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Use of Microhardness as a Simple Means of Estimating Relative Wear Resistance of Carbide Thermal Spray Coatings: Part 2. Wear Resistance of Cemented Carbide Coatings

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A selection of WC-Co and Cr_3C_2-25%NiCr coatings produced by plasma spray and high velocity oxygen fuel (HVOF) deposition techniques were subjected to various wear tests designed to simulate abrasion, cavitation, sliding, and particle erosion type wear mechanisms. All of the coatings were at least 200 µm thick and were deposited onto stainless steel substrates. In Part 1 of this contribution, the microstructures of the coatings were characterized and their mechanical properties were assessed using microindentation procedures. In this second part of the article, the behavior of the coatings when subjected to the various wear tests is reported and the utility of microhardness testing as an indication of relative wear resistance is discussed. It is shown that correctly performed, appropriate microhardness measurements are a good indication of abrasion resistance and sliding wear resistance, and also correlate well with cavitation resistance in Cr_3C_2-NiCr. The measurements were less useful for predicting erosion resistance for both Cr_3C_2-NiCr and WC-Co, however, and for abrasion resistance when WC-Co was ground against SiC. Here the contribution of micromechanisms involving fracturing and brittle failure is greater than that indicated by the coating microhardness, which is essentially a measurement of resistance to plastic deformation under equilibrium conditions.

Keywords carbides, coatings, Cr_3C_2-NiCr, microhardness, WC-Co, wear

1. Introduction

Wear can be understood as being the accumulated degradation of surfaces resulting from interaction and relative motion (tribology). Several wear mechanisms have been identified,[1] but real-life examples of wear usually are the result of two or more of these idealized processes. In addition, wear processes often occur together with other stresses such as thermal cycling and chemical attack (corrosion). This often results in accelerated degradation. Because wear occurs at component surfaces, there are major advantages in applying wear-resistant materials such as coatings, rather than using them as the bulk materials from which components are manufactured. These advantages include economies of material, weight, and cost.

Real wear is both system dependent and poorly understood; therefore it is difficult to predict the relative wear resistance of different coatings manufactured by different techniques for any particular wear scenario. Yet, to optimize spray parameters, and for the selection of the most appropriate feedstocks, spraying techniques, fuel gases, gas pressures, and other spray parameters, such predictions are necessary.

Improving the wear resistance of a coating can increase the life of the coated component. Because of the inherent coating costs and the possible reduction in downtime of the machinery or plant in which many coated components act, these improvements have major financial significance.[2]

The microhardness of coatings has often been used as a first indication of their wear resistance. This article discusses the appropriateness of this practice by examining the correlation between coating microhardness and wear resistance in a variety of wear tests designed to be indicative of different wear processes.

2. Experimental

2.1 Wear Tests Used

The wear tests used in this study were chosen mostly because of their simplicity and because they used common laboratory and industrial equipment such as automated polishing machines, ultrasonic baths, and sand blasting equipment. In addition, sliding wear was measured using special equipment.

There are, of course, standard testing procedures for wear of cemented carbides, e.g., ASTM B 611,[3] but these were designed to provide information on the behavior of sintered components. Their appropriateness for testing of thermal spray coatings has not been established.

2.2 Coatings Used

Six Cr_3C_2-25%NiCr coatings, five WC-%17Co coatings, and one WC-12%Co coating were used in this work. WC-Co is the most widely used thermal spray coating for wear-resistant appli-

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Table 1 Details of Coatings Subjected to Wear Simulations

Code Number	Material	Powder Type and Manufacturing Route	Manufacturing Process	Microhardness as Performed by Sulzer Metco, VH_{300}
A	WC-12%Co	Diamalloy 2004, sintered	HVOF H_2 sprayed (DJ 2600)	1231
B	WC-17%Co	73 NS-1, spray dried, sintered	Plasma spray Ar/H_2	937
C	WC-17%Co	73 NS-1, spray dried, sintered	Plasma spray Ar/He	930
D	WC-17%Co	Diamalloy 2005, spray dried, sintered	HVOF H_2 sprayed (Diamond Jet)	959
E	WC-17%Co	Diamalloy 2005, spray dried, sintered	HVOF C_3H_8 sprayed (Diamond Jet)	884
F	WC-17%Co	Diamalloy 2005, spray dried, sintered	HVOF natural gas sprayed (Diamond Jet)	1154
G	Cr_3C_2-25%NiCr	430 NS, self-fusing nickel alloy blend	Plasma spray Ar/H2	543
H	Cr_3C_2-25%NiCr	430 NS, self-fusing nickel alloy blend	Plasma spray Ar/He	524
I	Cr_3C_2-25%NiCr	Diamalloy 3004 blend	HVOF H_2 sprayed (Diamond Jet)	680
J	Cr_3C_2-25%NiCr	Diamalloy 3004 blend	HVOF C_3H_8 sprayed (Diamond Jet)	629
K	Cr_3C_2-25%NiCr	Diamalloy 3004 blend	HVOF natural gas sprayed (Diamond Jet)	866
L	Cr_3C_2-25%NiCr	Amdry 5260, spheroidal, agglomerated, and densified	HVOF H_2 sprayed (DJ 2600)	952

cations. Cr_3C_2-25%NiCr is generally used at higher temperatures and under corrosive conditions, where WC-Co is susceptible to degradation.

The coatings were all supplied by Sulzer Metco (Wohlen, Switzerland), using powders and coating deposition equipment of their own manufacture as summarized in Table 1. Full metallographic details of these coatings are given in Part 1 of this two-part contribution.

2.3 Microhardness Testing

Knoop microhardness testing was performed on the coating surface using a 500 g force. Twenty clearly defined indentations were made in two orthogonal directions. Justification for this nonstandard procedure and full results obtained are given in Part 1 of this two-part contribution.

2.4 Evaluation of Abrasion Resistance

Coating samples were ground against both 220 grit SiC grinding papers and a 220 grit fixed diamond-grinding disk mounted on a Rotoforce 4 automatic polisher with 10 in. grinding plates, all manufactured by Struers (Cleveland, OH). This grinding/polishing machine allows up to six samples to be ground at once, each sample being individually direct-loaded to a set grinding force. The operator can set polishing speeds, the type and quantity of lubricant, the duration of polishing runs, and the direction of rotation of the sample holder with respect to that of the grinding surface. By varying these parameters, and the grinding material and its grain size, a wide-variety of abrasive wear conditions can be simulated. The weight loss resulting from the grinding procedure was measured using a model 125A digital weighing scale (Precisa, Dietikon, Switzerland), precise to 1×10^{-7} kg.

Disks of 25 mm diameter were cut out of the specimen coatings using a plasma erosion cutting technique that causes minimal damage to the coating. These sample disks were held in aluminum cups, and were ground against the SiC papers and the diamond platen, using water for cooling and lubrication. The samples were washed with alcohol, dried, and weighed. Because no mounting resins were used, the weight loss of the samples is a direct measurement of accumulated abrasive wear.

The six WC-Co coating specimens were ground simultaneously, as were the six Cr_3C_2-25%NiCr specimens. Grinding runs were generally 2 min long. Between runs, a fresh SiC paper was used, or when grinding against the diamond platen, the platen was dressed with the grinding stick supplied for that purpose. Although attempts were made to standardize the polishing procedure, in practice this is of little consequence because each set of samples experienced identical polishing treatment in each run. The applied load chosen was generally 30 N, but was also varied to 10 N.

A similar two-body abrasion test was described by Barbezat et al.[4] and was used on various oxide coatings. The advantage of the system used here is that six coatings can be tested at the same time, and under identical conditions.

The samples were weighed to determine weight loss per grinding session. The measured wear per run was at least 10 mg per sample. Between six and eight grinding sessions and material loss measurements were made per carbide set, per polishing medium. The nearest ASTM standard to this procedure is probably ASTM G132-96, Standard Test Method for Pin Abrasion Testing.

2.5 Sliding Wear Simulation

A standard hemispherical-tipped, conical, Rockwell diamond indenter loaded with 1 kg force was dragged back and forth with velocity v = 0.2 mm/s across the polished surface of the carbide coatings, using an in-house developed scratch tester, which has been described.[5] Twenty cycles were performed to produce each wear track. Three wear tracks were made for each sample.

The topography and size of the resulting wear tracks were measured using a Surtronic profilometer (Taylor Hobson, Leicester, UK), which made several passes across each wear track. Several readings were made per wear track, and average measurements were recorded to a precision of 1×10^{-7} and 1×10^{-5} m, respectively, i.e., one significant figure less than the capability of the equipment. The widths of the wear tracks were also measured using the optical microscope of a microhardness tester (magnification ×400, Matuzawa, Tokyo, Japan).

2.6 Erosion Simulation—Grit-Blasting

Samples of known geometry were sandblasted with coarse SiC grit (type N-24) using workshop sandblasting equipment, and the weight loss of samples was measured. The experiment

Table 2 Total Material Loss and Relative Rankings (Best to Worst) for Abrasive Wear of WC-Co and Cr_3C_2-NiCr Samples; Samples Are Arranged in Order of Increasing Microhardness

Specimen	Microhardness, HK_{500}	Diamond Weight Loss, g	Diamond Ranking	Silicon Carbide Weight Loss, g	Silicon Carbide Ranking
WC-Co Coatings					
E	926	0.5611	6	0.0138	1
B	949	0.5465	5	0.0217	5
C	965	0.4921	4	0.0233	6
D	1034	0.4674	3	0.0145	3
F	1113	0.4421	2	0.0190	4
A	1254	0.4057	1	0.0156	2
Cr_3C_2-25%NiCr Coatings					
G	458	0.4508	6	0.1428	6
H	497	0.3726	5	0.0936	5
I	617	0.3316	4	0.0835	4
J	652	0.202	2	0.0702	3
K	765	0.2278	3	0.0566	2
L	847	0.1018	1	0.0422	1

was designed to simulate the type of damage occurring when sand and similar materials are ingested into jet engines as airplanes take off and land in sandy regions of the world.

Two sets of ground sample coatings (25 mm diameter disks) were sandblasted for controlled time periods. One set was sandblasted with the samples held perpendicularly to the spraying direction and the second set was performed with the sandblasting at a low angle to coating surface. Before the experiment was started, the blasting grit was replaced with fresh material. The samples were grit-blasted for two minutes each.

2.7 Cavitation

Cavitation erosion is the type of wear that occurs in pipes and on ship propellers, resulting from bubble formation and implosion on the component surface.[6] The use of an ultrasonic vibrator for simulation of cavitation wear for thermal spray coatings has been reported in the literature.[7]

Disks of 25 mm diameter of each sample coating were polished, cleaned, dried, and weighed using a model 40 SM-200A digital scale (Precisa), precise to 1×10^{-8} kg. After the samples were weighed, they were placed coating side up and left in a model 2200 ultrasonic bath (Branson, Danbury, CT) filled with tap water, temperature 60 °C, for 24 h. The samples were removed, washed, rinsed with ethanol, dried, and weighed again. The weight losses were taken as being indicative of cavitation wear rates.

3. Results

3.1 Microhardness

The average microhardness values and standard deviations per coating, and comparison to average Vickers microhardness as measured on the coating cross sections, were given in Part 1. Analysis of variance (ANOVA) shows that the differences in microhardness between the different coating samples are statistically significant. In Table 2, the average microhardness values are summarized.

3.2 Abrasion

Abrasion was simulated by grinding coating sample disks against SiC and diamond counter-surfaces, as described in Section 2.4. The total weight losses for both sample sets against the two counter-media are given in Table 2. In both cases, lowering the load applied during grinding lowered the rate of material removal.

The total wear for each coating is shown as a function of microhardness in Fig. 1. For all coatings, the rate of wear when grinding against the diamond platen is much greater than when grinding against SiC. This reflects the relative hardness and aggressiveness of the abrasive.

Examination of the ground surfaces of the coatings with a low-powered optical microscope revealed that for the WC-Co samples ground against SiC, the coatings were not ground flat with 10 min of grinding. This was also true for the Cr_3C_2-25%NiCr coating sample L. This shows the importance of high hardness in resisting wear. If the counter-surface is of lower hardness than the protected surface, one can expect that the abrasive wear of the protected surface will be negligible.

The Cr_3C_2-NiCr samples ranked almost identically in terms of their Knoop surface microhardness values and their abrasion resistance, as defined in terms of loss of material during grinding against both SiC papers (220 grit) and fixed diamonds platen.

In general, plasma sprayed samples exhibited higher wear rates than the high velocity oxygen fuel (HVOF) equivalents. With the WC-Co samples, very little wear occurred when ground against SiC, but significant wear resulted from grinding against the diamond counter-body. The ranking in terms of material loss is very different with the two counter-body materials. When WC-Co is abraded against diamond, the ranking of abrasion resistance is identical to the indentation hardness ranking. However, when WC-Co is abraded by SiC, not only is very little material removed, but the ranking (relative wear resistance) is also very different from the microhardness ranking (Table 2 and Fig. 1).

If one examines the HVOF sprayed WC-17% Co samples separately from the plasma sprayed equivalents, one sees that the order of the HVOF samples is reversed as the grinding medium is changed. This inversion also occurs for the two plasma sprayed samples (Fig. 2 and 3). These results indicate that the dominant wear mechanism is different for the two grinding media. Apparently, when abrading against diamond, a harder medium, the difference in hardness between coating and abrasive is

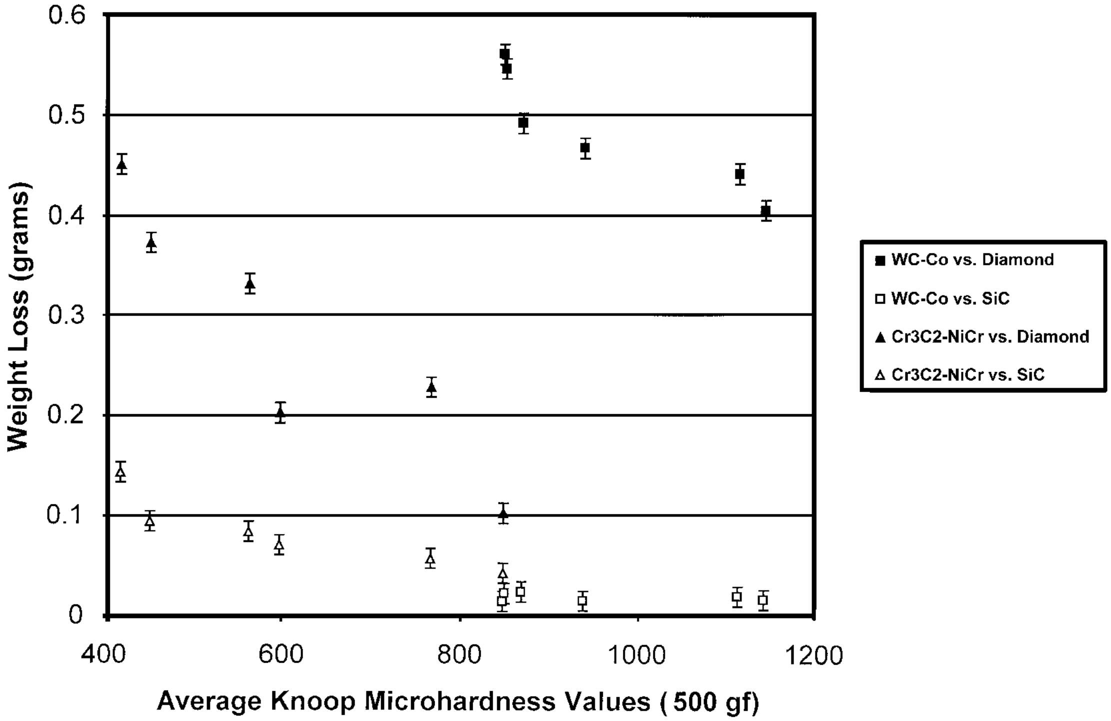

Fig. 1 Comparison of accumulated abrasive wear with Knoop microhardness for coatings

the main factor determining the rate of wear. When grinding against softer SiC however, the hardness of the coating is not the main criterion that determines the wear rate of the coatings, although the HVOF deposited coatings still out-performed those deposited by the plasma spray process.

The ground surfaces of the various coatings were examined by scanning electron microscopy (SEM). Clear differences were apparent in the scratches produced by the two abrasion media for the various coatings. In general, the plasma sprayed coatings featured a coarser microstructure, and both diamond and SiC caused deep, uneven scratches, indicative of material having been gouged out in chunks, with clear indication of brittle failure. The width of the scratches tended to be greater for the Cr_3C_2-25%NiCr coatings than for the WC-17%Co.

When the HVOF coatings were examined, differences could be seen between the types of damage produced by the two abrasive media. Reproduced in Fig. 4(a-d) are SEM microphotographs of samples D and J abraded with SiC and diamond. Figure 4(a) shows the resulting damage when sample D, which is WC-17%Co sprayed with HVOF, is abraded against SiC. The scratches are uneven, showing that particles were gouged out by the abrasive, with brittle damage being clearly evident. In Fig. 4(b) the same coating abraded with diamond is shown. Here the scratches are more numerous and more material is removed, but the scratches themselves are much smoother. The damage in this case is more ductile, or plastic in nature. In Fig. 4(c) and (d), SEM microphotographs of sample J (Cr_3C_2-25%NiCr sprayed with HVOF) abraded with SiC and diamond are shown. With both media the scratches are quite smooth. It appears that in both cases, because the Cr_3C_2-25%NiCr coating is abraded by a harder material, the resulting wear mechanism is ductile in nature.

Holmberg and Matthews point out[8] that for plowing of a coating to occur, the abrading medium must be harder than the coating. By applying a WC-Co coating to a component, even such hard abrasives as SiC particles cannot plow the component surface. Indeed, SiC is not recommended for grinding hard materials (microhardness value [HV] > 800) when preparing metallurgical samples, and when used, the rate of wear is minimal. However, WC-Co coatings do suffer some wear and need replacing from time to time, even when they are not exposed to damage from harder materials. When plowing is eliminated, hard phase pullout and microfracture are the dominant wear mechanisms.

Accurate microhardness measurements indicate susceptibility to plastic deformation. This is the dominant wear mechanism when coating is abraded by a harder counter-body. Once a coating is harder than the counter-body, this mechanism is eliminated and other wear mechanisms dominate. Providing the coating material is hard enough, microhardness is not the best indicator of wear resistance and will not provide the best indication of relative coating life. It could well be that the wear resistance ranking shown against a material such as SiC is much more useful in predicting relative wear resistance of hard coatings in industrial use.

3.3 Sliding Wear

In Table 3, the dimensions of the wear track typical cross sections are summarized. The coefficients of friction measured during sliding operation and Knoop microhardness values are also listed. Coatings A and L were not measured in this experiment.

The tabulated measurements refer to dimensions indicated in

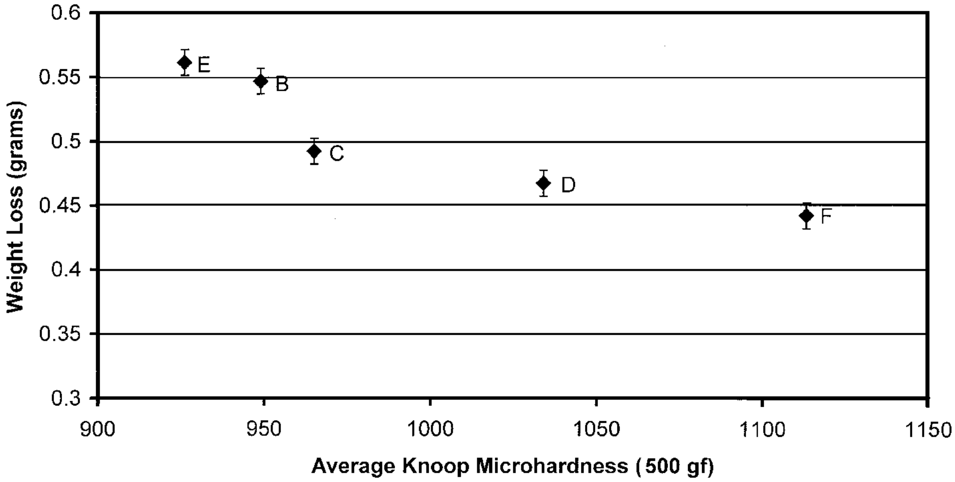

Fig. 2 Comparison of accumulated abrasive wear with microhardness where WC-17%Co is ground against diamond counter-surface. Each coating is identified.

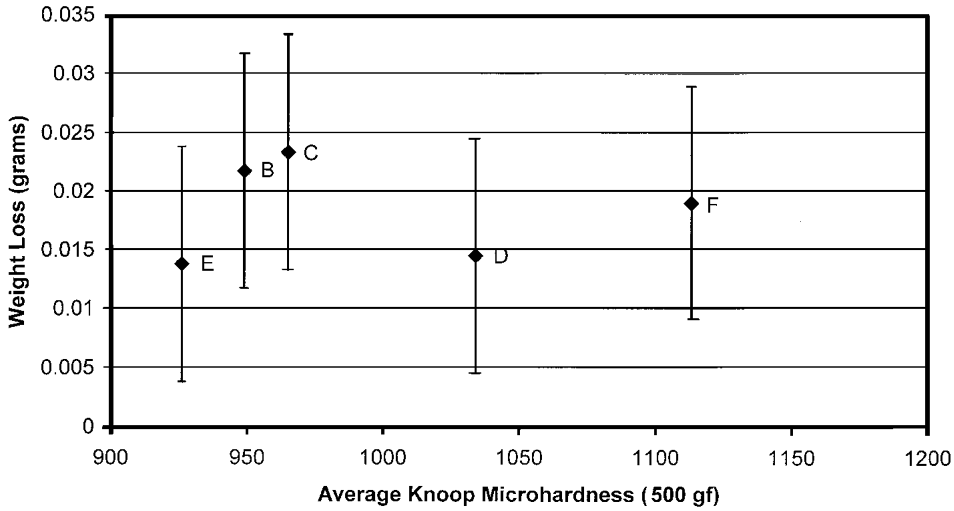

Fig. 3 Comparison of accumulated abrasive wear with microhardness where WC-17%Co is ground against silicon carbide counter-surface. Each coating is identified.

Fig. 5, a schematic of the cross section through wear track. The depth of wear track plotted against microhardness is shown in Fig. 6. Good correlation is shown.

The L_2 dimension is taken as being the best indication of the relative extent of sliding wear. The profilometer is more precise in the vertical dimension, and there is a degree of subjectivity regarding optical measurements of scar widths. The ranking of the L_2 dimension, Table 5, summarizes the relative wear-resistance of the coatings in the various wear tests performed.

The WC-Co coatings out-performed those made from Cr_3C_2-25%NiCr, and there is a good correlation between microhardness and degree of wear as measured by the depth of wear tracks produced. Coating E performed somewhat better than would be expected from its low microhardness, however. SEM examination of the wear tracks revealed that dominant wear processes occurring varied between the different coatings. Further inspection of the wear tracks produced on plasma sprayed WC-Co showed that for coating B, the dominant deformation mechanism was plastic deformation. In coating C there was evidence of failure of the matrix-carbide interface, leading to loss of carbide particles. The wear tracks made on WC-Co coatings produced by HVOF also featured different wear mechanisms. Within the wear track on coating E, broken carbide particles are in evidence, but there is no indication of plastic deformation. In coating F, however, there is significant crack propagation tangential to the wear track, with cracks appearing to propagate primarily along the matrix-carbide interface. In the wear tracks produced for coating D, splats that feature less retention of hard phase, presumably indicating overheating and greater dissolution of hard phase during spraying, exhibit greater plastic deformation, whereas areas featuring more retention of hard carbide particles contain more fractured particles and less plastic deformation. An SEM microphotograph of part of the wear track produced on coating D is shown in Fig. 7. Here damage result-

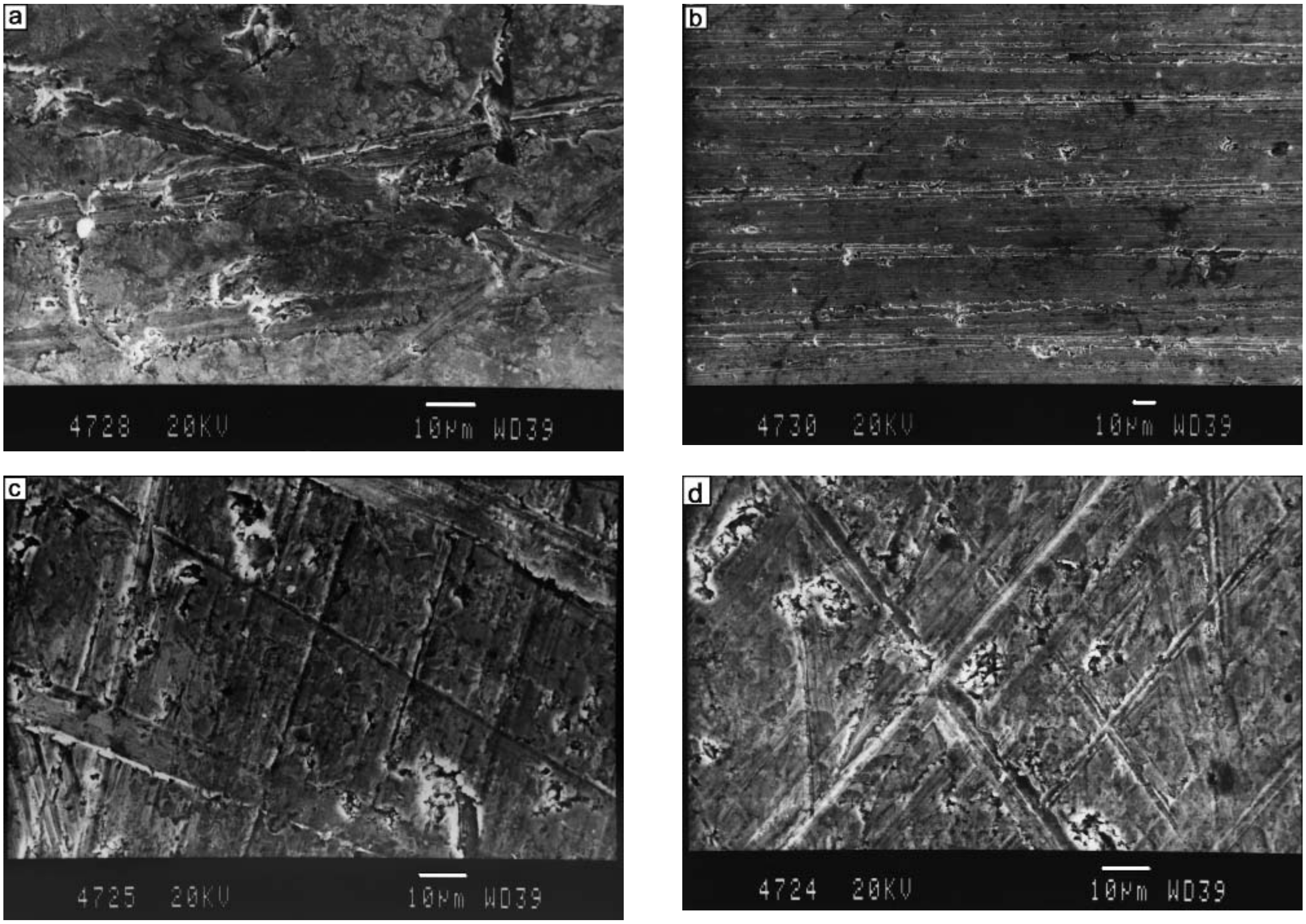

Fig. 4 **(a)** SEM microphotograph of resultant surface damage from abrading sample D (WC-17%Co coating sprayed with HVOF using H_2 fuel) with 220 grit SiC. **(b)** SEM microphotograph of resultant surface damage from abrading sample D (WC-17%Co coating sprayed with HVOF using H_2 fuel) with 220 grit diamond. **(c)** SEM microphotograph of resultant surface damage from abrading sample J (Cr_3C_2-25%NiCr coating sprayed with HVOF using C_3H_8 fuel) with 220 grit SiC. **(d)** SEM microphotograph of resultant surface damage from abrading sample J (Cr_3C_2-25%NiCr coating sprayed with HVOF using C_3H_8 fuel) with 220 grit diamond

Table 3 Dimensions of Wear Tracks (Fig. 5); Coatings Are Arranged in Order of Increasing Microhardness for Each Material Type in Turn

Specimen	Coefficient of Friction	Knoop	Width, mm (a)	*H*, mm	*h*, mm	*b*, mm	L_1, µm	L_2, µm
WC-17%Co Coatings								
E	0.1	926	0.09	0.08	0.06	0.32	0.4	0.5
B	0.13	949	0.07	0.09	0.06	0.28	0.4	0.7
C	0.11	965	0.07	0.07	0.06	0.22	0.2	0.6
D	0.1	1034	0.06	0.09	0.06	0.17	0.2	0.4
F	0.09	1113	0.07	0.05	0.05	0.17	0.1	0.3
Cr_3C_2-25%NiCr Coatings								
G	0.18	458	0.12	0.11	0.09	0.38	0.8	1.5
H	0.17	497	0.11	0.11	0.09	0.41	1.1	1.25
I	0.23	617	0.11	0.11	0.06	0.20	0.6	0.7
J	0.18	652	0.11	0.10	0.07	0.25	0.5	0.8
K	0.11	765	0.09	0.09	0.06	0.18	0.2	0.5

(a) Measurement of wear track by optical microscopy.

ing from both plastic and brittle wear mechanisms is in evidence.

Examination of the wear tracks on the Cr_3C_2-25%NiCr coatings revealed that in all cases, plastic deformation was the main wear mechanism. In the plasma sprayed coatings there was evidence of material having been gouged out by the plowing dia-

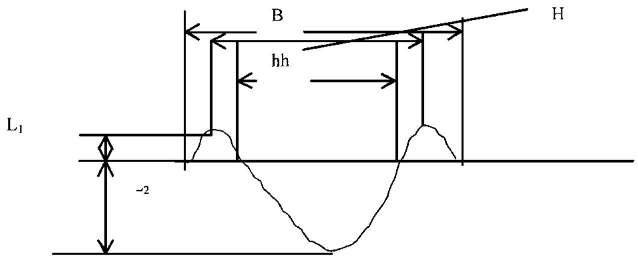

Fig. 5 Annotated cross section through wear track

mond. Coating K suffered the least wear damage exhibited by any of the Cr_3C_2-25%NiCr coatings; the wear track resembling those formed on the WC-17%Co coatings.

3.4 Erosion

The six coatings of each material type were arranged in a group and sandblasted simultaneously. There was some indication that the sandblasting equipment suffered random partial blockages. This presumably resulted in variation of both the throughput of grit particles and their acceleration. Thus, there is lack of repeatability in the experiment. The material losses suffered at both high and low particle-impingement angles are shown for the two types of coatings in Table 4; their relative rankings are listed.

The absolute values for the two orientations cannot be compared because precise control was lacking. However, the weight losses seem to indicate that under these conditions, hardness is not the only criterion determining rate of wear, and it is a poor indicator of relative wear.

The coatings were examined by SEM. In Fig. 8, SEM microphotographs of the grit-blasted surface of coating J (Cr_3C_2-25%NiCr sprayed with HVOF) are shown at both low and high magnifications. The sample surface appears rough and cratered. The damage is indicative of brittle failure mechanisms.

3.5 Cavitation

The weight losses suffered for each sample after 24 h submersion in tap water in an ultrasonic bath are shown in Fig. 9. From examination of the samples, it is evident that some of the material loss is from the uncoated side of the specimen, and from its edge. Thus, total sample weight loss is not a good indication of coating performance with samples of this type. It is clear, however, that Cr_3C_2-25%NiCr outperforms the WC-Co samples, and it would appear that the WC-12%Co sample performs better than the WC-17%Co samples.

Visual inspection of the samples after the cavitation simulation showed discoloration of the WC-Co samples. This indicated that corrosion mechanisms play an important role in the overall damage. Possibly there is enhanced corrosion resulting from the cavitation mechanisms causing pit corrosion or similar behavior. That Cr_3C_2-25%NiCr coatings proved more corrosion resistant than WC-Co is not surprising. They are often substituted for WC-Co in applications where Co tends to oxidize.

A close examination of the polished surfaces of the Cr_3C_2-25%NiCr coatings reveals that the two plasma sprayed samples (G and H) appear spotted because of pits being formed on the surface. There are traces of similar damage on sample K. All of the above coatings (G, H, and K) and sample I appear dulled, whereas samples J and L retained shiny appearances. If coatings are ranked in order of cavitation damage as determined from visual inspection, the sample order is L, J, K, I, H, and G., which correlates reasonably well with the microhardness ranking for the coatings.

The coatings were examined under SEM. Similar types of wear were seen in all coatings, with the surfaces exhibiting crater-like damage. The wear mechanism is evidently the removal of flake-like particles, with the size of the flakes and the density of craters per unit area varying from coating to coating. In Fig. 10(a,b), respectively, SEM microphotographs of the resulting damage to coatings D (WC-17%Co deposited by HVOF) and G (Cr_3C_2-25%NiCr deposited by plasma spray) are shown. In both images, the wear loss mechanism is clearly that of the delamination of flakes of material. It would appear that the dominant mechanism for the surface degradation of these layered coating structures when subjected to cavitation-type wear, is by brittle failure of the bonding layer between splats.

4. Discussion

4.1 Comparing Microhardness With Wear Rates

In Table 5, the Knoop microhardness rankings versus the various wear tests for the WC-Co and Cr3C2-NiCr samples are summarized.

For the Cr_3C_2-NiCr samples, there is good correlation between the microhardness ranking and their ranking for abrasive wear resistance against both SiC and diamond grinding papers. Similar good agreement is shown against the cavitation wear ranking as simulated using the ultrasonic bath, and against the scratch test ranking. With grit blasting, which simulates dry particle erosion, the results are very different.

For WC-Co, the correlation between microhardness ranking is very good for abrasion resistance against diamond and sliding wear. It is not good for dry particle erosion, abrasion against SiC, or cavitation wear.

Provot et al.[9] found very low wear rates when measuring abrasive wear of WC-Co coatings against softer counter-bodies using a CSM (Olten, Switzerland) pin-on-disk apparatus. They report that they experienced difficulties in making "significant comparisons" between the WC-Co coatings produced by different technologies. In this research, because abrasive particles were used rather than a spherical counter-body, and the samples were worn and weighed several times, there is confidence that the ranking obtained has significance. When using a harder (WC-Co) counter-body, Provot et al. found that HVOF coatings outperformed those deposited by APS.

In a two-body abrasion test against SiO_2 (220 mesh), Clarke et al.[10] report a clear correlation between abrasive wear resistance and microhardness for WC-12%Co deposited by air plasma spraying (APS). Examined HVOF coatings of similar hardness values to the APS coatings exhibited significantly better wear resistance. Clearly, when abrading WC-Co against a softer particulate abrasive, microhardness is not the only consideration determining wear resistance.

Wang[11] showed that for a variety of coating materials, in-

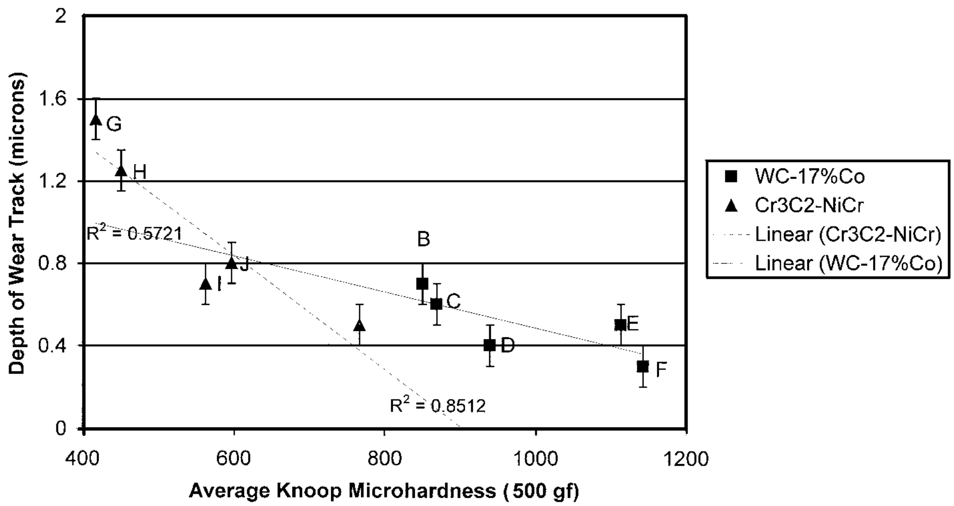

Fig. 6 Comparison of depths of wear tracks with Knoop microhardness for coatings

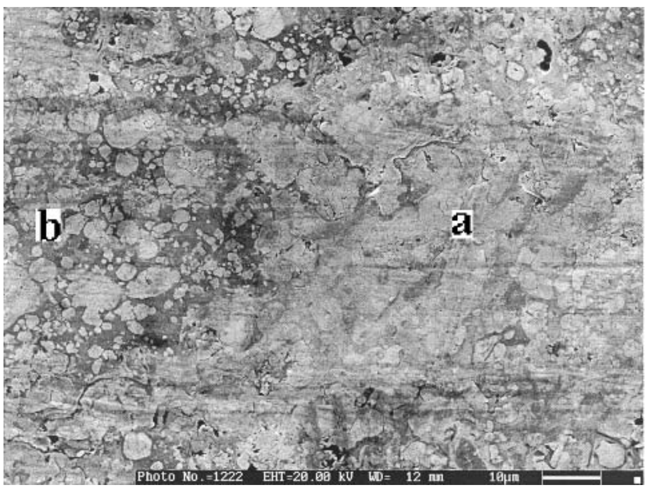

Fig. 7 SEM microphotograph of part of the wear track produced on coating D (WC-17%Co sprayed with HVOF using H_2 fuel). Notice **(a)** region of plastic deformation, and **(b)** region showing brittle damage and cracked carbides.

cluding WC-Co and Cr_3C_2-NiCr, detonation gun (D-gun) coatings outperformed APS coatings of the same material, both in terms of microhardness and wear resistance. When all samples of the different coating material types are compared with each other, however, the good correlation between microhardness and wear resistance is lost. This implies that the wear processes occurring in a given abrasive system are to some extent material dependent and do not only reflect microhardness.

The present research indicates that microhardness does not correlate well with dry particle erosion wear. What is true for particle impingement is probably true for all types of impact wear. Nerz et al.[12] found poor correlation between microhardness and solid particle erosion for the various Cr_3C_2 coatings they examined. Likewise, Shui et al.[13] found that there was no direct correlation between hardness and wear rates for the coatings that they examined using tests designed to simulate erosion by coal particle impingement in energy producing systems. They also showed different degradation mechanisms occurring and dominating as the conditions were changed. The ranking for low angle and high angle impacts were very different. This indicates that different mechanisms occur with different impact angles.

Martinella et al.[14] measured the erosion resistance of Cr_3C_2 and NiCrAlY thermal spray coatings by SiO_2 particle bombardment. They found good resistance to normal impacts for coatings that performed poorly under glancing angle (25°) impact, yet coatings that performed well under glancing impacts performed badly under normal impact. Similarly, Wood et al.,[15] when examining the sand erosion performance of D-gun applied carbide coatings, also found that there was a different ranking at different impingement angles. They proposed that at high angles, the dominant mechanism of degradation for their coatings was one of crack formation with material loss occurring as cracks interlink, thereby isolating and separating particles of material. At low angles, microcutting and plowing were the dominant wear mechanisms.

Also of interest are the results obtained by Su and Lin.[16] These workers examined the wear resistance of carbide-coated steels in dry sliding wear against steel, and found that Cr_3C_2-NiCr outperformed WC-Co. They discovered that a thin layer of steel was smeared onto the Cr_3C_2-NiCr and acted as a lubricant.

The rankings shown for the different wear simulations are indicative that different micromechanisms of wear dominate in the various simulations. Where sliding wear occurs against a harder counter-body, microcutting or plowing appears to be the dominant mechanism, and microhardness is a good indication of the resistance of the material to this kind of degradation. In other wear systems, surface fatigue or adhesive wear may dominate. It is the domination of alternative wear mechanisms that is the likely cause of the different rankings seen when sand-blasting, as the blasting angle changes, or when abrading WC-Co against the softer SiC.

Li et al.[17] found that impact wear increased in the order HVOF, APS Ar/He, and APS Ar/H_2 for Cr_3C_2-25%NiCr coatings. They explained this as being largely due to structural defects, decreasing density, and increasing porosity of the coatings. With the exception of coating I, which displayed a very brittle nature, the Cr_3C_2-25%NiCr samples examined here suffered degradation in the same order, at least with regard to high angle erosion. This correlation confirms that the experimental results of Li et al. reflect other impact wear systems. It is also true that porosity both facilitates cracking and lowers microhardness. It would appear that microhardness is some indication of impact and particle erosion resistance, but it is not the only indication. For wear of these types, brittleness plays a greater role than it does for abrasion resistance and sliding wear. Wang and Luer[18] showed that the erosive impact resistance of Cr_3C_2-25%NiCr varies significantly with temperature and angle. This also confirms that different mechanisms dominate the extent of wear under different conditions.

4.2 Wear Mechanisms

In general, wear is the accumulated loss of material and dimensional changes of a component over the course of time, resulting from mechanical degradation of the surface. It depends on the type and magnitude of the mechanical stresses applied, the time over which those stresses act, and the resistance of the surface to those stresses. This resistance depends on the structural integrity and the basic material properties of the surface. These properties are usually considered to be (1) resistance to plastic deformation, of which indentation hardness (*H*) is essentially a measure; (2) resistance to elastic deformation or stiffness, which is usually referred to as the Young's modulus (*E*); and (3) susceptibility to crack propagation or brittleness (*K* or equivalent). These properties are in turn determined by the phases present, their relative proportions, intergrain adhesion, porosity, and the grain size, shape, and distribution.

The response of the coating surface to microindentation is also determined by these qualities. When indenting thermal spray coatings in which pores are found within the volume of material that is stressed, the material under the indenter experiences compaction, facilitated by material flow due to giving of the weakest link. This may be plastic deformation of the metal matrix as occurs in hardness testing of regular metallic materi-

Table 4 Particle Erosion of WC-Co and Cr_3C_2-NiCr Coating Samples; Coatings Are Tabulated in Order of Increasing Microhardness for Each Coating Type

Specimen	Knoop Microhardness, HK_{500}	Sandblast, Perpendicular Weight Loss, g	Ranking	Sandblast, Low Angle Weight Loss, g	Ranking
WC-Co Coatings					
E	926	0.0208	1	0.0084	2
B	949	0.0522	5	0.0117	4
C	965	0.0516	4	0.0123	5
D	1034	0.0461	3	0.0155	6
F	1113	0.0589	6	0.0099	3
A	1254	0.0432	2	0.0046	1
Cr_3C_2-NiCr coating					
G	458	0.0602	4	0.0044	4
H	497	0.0685	5	0.0043	3
I	617	0.114	6	0.005	6
J	652	0.0231	1	0.0033	2
K	765	0.0503	2	0.0047	5
L	847	0.0558	3	0.0016	1

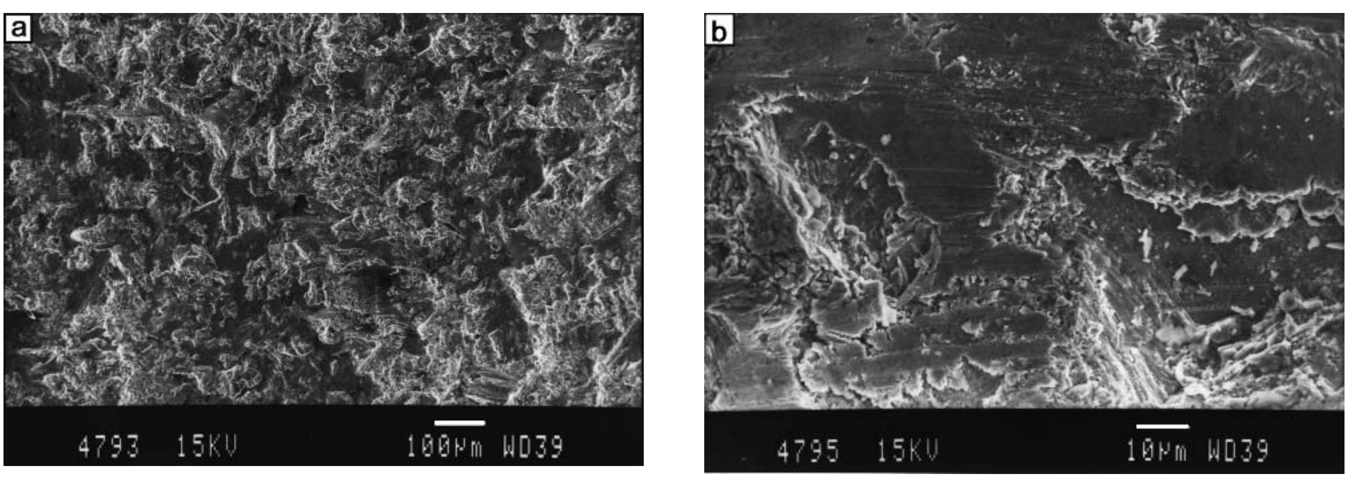

Fig. 8 SEM microphotograph of coating J (Cr_3C_2-25%NiCr coating sprayed with HVOF using C_3H_8 fuel) after grit blasting. **(a)** Low magnification, showing that the sample surface is very rough and cratered. **(b)** High magnification, showing that the damage is of a brittle nature.

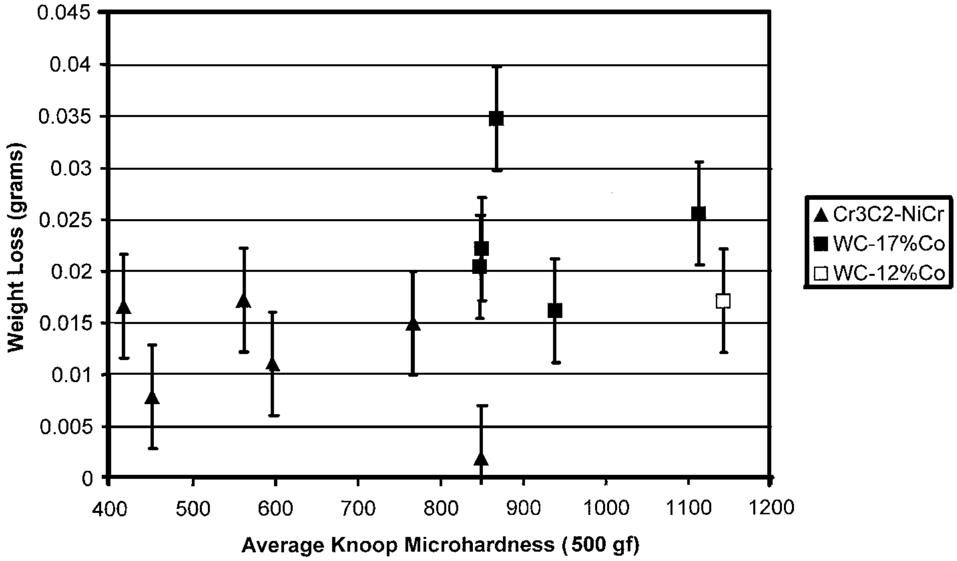

Fig. 9 Comparison of accumulated cavitation wear with Knoop microhardness for the coatings

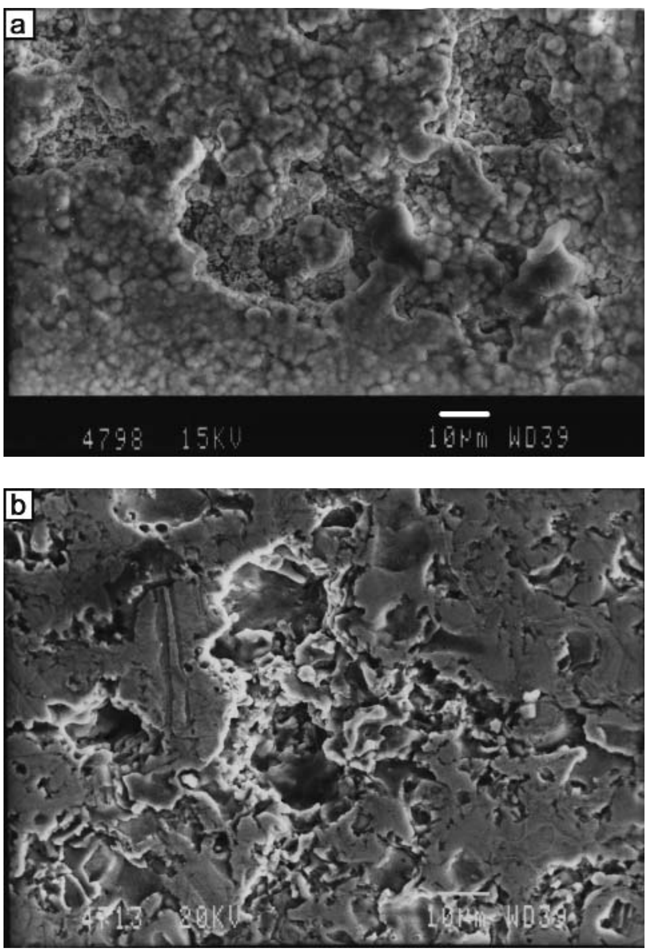

Fig. 10 Cavitation damage to **(a)** surface of coating D (WC-17%Co sprayed with HVOF using H_2 fuel), and **(b)** surface of coating G (Cr_3C_2-25%NiCr sprayed with APS using Ar/H_2). In both cases, brittle failure mechanisms are in evidence, with material having flaked away.

als, but is likely to be failure of the matrix reinforcement adhesion, and may involve cracking of the hard phase particles. Apart from compaction, for every indentation performed, different mechanisms act to enable material flow and to accommodate the indenter probe. The particular mechanisms locally available in the stress field of the indentation, their activation energies, and the extent to which they can act will determine the size of the indentation formed. Perhaps the best way to conceptualize the hardness indentation of a material is that proposed by Gilman, i.e., "considered as a strength microprobe."[19] The favorable surface deformation mechanisms for accommodating the indenter penetration will often be the most favorable deformation mechanisms when a surface is subjected to various forms of wear attack. One can expect, therefore, that measured microhardness (inverse of indentation size) will indicate wear resistance to some extent.

All static indentation testing (such as the microhardness test) is designed to provide conditions compatible with plastic flow that eliminate sudden impacts, minimizing cracking phenomena. Thus, where subjected to a type of wear wherein the dominant mechanism involves damage due to cracking, a brittle microstructure will show more susceptibility to wear than would be indicated merely by examination of the measured microhardness values.

Unfortunately, the common practice when performing Vickers microhardness testing is to discount all (or badly) cracked indentations, and only measure sharp (or reasonable) indents. By discounting results of microindentation probing indicative of severe brittleness, the microhardness values generated are selective of the areas more susceptible to plastic deformation, and as such, the microhardness values generated will be too high. This practice thus makes microhardness statistics even less indicative of wear resistance behavior. Sometimes, these cracked indents may be unmeasurable, and the experimenter has no choice but to discount the test. However, the resulting "average microhardness" with or without a measure of spread such as standard deviation or range is not a true average response of the material.

Table 5 Summary of Various Wear-Resistance Rankings for WC-17%Co and Cr_3C_2-25%NiCr Coating Samples

Rank	Microhardness Knoop 500 g	Abrasion Wear: Against 220 SiC Papers	Abrasion Wear: Against 220 Grit Diamond Platen	Sliding Wear (a), Depth of Wear Track	Sandblasting: Perpendicular	Sandblasting: Low Angle	Cavitation
WC-Co Coatings							
1	A	E	A	…	E	A	D (b)
2	F	A	F	F	A	E	A (b)
3	D	D	D	D	D	F	E (b)
4	C	F and B	C	E	C	B	B (c)
5	B	…	B	C	B	C	F (c)
6	E	C	E	B	F	D	C (c)
Cr_3C_2-NiCr Coatings							
1	L	L	L	…	J	L	L
2	K	K	J	K	K	J	J
3	J	J	K	I	L	G and H	K
4	I	I	I	J	G	…	I
5	H	H	H	H	H	K	H
6	G	G	G	G	I	I	G

(a) Coatings A and L were not tested.
(b) Significant corrosion apparent.
(c) Slight corrosion apparent.

The utility of microhardness statistics as indicators of wear resistance for any particular wear process will depend on how similarly the relative contributions of the various surface deformation mechanisms contribute to the two processes. If microhardness indentation is a good analogy for wear process in terms of the relative contributions of the deformation mechanisms, there will be a good correlation and the microhardness values generated will be good indication of wear. If this is not the case, the correlation will not be as good.

In general, wear effects due to relative movement between two surfaces in constant contact (such as sliding wear, abrasion, and fretting) are dominated by plastic deformation mechanisms and microhardness is a fair indication of material performance. This is particularly true where the counter-body is harder (i.e., more resistant to plastic deformation). Where the wear occurring is the result of multiple impacts, the susceptibility of the material to crack initiation and propagation is more significant. Thus, for evaluating the wear resistance of components subjected to particle erosion (such as piston heads and rock-hammer facing materials), microhardness is less valuable an indication of relative wear resistance. If note is also taken of the susceptibility to cracking during microhardness testing by either measuring or merely noting the occurrence of cracks, greater utility can be made of the technique.

4.3 Expressing Wear as a Function of $H^{1/2}K^{2/3}$

For bulk ceramic material, Evans[20] proposed that abrasive wear resistance depends on $H^{1/2}K^{2/3}$, where H is hardness and K is the fracture toughness of the ceramic. WC-Co is the coating material of choice for combating severe wear stresses. So-called semiempirical equations have been derived that relate generalized wear resistance to the fundamental mechanical properties for sintered carbides. An example of this type of equation is

$$W = \alpha\,(K_{1c}^{3/8}H^{1/2})\left(\frac{V_f^{Co}}{1 - V_f^{Co}}\right) \qquad \text{(Eq 1)}$$

where W is erosive or abrasive wear, K_{1c} is indentation fracture toughness, and V_f^{Co} is the volume fraction of cobalt in the composite. H and K parameters for bulk WC-Co samples of various grain sizes, manufacturing routes, and matrix extents were determined by Schubert et al.[21] This equation has been applied by some researchers to model the wear resistance of cemented carbide thermal spray coatings.[22] Despite their conclusions to the contrary, the evidence shown in the graphs they provide do not show a good correlation.

Although it may be possible to accurately determine quantitative statistics that reflect coating bulk properties such as H and K_{1c} using some of the various techniques that have been proposed, it would be unlikely that these values would model the local degradation damage occurring on the coating surface at the scale of the microstructure during any particular wear process. The fact that simple changes such as the type and hardness of the counter-body material in an abrasion test affect the relative wear of different coatings indicates that the approach has poor predictive utility.

As described in Part 1 of this two-part contribution, it proved impossible to produce Palmquist cracks on the polished surface under 30 kg force load in accordance with the relevant standard.[23] The load is too high, with the crack patterns produced varying widely because the cracks reach to, and are deflected by, the tougher substrate. Clearly, this was of no value in predicting either coating bulk brittleness or the likelihood of brittle fracture mechanisms at the coating surface when subjected to tribological attack.

Derivations of fracture toughness values (K_{1c}) from indentation crack lengths are based[24] on the classic derivation by Griffith.[25,26] The model can be applied to cracks formed when indenting relatively homogeneous and isotropic materials such as glass and sintered ceramics. As summarized by Quinn,[27] even for bulk ceramic materials the K_{1c} values calculated from Palmist crack measurements are only accurate to within 30-40%. This is a consequence of K_{1c} being proportional to (crack length c)$^{3/2}$, so a small variation in c (or its measurement) is expanded greatly. Furthermore, it may also be noted that there are many alternative equations to calculate K_{1c} values from indentation crack lengths.

Apart from these general difficulties, there are additional experimental problems in determining indentation fracture toughness for thermal spray coatings. As described in Part 1 and mentioned above, when indenting in the direction of wear attack, i.e., the surface of the coating, the cracks resulting from Vickers indentation do not resemble classic Palmquist cracks. This is because the relative thinness of the coating allows the stress field to reach the coating-substrate interface. Cracks propagate along this interface and rebound from it. The resultant crack patterns seen on the coating surface are so different from those formed by indenting into a continuum of isotropic material, that all of the theory behind deriving K_{1c} from crack lengths is inappropriate.

Conversely, De Palo et al.[28] performed this procedure on the polished cross section. Here the resultant cracks are very much longer in the direction parallel to the interface than perpendicular to it. The reasons for such fracture behavior are clear. Perpendicular to the interface, the thin coating is constrained by metallic substrate on one side, and by mounting resin on the other. The cracks do not propagate in a continuum of material and the model is again inappropriate. These workers ignored the perpendicular cracks and derived K_{1c} from the crack lengths along the interface. We believe that to use results generated as a true indication of coating brittleness and to then attempt to correlate the statistic derived to surface wear degradation is unrealistic. Thermal spray coatings have a layered structure. What is measured here is clearly the susceptibility of crack propagation along the intersplat interfaces, parallel to the substrate. In a similar manner to the relative ease with which wood can be split along the grain, cracks will preferentially propagate along the direction of least resistance, usually intersplat boundaries. Unless the dominant wear mechanism is failure of the coating due to splat delamination and flaking of the coating, any correlation between wear and K_{1c} will be coincidental.

Working with 1 kg loads and a Vickers indenter on the polished surface, we attempted to determine the crack resistance using a variation of the modified crack length determination. No attempt was made to differentiate between radial and median cracks, nor were multiple indentations performed until acceptable cracking patterns were produced. Rather, the extent of cracking in tangential directions parallel to the two indentation diagonals was measured. The results obtained are discussed in Part 1 of this two-part contribution.

It is clear that the extent of cracking is indicative of the volume damaged by the indentation, reflecting the brittleness of surface regions. However, the effects of (1) the various uncertainties in measuring crack lengths, (2) the dubious relevance of the statistic, (3) the probable influence of polishing technique, (4) selectivity in choosing areas away from surface pores, and (5) their effect on crack blunting, combine to make this technique very unsatisfactory.

The existence or otherwise of severe cracking for Knoop indentation was also examined as an indication of susceptibility to cracking. Crack lengths were not measured and so the technique is certainly highly load dependent. Nevertheless, it was believed that for ranking purposes only, as an indication of brittleness, the technique has some utility. These two brittleness rankings are tabulated in Part 1. Both rankings indicate that coating I was very brittle. Dry particle erosion as simulated by sandblasting is a good example of the type of wear for which knowledge of brittleness is valuable in making a choice of wear combating material. Indeed coating I performed the worst in both high and low angle particle-erosion tests. In fact, if the rankings for both high and low angle impingement is considered together, the brittleness index calculated is a reasonable indication of impact wear susceptibility.

It is appreciated that each wear process may be modeled by a semiempirical equation generated by linear regression of average H, E, and K values. However, the relative susceptibility of the coatings to wear will change with minor changes in the wear process because different underlying mechanisms contribute to the total wear to different relative extents, and thus the wear-resistance ranking will vary. Such equations include wear process, coating type, and condition-specific parameters, and in general, the effort involved in their derivation far surpasses their usefulness, and is not justified for thermal spray coatings.

Under different wear conditions, the relative importance of the various materials parameters in combating wear varies. Thus, some workers[22] have been a little ambitious in their attempts to find a general equation for wear that links fundamental material properties with general erosive and abrasive wear rates. This is particularly true because the two processes generally depend on H (measure of plasticity) and K (measure of brittleness) to very different extents.

As discussed by Horszt,[29] application of the scientific analytical approach to wear systems is often inappropriate, and a systems approach is often more suitable. Indeed, Habig[30] showed that even for simpler systems such as steels, by changing the dominant wear mechanism the ranking of three steels changes, with each of four predominant wear mechanisms producing a different ranking. The hardness of the steels is a material property and is not wear mechanism dependent. This clearly indicates that hardness (or resistance to plastic deformation) is not the only contributing factor in determining wear.

5.4 Alternative Approaches for Determining Wear Resistance

Note that the wear tests indicated here are all less labor intensive than microhardness determination, particularly when multiple testing is required. The use of several wear tests in combination enables various coatings to be ranked in terms of their average apparent wear resistance, and may be more meaningful than measuring and using microhardness as an indication of quality.

Certainly, for coating selection and optimization for a particular application, it is required to characterize the types of wear stresses and likely failure mechanisms involved. Ideally, a special rig should be devised to simulate the wear conditions appropriate to the application. This is not trivial. A discussion of the approach used by tribology laboratories was given by Wüthrich.[31]

6. Conclusions

When thermal spray coatings are microindented, plastic deformation is the prime materials response that allows penetration of the indenter. Unlike the hardness determination for bulk met-

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als, the microhardness response of thermal spray coatings is also influenced by and is thus in part a measure of porosity and brittleness.

To the extent that the dominant deformation mechanisms occurring during microindentation of thermal spray coatings are the dominant mechanisms occurring during a particular wear process, microhardness will be a good indication of wear resistance. This is generally the case when the coatings are subjected to abrasion or sliding wear against harder materials. The dominant wear processes that occur on a hard coating when in contact with a softer counter-body are not plastic deformation, and microhardness is thus not a good indication of wear resistance ranking. Similarly, for impact and cavitation wear processes, the correlation between microhardness and wear rate is poor. This is due to the relative significance of strain rate effects and brittle microfailure mechanisms.

For wear mechanisms that are more closely linked to local brittle failure of the coating surface than is indicated by microhardness statistics, an indentation brittleness ranking can be used to identify coatings likely to perform badly. The simpler the technique, the greater its utility; thus, a simple counting up of indentation failures is preferable to measuring crack lengths as a means of identifying coatings susceptible to brittle forms of damage.

In general, microhardness is a good first indication of likely wear resistance when no other information is available. If microhardness data are supplemented by an indication of brittleness, a more informed decision could be made. There is no simple correlation between hardness and general wear resistance, however, and a simple analogous wear simulation may provide greater insight into the likely response by coatings when under a specific type of attack than merely relying on microhardness values.

Because all wear types are fundamentally functions of basic material parameters such as plasticity or hardness, elasticity, and brittleness, for many fairly steady wear states, it may be possible to construct empirical equations linking Young's modulus (E), hardness (H), brittleness (K), and time (t) to the rate of wear. Unfortunately, equations of this type have no general applicability, and even fairly small changes in any of the many variables that affect any particular wear process will have an effect on the wear rate that is often impossible to predict. In addition, different wear types may operate by very different mechanisms, and real coatings are not only subjected to tribological attack mechanisms, but are often also subjected to chemical attack and thermal cycling as well. How these stresses contribute to the extent of wear is difficult to predict, thus the authors believe that such empirical type equations have little utility, and the effort to obtain results far surpasses the worth of the equations.

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