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Anodic polarization and corrosion of cemented carbides with cobalt and nickel binders

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The polarization of pure cobalt, nickel and tungsten, and hardmetals based on WC/Co and WC/Ni, in a solution of 0.01 M H_2SO_4 + 0.99 M Na_2SO_4 (pH 2.55), has been investigated using potentiodynamic and metallographic techniques. Pure cobalt dissolved rapidly, nickel had an excellent passivity, while tungsten had a high degree of passivity over the whole potential range up to 2.0 V (SCE). Extensive dissolution of WC was observed metallographically at potentials in the range 0.6 to 1.4 V (SCE). The polarization of WC/Co hardmetals reflected mainly the behaviour of the binder phase modified by the presence of tungsten in the binder and passivating film. The effects of the carbon in the binder are discussed in relation to the tungsten in the binder. Tungsten carbide grain size, and the presence of TaC and TiC, had no noticeable effects. Hardmetals with nickel binders had a superior performance compared with cobalt binders. Chloride in the solution had a relatively small effect.

1. Introduction

Commercial hardmetals are based on the WC/Co system in which hard carbide particles are bound together by a tough metal matrix. Some of the carbide dissolves in the cobalt to form a Co–W–C solid solution [1], and the carbide/carbide interfaces are separated by, on average, half a monolayer of cobalt which is localized in monolayer regions [2]. The WC/Co hardmetals have the highest impact toughness of all hardmetals, and this, combined with a high thermal conductivity, excellent wettability and the relative ease of producing components of a consistent quality on an industrial scale, make them the most generally useful of hardmetals. But for an increased resistance to the most severe wear, oxidation, and corrosion, and for special applications, there has been a continuous development to replace the WC phase by carbo-nitrides and the cobalt phase by nickel and various alloys, and to introduce other cermets, notably based on TiB_2, or toughened ceramics [3, 4].

Corrosion resistance is not usually considered a prime requirement of hardmetals, but it is important in the use of hardmetals in mechanical seals and valves in industrial pumps and in sea water [5–7], drilling in geothermal brines and mine waters [8], cutting tools and metal finishing operations [8–10], and, from the opposite point of view, in metal recycling where it is necessary to dissolve the binder to release the carbide [8]. The comparatively poor corrosion resistance of cobalt [11], has led to the use of nickel, Ni–Cr and Ni–Cr–Mo binders [5–7]. Nickel is more corrosion resistant than cobalt [11] while chromium readily forms a protective film. Presumably molybdenum is present to enhance the pitting resistance to chloride, but few detailed studies have been made and, more generally, there is only a limited amount of information on the corrosion behaviour of hardmetals [5–8, 10, 12, 13]. Thus the present work investigates in a broad way, the polarization and corrosion behaviour of a number of hardmetals in acids and waters.

2. Experimental procedure

The pure cobalt, nickel and tungsten metals had maximum impurities of 0.002, 0.001 and 0.1%, respectively. The hardmetals were kindly supplied by B. Roebuck, National Physical Laboratory, and the available details are shown in Table I. Solutions were prepared from Analar reagents and distilled water. The solution used in most of the experiments was 0.01 M H_2SO_4 + 0.99 M Na_2SO_4 with a pH 2.55 and will be considered as the standard solution in the present work. Oxygen-free nitrogen was used to deaerate the solutions.

A standardized potentiodynamic polarization procedure was used. In outline, a specimen was vacuum sealed with Araldite in a PTFE holder and polished to a 1 μm diamond finish. This was the working electrode of a cell consisting of a saturated calomel reference electrode (SCE) and a platinum gauze auxillary electrode in an open beaker. The solution was deaerated by bubbling nitrogen through the solution for 40 min before the specimen was inserted, and then continued during the experiment. After 5 min the corrosion potential, E_{corr}, was taken. The specimen was then chemically cleaned by hydrogen at -1.3 V (SCE) for 10 min before the potential was anodically ramped at 1 mV sec^{-1}. To minimize concentration effects, the solution was magnetically stirred.

Standard scanning electron microscopy and other metallographic techniques were used. The hardmetals were cut with a diamond wheel, ground, and then polished on a diamond-impregnated copper lap.

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TABLE I Composition and properties of the hardmetals*

Sample	Composition (wt %)					Grain size (μm)	Density ($Mg\,m^{-3}$)	HV30
	Binder			Carbide†				
	Co	Ni	C	TaC	TiC			
6CoF	6	–	–	–	–	1.44	15.01	1540
6CoC	6	–	–	–	–	4.81	15.08	1230
11CoF	11	–	–	–	–	1.41	14.45	1325
11CoC	11	–	–	–	–	5.12	14.44	1108
10Co(lc)	10	–	low	10	2	1.5	14.02	1540
10Co(hc)	10	–	high	10	2	1.5	13.88	1480
13Co(lc)	13	–	low	13	13	1.3	10.98	1520
13Co(hc)	13	–	high	13	13	1.3	10.92	1440
10Ni	–	10	–	–	–	1.8	14.6	1200
10NiCo	7	3	–	–	–	1.6	14.65	1300

*Supplied by B. Roebuck, National Physical Laboratory.
†Balance WC.

3. Results

Anodic polarization curves for pure cobalt, nickel and tungsten are shown in Fig. 1 and various parameters from the curves are collected in Table II along with other information. Overall, it is clear that cobalt has a very poor corrosion resistance. Up to a point A, the pink coloration of Co^{2+} appears next to the surface but this gradually disappears as the surface is progressively covered by a jet-black film in the region A to B. At C the film broke away and rapid evolution of oxygen occurred above point D. The reverse scan followed approximately the forward scan. Nickel was passivated with a very low value of i_{pass} (Table II), and above about 0.8 V evolution of oxygen occurred. Tungsten passivated readily and the electronic conductivity of the film was sufficiently low to prevent oxidation of the solution.

Polarization curves for the WC/Co hardmetals with 6 and 11% Co, for both fine and coarse carbide grains, were similar and the results for the WC (coarse)/11% Co sample are shown in Fig. 2, and parameters from all four hardmetals are included in Table II. In contrast to the pure cobalt, the hardmetal has a small amount of passivation on the forward scan and, most markedly, a substantial passivation on the reverse scan (Fig. 2), while the film on the surface was grey.

TABLE II Corrosion parameters of pure metals and hardmetals in a solution 0.01 M H_2SO_4 + 0.99 M Na_2SO_4

Sample	Chloride in solution (M)	E_{corr}* (V)	E_{crit} (V)	log i_{crit} ($A\,m^{-2}$)	log i_{pass} ($A\,m^{-2}$)
Co	–	−0.460	−0.1	3.3	–
Ni	–	−0.246	0	0.36	−1.01
W	–	−0.310	–	–	–
6CoF	–	−0.430	0	2.23	1.80
6CoC	–	−0.406	0	2.35	1.69
11CoF	–	−0.413	0	2.62	2.16
11CoC	–	−0.430	0	2.67	2.16
10Co(lc)	–	−0.371	−0.1	2.35	0.88
10Co(hc)	–	−0.412	0	2.54	2.02
13Co(lc)	–	−0.377	−0.12	1.87	0.60
13Co(hc)	–	−0.405	−0.05	2.8	2.1
10Ni	–	−0.197	0.08	−0.03	−0.4
10NiCo	–	−0.294	0.05	1.43	0.05
11CoF	0.5	−0.374	−0.5	2.69	2.15
10NiCo	0.1	−0.301	0.05	1.48	0.45
10Ni	0.5	−0.248	−0.5	0.66	0.01
10Ni	0.1	−0.230	0.15	0.28	−0.14
Ni	0.1	−0.223	0.05	0.68	−0.53

*With respect to the SCE.

TaC and TiC in the hardmetal had little effect on the polarization behaviour (Table II). Carbon dissolved in the binder had, however, a marked effect. In both the 10 TaC/2TiC/10Co and 13TaC/13TiC/13Co hardmetals, those with the lower concentration of carbon in the binder had a much lower value of i_{crit} and i_{pass} and a significantly higher value of E_{corr} (Fig. 3 and Table II).

Hardmetals with nickel and Ni–Co binders had a very limited passivation range compared with pure nickel (cf. Figs 4 and 1, and see also Table II) and also a region of secondary passivation (Fig. 4). However, in comparing the parameters of the hardmetals and pure nickel it must be remembered that nominal current densities are used, and so if the only or major process is the dissolution of the binder, then the true dissolution rate would be much higher.

Typically the presence of chloride in the solution increases the dissolution rate (Table II). In the case of cobalt binders, the rate is so high that the influence of

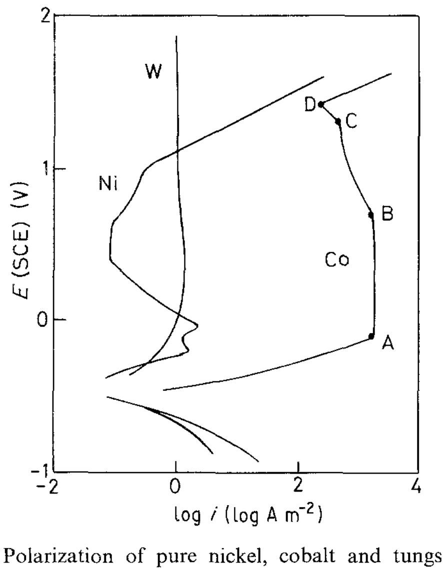


Figure 1 Polarization of pure nickel, cobalt and tungsten. For reference to the letters A to D, see the text.

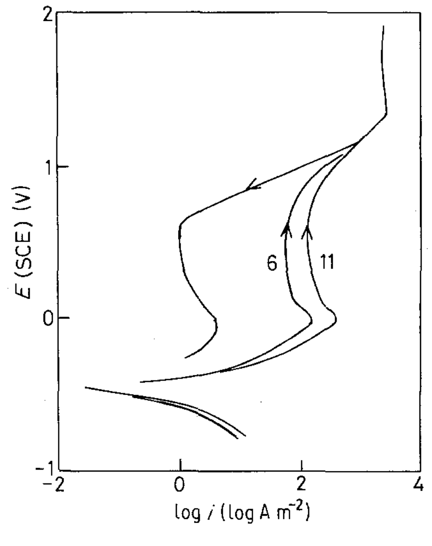


Figure 2 Polarization of hardmetal WC(fine) with 6 and 11% Co binder. Note the reverse scan.

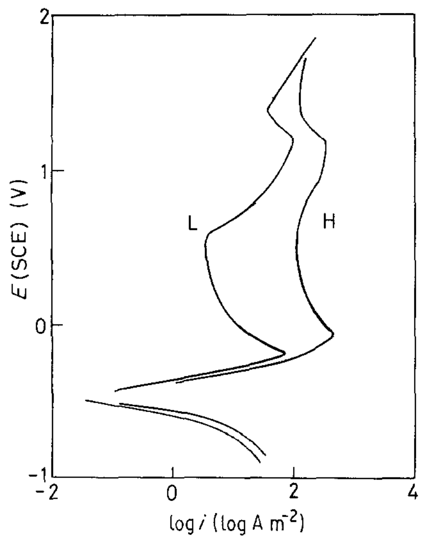


Figure 3 Polarization of the WC hardmetal containing 13TiC/13TiC/13Co with the binder containing low (L) and high (H) amounts of carbon.

chloride is negligible, but it appears that above about 1.2 V a film is formed which is protective against chloride attack at lower potentials, and the reverse scan then follows the pattern of Fig. 2.

Scanning electron micrographs of the WC(coarse)/11% Co hardmetal in various conditions are shown in Fig. 5. The surface in the as-polished conditions is shown in Fig. 5a, and the surfaces after the specimens had been chemically cleaned at -1.3 V (SCE) and then taken immediately to various anodic potentials (see Fig. 2) and held for 30 min, are shown in Figs 5b to e. At E_{crit} there has been extensive dissolution of the binder and some attack of the carbide (Fig. 5b). In the passive range, all the grains have been attacked and dissolution of the carbide is substantial (Fig. 5c). At a potential of 1.2 V a thick film formed on the surface. The surface of the grey film is shown in Fig. 5d and when this was scraped away there was a very thin, adherent, blue film on the hardmetal (Fig. 5e). It is seen that considerable attack on the carbide has occurred. We may note that the outer grey film showed little relation to the underlying carbide grains (cf. Figs 5d and e).

Metallographic sections of the hardmetals that had been potentiostatically dissolved (see above) typically had a layer of carbide grains denuded of binder. Two examples are shown in Fig. 6 and the data are presented in Table III. In Fig. 6b the dark space at the bottom is the region that had been occupied by the thick layer of reaction product (see Fig. 5d) which has been removed during polishing.

4. Discussion

Anodic films on cobalt may consist of an inner layer of CoO, and an outer layer of variable composition $Co_{3-x}O_4$ depending on the potential [14]. In a given situation there are many possibilities [15], and for our present purposes we may consider the decrease in current density from B to C (Fig. 1) during polarization of cobalt due to a change in the nonstoichiometry and properties of the film. After the film has ruptured, the inflexion at C (Fig. 1) we take to be due to the absorption of oxygen on the freshly exposed metal surface [16], before evolution of oxygen occurs at higher potentials. The shape of the curve and the very low values of i_{pass} are characteristic of the behaviour of nickel. Tungsten has a value of i_{pass} considerably below that of cobalt (Fig. 1), and this, together with the stability of the passive state over a large potential range, appears to be due to a passive film of, or based on, WO_3 ([15], p. 282).

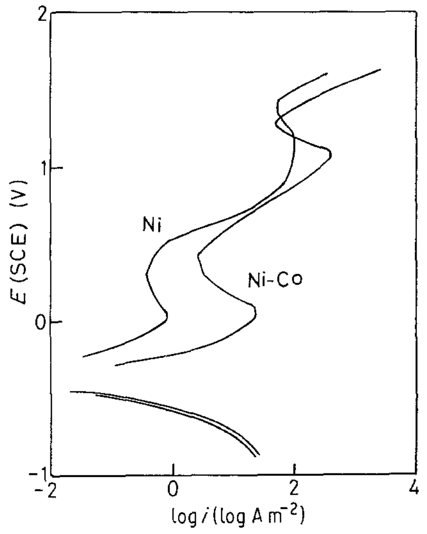


Figure 4 Polarization of WC/Ni and WC/Ni-Co hardmetals.

Tunsten in the binder dissolves according to

$$W + 4H_2O = WO_4^{2-} + 8H^+ + 6e$$

in the amounts expected based on the solubility of tungsten in cobalt [8]. On the basis of a mass balance it was also considered that the WC dissolved according to

$$WC + 6H_2O = WO_4^{2-} + CO_2 + 12H^+ + 10e$$

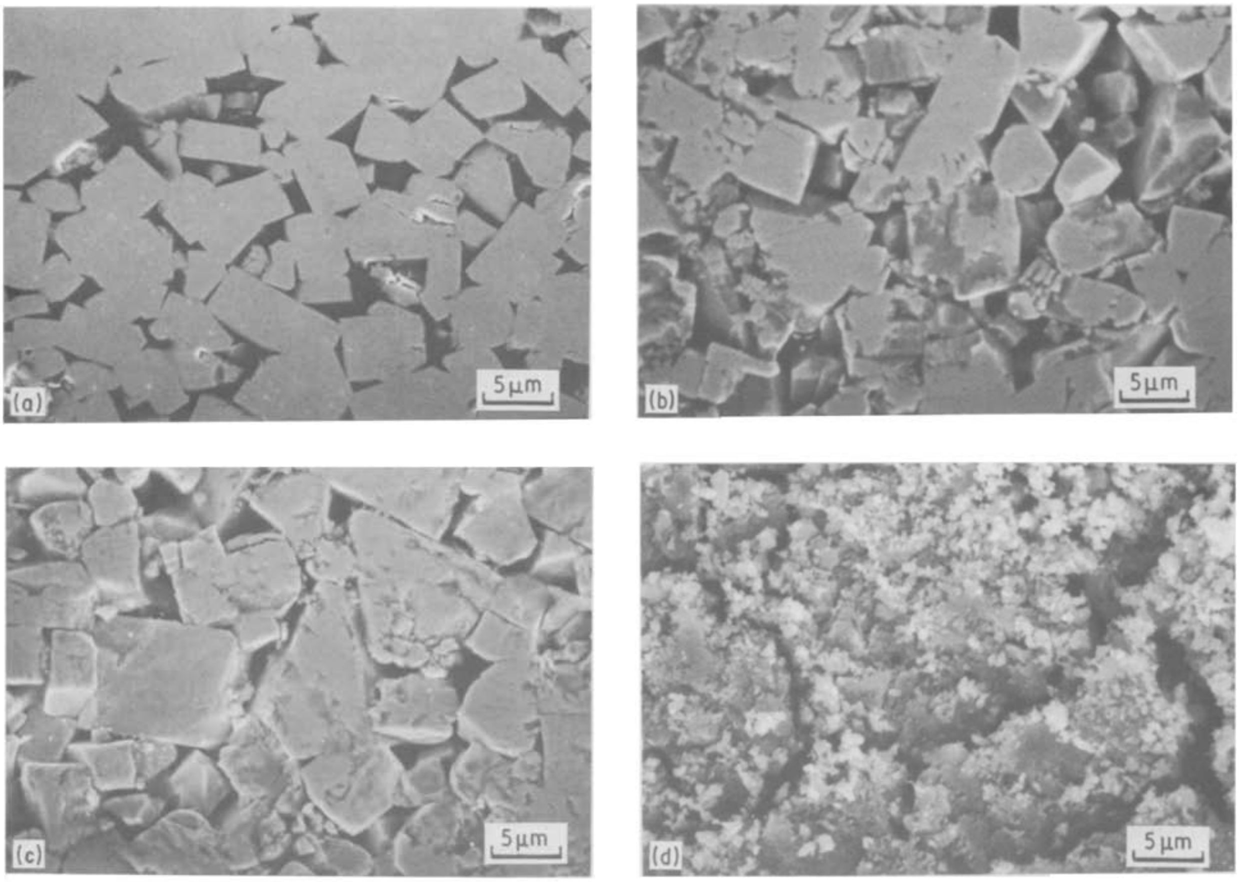
at potentials positive to the reversible potential $E^{\theta}(\mathrm{SCE}) \approx 0$ V [8]. The present results (Figs 5 and 6) demonstrate that WC dissolves in substantial amounts at 0.6 V and above. At the highest potential investigated (1.2 V), it is clear that the rate of dissolution of the WC is similar to that of the binder and so no denuded layer of carbide grains occur (Fig. 6b and Table III).

After allowance has been made for the fraction of the surface occupied by the binder in the hardmetal, the polarization behaviour of the WC/Co hardmetals generally follows the behaviour of pure cobalt (cf. Figs 2 and 1, and see Table II). The small amount of passivation appears to be due to incorporation of some tungsten into the film, and the unusually pronounced degree of passivation on the reverse scan

TABLE III Depth of the layer denuded of binder in a WC(coarse)/11Co hardmetal after holding at for 30 min at various potentials in the standard solution

Potential, E(SCE)(V)	Mean*	S.D.
0.0	98	13.6
0.6	48	5.0
1.2	< 1.0	–

*On six measurements.



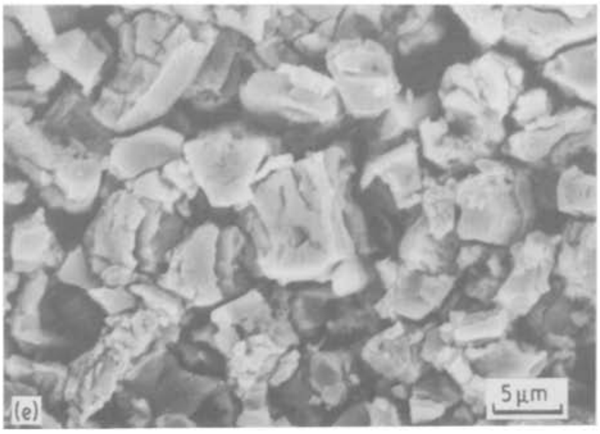


Figure 5 Surface of the WC/Co hardmetal (a) as polished; and after holding potentiostatically for 30 min at (b) 0.0 V, (c) 0.6 V, (d) and (e) 1.4 V. Note (d) shows the surface of a thick film that formed, and (e) shows the hardmetal surface after the film had been scraped away. SEM.

(Fig. 2) will be due to the formation of a WO_3 film at high potentials (Figs 5d and e) which is stable and protective at lower potentials. The effect of carbon in the binder phase on the polarization behaviour (Fig. 3) is also related to the presence and effects of dissolved tungsten. For the reaction $WC = W + C$ there is the equilibrium $[W][C] =$ constant [1]. And so the low concentration of carbon in the binder will mean the presence of a high concentration of tungsten in the binder, and a correspondingly higher degree of passivation (Fig. 3).

The impure nickel of the binder is not as effective over the whole potential range as would be expected from the behaviour of pure nickel (Fig. 4), but fortunately the effect is not too large in the lower potential ranges that may be expected in service. In the same potential range, the presence of 30% Co in the nickel binder substantially increases the current densities and this suggests a serious decrease in the resistance to corrosion. Chloride has a surprisingly small effect on the polarization behaviour (Table II). We take this to be mainly due to the tungsten promoting the formation of a film which is resistant to chloride.

5. Conclusions

From the present work on the anodic polarization of various pure metals and hardmetals in a standard solution of 0.01 M H_2SO_4 + 0.99 M Na_2SO_4 (pH 2.55) and the associated metallographic work the following conclusions are drawn.

1. Passivation of the pure metals nickel, tungsten and cobalt is excellent, good, and zero, respectively. Tungsten exhibits good passivation over a very wide potential range.

2. In the WC/Co-based hardmetals, the binder phase is selectively dissolved at about 0 V (SCE). WC also dissolves at potentials of 0.6 V and above. Above the passive range the rate of dissolution of WC is similar to the rate of dissolution of the binder.

3. The general polarization behaviour of the WC/Co-based hardmetals reflect mainly the behaviour of the binder and this follows the high dissolution rate of pure cobalt over the potential range. Dissolved tungsten induces a small amount of passivation on the forward sweep, and the film formed at high potentials has a pronounced degree of protection during the reverse sweep at lower potentials. Low amounts of

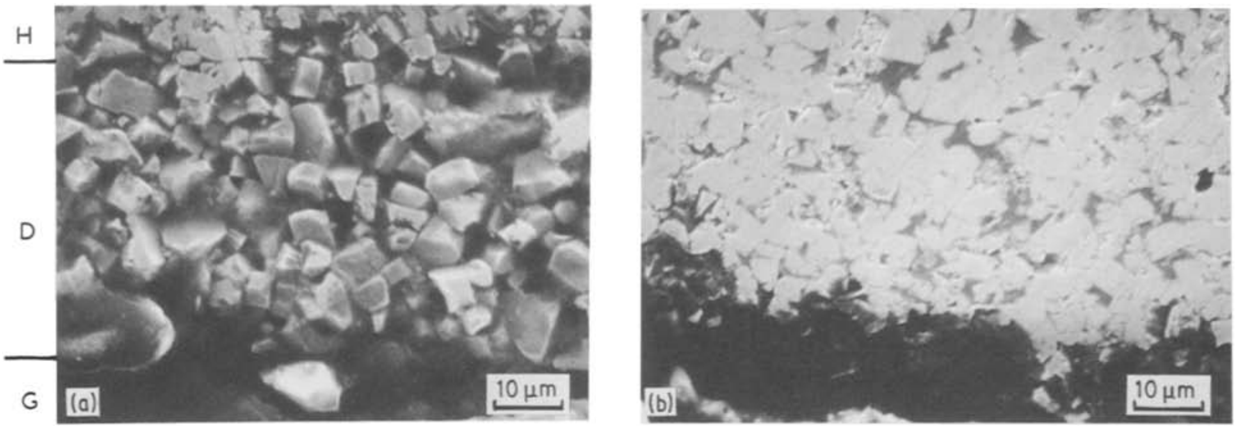


Figure 6 Sections of the specimens potentiostatically dissolved at (a) 0.06 V and (b) 1.4 V. H = unattached hardmetal, D = layer of carbide denuded of binder, and G = a gap between the denuded layer of carbide grains and the mounting medium. SEM.

carbon in the binder promote a more protective film. Neither WC grain size nor the presence of TaC and TiC has any noticeable effect.

4. A nickel binder was more corrosion resistant than cobalt binder, but its performance was less than that expected by comparison with pure nickel.

5. Chloride in solution had a relatively small effect.

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