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Corrosion, erosion–corrosion, and the flexural strength of WC–Co hardmetals

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The corrosion of commercial hardmetals containing 6, 8 and 10% Co with small additions of Cr_3C_2 and VC, in solutions of pH 1, 3, 5 and 10, and in a cutting fluid of pH 8.6, has been investigated using weight loss, atomic absorption spectroscopy, and metallographic techniques. For a surface area 420 mm^2, at 20 °C, the amount of cobalt dissolved in pH 5 and 10 solutions was less than 0.05 mg per day and in the cutting fluid was less than 0.05 mg in 7 days. Salt in the water increased the corrosion rate in the pH 10 solution by over five times. Corrosion was highest in the hardmetal containing VC. Corrosion in a pH 1 solution at 20 °C for 24 h (weight loss about 1 mg) did not affect the mean strength of the hardmetals. Erosion by alumina balls during corrosion increased the corrosion rate in the pH 1 solution by 16 to 29 times, formed a thick layer of WC denuded of cobalt, and reduced the strength of the eroded–corroded hardmetals by 0.54 to 0.76 times.

1. Introduction

Cemented carbides are used for their outstanding resistance to wear. In many cases they must also have a high resistance to corrosion. This is obvious in severe and demanding conditions such as drilling in acid and aggressive environments [1–7], but it is also important when only very small amounts of the cobalt binder dissolve in the grinding fluids during typical machining operations [8]. Cobalt corrodes readily in many aqueous solutions [9], and while this is modified by various alloying additions [6, 7], the corrosion rate in some applications is unacceptably high, and hardmetals with a nickel binder and, consequently with a considerably increased resistance to corrosion, have been introduced [1, 2, 6].

Corrosion of cemented carbides is most easily measured and characterized by simple immersion testing. Electrochemical techniques have also been used to determine the corrosion behaviour of hardmetals, but they are more complicated to operate and require more interpretation [6, 7]. All such accelerated tests need careful interpretation with respect to service performance. In practice, the situation is further complicated inasmuch as the conjoint action of wear and corrosion may increase the amount of wear and/or corrosion far more than that measured in the separate corrosion and wear tests. In addition, corrosion and wear may influence the mechanical properties of the hardmetals. Conjoint action of corrosion and wear, and the effect of corrosion on the mechanical properties of hardmetal have not previously been studied. The present work, therefore, investigated the corrosion behaviour of three commercial hardmetals under simple immersion conditions and under corrosion–erosion conditions to simulate, at least in part, the action of wear in removing any possible protective corrosion products, and the effect of corrosion and erosion–corrosion on the flexural strength of the hardmetals.

2. Experimental procedure

The hardmetals, kindly supplied by Sandvic (UK) Ltd, Coventry, were drill blanks 39 mm long and 3.28 mm diameter (surface area 420 mm^2) and the available data are shown in Table I. Distilled water and Analar reagents were used to make the solutions. Sulphuric acid or sodium hydroxide was added to distilled water until the required pH, as measured on a pH-meter, was obtained.

Individual specimens were corroded in 20 ml of solution in a test tube. The amount of corrosion was so small that problems associated with saturation were not expected. Erosion–corrosion of batches of 11 specimens occurred in 220 ml of solution with 75 alumina balls held in a plastic jar of diameter 73 mm and rotated horizontally along the axis at 100 revolutions per minute. The balls, diameter 10 mm, with the 11 specimens filled the jar to a height of 37 mm along the diameter of the jar, and the solution covered the balls to a further height of 5 mm. Before testing the specimens were degreased and weighed to 0.1 mg, and after testing, the specimens were washed in distilled water and then in acetone, dried, and weighed.

Standard metallographic techniques, scanning electron microscopy (SEM), EDAX analysis, and atomic absorption spectroscopy (AAS) were used. The sensitivity of the AAS was approximately 0.05 mg cobalt.

3. Results and discussion

Results for the measured weight losses and the equivalent mass losses of the dissolved cobalt measured by

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TABLE I Composition and properties of the hardmetals

Sample	Sandvic grade	Cobalt (wt %)	Additions (wt %)	Grain size (µm)
6fCC3	H6F	6	$0.3Cr_3C_2$	0.8
8uCC4VC6	8uF	8	$0.4Cr_3C_2$ + 0.6VC	0.4
10fCC5	H10F	10	$0.5Cr_3C_2$	0.8

atomic absorption spectroscopy (AAS) are shown in Table II. All the corroded and eroded specimens were examined metallographically. When extensive corrosion of the cobalt had occurred the WC denuded layer has a relatively even thickness (Fig. 1), and results for the thickness of the denuded layers are shown in Table III. The strength of the as-manufactured drill blanks, and after corrosion for 24 h and erosion–corrosion for 6 h in a pH 1 solution at 20 °C, are shown in Table IV.

Corrosion was most extensive in the pH 1 solution after 6 h at 80 °C (Table II). The results obtained under this condition by weight loss and by AAS are in good agreement (Table II). Only a small amount of cobalt remains in the denuded layer (Table IV), and loss of cobalt for the 6, 8, and 10% Co hardmetals is 4.6, 15.3, and 12.8 mg, respectively. These are in excellent agreement with the values 4.65, 16.50 and 13.00 measured using AAS (Table II) thus confirming the accuracy of the measurements. Results obtained by AAS are more sensitive (to 0.05 mg) than those obtained by weight loss (to 0.1 mg) and are considered to be more accurate inasmuch as the AAS measures only the amount of cobalt in solution whereas the weight loss might measure other substances (see later under erosion–corrosion). Overall, corrosion in pure solutions followed the prediction of the Co–H_2O Pourbaix diagram [9]; corrosion occurred in acid solutions and passivation occurred in neutral and alkaline solutions. In the cutting fluid (pH 8.6) the amount of cobalt dissolved from the 8% Co alloy after 168 h at 20 °C was less than 0.05 mg, and after 168 h at 80 °C it was 0.09 mg (Table II). After corrosion at 20 °C in the cutting fluid there was no evidence of the presence of corrosion pits, but after corrosion at 80 °C corrosion pits were occasionally present and the maximum depth observed was 6 µm.

In general, the alloy containing VC has the highest corrosion rate. This is particularly so for the tests conducted at 80 °C (Table II). Similar results were obtained using electrochemical techniques [7] when in a more detailed and broader study it was concluded that the presence of vanadium interfers with the passivation conferred by small amounts of chromium on the cobalt binder.

Salt in the water (3.0 wt % NaCl) increased the

TABLE II Corrosion of commercial WC–Co hardmetals under corrosion (static) and erosion–corrosion conditions

Test		Solution[a]		Sample[b]	Specimen weight loss (mg)[c]		Dissolved cobalt (mg)	
Type	Duration (h)	pH	Temperature (°C)		During test	per 24 h	During test	% Total wt loss
Static	24	1	20	6	1.1	1.1	1.08	98
				8	1.1	1.1	1.02	93
				10	0.9	0.9	0.80	89
Static	6	1	80	6	5.8	23.2	4.65	80
				8	20.6	82.4	16.50	80
				10	15.5	62.0	13.00	84
Erosion–corrosion	6	1	20	6	–	–	4.67	–
				8	–	–	4.16	–
				10	–	–	5.79	–
Static	24	3	20	6	0.3	0.3	0.20	66
				8	0.5	0.5	0.26	52
				10	0.4	0.4	0.25	63
Static	6	3	80	6	0.2	0.8	0.13	65
				8	0.4	1.6	0.26	65
				10	0.3	1.2	0.18	60
Static	24	5	20	All	< 0.1	< 0.1	< 0.05	—
Static	6	5	20	All	< 0.1	< 0.4	< 0.05	—
Static	24	10	20	All	< 0.1	< 0.1	< 0.05	—
Static	6	10	80	All	< 0.1	< 0.4	< 0.05	—
Static	24	10 + 3% NaCl	20	6	0.4	0.4	0.24	60
				8	0.4	0.4	0.20	50
				10	0.6	0.6	0.32	53
Static	6	10 + 3% NaCl	80	6	0.4	1.6	0.17	43
				8	0.3	1.2	0.16	53
				10	0.3	1.2	0.12	40
Static	168	8.6[d]	20	All	< 0.1	< 0.1	< 0.05	—
Static	168	8.6[d]	80	8	< 0.1	< 0.1	0.09	—

[a] All distilled water solutions except as given for the addition of 3 wt % NaCl, or the cutting fluid

[b] 6 = 6% Co in sample 6fCC3, etc. see Table I

[c] Each specimen area 420 mm^2. The 24 hour weight loss for the 6 h tests is for comparison and calculated assuming a linear corrosion rate. Dissolved cobalt is an average of 11 specimens for the erosion–corrosion tests.

[d] Cutting fluid.

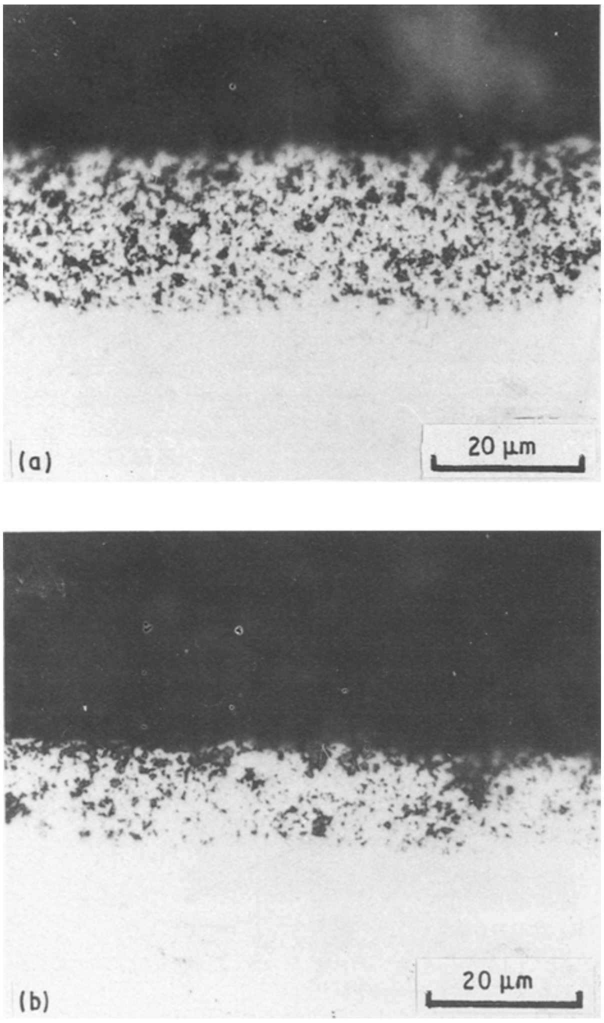

Figure 1 The WC–Co skeleton layer formed on a 6% Co hardmetal after (a) corrosion for 6 h in a pH 1 solution at 80 °C, and (b) erosion–corrosion for 6 h in a pH 1 solution at 20 °C, unetched.

corrosion rate in pH 10 solution by over 5 times (Table II) and caused the surface to have a slightly roughened appearance. In section, however, no evidence of pitting was observed. It may be noted that in acid solution (pH 2.5) the presence of 3.0 % NaCl only increased slightly the corrosion rate [7].

In terms of the results obtained by AAS the effect of erosion on the amount of corrosion in the pH 1 solution at 20 °C for 24 h was (4 × 4.67)/1.08 = 17.3, (4 × 4.16)/1.02 = 16.3, and (4 × 5.79)/0.80 = 29.0 times for the hardmetals with 6, 8, and 10% Co respectively (Table II). Hence the increase in corrosion for this type of erosion is considerable. It should be noted that the effect of the wear process is not one of simple abrading the surface since a substantial thickness of denuded WC protects the dissolution site from the direct impact of the alumina balls.

Corrosion does not affect the mean strength of the hardmetals (Table III). In contrast, erosion–corrosion has a considerable effect, and under the present conditions it reduces the strength of the as-received 6, 8, and 10 % Co hardmetals by 1919/3566 = 0.54, 2264/3477 = 0.65, and 3158/4181 = 0.76 times, respectively (Table III). It is not clear why the reduction in strength is greatest with the 6 % Co hardmetal and least with the 10 % Co hardmetal, but it is probably due to the denuded WC skeleton which is thickest (14 µm) on the 6 % sample and thinnest (9 µm) on the 10 % sample (Table III).

It is seen that the thickness of the WC skeleton worn away during erosion–corrosion is 10, 6, and 10 µm for the 6, 8, and 10 % Co alloys, respectively (Table III). Although the present evidence is limited, it is suggested that this could well be due to the size of the carbide particles since the 8 % Co alloy had an ultrafine grain size (Table I), and might therefore, form a stronger WC–WC bond during sintering.

Corrosion is a property of the system and it depends on such factors as the geometry of the material and the flow conditions of the environment. Wear is also a property of the system and it depends critically on the precise wear conditions. The conjoint action of corrosion wear is clearly a complex property, and to characterize the corrosion properties of hardmetals in a simple and meaningful way requires at least two tests: one to characterize the dissolution rate and material damage under defined conditions, and a second test to characterize the dissolution rate and material damage under the action of a defined wear process. The useful-

TABLE III The WC skeleton layer denuded of cobalt formed on the surface of specimens after corrosion or erosion–corrosion in pH 1 solutions

Sample	Cobalt[a] (wt %)	Measured depth (µm)	Equivalent cobalt[b] (wt %)	AAS cobalt[c] (mg)	Equivalent depth[d] (µm)	Eroded depth[e] (µm)	Fraction eroded
Corroded 6 h in pH 1 solution at 80 °C							
6	0.5	23	4.6	4.7	–	–	–
8	0.2	56	15.3	14.5	–	–	–
10	0.3	38	12.8	13.0	–	–	–
Eroded–corroded 6 h in pH 1 solution at 20 °C							
6	–	14	2.7	4.7	24	10	0.42
8	–	11	2.7	4.2	17	6	0.35
10	–	9	2.7	5.8	19	10	0.53

[a] From EDAX analysis of layer.
[b] Calculated from the depth of the measured layer.
[c] From Table II.
[d] Calculated from AAS Co result.
[e] Eroded depth = Equivalent depth – measured depth.

TABLE IV Effect of corrosion and of erosion–corrosion on the flexural strength of some WC–Co hardmetals

Sample condition[a]	Sample	Modulus of rupture (MPa)[b] mean	S.D.	C of V	Weibull modulus
As-received	6	3566	727	20.4	4.1
As-received	8	3477	318	9.2	10.5
As-received	10	4181	192	4.6	20.4
Corroded	6	3207	237	7.4	12.9
Corroded	8	3515	432	12.3	6.0
Corroded	10	4044	379	9.4	10.1
Eroded–corroded	6	1919	144	7.5	12.8
Eroded–corroded	8	2264	223	9.9	9.4
Eroded–corroded	10	3158	919	29.0	3.2

[a] As-received drill blanks; corroded at 20 °C in pH 1 solution; eroded–corroded 6 h at 20 °C in pH 1 solution.
[b] Mean of 10 samples; C of V = ((S.D.)/mean) × 100.

ness or otherwise of the tests would then depend on the extent they relate to industrial experience.

4. Conclusions

From the present work on the corrosion and erosion–corrosion of WC–Co hardmetals containing 6 % Co with 0.3 % Cr_3C_2, 8 % Co with 0.4 % Cr_3C_2 and 0.6 % VC, and 10 % Co with 0.5 % Cr_3C_2, of surface area 420 mm^2, we conclude the following.

1. Static corrosion at 20 °C in solutions of pH 1, 3, 5 and 10 was 0.80 to 1.08, 0.20 to 0.26, < 0.05, and < 0.05, mg per day, respectively. Corrosion in the pH 1 solution for 6 h at 80 °C was 5.8, 20.6 and 15.5 mg for the 6, 8, and 10 % Co alloys, respectively. Salt in the pH 10 solution increased the amount of corrosion by over five times.
2. Static corrosion at 20 and 80 °C in a cutting fluid of pH 8.6 was 0.05 and 0.09 mg, respectively, after 7 days.
3. The hardmetal with 0.6 % VC in the binder had the highest corrosion rate.
4. Corrosion in pH 1 solution at 20 °C for 24 h (about 1 mg weight loss) did not affect the mean strength of the hardmetals.
5. Erosion by impacting alumina balls increased the corrosion rate in pH 1 solution at 20 °C for 6 h for hardmetals containing 6, 8, and 10 % Co by 17, 16 and 29 times, respectively.
6. Erosion–corrosion reduced the flexural strength of hardmetals containing 6, 8, and 10 % Co by 0.54, 0.65 and 0.76 times, respectively.

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