostatic polarization measurements, thermal sprayed coatings were polished down to Ra ~ 40 nm measured by white light interferometer (WYKO NT 3300). SEM investigations on cross section revealed that the coating thickness is still around 150 μ m after polishing. Image analyses were done on SEM micrographs of cross sections to estimate the percentage of porosity in the coatings. In case of thermal sprayed coatings porosity is unavoidable. There are different kinds of pores which are generally present in the thermal sprayed coatings and among them the following four kinds of pores are most frequently encountered, namely (i) open porosity, (ii) closed porosity, (iii) interconnected porosity and (iv) 'through coating' porosity. Among these four kinds of pores, 'through coating' pores are most dangerous one, as they can lead the electrolyte to the substrate where preferential corrosion of the substrate, that is crevice corrosion, may take place. These different kinds of pores are shown schematically in Fig. 1.

2.2. Experimental procedures

The experimental set-up used to perform electrochemical tests consists of a Solartron 1287 potentiostat (producer: Solartron Analytical, USA), a frequency analyzer (producer: Solartron Analytical, USA), and an electrochemical cell. The flat test samples were covered with an electrical insulating cover prior to electrochemical tests leaving an area of 1 cm^2 exposed to the electrolyte. A three electrode setup was used consisting of a flat test sample used as working electrode, a platinum grid used as counter electrode, and a

Ag/AgCl 3M KCl (SCE = +0.207 V vs. SHE) reference electrode. The electrolyte was artificial seawater prepared according to the ASTM D-1141 standard with following composition: 29.221 g/L NaCl, 1.544 g/L CaCl₂, 11.182 g/L MgCl₂, 0.168 g/L NaHCO₃, and 0.021 g/L Na₂CO₃. The pH was 7.8, and electrochemical tests were performed at 23 °C. The cell content was 20 ml, and fresh solution was used in each test.

Open circuit potential measurements (OCP) were carried out for 1 hour starting on immersion. During the potentiodynamic polarization measurements, the working electrode potential was scanned from - 0.5 V up to +1.0 V vs. SCE with a Solatron 1287 electrochemical interface at a rate of 1 mV/s. Then, the potential scan was reversed down to - 0.8 V vs. SCE at the same rate. Potentiostatic polarization measurements were carried out at + 0.2 V vs. OCP for 300 seconds starting at stable open circuit potential. EIS measurements were carried out as follows: The samples were immersed in the electrolyte, and the potential stabilized for 1 hour before the start of EIS measurements. AC impedance data were obtained with a Solartron 1287 impedance gain-phase analyzer coupled to a Solartron 1255 electrochemical interface. The obtained data were analyzed by Corrview and Zview software (producer: Solartron analytical). A sinusoidal a.c. perturbation of 10 mV amplitude (r.m.s.) was applied to the open circuit potential (OCP) of the working electrode via the Solartron 1287 electrochemical interface. A frequency range of 100 kHz down to 0.001 Hz was scanned. All electrochemical tests were performed at room temperature and under unstirred conditions.

It is important to note that, all electrochemical measurements were repeated three times with fresh solution in each case. A good reproducibility was obtained.

The sample surfaces were characterized with scanning electron microscopy (Philips XL30 FEG) coupled to energy-dispersive X-ray spectroscopy (EDAX), TEM (Philips CM 200 FEG), and image analysis (Leica Qwin software).

3. Result and Discussion

3.1 Coating characterization

The microstructure of different WC-Co coatings investigated is shown as top views on polished samples in Fig. 2. Angular WC particles are embedded in the metallic matrix and homogeneously distributed. Pores in the coatings appear generally as dark phases. Typical coating properties are shown in Table 1. Image analyses of such cross sections revealed that micron-sized WC-Co coatings contain less than 0.5 % porosity. On the contrary, nanostructured coatings contain up to 3.8 % porosity. This amount of porosity is still large and could be lowered on further optimization of the HVOF spraying conditions. The hardness of these three types of coatings is comparable (HV₃₀₀ ~ 1200 Vicker's). The coatings deposited on low carbon steel substrate exhibit a good adhesion strength (> 60 MPa) determined by pull test.

Dark field TEM images of the Co metallic binder and WC particles in the nanostructured WC-Co coating are shown in Fig. 3. The size of the WC particles in these nanostructured coatings varies between 12 to 18 nm and for Co it is 20 to 28 nm. This confirms the retention of the nano-size WC particles in the coatings deposited by HVOF from nanosized powder.

3.2 Open circuit potential measurements

The open circuit potential of as-received HVOF micron sized and nanostructured WC-12Co coatings immersed in artificial sea water are shown in Fig. 4. Fig. 4(a) was on coated alumina substrates, while Fig. 4(b) was obtained on coated low carbon steel substrates. The open circuit potential stabilizes quickly on immersion with some small intermittent fluctuations. The relative evolution of open circuit potential can be explained based on the Pourbaix diagram [16], keeping in mind that such diagrams are theoretical ones and only valid for elements at thermodynamic equilibrium in water. Therefore it is not possible to apply the Pourbaix diagram directly since in this case W is present as a compound, and Co and Al may also be present as an alloy. However, according to literature [17 - 19] it is fair enough at this point to assume that mainly Co is expected to dissolve. Under the present test conditions (pH 7.8 at 23° C), W is at the boundary between passivation and dissolution, Co is in the dissolution region, while Al is in the passive region. The open circuit potential of nanostructured WC-12Co coating deposited on alumina substrate is almost 100 mV lower than the one of micron sized WC-12Co coating deposited on the same type of substrate. Since the coating composition is the same in both cases, and since porosity can not affect the open circuit potential of coatings deposited on such a ceramic substrate, the lowering of the open circuit potential noticed can be linked reasonably to the nanostructuring. Indeed, in HVOF nanostructured WC-12Co coatings, a higher amount of grain boundaries are exposed to the electrolyte than in HVOF micron sized WC-12Co coatings. As a result more reaction sites are available, and the open circuit potential is anodic compared to HVOF micron sized WC-Co coating, assuming that the oxygen flux is constant. On the other hand, the addition of Al to HVOF nanostructured WC-12Co coating increases the potential to a limited extent (about 30 mV) compared to HVOF nanostructured WC-12Co coatings. This may be due to the passivation effect of Al at pH 7.8, as revealed by the Pourbaix diagram in the case of pure Al. This phenomenon is shown schematically in Fig. 5.

In comparison to coatings deposited on alumina substrate, the open circuit potential of the HVOF micron sized WC-12Co coatings deposited on low carbon steel decreases by about 50 mV. The open circuit potential of the HVOF nanostructured WC-12Co and WC-12Co-2Al coating increases by 55 mV and 30 mV respectively. This small shift of the open circuit potential is probably due to a different coating growth mechanism. Indeed, the heat flux during thermal spraying on low carbon steel substrate can diffuse through the substrate by which the cooling rate of the deposited splashes increase. On the contrary, on alumina substrates, the heat accommodates in the deposited splashes and the cooling rate lowers.

The open circuit potential of low carbon steel is anodic by about 200 mV compared to the HVOF micron sized WC-12Co coating. Since the open circuit potential of HVOF micron

sized and nanostructured WC-12Co based coatings deposited on low carbon steel substrate is not largely different from the ones deposited on alumina substrates, it is unlikely that the coatings contain 'through coating pores'. However, this does not rule out the role of other porosities in the coatings and effect of open pores/ interconnected pores can be considered.

3.3 Chronoamperometric investigation regarding coating degradation

Chronoamperometric measurements at + 0.2 V vs. OCP were triplicated on polished coatings (Ra ~ 40 nm) deposited on low carbon steel substrates. A representative chronoamperometric measurement on nanostructured HVOF WC-12Co coating is shown in Fig. 6. Dashed line aa' in Fig. 6 represent the current evolution during dissolution of coating constituents whereas the line bb' represent repassivation. Thus the resulting curve is the summation of these two process as denoted in Fig. 6 as (I) dissolution region and (II) repassivation region. At the start of the experiment, the anodic dissolution of coating constituents dominates over cathodic repassivation and as a result the current increase with time. After some time, around 17 s in present case, the scenario reverse. Now cathodic repassivation dominates over anodic dissolution and the current decrease and stabilise with time that is the system became in dynamic equilibrium. A comparison of chronoamperometric measurements for different micron sized and nanostructured HVOF WC-12Co coatings is shown in Fig. 7. In the case of nanostructured HVOF WC-12Co-2Al coating and micron sized HVOF WC-12Co coating, the repassivation region starts earlier than on the nanostructured HVOF WC-12Co coating. This indicates a higher reactivity of the nanostructured HVOF WC-12Co coating in the electrolyte prolonging the anodic dissolution process.

From these current vs. time curves, the charge passed through the apparent exposed area of the coatings (1 cm^2) at the applied anodic potential, was calculated as:

$$Q = \int_{t_0}^{t_{300}} It$$
 (1)

with Q the charge passed through the coating in Coulomb (C), I the current at a given potential in ampere (A), and t time in second (s). The charge passed through the HVOF micron sized WC-12Co coating is 0.06 C and much lower than on HVOF nanostructured WC-12Co-2Al (0.24 C) and nanostructured WC-12Co coating (0.61 C). After the chronoamperometric measurements, the morphology of the coating surface was investigated by SEM as shown in Fig. 8, were used to determine the length of the particle-matrix interface by image analysis. The charge passed through the coatings during potentiostatic polarization is plotted versus that length of the particle-matrix interface in Fig. 9. The spread on data was obtained through standard deviation of results of three independent chronoamperometric measurements under identical set of test parameters.

It should be noted that the length of the particle-matrix interface in nanostructured coatings deviates from the theoretical one (~ $10^9 \,\mu$ m/cm²) due the instrumental limitation. However, it confirms the claim that nanostructured coatings have a larger particle-matrix interface than micron sized ones. The electrochemical attack on micron sized coatings is thus confined within fewer interfaces than in nanostructured coatings. This dissipated anodic charge is thus most probably due to the oxidation of metallic cobalt matrix according to equation 2, since in artificial sea water W is almost inert [20].

$$Co \rightarrow Co^{++} + 2e^{-}$$
 (2)

3.4 Potentiodynamic polarization investigation to unravel passivation-repassivation behaviour of HVOF nanostructured WC-12Co coatings

In order to find out the detailed role of passivation-repassivation of WC-12Co coatings, potentiodynamic polarization measurements were carried out as described hereafter.

Potentiodynamic polarization curves (out of triplicated tests) recorded in artificial sea water on HVOF micron sized and nanostructured WC-12Co based coatings deposited on alumina substrates are shown in Fig. 10. Nanostructuring causes a shift of the anodic polarization curves to higher current density compared to micron sized coatings (Fig. 10). Since the sample size exposed to the electrolyte was identical, the cathodic and/or anodic reactions are enhanced compared to micron sized coating. This may be due to the effect of porosity (not 'through coating pores') and/or nanostructuring of the coating. On alumina substrate E_{corr} of micron sized WC-12Co coating is about -0. 44 V vs. Ag/AgCl, while it is around -0.54 V vs. Ag/AgCl and -0.53 V vs. Ag/AgCl respectively for nanostructured WC-12Co and WC-12Co-2Al coatings. This observation is in line with the open circuit potential measurements.

Potentiodynamic polarization measurements on as-received HVOF micron sized WC-12Co deposited on low carbon steel and uncoated low carbon steel substrate are shown in Fig. 11. The coating shows a limited passivation-repassivation behaviour, and the coating is more noble then the low carbon steel. This type of limited passivation-repassivation behaviour of WC-Co coatings is termed as pseudo-passivity in some literature [17]. Like in the case of Fig. 10, nanostructuring of WC-12Co coating also shifts the potentiodynamic polarization curve (Fig. 11) shifted to higher current density (from $\sim 10^{-10}$ ³ A/cm² to ~ 10^{-2} A/cm²) and a lower corrosion potential (E_{corr} from - 0.49 V vs. Ag/AgCl to - 0.53 V vs. Ag/AgCl) is noticed compared to micron sized WC-12Co coating deposited on low carbon steel. The addition of Al as alloying element to a HVOF nanostructured WC-12Co coating (Fig. 11) causes a further shift of the E-i curve towards high current density (from ~ 10^{-2} A/cm² to ~ 10^{-1} A/cm²) while E_{corr} is almost unaffected (E_{corr} from - 0.53 V vs. Ag/AgCl to - 0.50 V vs. Ag/AgCl). When exposed to a corrosive media, usually a preferential attack of metallic materials takes place at grain boundaries. Nanostructured coatings have, in comparison to micron sized coating, a high grain boundary density, and thus a larger area undergoing anodic dissolution. At the same time, nanostructured coatings are characterized by small cathode and anode surfaces resulting in an evenly distributed localized corrosion what may be beneficial in terms of corrosion resistance. This phenomenon is supported by the work of Tao et al. [21] who investigated pulse electrodeposited nanocrystalline copper in 0.1 M NaOH solution and showed that nanocrystalline copper exhibits a higher corrosion resistance then microcrystalline copper in that alkaline electrolyte (no pH was mentioned!). A literature survey of the E_{corr} and I_{corr} values of some micron sized and nanostructured materials is summarized in Table 2.

During anodic polarization, the formation of various oxide films was observed on WC-12Co coatings. WC phases act as cathode in contact with Co, which acts as anode. According to [22], a passive surface layer mainly consisting of WO₃ is built on WC coating which can be cathodically reduced again [22], whereas Co can oxidize to CoO, forming an inner layer, and to $Co_{3-x}O_4$ as an outer layer on Co in aqueous solution of 5 x 10^{-1} mol dm⁻³ sulphuric acid [23]. The observed enhanced Co dissolution occurs thus due to the unfavorable surface ratio of anodic to cathodic sites. In parallel, the cathodic reaction, i.e. the reduction of oxygen or hydrogen will take place on the WC phase, which is thereby 'in principle' protected against electrochemical dissolution.

According to classic corrosion theory, nanostructuring of materials should accelerate corrosion by forming more micro electrochemical cells across the huge amount of grain boundaries [24]. According to literature, the effect of nanostructuring on the corrosion behavior varies among metal systems and corrosion environments [17, 18] as summarized in Table 2. Therefore it is difficult to predict the electrochemical behavior of nanostructured materials from the one of coarse-grained polycrystalline counterparts [25-27]. Recently Wang *et al.* [28] investigated the corrosion resistance of nanocrystalline Co coatings obtained by pulse reverse electrodeposition. They clearly showed that in weekly acid to weekly basic media, nanocrystalline Co coatings exhibited an improved corrosion

resistance in term of E_{corr} compared to coarse grain Co coatings (see Table 2). They attributed that to the higher grain boundary density in nanocrystalline materials that allows a quick formation of a stable and protective passive film. But in strong acidic media [28], the scenario was completely the opposite one. In that case, corrosion rate accelerates by providing a high density of active sites (grain boundary) for preferential attack.

The reduction of the corrosion current on nanostructuring was also noticed in the presently investigated HVOF nanostructured WC-12Co based coatings compared to HVOF micron sized WC-12Co coating in artificial sea water. In Table 3, E_{corr} and I_{corr} values were calculated according to Tafel plot [17] from potentiodynamic polarization experiments.

3.5 Investigation on dissolved coating constituents through ICP analyses

After open circuit potential, chronoamperometric, and potentiodynamic polarization measurements on the coatings deposited on low carbon steel, the electrolytes were analyzed by ICP-AES technique to identify and to quantify the different dissolved elements. The chemical analyses were carried out for three times to check reliability. A good reproducibility was obtained (Fig. 12). The ICP-AES measurements revealed the presences of only Co and W in the electrolytes in all cases and Al or Fe were not detected in the electrolytes. According to literature [17], in neutral solution like artificial sea water pH 7.8 at 23° C, the corrosion process of WC-12Co coatings consists mainly of Co

dissolution. Dissolution of WC becomes more significant at alkaline pH. Degradation is mainly the result of a selective uniform dissolution of the metallic phases (mainly Co) and not of a localized corrosion because of the poor passivation ability of Co (except at alkaline pH). The galvanic coupling between the Co binder and WC accelerates Co dissolution and hinders the WC dissolution compared to pure compounds. Indeed, a same scenario was observed in this work and it was more pronounced on nanostructured coatings. In nanostructured coatings, there is a high dissolution of Co but a low dissolution of W, compared to micron sized ones. This is due to high amount of grain boundaries in nanostructured coatings so that, as a consequence, more galvanic couples are active leading to a subsequent higher Co-dissolution.

The occurrence of galvanic coupling in HVOF micron sized WC-12Co coating was previously reported by Monticelli *et al.* [29]. The cobalt dissolution rate in the cermet was found to be faster than on bulk cobalt as a consequence of the alloying with the carbide [29-31]. The addition of Al to nanostructured WC-12Co coating tends to lower the Co dissolution may be due to its alloying effect. Moreover the evolution of cobalt dissolution noticed (Fig. 12) in ICP measurement is in line with the evolution in charge passed during chronoamperometric measurements (Fig. 7): lower for micron sized WC-12Co-2Al coating.

In view of above discussion, the higher Co dissolution noticed on HVOF nanostructured WC-12Co based coatings (Fig.12) compared to HVOF micron sized WC-Co coating

could be explained in view of chronoamperometric and potentiodynamic results observations in two ways:

- (i) The composition of the metallic matrix differs in nanostructured from the one in micron sized WC-12Co coatings as a result of the elaboration process. The metallic matrix is more 'reactive' in nanostructured coatings due to a higher grain boundary density.
- (ii) Corrosion occurs mainly at the matrix/WC interfaces as a result of galvanic effects between cathodic WC and anodic Co. The higher total length of the interfaces in nanostructured WC-12Co coatings explains than the higher amount of dissolved cobalt.

3.6 Electrochemical impedance spectroscopy (EIS) investigation regarding coating porosity and degradation mechanisms

The corrosion resistance of a coated material is evaluated as a coating/substrate system. In the case of a noble coating deposited on a lesser noble substrate, the substrate has a stronger corrosion tendency and corrosion of the substrate takes place in preference to coating corrosion when both materials are exposed to an electrolyte. Consequently impermeability of the noble coating determines the protective performance of the coating/substrate system rather than its corrosion resistance. In that respect, the objective of this section is to use electrochemical impedance spectroscopy (EIS) to unravel the corrosion mechanisms of the HVOF WC-Co coatings as well as to disclose the role of coating constituents and substrates.

The EIS Nyquist plots recorded on different coatings on both ceramic and low carbon steel substrate are shown in Fig. 13 and a zoom-in as an insert. In the case of HVOF micron sized WC-Co coatings, there is a small capacitive loop at high frequency followed by a large capacitive loop at low frequency. In the cases of HVOF nanostructured WC-12Co and WC-12Co-2Al coatings and uncoated low carbon steel (LCS), there is only one capacitive loop in the whole frequency range. In all cases, the EIS spectra are similar in shape but differ in magnitude, except for the micron-sized WC-12Co coating at low frequency. This means that the corrosion mechanisms of the different materials are the same but the reaction rate varies. It was reported earlier that the EIS spectrum recorded on cermet based coatings is strongly influenced by the coating morphology and porosity [2, 8, 30 -31]. The dissolution of the metallic substrate strictly depends on the presence of 'through coating' pores. Then the micro-galvanic effects between substrate and coating can become important [232]. According to Saengera et al. [3] a 'through coating' pores can only be achieved when the WC-12Co matrix is globally conductive, what implies that the Co matrix has to be connected by some percolation and that electrolyte reaches the substrate by a wetting process throughout the pores.

In this investigation it is clear from the EIS spectra in Fig. 13 that the micron-sized WC-12Co coating undergoes a different corrosion mechanism than the nanostructured ones. The micron sized WC-12Co coating has a very low (0.5%) porosity level. A large capacitive loop at low frequency on such WC-12Co cermet coatings was also reported by Saengera *et al.* [3]. This means that after an initial interaction between coating and electrolyte, the pore walls became active. In the case of nanostructured WC-12Co based coatings, the porosity is high (up to 3.8%) and the porosity affects the EIS spectra. There is only one capacitive loop in the whole frequency range indicating an on- going reaction between coating and electrolyte, and a filling up of pores. The spectra show a higher polarization resistance for micron sized coatings compared to nanostructured coatings. This is due to the fact that in nanostructured coatings a higher grain boundary density is available as well as more pores. On the other hand, on low carbon steel (LCS) a representative capacitive loop is noticed in agreement with [33].

The equivalent circuit of the impedance spectrum shown in Fig. 14 was proposed by Saengera *et al.* [3] for plasma sprayed micron sized WC-Co coating, and by Liu *et al.* [32] for PVD processed TiN coating. WE and RE denote the working and reference electrode respectively. This type of equivalent circuit is most frequently used to interpret the EIS data obtained on thermal sprayed micron sized WC-12Co based coatings [3]. The circuit components represent the 'overall electrochemical behaviour' of the coating surface, where R1 is solution resistance, R2 is overall transfer resistance, and R2+R3 is the polarization resistance of the coating. The constant phase element in the equivalent circuit was used instead of capacitance which represents the building up of charges in the coating surface as well as pores.

Considering the capacitive loops recorded at high frequency, a depression is noticed in the case of nanostructured WC-12Co based coatings compared to micron sized ones. The presence of depressed semicircles has been explained by a number of phenomena, like heterogeneity of the material, contamination, surface morphology etc. depending on the nature of the system investigated [35]. However, the common trend among these explanations is that some property of the system is not homogeneous or that there is a distribution (dispersion) of some physical property of the system. In this case, it is most likely that this dispersion in the capacitive loop is due to the presence of pores or the formation of non-uniform reaction layers. Therefore, the pure double layer capacitance (C_{dl}) is replaced by a constant phase element, *CPE* [36]. Mathematically, the *CPE's* impedance is given by equation (6.3) [35]:

$$Z_{CPE} = \frac{1}{Q^{\circ}(j\omega)^{\alpha}}$$
(3)

with Q° (S·s^{α}) the CPE coefficient and has the numerical value of the admittance (1/|Z|) at $\omega = 1$ rad/s, ω the angular frequency ($\omega = 2\pi f$), f the frequency applied during impedance measurements, and α the CPE exponent. When $\alpha = 1$, this is the same equation as that for the impedance of a capacitor, where $Q^{\circ} = C$.

$$Z_{CPE} = \frac{1}{Q^{\circ} j\omega} = \frac{1}{Cj\omega}$$
(4)

When α is close to 1, the *CPE* resembles a capacitor, but the phase angle is not 90°. It is constant and somewhat less than 90° at all frequencies and if $\alpha = 0.5$, a 45° line is

produced on the complex-plane graph, indicative of a diffusion controlled process (Warburg impedance).

The main problem in the use of available software with *CPE* is that the capacity, obtained by fitting procedure, does not have the dimensions of a capacity, *i.e.*, F cm⁻², or Ω^{-1} cm⁻²s, but dimensions given in Ω^{-1} cm⁻² s^{α} [30, 37, 38]. Hsu *et al.* [39] developed an equation for correction of capacity to its real value, in the case of parallel connection of *CPE* and *R*, by using equation 5:

$$C_{dl} = Q^{\circ} (\omega_{\text{max}})^{\alpha - 1}$$
 (5)

where $\omega_{\text{max.}}^{"}$ represents the frequency of the maximum on the $-Z^{"}$ vs. ω dependence, which is independent of the exponent α , while Q° represents the result of fitting. In this case, equation 5 was used to calculate the capacitance which is summarized in Table 4 along with other electrochemical parameters obtained by fitting the EIS data shown in Fig. 13 according to the equivalent circuit shown in Fig. 14. The impedance, Z of that equivalent expressed as:

$$Z = R1 + \frac{1}{\frac{1}{\frac{1}{\frac{1}{R3} + Q^{\circ} 2(j\omega)^{\alpha^{2}}} + R2}} + Q^{\circ} 1(j\omega)^{\alpha^{1}}}$$
(6)

where *R*1 is the solution resistance between working and reference electrodes, $Q^{\circ}1$ and $Q^{\circ}2$ are the CPE coefficients of coating and pores respectively, $\alpha 1$ and $\alpha 2$ are dimensionless numbers, *R*2 is the overall transfer resistance, and *R*2+*R*3 is the polarization resistance.

From Table 4 and Fig. 15, it seems that the capacitance (C1) on HVOF micron sized WC-12Co coating is lower compared to HVOF nanostructured WC-12Co based coatings deposited on in both alumina and low carbon steel. The physical significance of this is that a larger charge builds up in the nanostructured coatings preferably along particle/matrix boundary. When this charge build up exceeds a certain limit, it causes the dissolution of the matrix phase which in turn reduces the overall transfer resistance against corrosion. This is evident if we compare the overall transfer resistance (R2) which is higher for micron sized than for nanostructured coatings deposited on both substrates (Fig. 15). The polarization resistance (R2 + R3) of the different nanostructured WC-12Co coatings is low compared to the one of micron sized WC-12Co coatings and the one of low carbon steel. This decrease in polarization resistance is probably due to the penetration of electrolyte within the coating and movement of ionic species in pores what increases the apparent coating conductivity. Thus wetting of particle/matrix interfaces and pores creates conducting paths at different depths within the coating as stated in literatures [39-42].

These EIS investigations also indicate the absence of any 'through coating' pores. 'Through coating' pores will allow the electrolyte to react with the substrate and influence the spectra and moreover the substrate will increase the polarization resistance of the coating system as a whole, but this is not the case. This claim is also supported by the fact that, there was no Fe dissolved (from the substrate) in the electrolyte, after electrochemical tests. So we can conclude that, in the present case it is unlikely that there is any influence of substrate on the electrochemical behavior of the coating. In other words, 'through coating' pores are probably not present.

However, this is not the only fact which influences the electrochemical behaviour of the coatings. Other parameters like surface composition, homogeneity etc. also play a role. The role of Al in the WC-12Co nanostructured coating is not yet explicitly evident but it seems to reduce the Co dissolution from the matrix (Fig. 12). There may be two possible reasons for that:

- (i) Al mainly resides at the particle boundaries and causes a galvanic coupling with other coating constituents, and
- (ii) Al is inserted in the matrix and generates a kind of protective film properties of different effectiveness.

The first hypothesis was checked by TEM and elemental analyses mapping as described here after. In order to carry out an in-depth TEM investigation of HVOF nanostructured WC-12Co-2A1 coatings, several samples were prepared by metallographic sample preparation technique [43], followed by ion milling (producer: Gatan, Model 600). First of all, a represented coating area was selected showing several WC particles. Then mapping of W, Co and Al elements were carried out in that area as shown in Fig. 16 along with corresponding TEM picture. The elemental mapping clearly confirms that, Al is distributed around the WC particles. Such a distribution of Al may cause a galvanic coupling with W and Co and contribute to enhance Co dissolution from the matrix.

These two hypotheses can be further confirmed by a detailed AFM investigation which can be an interesting starting point of future research. Furthermore, it has shown in [44] that the addition of Al to nanostructured WC-12Co coatings is beneficial in terms of wear resistance of the coating.

6.8 Conclusion

In this research, nanostructured WC-12Co cermet coatings were investigated by chemical and electrochemical techniques, and compared to micron sized WC-12Co cermet coating and low carbon steel (LCS). The influence of pores in the coatings and the effect of alloying element were looked for.

The experimental results show that the open circuit potential of micron sized WC-12Co coating is more cathodic compared to the nanostructured WC-12Co and WC-12Co-2Al coating, and this was related to a lower gain boundary density. Polarization experiments revealed indeed that nanostructuring reduces the corrosion potential and that no true passivation-repassivation behavior was detected. From ICP analyses it was shown that

nanostructuring enhances the dissolution of Co but decreases the dissolution of W compared to micron sized coatings. Due to the presence of higher particle/matrix interface in nanostructured coatings, the localized corrosion attack on the matrix is higher but it is more evenly distributed. The electrical charge passed in chronoamperometric tests through nanostructured coatings is higher compared to micron-sized coatings though the overall attack become less aggressive compared to micron-sized coatings. The EIS-investigation revealed that the polarization resistance of nanostructured WC-12Co based coatings is slightly reduced compared to micron-sized WC-12Co coatings. Moreover nanostructuring reduces the corrosion potential and enhances the Co dissolution. Thought the coatings contain a certain amount of pores, it is unlikely that pores in HVOF coatings investigated are 'through coating' pores. There is thus no risk of substrate exposure to the electrolyte. The role of Al on the electrochemical behaviour of nanostructured HVOF WC-12Co coating is not yet explicitly clear although it increases wear resistance.

Acknowledgement

The authors acknowledge the support of European Growth 2003-2006 project entitled Nanospraying (contract G5RD-CT-2002-00862) under which the work has carried out. A. K. Basak also acknowledges Katholieke Universiteit Leuven for providing fellowship to carry out part of the work.

References

[1] J. Kawakita, S. Kuroda, T. Fukushima, Thermal Spray 2003: Advancing the Science and Applying the Technology, (Ed.) C. Moreau and B. Marple, Published by ASM International, Materials Park, Ohio, USA, 2003, 353.

[2] A. K. Basak, P. Matteazzi, M. Vardavoulias, J.-P. Celis, Wear 261 (2006) 1042.

[3] R. Saengera, D. Martina, C. Gabriellib, Surface and coatings technology 194 (2005)335.

[4] S. M. Mirabedini, S. Moradian, J. D. Scantlebury, G. E. Thompson, Iranian polymer journal 12 (4) (2003) 261.

[5] C. Gabrielli, Use and applications of electrochemical impedance techniques, Technical Report, Solartron, Farnborough, 1990.

[6] J. P. Candy, P. Fouilloux, M. Keddam, H. Takenouti, Electrochima Acta 27 (1982)1585.

[7] C. Gabrielli, F. Huet, A. Sahar, G. Valentin, J Journal of applied electrochemistry 24 (1994) 481.

[8] M. Kaiser, K. D. Beccu, M. R. Gutjahr, Electrochima Acta 21 (1976) 539.

[9] C. A. Achete, L. F. Senna, T. Hirsch, F. L. Freire Jr., Surface and coating technology 94 (1997) 390.

[10] C. Liu, Q. Bi, A. Matthews, Corrosion science 43 (2001) 1953.

[11] J. M. Guilemany, J. Fernandez, J. Delgado, A. V. Benedetti, F. Climent, Surface and coating technology 153 (2002) 107.

[12] S. H. Ahn, Y. S. Choi, J. G. Kim, J. G. Han, Surface and coating technology 150 (2002) 319.

[13] S. Frangini, A. Masci, A. d. Bartolomeo, Surface and coating technology 149 (2002)279.

[14] J. Hess, Coating world, 36 (1999) 33.

[15] P. Matteazzi, M. Alcala, Materials science and engineering A 230 (1997) 161.

[16] M. Pourbaix, Diagrammes d'équilibres électrochimiques et applications expérimentales, Publ. Bruxelles: Centre Belge d'Etude de la Corrosion (1966).

[17] S. Sutthiruangwong, G. Mori, R. Kosters, Int. J. Ref. Metals & Hard Materials 23(2005) 129–136.

[18] S. Hochstrasser(-Kurz), Y. Mueller, C. Latkoczy, S. Virtanen, P. Schmutz, Corrosion Science 49 (2007) 2002–2020.

[19] K. M. Andersson, L. Bergstom, Int. J. Ref. Metals & Hard Materials 18 (2000) 121-129.

[20] E. V. Westing, PhD Thesis, Technical University of Delft, (1992).

- [21] S. Tao, D. Y. Li, Nanotechnology, 17 (2006) 65-73.
- [22] J. D. Voorhies, J. Electrochem. Soc. 119 (1972) 219-227.
- [23] H. Scholl, B. Hofman, A. Rauscher, Electrochim. Acta 37 (1992) 447-452.
- [24] V. S. Saji, J. Thomas, Current Science, 92 (1) (2007) 51-55.
- [25] R. Rofagha, R. Langer, A. M. El-Sherik, Scripta Metall. Mater., 25 (1991) 2867-2875.

[26] M. Schneider, K. Pischang, H. Worch, G. Fritsche, P. Klimannek, Mater. Sci.Forum, 343–346 (2000) 873-881.

[27] S. G. Wang, C. B. Shen, K. Long, T. Zhang, F. H. Wang, Z. D. Zhang, J. Phys. Chem., B 110 (2006) 377-388.

[28] L. Wang , Y. Lin, Z. Zeng, W. Liu, Q. Xue, L. Hu, J. Zhang, Electrochimica Acta, 52 (2007) 4342-4350.

[29] C. Monticelli, A. Frignani, F. Zucchi, Corrosion Science, 46 (2004) 1225-1234.

[30] A. M. Human, H. E. Exner, Int. J. Ref. Metals & Hard Materials 15 (1997) 65-76.

[31] S. P. Pednekar, Corrosion, 53 (10) (1997) 813-821.

[32] A. Neville, T. Hodgkiess, J. Am. Ceram. Soc., 62 (8) (1999) 2138-2145.

[33] A. Collazo, X. R. Novoa, C. Pérez, Electrochimica Acta, 44 (1999) 4289-4295.

[34] C. Liu, A. Leyland, S. Lyon, A. Matthews, Surf. Coat. Technol., 76-77 (1995) 615-624.

[35] J. R. Macdonald, W. R. Kenen, Impedance Spectroscopy Emphasizing Solid Materials and Systems, Publ. Wiley-Interscience, ISBN 0-47183-122-0 (1987).

[36] S. Skale, V. Dolec'ek, M. Slemnik, Corrosion Science, 49 (2007) 1045–1055.

[37] S. F. Mertens, C. Xhoffer, B. C. De Cooman, E. Temmerman, Corrosion, 53 (1997)381.

[38] G. O. Ilevbare, J. R. Scully, Corrosion, 39 (1983) 466.

[39] C. H. Hsu, F. Mansfeld, Corrosion, 57 (2001) 747.

[40] F. Deflorian, L. Fedrizzi, D. Lenti, P. L. Bonora, Prog. Org. Coat., 22, (1993) 39-45.

[41] M. Kendig, F. Mansfeld, T. sai, Corrosion Science, 23, (1983) 317-325.

[42] B. J. Hepburn, L. M. Callow, J. D. Scantlebury, J. Oil & Colour Chem. Association, 7 (1984) 193-205.

[43] D. B. Williams, C. B. Carter, Transmission electron microscopy: A text book for materials science, Pub. Pienum press, NewYork (1996), ISBN 0-306-45247-2.

[44] A. K. Basak, S. Achanta, M. De Bonte, J. P. Celis, M. Vardavoulias, P. Matteazzi,Trans. Inst. Metal Finishing (IMF), 85 (6) (2007) 32-40.

List of tables

Table 1: Typical properties of the investigated micron sized and nanostructured HVOFWC-Co coatings.

Table 2: E_{corr} and I_{corr} values of different micron sized and nanostructured materials measured according to Tafel plot from potentiodynamic polarization measurements.

Table 3: E_{corr} and I_{corr} values calculated according to Tafel plot from potentiodynamic polarization experiments on HVOF micron sized (μ) and nanostructured (nc) WC-12Co coatings deposited on alumina and low carbon steel.

Table 4: Electrochemical parameters obtained by fitting the EIS spectra in Fig. 13 with the equivalent electrical circuit shown in Fig. 14. EIS measurements were done in artificial sea water pH 7.8 at 23° C.

List of figure captions

Fig. 1: Schematic of different kind of pores usually present in HVOF sprayed micron sized and nanostructured WC-12Co coatings.

Fig. 2: SEM (top view) of polished section of micron sized and nanostructured HVOF WC-12Co coatings with Ra ~ 40 nm.

Fig.3: TEM dark field images of nanostructured HVOF WC-Co coating which revealed the retention of nanosize WC grains in the deposited coating.

Fig: 4: Evolution of open circuit potential of HVOF micron sized and nanostructured WC-12Co based cermet coatings and low carbon steel with immersion time in artificial sea water (pH 7.8 at 23° C): (a) coatings deposited on alumina and (b) on low carbon steel. All the results were triplicated.

Fig. 5: Schematic of the anodic and cathodic process in the micron sized and nanostructured WC-12Co coatings immersed in artificial sea water pH 7.8 at 23° C.

Fig. 6: Evolution of current during chronoamperometric measurements at + 0.2 V vs. OCP on nanostructured HVOF WC-12Co coatings deposited on low carbon steel substrates (1 cm² testes area) and tested in artificial sea water pH 7.8 at 23° C.

Fig. 7: Evolution of current during chronoamperometric measurements at + 0.2 V vs. OCP on HVOF micron sized and nanostructured WC-12Co coatings deposited on low carbon steel substrates and tested in artificial sea water electrolyte with pH 7.8 at 23° C.

Fig. 8: Top view SEM micrographs of HVOF micron sized and nanostructured WC-12Co coatings deposited on low carbon steel substrate after chronoamperometric measurements at + 0.2 V vs. OCP for 300 s in artificial sea water with pH 7.8 at 23° C.

Fig. 9: Characteristic structural length in HVOF micron sized and nanostructured WC-12Co coatings vs. dissipated charge during chronoamperometric measurements at + 0.2 V vs. OCP for 300 s in artificial sea water with pH 7.8 at 23° C.

Fig. 10: Potentiodynamic polarization measurements at scan rate 1 mV/S in aerated artificial sea water pH 7.8 at 23° C recorded on HVOF micron sized and nanostructured WC-12Co based cermet coatings deposited on alumina.

Fig. 11: Potentiodynamic polarization measurements at scan rate 1 mV/S in aerated artificial sea water pH 7.8 at 23° C recorded on HVOF micron sized and nanostructured WC-12Co coatings deposited on low carbon steel as well as on uncoated low carbon steel.

Fig: 12: ICP-AES analyses of electrolytes after open circuit potential (OCP test for 3600 s), potentiostatic polarization (PS test for 300 s), and potentiodynamic polarization (PD at

1 mV/S scan rate) measurements on HVOF micron sized and nanostructured WC-12Co based cermet coatings deposited on low carbon steel. Neither Al nor Fe was detected.

Fig. 13: EIS Nyquist plot recorded on HVOF micron sized and nanostructured WC-12Co based coatings on (a) alumina and (b) low carbon steel substrate over a wide frequency range at open circuit potential in artificial sea water pH 7.8 at 23° C.

Fig. 14: Schematic of the equivalent circuit to fit the EIS spectra shown in Fig. 13, with R1 is solution resistance, R2 is overall transfer resistance, R2 + R3 the polarization resistance, and CPE is constant phase elements.

Fig. 15: Overall charge transfer resistance (R2) and capacitance (C1) on different HVOF micron sized and nanostructured WC-12Co based coatings deposited on alumina and low carbon steel along with uncoated bulk low carbon steel during EIS measurement in artificial sea water pH 7.8 at 23° C.

Fig. 16: TEM and elemental mapping on HVOF nanostructured WC-12Co-2Al coating.

Fig. 1: Schematic of different kind of pores usually present in HVOF sprayed micron sized and nanostructured WC-12Co coatings.



Fig. 2: SEM (top view) of polished section of micron sized and nanostructured HVOF WC-12Co coatings with Ra ~ 40 nm.



Fig.3: TEM dark field images of nanostructured HVOF WC-Co coating which revealed the retention of nanosize WC grains in the deposited coating.



Fig: 4: Evolution of open circuit potential of HVOF micron sized and nanostructured WC-12Co based cermet coatings and low carbon steel with immersion time in artificial sea water (pH 7.8 at 23° C): (a) coatings deposited on alumina and (b) on low carbon steel. All the results were triplicated.



Fig. 5: Schematic of the anodic and cathodic process in the micron sized and nanostructured HVOF WC-12Co coatings immersed in artificial sea water pH 7.8 at 23°





Fig. 6: Evolution of current during chronoamperometric measurements at + 0.2 V vs. OCP on nanostructured HVOF WC-12Co coatings deposited on low carbon steel substrates (1 cm² testes area) and tested in artificial sea water pH 7.8 at 23° C.



Fig. 7: Evolution of current during chronoamperometric measurements at + 0.2 V vs.
OCP on HVOF micron sized and nanostructured WC-12Co coatings deposited on low carbon steel and tested in artificial sea water electrolyte with pH 7.8 at 23° C.



Fig. 8: Top view SEM micrographs of HVOF micron sized and nanostructured WC-12Co coatings deposited on low carbon steel substrate after chronoamperometric measurements

at + 0.2 V vs. OCP for 300 s in artificial sea water with pH 7.8 at 23° C.



Fig. 9: Characteristic structural length in HVOF micron sized and nanostructured WC-12Co coatings vs. dissipated charge during chronoamperometric measurements at + 0.2 V



vs. OCP for 300 s in artificial sea water with pH 7.8 at 23° C.

Fig. 10: Potentiodynamic polarization measurements at scan rate 1 mV/S in aerated artificial sea water pH 7.8 at 23° C recorded on HVOF micron sized and nanostructured



WC-12Co based cermet coatings deposited on alumina.

Fig. 11: Potentiodynamic polarization measurements at scan rate 1 mV/S in aerated artificial sea water pH 7.8 at 23° C recorded on HVOF micron sized and nanostructured WC-12Co coatings deposited on low carbon steel as well as on uncoated low carbon





Fig: 12: ICP-AES analyses of electrolytes after open circuit potential (OCP test for 3600 s), potentiostatic polarization (PS test for 300 s), and potentiodynamic polarization (PD at 1 mV/S scan rate) measurements on HVOF micron sized and nanostructured WC-12Co based cermet coatings deposited on low carbon steel. Neither Al nor Fe was detected.



Fig. 13: EIS Nyquist plot recorded on HVOF micron sized and nanostructured WC-12Co based coatings on (a) alumina and (b) low carbon steel substrate over a wide frequency range at open circuit potential in artificial sea water pH 7.8 at 23° C.



Fig. 14: Schematic of the equivalent circuit to fit the EIS spectra shown in Fig. 13, with R1 is solution resistance, R2 is overall transfer resistance, R2 + R3 the polarization resistance, and CPE is constant phase elements.



Fig. 15: Overall charge transfer resistance (R2) and capacitance (C1) on different HVOF micron sized and nanostructured WC-12Co based coatings deposited on alumina and low carbon steel along with uncoated bulk low carbon steel during EIS measurement in artificial sea water pH 7.8 at 23° C.



Overall charge transfer resistance, R2(ohm cm²)

Fig. 16: TEM and elemental mapping on HVOF nanostructured WC-12Co-2Al coating.



Table 1: Typical properties of the investigated micron sized and nanostructured HVOF

WC-Co coatings.

	Coating properties					
	Porosity	Adhesion	Thickness	Vickers' hardness (HV ₃₀₀)		
Type of	by image	on substrate	by SEM on			
coatings	analysis	by pull test	cross-section			
	(%)	(MPa)	(µm)			
m WC-Co	< 0.5	> 60	150 ± 20	1208 ± 162		
n WC-Co	3.6 ± 1.1	> 60	185 ± 26	1044 ± 187		
n WC-Co-Al	3.8 ± 0.8	> 60	199 ± 21	1215 ± 159		

Table 2: E_{corr} and I_{corr} values of different micron sized and nanostructured materials measured according to Tafel plot from potentiodynamic polarization measurements.

Materials	Test	E _{corr}	Icorr	Reference
	conditions	(mV vs. SCE)	(µA/Cm ²)	
Electrodeposited micron	0.1 M	- 230	8.8	21
sized Cu (2 µm)	NaOH			
Electrodeposited		- 248	3.6	
nanocrystalline Cu (56 nm)				
Electrodeposited micron	3.5 wt %	- 812	13.63	28
sized Co	NaCl			
Electrodeposited		- 736	11.18	
nanocrystalline Co (18 nm)				
Sintered WC-10Co	aerated	- 609	100	17
Sintered WC-10Co-1Cr	1 N	- 503	3	
Sintered WC-10Co-1Cr	sulfuric	- 583	160	1
Sintered WC-10Co-5VC	acid	- 586	160	

Table 3: E_{corr} and I_{corr} values calculated according to Tafel plot from potentiodynamic polarization experiments on HVOF micron sized (μ) and nanostructured (nc) WC-12Co

Substrate	HVOF coating	E _{corr}	I _{corr}	
		(V vs. Ag/AgCl)	(x 10 ⁻⁵ A/cm ²)	
	μ WC-12Co	- 0.44	3.30	
Alumina	nc WC-12Co	- 0.56	6.79	
	nc WC-12Co-2Al	- 0.53	6.65	
Low carbon steel	μ WC-12Co	- 0.49	3.10	
	nc WC-12Co	- 0.53	6.45	
	nc WC-12Co-2Al	- 0.50	6.73	
Low carbon steel	_	- 0.72	1.12	

coatings deposited on alumina and low carbon steel.

Table 4: Electrochemical parameters obtained by fitting the EIS spectra in Fig. 13 with the equivalent electrical circuit shown in Fig. 14. EIS measurements were done in artificial sea water pH 7.8 at 23° C.

EIS	HVOF coating				Low		
parameters	μ WC-12Co		nc WC-12Co		nc WC-12Co-2Al		carbon
	On	On	On	On	On	On	steel
	alumina	LCS	alumina	LCS	alumina	LCS	(for
							reference)
$R1(\Omega cm^2)$	6.88	6.26	8.21	10.74	18.20	6.00	9.55
$Q^{\circ}1(\mathbf{S}\cdot\mathbf{s}^{\boldsymbol{\alpha}})$	0.00122	0.00120	0.00270	0.00833	0.00449	0.00861	0.00708
$C1(\mathbf{mF cm}^{-2})$	1.30	1.28	2.88	6.63	4.22	2.85	6.34
α1	0.857	0.854	0.866	0.751	0.967	0.600	0.760
$R2(\Omega cm^2)$	897.4	896.7	544.3	12.05	134.9	31.3	829.2
$Q^{\circ}2(\mathbf{S}\cdot\mathbf{s}^{\boldsymbol{\alpha}})$	0.00586	0.00701	-	0.01586	0.01226	0.01840	-
$C2(\mathbf{mF cm}^{-2})$	24.46	33.17	-	183.62	18.31	45.09	
α2	0.690	0.663	-	0.517	0.826	0.784	-
R3 (Ωcm ²)	5105	5447	-	469.2	468.2	649.4	-