Corrosion Behavior of WC-Co in High Sulphate Content

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Abstract. Cermet alloys are a combination of ceramic and metal. Therefore, cermets exist in high corrosion resistance in aqueous media. However, because of the nature of cermet alloys, which have a metal and ceramic composition, the corrosion rate is complex to identify. The corrosion attack could be assessed by calculating the corrosion rate or through electrochemistry evaluation. Generally, the corrosiveness of media increased as the anions contents increased. This paper presents the corrosion mechanism of cobalt tungsten-carbide (WC-Co) exposed to a high concentration of sulphate in the salinity of seawater. The solution (media) was prepared according to the same composition as seawater including pH, salinity and dissolved oxygen. The corrosion rate was then identified and the corrosion mechanism revealed. The corrosion rate was identified at 4°C, 20°C, 50°C and 80°C and compared with the corrosion rate of WC-Co in seawater. The results revealed that sulphate has an inhibiting effect that minimises the corrosion attack on WC-Co. The corrosion rate decreased as the sulphate content in seawater increased, and an increase in the temperature increased the corrosion attack on WC-Co.

Introduction

Cermet alloy is the name given to a composite material composed of ceramic (cer) and metallic (met) materials [1]. A cermet is ideally designed to have the optimal properties of both a ceramic, such as high temperature resistance and hardness, and those of a metal, such as the ability to undergo plastic deformation. The metal is used as a binder for an oxide, boride, or carbide. Generally, the metallic elements used are nickel, molybdenum, and cobalt. Depending on the physical structure of the material, cermets can also be metal matrix composites; however, cermets are usually less than 20% metal by volume [2]. Corrosion is the physicochemical interaction between a metal and its environment that results in changes in the properties of the metal, and which may lead to significant impairment of the function of the metal, the environment, or the technical system, of which these form a part. It is known that every substance interacts differently with the environment in which it is used. Furthermore, each ionic species present in the environment behaves uniquely. To date, although no general theory has been established that accounts with certainty for the corrosion interaction between metals and the environment, it is realised that there is more than one factor that influences the corrosion of metals in aqueous solutions. This makes it necessary to study the effects of the ions in the solution on the corrosion phenomenon, with due consideration to such factors as the type of metal and anions. In this study, a cermets alloy cobalt (Co)-Tungsten Carbide (WC) was used to identify its characteristic in high sulphate compared to chloride aqueous media. A study found that the presence of these aggressive anions, Cl^- and SO_4^{2-} stimulates the anodic dissolution rate in both the active and pre-passive potential regions [3,4]. Pitting corrosion only observed in the presence of Cl^- anions and the effect of SO_4^{2-} anion exerts an indirect effect on increasing the cathodic reaction and influences the anodic reaction [4,5].

Methodology

Cyclic Potentiodynamic Polarisation (CPP) tests were carried out at four different temperatures: 4°C, 20°C, 50°C and 80°C in static conditions. The electrolyte was prepared according to the seawater composition and the sulphate content in the salinity of seawater was increased (Table 1). Specimens with an electrical connecting wire were embedded in a non-conducting resin and the exposed surface, with known area, was subsequently ground using SiC sandpaper and diamond polished to a 6-micron finish. The sample was held in each solution for 5 min before starting the experiment to stabilize the surface. The reference electrode used in all experiments was silver/saturated-silver-chloride (Ag/AgCl) half-cell, the potential of which, versus normal hydrogen electrode (NHE), is +0.197 V. The working electrode is the sample, and platinum is used as the counter electrode. This accelerated test method facilitates analysis of the kinetics of the corrosion reaction by controlling the potential between the reference and the working electrode, and maintaining the current in the external cell between the counter and the working electrode. The potential is controlled by a computer-controlled potentiostat and is shifted at a constant rate in the anodic direction from the open circuit potential (OCP), causing the working electrode to become the anode and causing electrons to be withdrawn there from.

Table 1. The composition of electrolyte

Component	Seawater	Solution with high sulphate content
Chloride (Cl-)	19.25	1.09
Sulphate (SO42-)	2.71	20.87
Magnesium (Mg2+)	1.30	1.30
Calcium (Ca2+)	0.42	0.42
Potassium (K+)	0.39	0.39
Sodium (Na+)	10.71	10.71
Concentration (mg/l)	34.78	34.78

Results and Discussion

Studies concerning the corrosion process of carbon steel coated with WC-Co cermets in seawater show that increasing the cobalt content from 12% to 17% provides more protection by changing the pore morphology from interconnecting the isolated pores [3]. Due to the heterogeneous microstructure and binder phase composition, the corrosion mechanisms of WC-Co are very complex, and only very little is known about the exact corrosion process taking place. This is in respect of the relationship behaviour between the electromechanical and in-service corrosion performance. Some researchers claim that the whole WC-Co surface does not behave equally active, and that the corrosion attack proceeds predominantly at locations where the WC phase has fallen out after localized initiation of corrosion has taken place. In addition, the corrosion of WC-Co is also controlled by the galvanic coupling of the anodic metallic binder to the cathodic ceramic phase, which exhibits electronic conductivity. Pure cobalt does not passivate and remains active with increasing potential [6]. Fig 1 presents the CPP of WC-Co in seawater. A film forms on Co (W,C) alloys causing the current to become relatively independent of potential but remaining very high. This behaviour is termed here as 'pseudo-passivation'. Investigations performed in aqueous solution, containing chloride ions, reveal that the whole WC-Co surface does not behave equally active, as the corrosion attack proceeds predominately at locations where the WC phase has fallen after localized initiation of corrosion has taken place. The corrosion behaviour of cermet alloys should be affected by the corrosion behaviour of its components, the galvanic effect of the WC-Co couple and the galvanic effect between the matrix regions of higher W concentration.
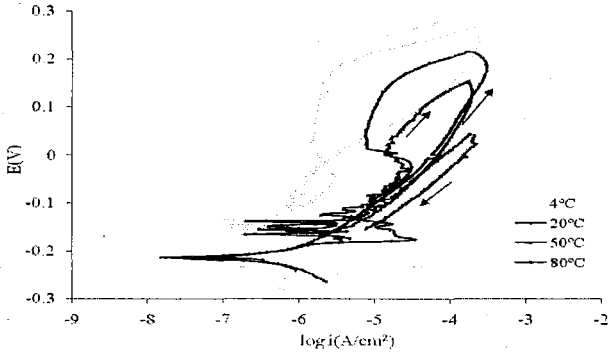
Figure 1. Cyclic polarisation of WC-Co in seawater

Anions as well as the structure of the surface, affect the anodic current-density potential curves in oxide-free dissolution, as in acid solutions. As explained before, cemented alloys consist of hard WC particles in a tough metallic matrix produced during a liquid phase sintering process. Therefore, corrosion attack will depend on the matrix and Co and the corrosion attacks. Fig 2 presents the CPP of WC-Co in high sulphate content compared to seawater (Fig 1). In all cermet alloys, the corrosion attack at the interface will produce an oxide layer. In terms of grain size, the smaller the grain size, the higher the corrosion resistance because the corrosion behaviour is strongly influenced by the WC dissolved in the Co binder, the C-Co increases with metallic content and binder composition [5]. Corrosion of WC-Co begins with active dissolution of Co in preferential sites, such as intersections of adjacent WC particles. The pseudopassivity proceeds via a passive process (oxide formation), pseudopassive (limitation of Co^{2+} diffusion), binder dissolution (active process), and, lastly, followed by localised corrosion. However, the reactions taking place on the hard metal surface are strongly dependent on the potential of the system. At open-circuit conditions or at small applied potentials, the binder phase undergoes selective dissolution, while it is only in the higher potential range that the dissolution of the WC phase takes place. At intermediate potentials (i.e. below the dissolution of the WC phase), the observations of different researchers diverge. Some authors report a passive behaviour of the composite, others claim a kind of pseudo-passive state, where the presence of non-adherent, but diffusion-inhibiting corrosion products leads to a limitation of current density [7,8]. Because the WC are more noble in oxidation potential compared to Co, a galvanic coupling between the two phases will force the anodic part of the overall corrosion reaction to proceed in the Co phase. Thus, Co dissolution occurs due to the unfavourable surface ratio of anodic compared to cathodic sites. In parallel, cathodic reaction occurs in oxygen, or hydrogen reduction will take place in the WC phase, and, consequently, protect the hard metals against corrosion.
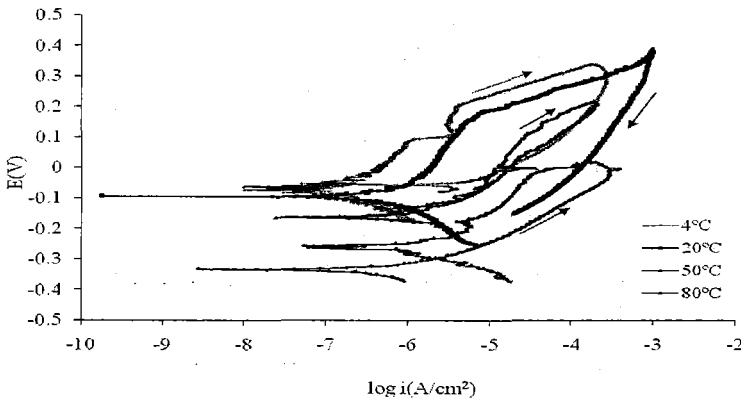

Figure 2. Cyclic polarisation of WC-Co in high sulphate content

Table 2 summarises the CPP data of WC-Co in seawater and high sulphate content. In both solutions, the corrosion rate increased as the temperature increased. However, in high sulphate content, the corrosion rate for WC-Co decreased compared to the corrosion rate in seawater. This shows that not all anions in seawater will accelerate the corrosion attack. As mentioned before, metals are susceptible to corrosion attack in chloride media, however, this research indicates that sulphate has an inhibiting effect on WC-Co.

Table 2. Cyclic Potentiodynamic Polarisation (CPP) data of WC-Co in seawater and seawater at high sulphate content

Solution	Temp. (°C)	Er (mV)	OCP (mV)	Ep (mV)	icorr (μA/cm2)	CR (mpy)
Seawater	4	260	-170	n/a	1.60	0.23
	20	213	-214	n/a	5.01	0.71
	50	151	-151	149	7.92	1.12
	80	36	-140	n/a	15.03	2.13
Seawater with high sulphate content	4	337	-62	-56	0.5	0.07
	20	364	-96	n/a	3.0	0.42
	50	206	-163	n/a	3.1	0.44
	80	11.98	-256	-333	3.2	0.45

Summary

The corrosion rate decreased as the sulphate content in seawater increased, and an increase in the temperature increased the corrosion attack on WC-Co.

Acknowledgement

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