

# Anodic polarization and corrosion of WC-Co hardmetals containing small amounts of Cr<sub>3</sub>C<sub>2</sub> and/or VC

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The anodic polarization and corrosion properties of commercial WC-Co hardmetals with different grain sizes and containing small amounts of Cr<sub>3</sub>C<sub>2</sub> and/or VC in acid (pH 2.8), acid/3% NaCl, and neutral 3% NaCl solutions, have been measured using potentiokinetic and linear polarization conductance techniques. An increase in grain size increased the passive current density. Small additions of Cr<sub>3</sub>C<sub>2</sub> increased substantially the corrosion resistance. Small additions of VC had little effect on the corrosion resistance, but in the presence of small additions of Cr<sub>3</sub>C<sub>2</sub> it reduced the beneficial effects of chromium.

## 1. Introduction

Hardmetals based on WC-Co alloys have an excellent combination of properties and are readily produced to a consistent quality on an industrial scale [1, 2]. Cobalt has a poor resistance to corrosion, and in applications such as mechanical seals and valves operating in seawater [3, 4], drilling in geothermal brines and mine waters [5], and cutting tools in metal finishing operations [5-7], there is a need for the hardmetals to be corrosion resistant, and the cobalt may be alloyed or replaced by nickel or nickel-based alloys [3, 4]. In contrast to the corrosion and performance of the hardmetals in service, there is a concern with the health hazards associated with the dissolution of cobalt from the hardmetals [8]. During grinding hardmetal tools, the presence of high temperatures and the large surface area of the debris results in rapid corrosion of the binder, and toxic amounts of ionic cobalt may form in the metal working fluid [8].

Corrosion is a complex property of a system which depends not only on the chemical and electrochemical factors involved but also on the geometrical and engineering aspects of the actual conditions of use; for example, during machining, the formation and accumulation of fine debris, the use of cleaning agents, the presence of adventitious substances, and stand-down conditions. An important point with respect to the corrosion of commercial hardmetals is that the presence of a relatively small amount of a substance added to the hardmetal to improve the fabrication or mechanical properties may greatly change the corrosion properties. Little is known about the effects of small additions on the corrosion behaviour of hardmetals, and the present work uses electrochemical tests to investigate the anodic polarization and corrosion properties of some commercial WC-Co hardmetals containing small amounts of Cr<sub>3</sub>C<sub>2</sub> and/or VC.

## 2. Experimental details

The hardmetals were kindly supplied by Sandvic Hard

Materials Ltd, Coventry, and the available data are shown in Table I. They were cut with a diamond wheel, ground, and then polished on a diamond impregnated copper lap. Analar reagents and distilled water were used to make the solutions. The solution 0.01 M H<sub>2</sub>SO<sub>4</sub> + 0.99 M Na<sub>2</sub>SO<sub>4</sub> adjusted to a pH 2.8 was used in most of the tests and will be considered the standard solution. Oxygen free nitrogen was used to deaerate the solution.

Electrochemical testing used a standardized potentiokinetic polarization procedure. In outline, a specimen was mounted in Araldite, polished on a hard cloth using a 1 μm diamond polish and lubricant, and then partly covered with insulating lacquer leaving an area about 30 mm<sup>2</sup> as the working electrode. The reference electrode area was a saturated calomel electrode (SCE) connected via a luggin capillary, and the auxiliary electrode was platinum gauze. The open beaker cell contained about 300 cm<sup>3</sup> of solution. Concentration gradients were minimized by using a magnetic stirrer, and the solution was deaerated by bubbling oxygen free nitrogen through the solution for 30 min prior to and then during the test. The working electrode was cathodically cleaned by reducing at -1.2 V (SCE) for about 5 min, and then the corrosion potential was allowed to stabilize for about 3 h. Anodic polarization from the corrosion potential was at 1 mV sec<sup>-1</sup> and current readings were taken every 20 mV.

Linear polarization conductance measurements were made by measuring the current flowing when the

TABLE I Composition and properties of the hardmetals

Sample	Sandvic grade	Cobalt (wt %)	Additions (wt %)	Grain size (μm)
6mZ	CP15	6	Nil	1.4
6cZ	CP47	6	Nil	3.0
6fVCl	CP6	6	0.1 VC	0.8
6fCC3	H6F	6	0.3 Cr <sub>3</sub> C <sub>2</sub>	0.8
8uCC4VC6	8uF	8	0.4 Cr <sub>3</sub> C <sub>2</sub> + 0.6 VC	0.4
10fCC5	H10F	10	0.5 Cr <sub>3</sub> C <sub>2</sub>	0.8

TABLE II Corrosion parameters of anodically polarized hardmetals

Sample	Solution	$E_{\text{corr}}^{(a)}$ (mV)	$E_{\text{crit}}$ (mV)	$i_{\text{crit}}$ ( $\text{Am}^{-2}$ )	$E_{\text{pass}}$ (mV)	$i_{\text{pass}}^{(b)}$ ( $\text{Am}^{-2}$ )
Co <sup>(c)</sup>	SS	-460	-100	2220	-	no passivation
W <sup>(c)</sup>	SS	-310	-	-	-	1.0
6mZ	SS	-387	-010	178	470	5.6
6cZ	SS	-378	-070	250	590	53.6
6fVC1	SS	-410	-050	173	250	19.4
6fCC3	SS	-360	000	73	250	1.0
10fCC5	SS	-361	050	254	410	1.45
10fCC5	SS	-388	080	245	400	1.48
8uCC4VC6	SS	-354	120	214	400	33.9
6cZ	SS + 3% NaCl	-340	000	286	640	85.7
6fCC3	SS + 3% NaCl	-313	-060	100	480	1.79
6fCC3	3% NaCl	-359	-110	470	570	4.8
8uCC4VC6	3% NaCl	-	180	266	~460	186

<sup>(a)</sup>electrode potentials with respect to SCE.

<sup>(b)</sup>minimum value.

<sup>(c)</sup>from [10].

potential was increased by 10, 20, -10 and -20 mV from the corrosion potential [9]. Details of the testing conditions are given along with the results.

### 3. Results

Polarization curves for some of the hardmetals are shown in Figs 1 to 4 and corrosion parameters from all the data are collected in Table II. Also included in Table II are results obtained elsewhere [10] on the polarization of pure cobalt and tungsten. Duplicate tests on sample 10CC5 produced results that were in close agreement, thus showing the reproducibility and validity of the test procedure.

In general terms, it is seen that the corrosion potentials fluctuate about an average value of -0.380 V, and this compares with the lower value of -0.460 V for pure cobalt. The values shown (Table II) were taken after about 3 h immersion, and these are some 30 to 50 mV lower than those observed after only about 5 min immersion, thus indicating the long time needed to reach equilibrium. Dissolution of the cobalt binder occurs preferentially (Fig. 5), and the critical current densities are seen to be, very approximately, proportional to the amount of cobalt binder in the hardmetal and not on the composition of the binder.

Pure cobalt does not passivate (it maintains the value  $i_{\text{pass}} = 2220 \text{ Am}^{-2}$  over a large potential range), and the tungsten has the low value  $i_{\text{pass}} = 1.0 \text{ Am}^{-2}$ . The hardmetals had a wide range of passivation current densities, and the effect of small alloying additions to the hardmetals on the values of  $i_{\text{pass}}$  show a clear pattern. The presence of chromium always decreased substantially  $i_{\text{pass}}$ , whereas the presence of vanadium at best had only a marginal effect, or at worst offset the beneficial effects of chromium. In the straight WC-Co samples (6mZ and 6cZ), the value of  $i_{\text{pass}}$  for the coarse grained hardmetal was much higher than that for the medium grain size hardmetal. The addition of 3% NaCl to the standard solution always increased the values of  $i_{\text{crit}}$  and  $i_{\text{pass}}$ . In neutral 3% NaCl solution the value of  $i_{\text{pass}}$  is increased and again we note the beneficial effect of small amounts of chromium.

Linear polarization conductance measurements at the corrosion potential after 15 min immersion are shown in Table III. The very close agreement between the 10 mV and 20 mV values indicates that the requirements for measuring the linear polarization conductance are satisfied and hence that the results are meaningful. For each hardmetal, the presence of salt in the standard solution increased slightly the corrosion rate whereas the corrosion rate in the neutral

TABLE III Linear polarization conductance measurements and corrosion rates of hardmetals after 15 min at  $E_{\text{corr}}^{(a)}$

Sample	Solution <sup>(b)</sup>	Polarization conductance (mS)		$i_{\text{corr}}^{(c)}$ ( $\text{Am}^{-2}$ )	Ratio $\left(\frac{i_{\text{corr}}(\text{sample})}{i_{\text{corr}}(6mZ)}\right)$
		10 mV	20 mV		
6mZ	SS	1.98	2.26	4.01	1
	SS + Salt	2.54	2.99	5.23	1
	Salt	0.31	0.34	0.62	1
6fVC1	SS	2.14	1.99	3.52	0.88
	SS + Salt	2.80	3.05	5.00	0.97
	Salt	0.46	0.39	0.72	1.16
6fCC3	SS	0.39	0.46	0.66	0.16
	SS + Salt	0.64	0.94	1.22	0.23
	Salt	0.18	0.17	0.27	0.44
8uCC6CC4	SS	1.21	1.17	1.58	0.39
	SS + Salt	1.71	1.65	2.23	0.42
	Salt	0.52	0.46	0.65	1.05

<sup>(a)</sup>see text for details.

<sup>(b)</sup>SS = standard solution, salt = 3 wt % NaCl.

<sup>(c)</sup> $I_{\text{corr}} = 0.035 \times (\text{polarization conductance})$ (from [9]);  $i_{\text{corr}} = I_{\text{corr}}/\text{area}$ .

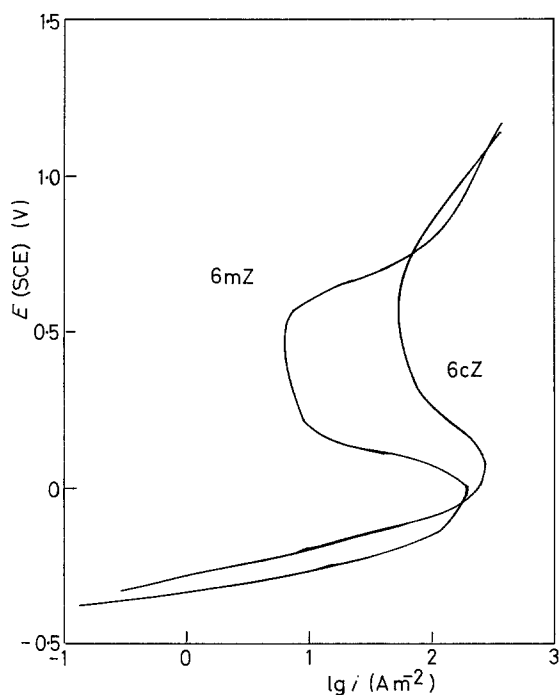


Figure 1 Anodic polarization of hardmetals with a coarse grain size (6cZ) and a medium grain size (6mZ) in pH 2.8 0.01 M  $H_2SO_4$  + 0.99 M  $Na_2SO_4$  solution.

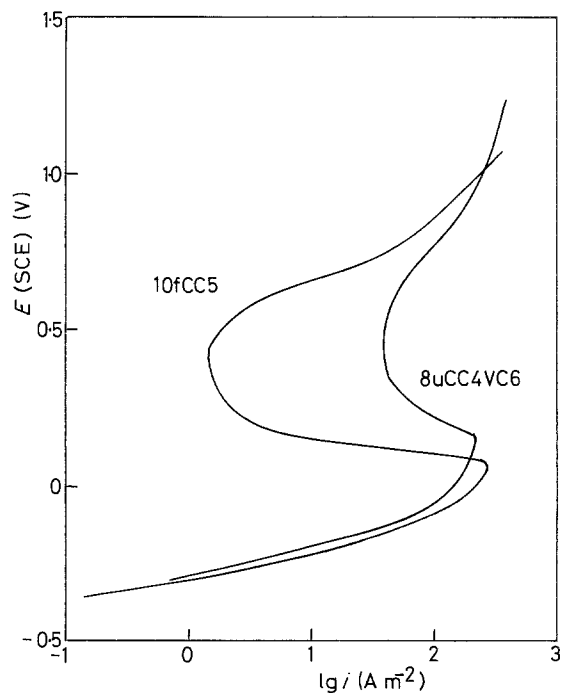


Figure 3 Anodic polarization of hardmetals with additions of 0.5%  $Cr_3C_2$  (10fCC5) and 0.4%  $Cr_3C_2$  + 0.6% VC (8uCC4VC6) in pH 2.8 0.01 M  $H_2SO_4$  + 0.99 M  $Na_2SO_4$  solution.

salt solution was always substantially lower than that obtained in the acid solutions. Chromium in the hardmetal always decreased the corrosion rate, while vanadium by itself had an indifferent effect or reduced the beneficial effect of chromium. It is important to note the procedure used to obtain these results. After polishing to a 1200 SiC grit finish the specimen was immersed in a deaerated standard solution and the polarization conductance measured after 15 min. The specimen was then washed well in distilled water, immersed in a fresh SS + salt solution, and the polarization conductance measured after about 5 min. The

specimen was then washed well in distilled water and immersed in fresh neutral 3% salt solution, and the polarization conductance measured after 5 min and then after 1 h. The results of the 5 and 60 min measurements were very close. The point here being that the surface conditions, and hence  $E_{corr}$ , change with time and it is possible that the surface conditions established in the standard solution may have influenced the results obtained in the other solutions. The present results indicate that the procedure did not influence the measurements significantly.

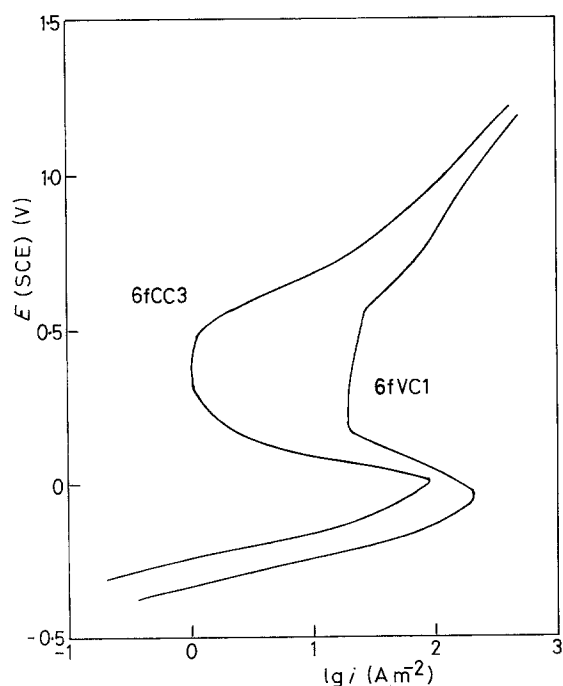


Figure 2 Anodic polarization of hardmetals with additions of 0.1% VC (6fVC1) and 0.3%  $Cr_3C_2$  (6fCC3) in pH 2.8 0.01 M  $H_2SO_4$  + 0.99 M  $Na_2SO_4$  solution.

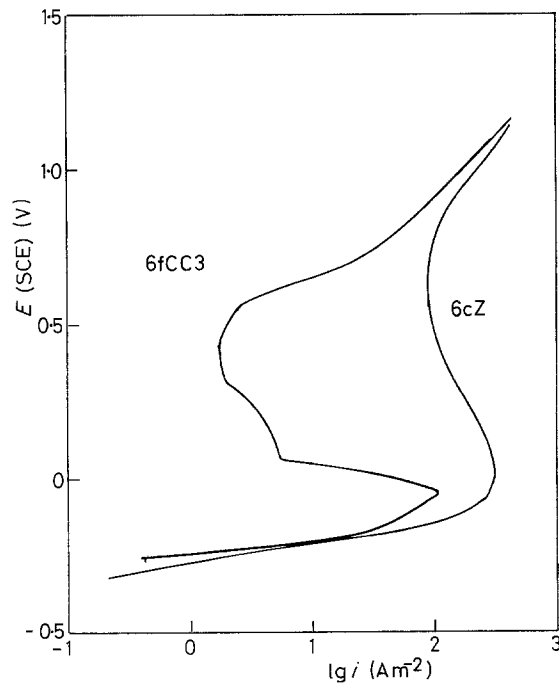


Figure 4 Anodic polarization of hardmetals with no additions (6cZ) and with 0.3%  $Cr_3C_2$  (6fCC3) in pH 2.8 0.01 M  $H_2SO_4$  + 0.99 M  $Na_2SO_4$  solution containing 3 wt % NaCl.

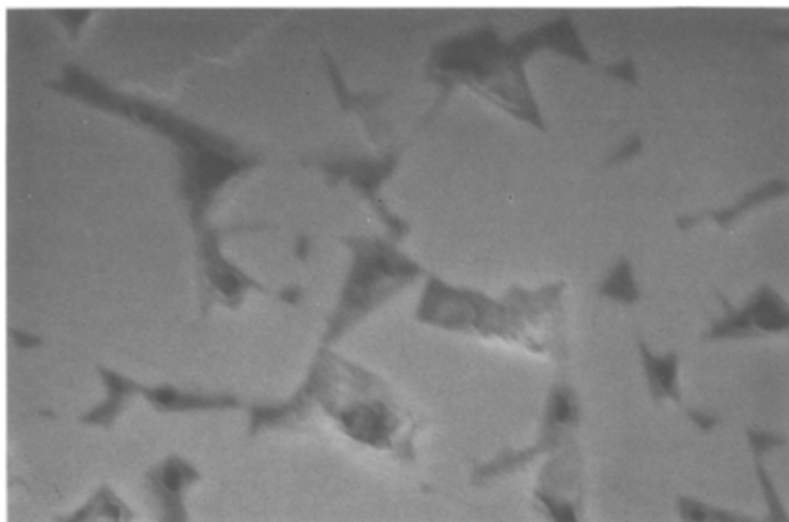
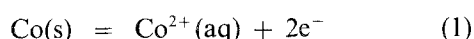


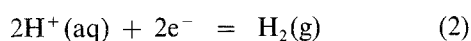
Figure 5 Scanning electron micrograph of hardmetal (6cZ) after anodically polarizing in pH 2.8 0.01 M H<sub>2</sub>SO<sub>4</sub> + 0.99 M Na<sub>2</sub>SO<sub>4</sub> solution. Marker 2 μm.

#### 4. Discussion

The corrosion potential is that at which the sum of the anodic currents is equal to the sum of the cathodic currents, and we assume that the reactions

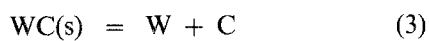


and



represent the anodic and cathodic processes in the present anaerobic conditions, although various adsorbed species, for example, sulphate, chloride, hydroxide, oxide, etc, may influence the surface and the value of  $E_{\text{corr}}$ . Nevertheless,  $E_{\text{corr}}$  for the hardmetals as a whole (about  $-0.380$  V) was substantially higher than that of pure Co ( $-0.410$  V). Tungsten carbide is catalytically active [11], and in terms of the Evans polarization diagram for the corrosion cell [12], the lower cathodic polarization would necessarily raise the value of  $E_{\text{corr}}$ .

Grain size had a pronounced effect on  $i_{\text{pass}}$  of the straight WC-Co hardmetals (Fig. 1 and Table II). In practice the binder is a ternary Co-W-C alloy since the dissolution reaction



always occurs. The amount of W in the binder depends on the grain size [13], and in addition, it is reasonable to suppose that a tungsten-rich rim exists next to the carbide. Tungsten passivates readily (Table II), and it seems that the poor passivation behaviour of the hardmetal with the coarse grain size is due either to the presence of less tungsten in the binder, or that the influence of the corrosion resistant rim does not extend into the central regions of the binder. At times it appeared that such a corrosion resistant rim did exist (Fig. 5), but the evidence was inconclusive.

Little is known about the composition of the binder phase in WC-Co alloys containing additional metals and carbides [13], and while it is speculation as to the detailed nature and effects of the additives in practice, nevertheless, it is clear that some or all of the additives will dissolve and distribute themselves among the phases. Anodic films on cobalt may consist of an inner layer of CoO and an outer layer of variable composi-

tion  $\text{Co}_{3-x}\text{O}_4$  depending on the potential [14]. Such cobalt oxides are not protective. Chromium, however, readily forms a very protective film of  $\text{Cr}_2\text{O}_3$ , and it is considered that the excellent corrosion resistance of sample 6fCC3 (Tables II and III) is due to formation of a chromium-rich or  $\text{Cr}_2\text{O}_3$  film on the surface of the binder. In contrast, the presence of vanadium has only a marginal effect on the corrosion behaviour of WC-Co alloys, and in hardmetals containing chromium the vanadium reduces the beneficial effects of the chromium, presumably by being incorporated in the passive film and interfering with the formation of  $\text{Cr}_2\text{O}_3$ .

#### 5. Conclusions

From the present work on the corrosion behaviour of WC-Co hardmetals containing small additions of  $\text{Cr}_3\text{C}_2$  and/or VC we conclude the following.

- (1) In acid solutions the cobalt binder dissolves preferentially.
- (2) In acid solutions,  $E_{\text{corr}}$  for WC-Co hardmetals is more noble than  $E_{\text{corr}}$  for pure cobalt.
- (3) In straight WC-Co alloys a hardmetal with a coarse grain size has a higher passive current density than a hardmetal with a medium grain size.
- (4) Small additions of  $\text{Cr}_3\text{C}_2$  to a WC-Co hardmetal increases substantially the corrosion resistance.
- (5) Small additions of VC to a WC-Co hardmetal has a marginal effect on the corrosion resistance. Small addition of VC together with  $\text{Cr}_3\text{C}_2$  reduces the beneficial effect of chromium.
- (6) Addition of 3 wt % NaCl to the acid solution only increases slightly the corrosion rate and passive current density.
- (7) The corrosion rate in neutral 3% NaCl solution is much less than that in acid solutions.

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