

Measurement Note

Ball Cratering as a Technique to Evaluate Microabrasion in Corrosive Media

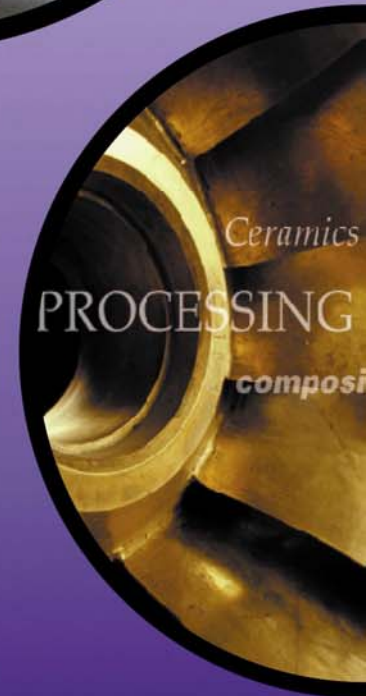
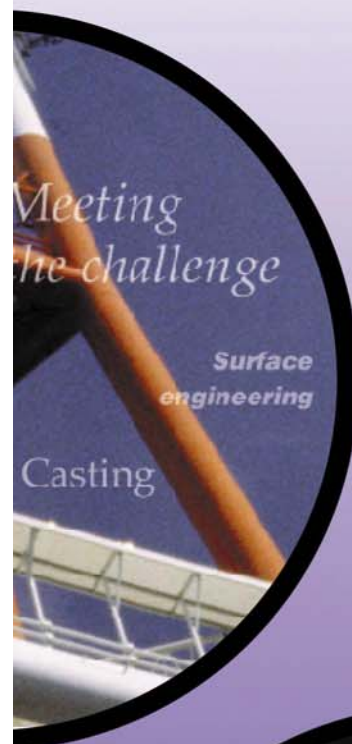
Summary

In micro-abrasion, the influences of corrosive carrier media on the mechanisms and severity of material removal are still poorly understood. This means that with a few notable exceptions, good models for the prediction of materials behaviour are still not readily available. Ball cratering is still a technique which is in its infancy, but is yet sufficiently developed for a test programme to be undertaken using corrosive media.

In this preliminary study, the technique has been applied to the micro-abrasion wear of selection WC-based hardmetals and a PVD coating. For the alkaline and neutral carrier media it was found that volume loss was inversely proportional to hardness. This was not in the case for the acidic media. Scanning electron microscopy of the wear surfaces indicated that the breakdown of the hardness-volume loss relationship in the acidic media was due to the coarser carbide grains (i.e. in the hardmetals of lower bulk hardness) remaining *in situ* rather than being removed by abrasive processes. Longer-term tests indicated that in the most acidic medium there were transients taking place in the material removal process, giving a higher wear rate at the start of a test.

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Introduction

WC based hardmetals and coatings are widely used in applications where both corrosion abrasion resistance are important. Abrasion resistance of hardmetals has been extensively researched over the past twenty to thirty years and the factors (mechanical and physical properties such as hardness and toughness; and microstructural parameters such as binder intercept and grain size) determining it are now reasonably well understood [1-4]. Corrosion resistance of hardmetals has also received a reasonable amount of coverage, but perhaps not to the same extent as abrasion. Despite this there has been little coverage on the interaction of wear and corrosion in hardmetals [5,6]. Where studies have been undertaken they have almost exclusively used macroscopic sized abrasants; this may not be appropriate for some applications dealing with fine corrosive slurries such as effluent pumps [7]. This Measurement Note describes a method that can be used to determine the wear mechanisms that take place in micro-abrasion with the conjoint action of corrosive media using optical measurement of craters and scanning electron microscopy to assess wear. The aim of this type of approach is that more knowledge about the wear mechanisms can be used to guide the development of new materials, and also to provide better ways of selecting materials for particular applications.

Experimental Method

Figure 1 shows the basic configuration of the ball tests. The ball is rotated against the test sample. Wear takes place to the sample and a crater is formed whose size provides a measure of the wear that has occurred. The abrasive tests reported herein are performed by dripping corrosive, abrasive, slurry into the contact between the ball and the sample.

Materials

In this preliminary investigation six WC/Co hardmetals and one TiN-coated stainless steel were examined (4 μ m PVD on 304 stainless steels). Details of the hardmetals tested are given in Table 1. The samples were 20 mm x 20 mm x 5 mm. One of the 20 x 20 mm faces of each sample was polished by standard metallographic techniques and then annealed *in vacuo* at 800°C for 1 hour in order to eliminate any possible residual stresses produced during sample preparation.

Before testing the polished face of the sample was cleaned by washing in detergent solution, rinsing in very hot water, and then blow-dried with compressed air. After every exposure this cleaning procedure was repeated and was also conducted before optical crater measurement and crater examination in the SEM.

Test System

The ball cratering test system that was used was a proprietary fixed ball system (Figure 1) with certain modifications; namely electrical isolation of the specimen (to give free-corroding conditions) and use of a Hastelloy C276 delivery tube to avoid delivery tube degradation, formation of reactants and modification of medium pH. The nozzle bore size was 1 mm. Slurry drips from the nozzle onto the rotating ball and is entrained into the ball/specimen contact patch. Fresh slurry is always used and a steady delivery rate is maintained by keeping the reservoir agitated with a magnetic stirrer.

The test conditions that were employed were:

- Abradant of angular silicon carbide, F1200 mesh size (4 μ m)
- Slurry concentration of 20% (vol.)
- Ball: WC-6% Ni, diameter 25 mm
- Applied load 0.2 N

The applied load and slurry concentration used were chosen to produce 3-body wear, good crater definition and no slurry starvation regions [8]. The samples were initially exposed to the various media, ranging from pH 1.1 to pH 13, outlined in Table 2 for a duration of 100 revolutions. conditions. Further experiments were also conducted at 250, 500, 750 and 1000 revolutions in the medium with the lowest pH; pH 1.1 sulphuric acid/ 20 vol. % SiC. These further tests were undertaken in order to determine whether or not an incubation period existed before steady state wear was achieved. Two of the WC-Co hardmetals were selected for examination by scanning electron microscopy; namely M6 and uc9. These two were selected as in terms of scale they are at the coarsest and finest extremes of the microstructural spectrum of the sample set tested.

Table 1, Details of hardmetals used.

Code	Co wt. %	d _{WC} , μ m	d _{binder} , μ m	HV ₃₀
macn9	6+3% Ni	0.23	0.1058	1683
M6	6	0.28	0.0952	1925
h10	10	0.41	0.205	1367
K5	6	1.31	0.4454	1487
M4	6	2.94	0.9996	1221
uc9	9	4.97	2.2862	996

Table 2, Details of slurries.

Medium	Abradant	Concentration
pH13 Ca(OH) ₂	4µm SiC	20% vol.
pH 6.3 deionised H ₂ O	4µm SiC	20% vol.
pH2.6 H ₂ SO ₄	4µm SiC	20% vol.
pH1.1 H ₂ SO ₄	4µm SiC	20% vol.

Results

A series of micrographs taken at a magnification of x5000 of wear surfaces of M6 and uc9 are shown in Figures 2 to 5. It can be seen that considerable damage to the surface of M6 in the form of removal of much of the cobalt binder phase on the surface and fracture of carbide grains has occurred after only 100 revolutions, regardless of slurry pH. In the case of uc9, close inspection reveals that preferential binder removal and pluckout, or undermining of the smallest grains becomes more prevalent with decreasing pH of the medium. However, the largest grains in uc9 appear to be undergoing a different, relatively mild wear regime in which is akin to polishing.

Examination of the exposed surfaces of uc9 at high magnification reveals more details of the wear mechanisms that are occurring; this is predominantly a 2-body regime – i.e. a scratching and grooving process. This is rather surprising, given that the applied load and slurry concentration ought to produce a 3-body (abrasive rolling) regime [8] under these conditions. However, data in the literature pertaining to expected regime in micro-abrasion were almost exclusively generated using either tool steels or TiN coatings on tool steel substrates.

A summary plot of volume loss vs. hardness on the Vickers scale measured using a load of 30 kgf is shown in Figure 6. There are two main points to note; firstly that, in general, wear increases with decreasing pH of the carrier medium of the slurry. The second point is that in the media of relatively high pH there is an inverse relationship between hardness and wear loss, but this

relationship is not seen in the more acidic media (pH2.6 and pH1.1). In Figures 7 to 10 plots of the inverse square root of both binder intercept and of WC grain size intercept are illustrated as a means of exploring in more detail the trends seen in Figure 6; it is clear that there is an inverse relationship between both microstructural size intercepts and hardness in the case of the hydroxide and deionised water-based slurries, but not in the case of the sulphuric acid media. Further tests were then conducted to establish whether there was any dependence on the relationship between the inverse square root parameters and test duration using the most acidic slurry. These additional tests were performed at 250, 500, 750 and 1000 revolutions; results of volume loss plotted against inverse square root of both binder intercept and WC grain size intercept are shown in Figures 11 to 14 and show that by 750 revolutions, an almost linear relationship between the inverse square root parameters and volume loss has developed, which is effectively a juxtaposition of the relationships seen in the short term tests (100 revolutions' duration) and the alkaline or approximately neutral media. Figure 15 illustrates the progressive increase in volume loss using the most acidic medium with time (up to 1000 revolutions). It shows clearly that in the finest grained materials (i.e. the largest values of inverse square root intercept) that volume loss proceeds in a linear manner, but this is not the case in the coarsest grained materials, where the initial wear rates are comparable with the other grades, but after 250 revolutions the wear rate becomes negligible. Samples whose intercepts are of an intermediate value exhibit behaviour which shows a progressive increase in wear, but one which is nevertheless sub linear. Given the effect of medium on these hardmetals, another material system was selected in which corrosive-conditions may be encountered; namely PVD TiN-coated 304 stainless steel, however there is little difference in volume loss between exposure to a pH6.3 (deionised water) based slurry and a pH1.1 slurry based on sulphuric acid, but as can be seen in Figure 16, the response to both slurries is approximately linear with respect to test duration.

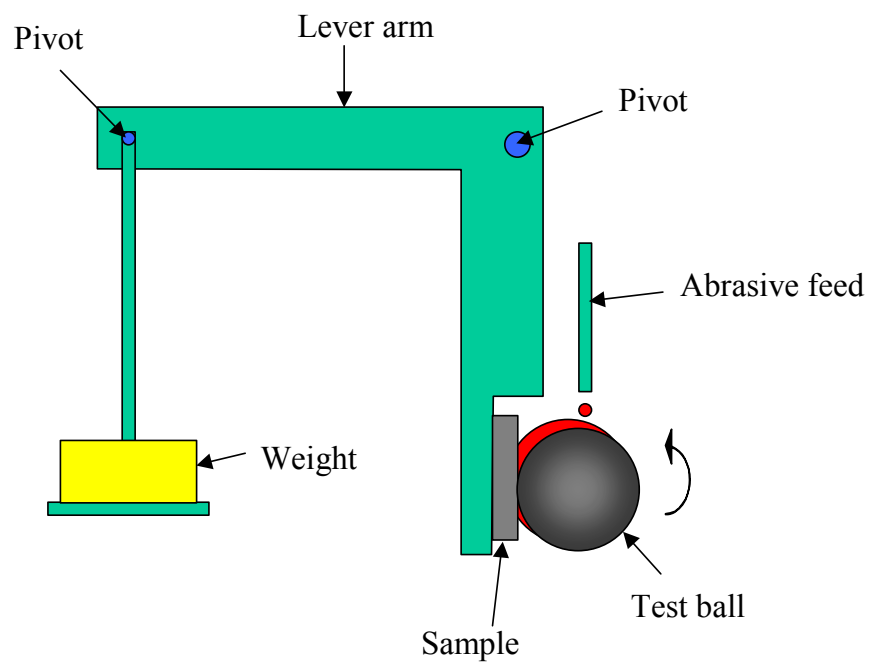


Figure 1, Schematic of ball cratering layout.

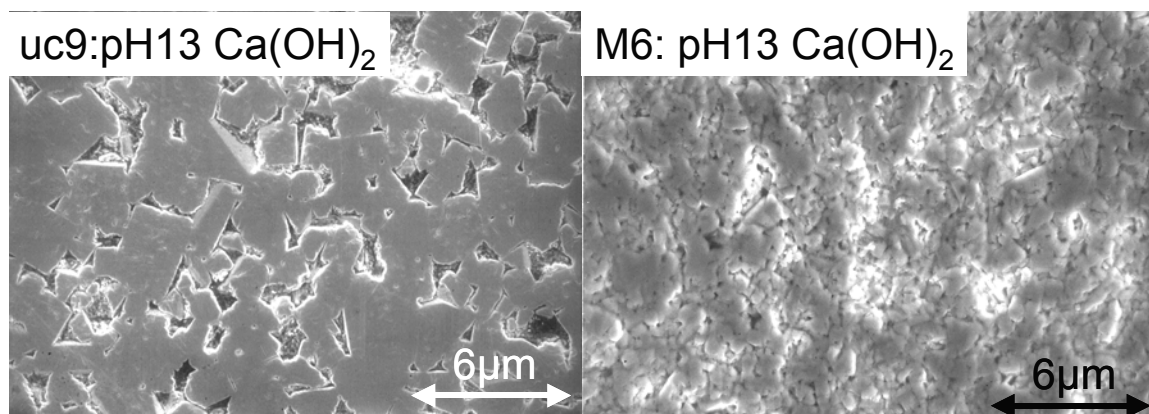


Figure 2, Wear surfaces of uc9 and M6 respectively produced by pH13 Ca(OH)_2 / 20% vol. SiC. 100 revolutions, applied load 0.2 N.

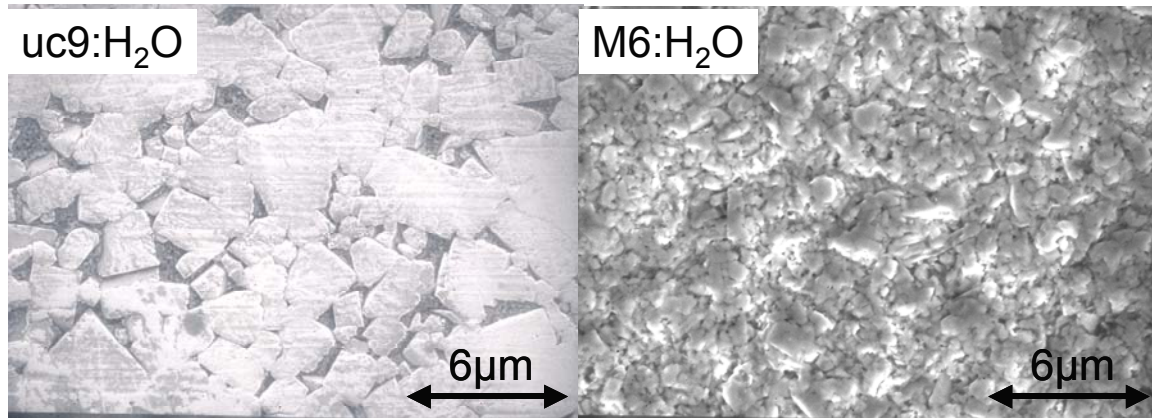


Figure 3, Wear surfaces of uc9 and M6 respectively produced by pH6.3 H₂O / 20% vol. SiC. 100 revolutions, applied load 0.2 N.

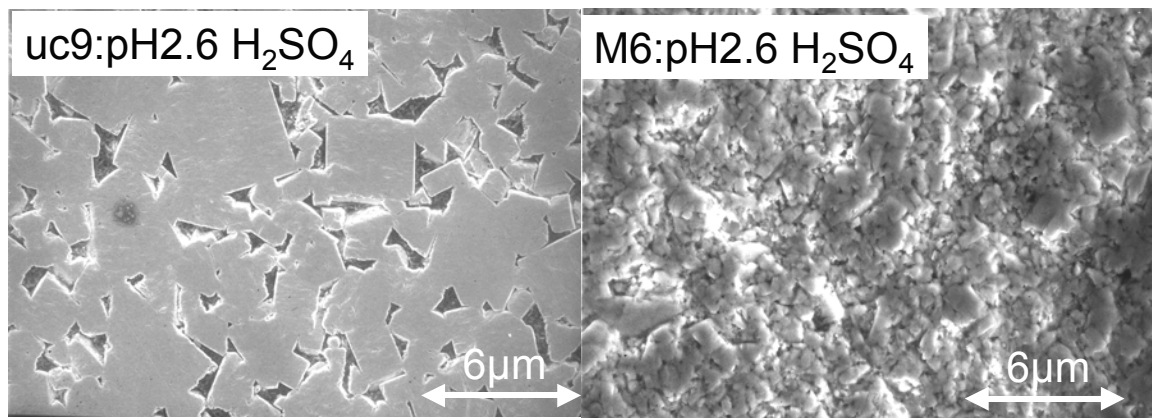


Figure 4, Wear surfaces of uc9 and M6 respectively produced by pH2.6 H₂SO₄ / 20% vol. SiC. 100 revolutions, applied load 0.2 N.

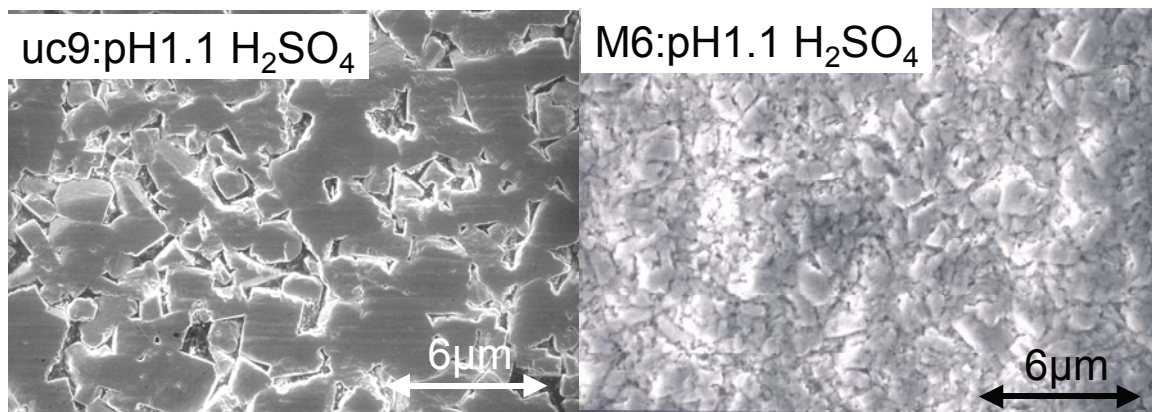


Figure 5, Wear surfaces of uc9 and M6 respectively produced by pH1.1 H₂SO₄ / 20% vol. SiC. 100 revolutions, applied load 0.2 N.

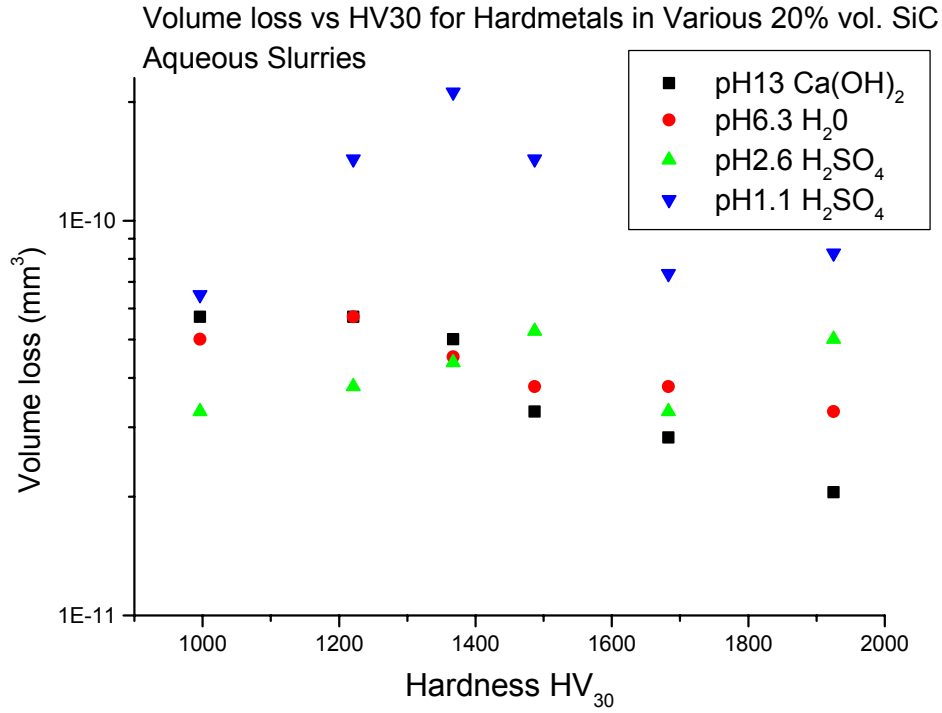


Figure 6, Summary plot of volume loss vs. HV30 for all slurries investigated; 100 revs with 0.2 N applied load against WC-6% Ni ball.

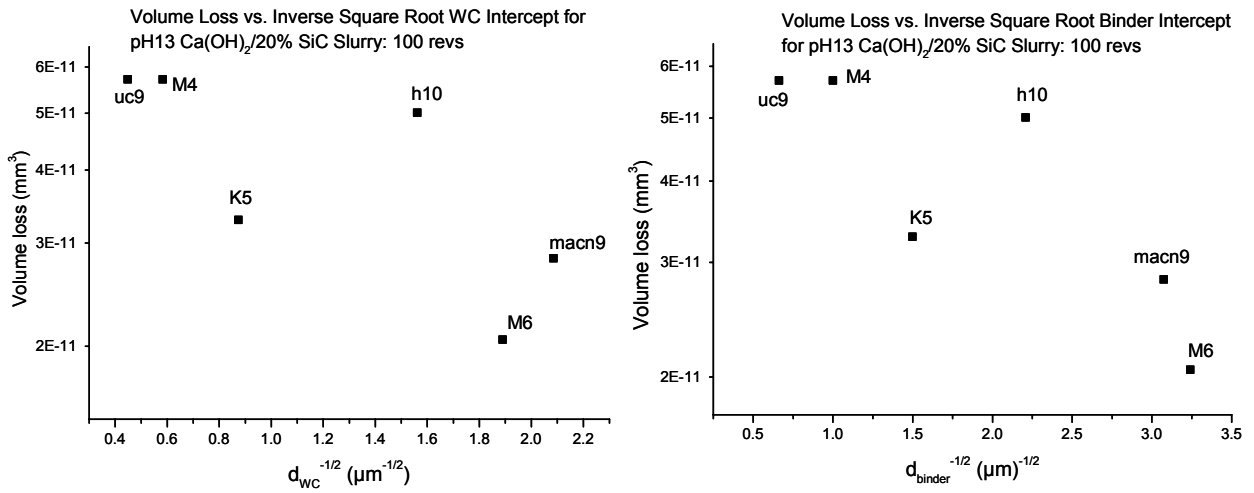


Figure 7, Plots of inverse square root WC grain intercept ($d_{WC}^{-1/2}$) and inverse square root binder intercept ($d_{Co}^{-1/2}$) for pH13 Ca(OH)₂ + 20% SiC slurry; 100 revs, 0.2 N applied load

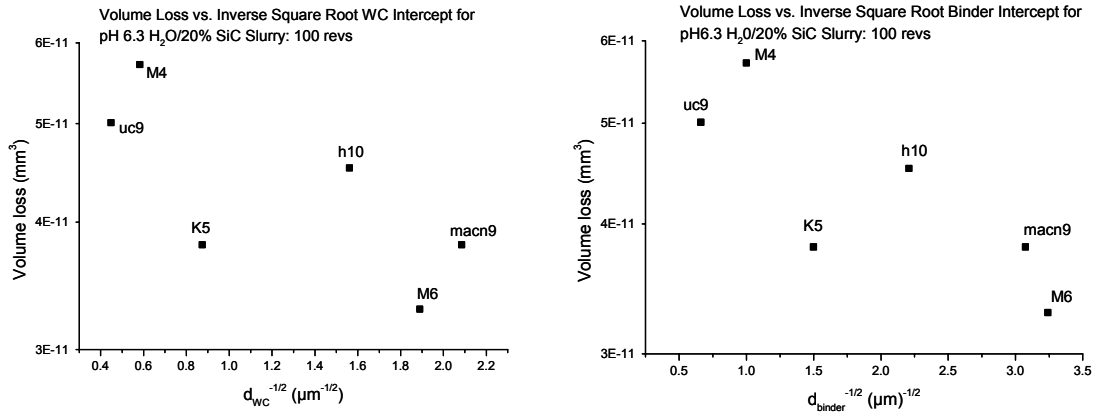


Figure 8, Plots of inverse square root WC grain intercept ($d_{WC}^{-1/2}$) and inverse square root binder intercept ($d_{Co}^{-1/2}$) for pH6.3 deionised water + 20% SiC slurry; 100 revs, 0.2 N applied load.

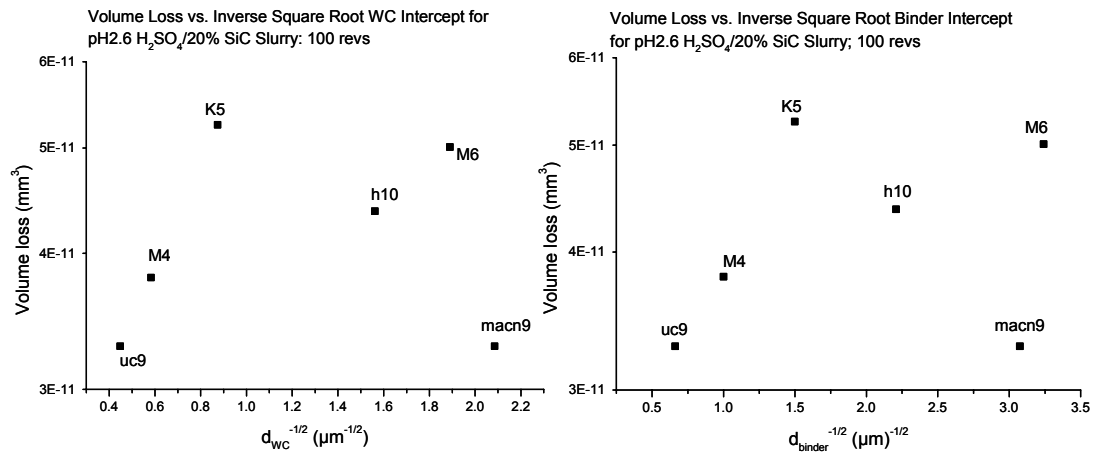


Figure 9, Plots of inverse square root WC grain intercept ($d_{WC}^{-1/2}$) and inverse square root binder intercept ($d_{Co}^{-1/2}$) for pH2.6 H₂SO₄ + 20% SiC slurry; 100 revs, 0.2 N applied load

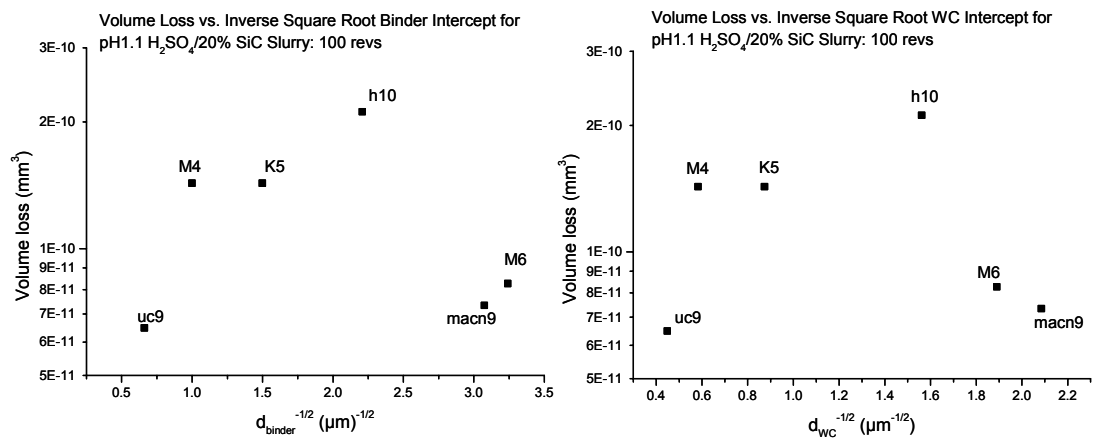


Figure 10, Plots of inverse square root WC grain intercept ($d_{WC}^{-1/2}$) and inverse square root binder intercept ($d_{Co}^{-1/2}$) for pH1.1 H₂SO₄ + 20% SiC slurry; 100 revs, 0.2 N applied load

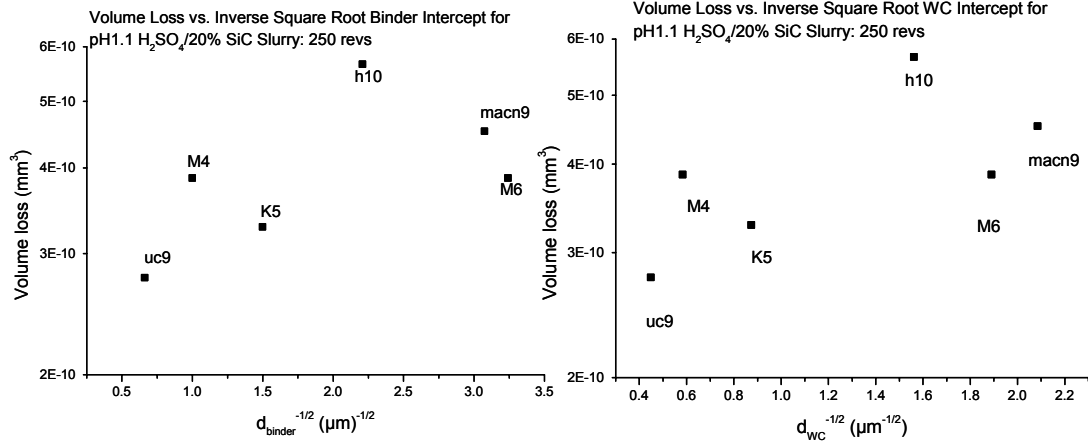


Figure 11, Plots of inverse square root WC grain intercept ($d_{WC}^{-1/2}$) and inverse square root binder intercept ($d_{Co}^{-1/2}$) for pH1.1 H₂SO₄ + 20% SiC slurry; 250 revs, 0.2 N applied load.

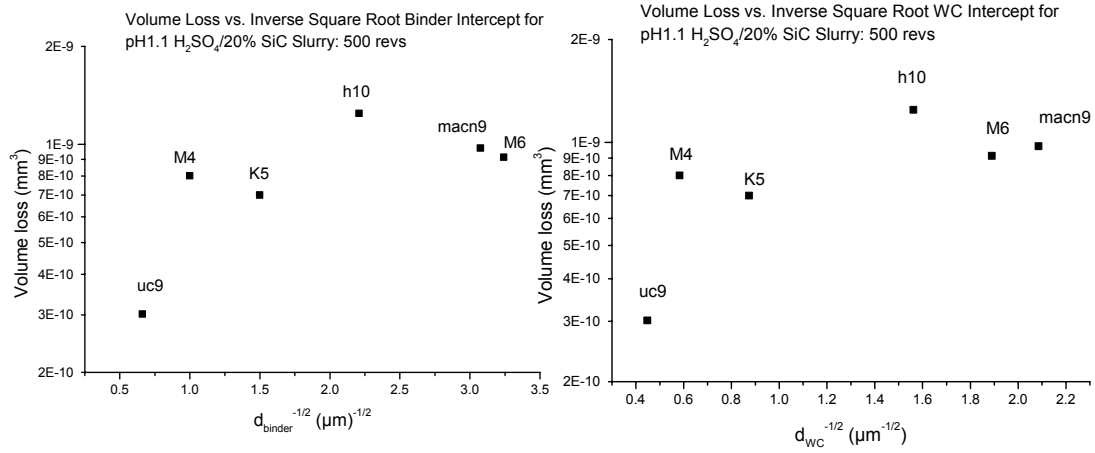


Figure 12, Plots of inverse square root WC grain intercept ($d_{WC}^{-1/2}$) and inverse square root binder intercept ($d_{Co}^{-1/2}$) for pH1.1 H₂SO₄ + 20% SiC slurry; 500 revs, 0.2 N applied load.

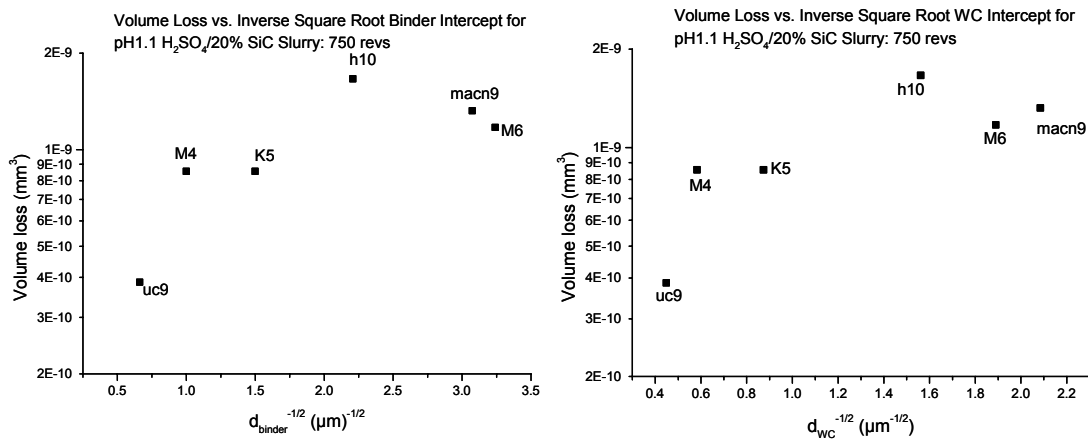


Figure 13, Plots of inverse square root WC grain intercept ($d_{WC}^{-1/2}$) and inverse square root binder intercept ($d_{Co}^{-1/2}$) for pH1.1 H₂SO₄ + 20% SiC slurry; 750 revs, 0.2 N applied load.

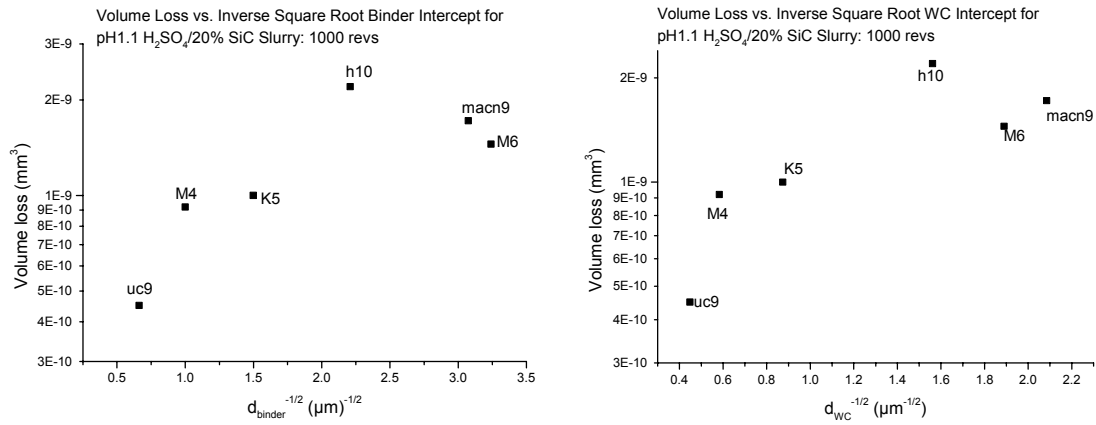


Figure 14, Plots of inverse square root WC grain intercept ($d_{WC}^{-1/2}$) and inverse square root binder intercept ($d_{Co}^{-1/2}$) for pH1.1 H₂SO₄ + 20% SiC slurry; 1000 revs, 0.2 N applied load.

Volume loss vs Test Duration in pH1.1 H₂SO₄/20% SiC Slurry; 0.2 N Applied Load Using WC-6% Ni Ball

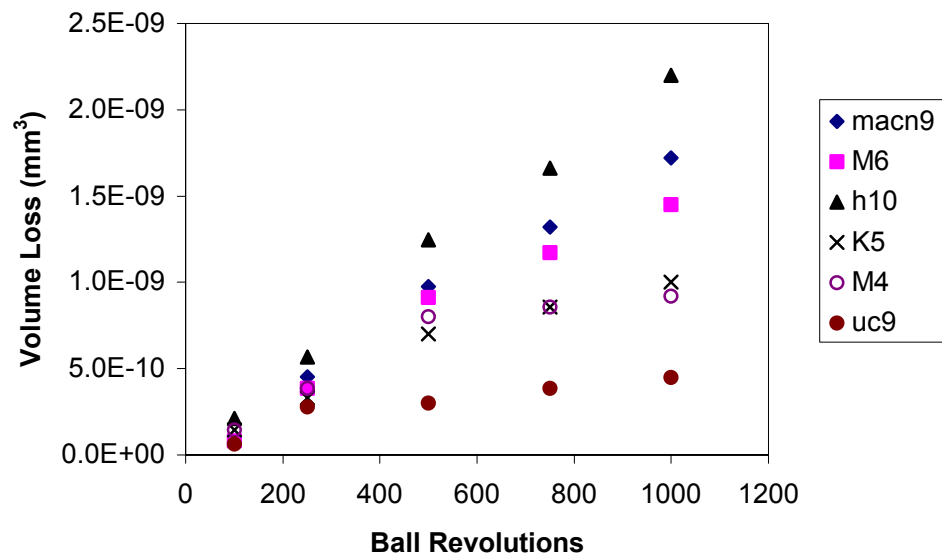


Figure 15, Plot of Volume loss vs Test Duration in pH1.1 H₂SO₄/20% SiC Slurry; 0.2 N Applied Load Using WC-6% Ni Ball.

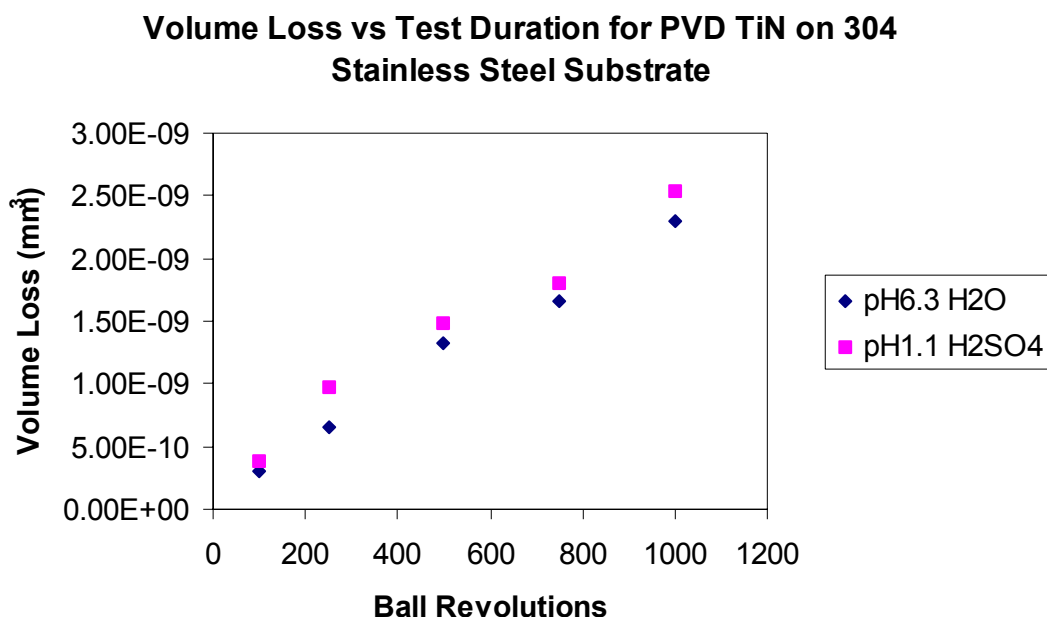


Figure 16, Plot of Volume loss vs Test Duration in pH1.1 H₂SO₄/20% SiC Slurry and pH6.3 H₂O/20% SiC Slurry; 0.2 N Applied Load Using WC-6% Ni Ball for PVD TiN coating on 304 stainless steel.

Conclusions

The ball cratering technique has proved to be an effective tool to investigate the performance and mechanisms of wear that occur in WC-based hardmetals using corrosive slurries containing microabrasdants. The preliminary results show :

- In general, volume loss increases with decreasing pH of the carrier medium
- For alkaline or approximately neutral conditions, volume loss is, for short term tests, inversely proportional to hardness
- When using acidic slurries, this relationship broke down due to accelerated wear in finer grain hardmetals by means of pluckout and undermining not occurring in the coarser grain materials; in the latter the larger grains remained *in situ*.
- Longer term tests in the most acidic medium indicated a complete reversal of the expected relationships between microstructural parameters and volume loss, suggesting the trends seen in short term tests were further accentuated.

Acknowledgements

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References

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