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Microhardness as a Simple Means of Estimating Relative Wear Resistance of Carbide Thermal Spray Coatings: Part 1. Characterization of Cemented Carbide Coatings

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A selection of WC-Co and Cr_3C_2-25%NiCr coatings deposited by plasma spraying and high velocity oxygen fuel (HVOF) were tested. The microstructures of the coatings were characterized, and their mechanical properties were assessed using Knoop microindentation procedures. The coatings were also subjected to various wear tests. All of the coatings were at least 200 μm thick and were deposited onto stainless steel substrates. The wear tests simulated abrasion, cavitation wear, sliding wear, and particle erosion wear.

In this first part of a two-part contribution, the microstructures of the coatings are characterized and a discussion on the evaluation of mechanical properties from the microindentation response is presented. The nature of microhardness testing as applied to thermal spray coatings is evaluated as a means of assessing resistance to plastic flow, elasticity, and brittleness. In Part 2, the results of the various wear simulations are reported, and the utility of microhardness as an indicator of wear resistance is examined.

Keywords carbides, Cr_3C_2-NiCr, Knoop, microhardness, Vickers, WC-Co

1. Introduction

Microhardness has been used for optimizing spray parameters,[1-3] and for quality control purposes.[4] It has been used to compare coatings supplied by different manufacturers,[5] and sprayed with different techniques.[6] It is believed by some to enable the quick estimation of coating strength[7] and the quality of spraying because defects such as nonmelted particle inclusions and porosity lower microhardness. Inherent in this usage is the assumption that hardness is a measure of quality.

Although valuable research into the microhardness of thermal spray coatings has been performed in the past on thermal barrier coatings,[8] where there is no obvious connection between microhardness and performance ability, microhardness is of most obvious relevance as an indication of wear resistance. As Pawlowski described it: "Hardness and microhardness are often used for the first approximation of coating wear resistance, which is by far the most important property in present application of thermal spray technology."[9] Brandt also maintained that "hardness and density are the major quality criteria for evaluating coatings."[10]

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There have been voices of dissent, however: Naerheim et al.[11] reported being "unable to obtain consistent and meaningful microhardness measurements for WC-Co thermal spray coatings."

In a series of previous publications, we have examined the empirical problems with microhardness testing with reference to cemented carbide thermal spray coatings.[12-14]

In this first part of a two-part contribution, a selection of WC-Co and Cr_3C_2-25%NiCr samples are characterized in terms of their microstructures and their response to microindentation. The use of microindentation techniques to assess elasticity and brittleness of thermal spray coatings is also discussed. In Part 2, the results of various wear simulations on these coatings are reported and correlated with the microhardness values reported here. The utility of microhardness as an indication of wear resistance is examined.

2. Coatings Used

Five WC-%17Co, one WC-12%Co coating, and six Cr_3C_2-25%NiCr coatings were supplied by Sulzer Metco (Wohlen, Switzerland). WC-Co is the most widely used thermal spray coating for wear-resistant applications, and Cr_3C_2-25%NiCr is generally used at higher temperatures and under corrosive conditions, where WC-Co is susceptible to degradation.

Details of the starting powders, the thermal spray processes, and the fuels used are summarized in Table 1 together with microhardness values as analyzed by Sulzer Metco in accordance with their standard practices.[12] Optical micrographs of the coatings are shown in Fig. 1.

Table 1 Basic Details Characterizing Coatings Analyzed in this Research

Code Number	Material	Powder Type and Manufacturing Route	Manufacturing Process	Appearance of the Microstructure	XRD Analysis and EDS on SEM: Main Phases Present	Porosity Measurements Based on Image Analysis of the Cross Section Microstructure (a)	Microhardness (b)
A	WC-12%Co	Diamalloy 2004 sintered	HVOF H2 sprayed (DJ 2600)	Low porosity, but not as good as F	WC and W_2C	1.5%	1231, 85
B	WC-17%Co	73 NS-1, spray dried, sintered	Plasma spray Ar/H_2	Poor retention of carbide particles; highest porosity of any of the WC-Co coatings; pore-size also larger	WC, W_2C, traces of η	<1%	937, 67
C	WC-17%Co	73 NS-1 Spray dried/ sintered	Plasma spray Ar/He	Good retention of carbide particles; less porosity than B, but more than any of the WC-Co coatings deposited by HVOF	WC, some free carbon, trace of W, Co, W_2C, η, WO, and unaccountable peaks, indicating impurities; Al, Si, and Ca detected using EDX, so probably contains Al_2O_3 and SiO_2	<1%	930, 69
D	WC-17%Co	Diamalloy 2005, spray dried, sintered	HVOF H_2 sprayed (Diamond Jet)	Slightly more porosity than E, but better than B and C	WC, W_2C, and W	0.3%	959, 54
E	WC-17%Co	Diamalloy 2005, spray dried, sintered	HVOF C_3H_8 sprayed (Diamond Jet)	Slightly better porosity than D, but much better than B and C	WC, W, and less W_2C than in 5 or X	1.1%	884, 77
F	WC-17%Co	Diamalloy 2005 spray dried, sintered	HVOF Natural Gas sprayed (Diamond Jet)	Lowest porosity of any of the WC-Co; similar pore size to D and E, but far fewer pores	WC, some W_2C, and trace of W, slight trace of η; non-resolved Co peak containing dissolved impurities	<1%	1154, 66.4
G	Cr_3C_2-25%NiCr	430 NS, self-fusing nickel alloy blend	Plasma spray Ar/H2	Slightly more retention of the unmelted particles than H; very high porosity apparent from examination of the coating surface; similar porosity as H, when cross sections are examined	Mostly Cr_7C_3, some Cr_2O_3, traces of Cr_3C_2	<2%	543, 43
H	Cr_3C_2-25%NiCr	430 NS, self-fusing nickel alloy blend	Plasma spray Ar/He	Less porosity than G apparent from examination of polished coating surface	Mostly Cr_7C_3, some Cr_2O_3, traces of Cr_3C_2	<2%	524, 43
I	Cr_3C_2-25%NiCr	Diamalloy 3004, blend	HVOF H_2 sprayed (Diamond Jet)	Similar porosity to J, but more sharply defined, less amorphous microstructure	Some Cr_7C_3, more Cr_2O_3 than in plasma sprayed coatings, some traces of Cr_3C_2	1.1%	680, 67

(a) Supplied by Sulzer Metco.
(b) As performed by Sulzer Metco VH_{300}; Average, Standard deviation.

(continued)

Table 1 Basic Details Characterizing Coatings Analyzed in this Research (continued)

Code Number	Material	Powder Type and Manufacturing Route	Manufacturing Process	Appearance of the Microstructure	XRD Analysis and EDS on SEM: Main Phases Present	Porosity Measurements Based on Image Analysis of the Cross Section Microstructure (a)	Microhardness (b)
J	Cr_3C_2-25%NiCr	Diamalloy 3004, blend	HVOF C_3H_8 sprayed (Diamond Jet)	Similar porosity to I, but microstructure indicates higher processing temperature	Cr_7C_3, more Cr_2O_3 than in plasma sprayed coatings, traces of Cr_3C_2; more Cr_2O_3, less Cr_7C_3 than in W	0.8%	629, 33
K	Cr_3C_2-25%NiCr	Diamalloy 3004, blend	HVOF natural gas sprayed (Diamond Jet)	More apparent porosity than I or J from examination of polished coating surface, but examination of the cross section indicates dense, finer microstructure	Cr_7C_3, more Cr_2O_3 than in plasma sprayed coatings, traces of Cr_3C_2; more Cr_7C_3, less Cr_2O_3 than in W8	<1%	866, 44.4
L	Cr_3C_2-25%NiCr	Amdry 5260, spheroidal, agglomerated, and densified	HVOF H_2 sprayed (DJ 2600)	Lowest porosity of any of the Cr_3C_2-25%NiCr examined	Cr_3C_2, some $Cr_{6.2}C_{3.5}N_{0.3}$, and Cr_7C_3	<1%	952, 44.5

(a) Supplied by Sulzer Metco
(b) As performed by Sulzer Metco VH_{300}; Average, Standard deviation.

3. Experimental

3.1 Analysis of the Microstructures

The microstructures of the coatings were examined by optical microscopy (OM) and scanning electron microscopy (SEM). Examination was performed on both the cross section and on the polished surface of each coating tested.

Photomicrographs of the cross-sections of the WC-Co coatings are shown in Fig. 1 and those of the Cr_3C2_3-NiCr coatings are shown in Fig. 2. The apparent porosity is very different in some of these coatings, depending on whether the cross section or the in-plane direction is examined. As demonstrated by Kharlanova et al.[15] and confirmed by us, both the apparent size and the apparent density of pores depend on polishing procedures. It is difficult to assess the extent of pullouts, and the use of the standard test methods[16] as developed for much denser cemented carbides are not really applicable. Alternative techniques such as mercury intrusion are not sensitive to closed pores.

Nevertheless, by comparing the polished surfaces and sections using similar preparation and observation techniques, an assessment of porosity is possible, which allows comparison between coatings. This may be done manually, comparing the appearance of the microstructure against known standards. Alternatively, computerized image analysis may be performed on magnified images of the coating microstructure. Porosity statistics of this nature as supplied by Sulzer Metco with the coating samples are also shown in Table 1.

Phase analysis was performed by x-ray diffraction (XRD) on an XRD system (Scintag, Thermo ARL, Waltham, MA), using Cu-Kα radiation. Figure 3 shows the XRD traces for the WC-12%Co coating A, Fig. 4 shows XRD traces for the various WC-17%Co coatings B-F, and Fig. 5 shows the XRD traces for the various Cr_3C2_3-NiCr coatings G-K.

3.2 Microhardness Testing

The samples were microhardness tested using a Knoop indenter under 500 g load on the polished coating surface, and also using a Vickers indenter and 1 kg loading. The equipment used was an MHT-1 tester (Matsuzawa, Tokyo, Japan).

After the samples were polished with successively fine polishing grit down to a final stage using 0.25 μm diamond paste, they were microindented on the polished coating surface using a Knoop indenter loaded with a 500 g force. Multiple indenting was performed in two perpendicular directions until 10 clearly defined indents that could be measured in both directions were produced.

Indents that were not clearly defined and measurable in both the major and minor diagonal directions were rejected, and the number of indents rejected was also recorded. From the ratio of discarded indents to acceptable ones, an indication of relative coating brittleness or susceptibility to severe indent cracking was made, and from the ratio of the indentation diagonals, an estimate of the local elastic modulus was made.

An intercomparison of relative brittleness or cracking susceptibility was also made from the extent of cracking around the Vickers microhardness indentations. Ten indentations were made using a 1 kg load. The diagonals of the indent were mea-

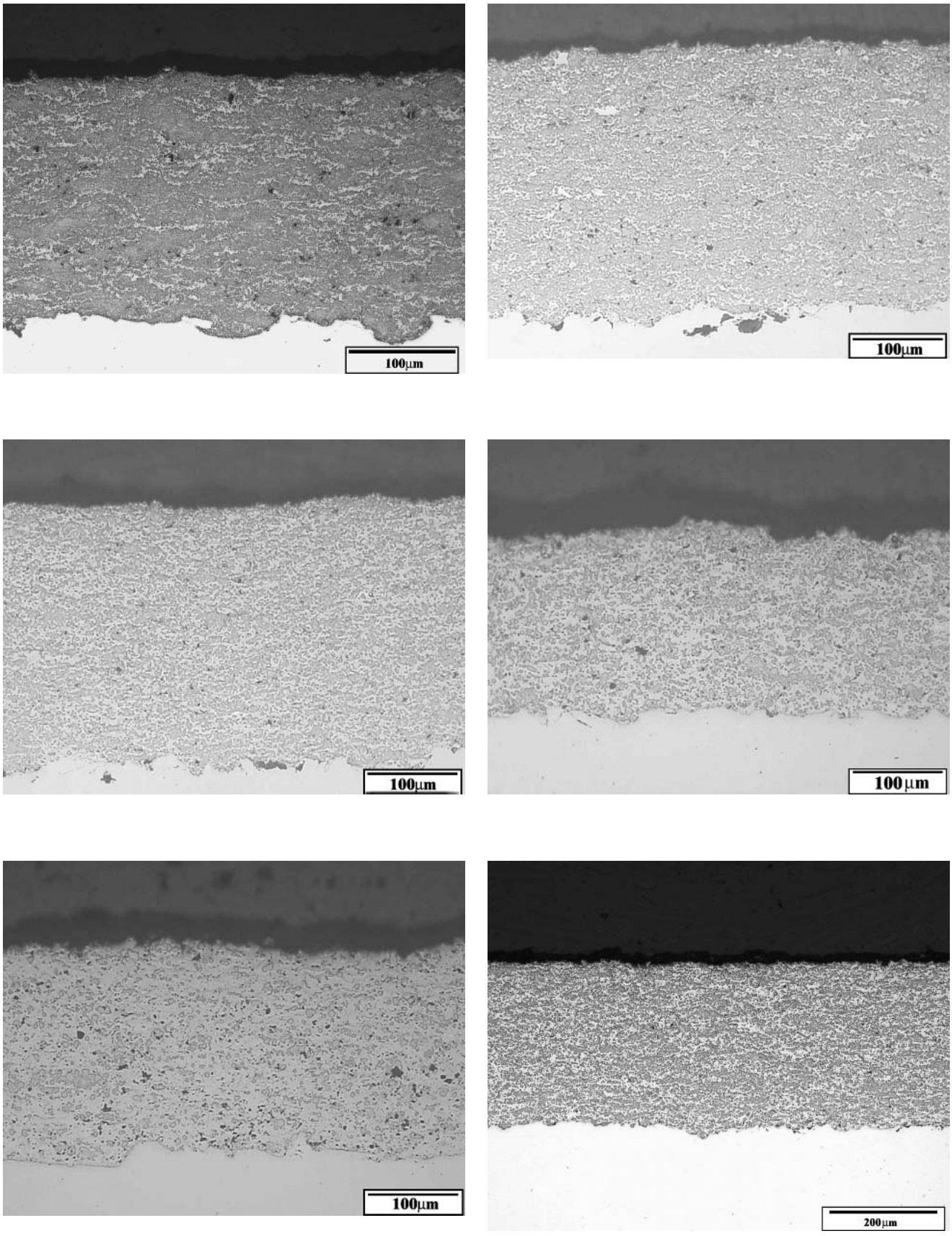

Fig. 1 Optical micrographs for the WC-Co coatings, as detailed in Tables 1 and 2

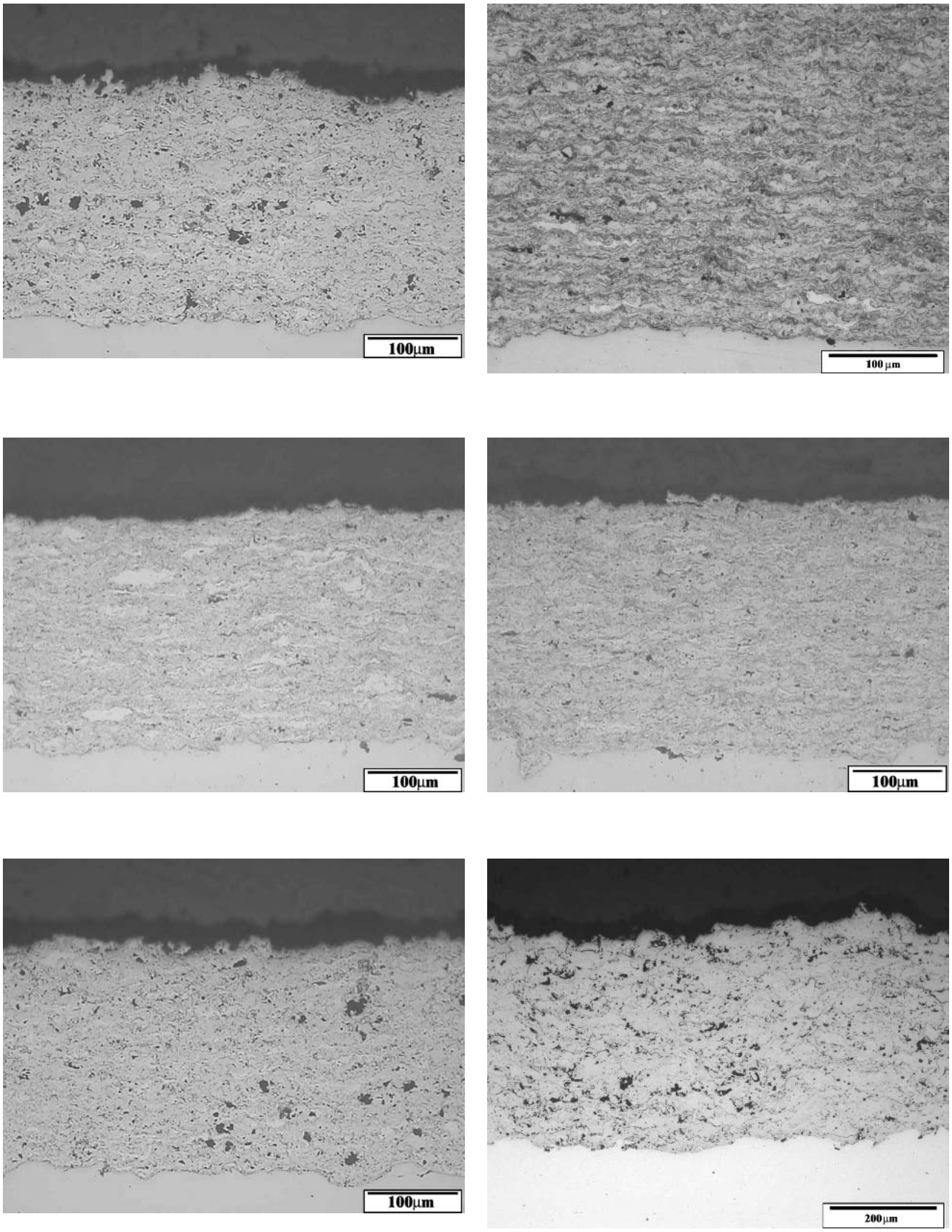

Fig. 2 Optical micrographs for the Cr_3C_2-25%NiCr coatings, as detailed in Tables 1 and 2

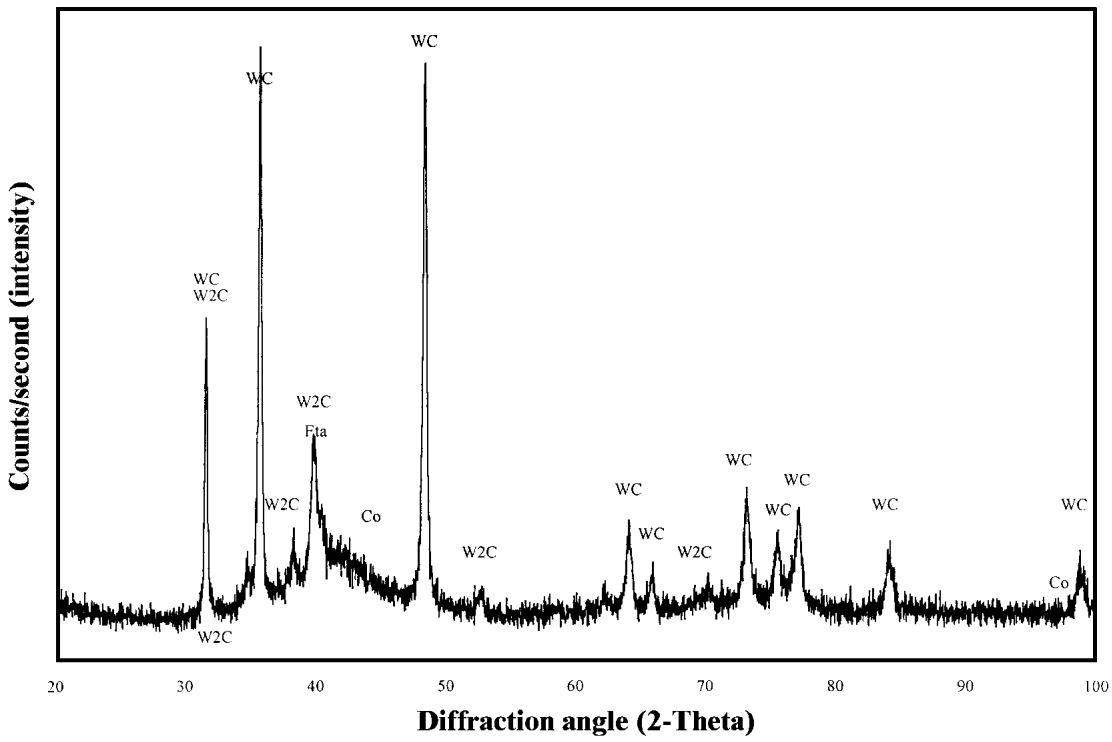

Fig. 3 XRD trace for WC-12%Co. The positions of peaks as a result of the various phases often seen are indicated.

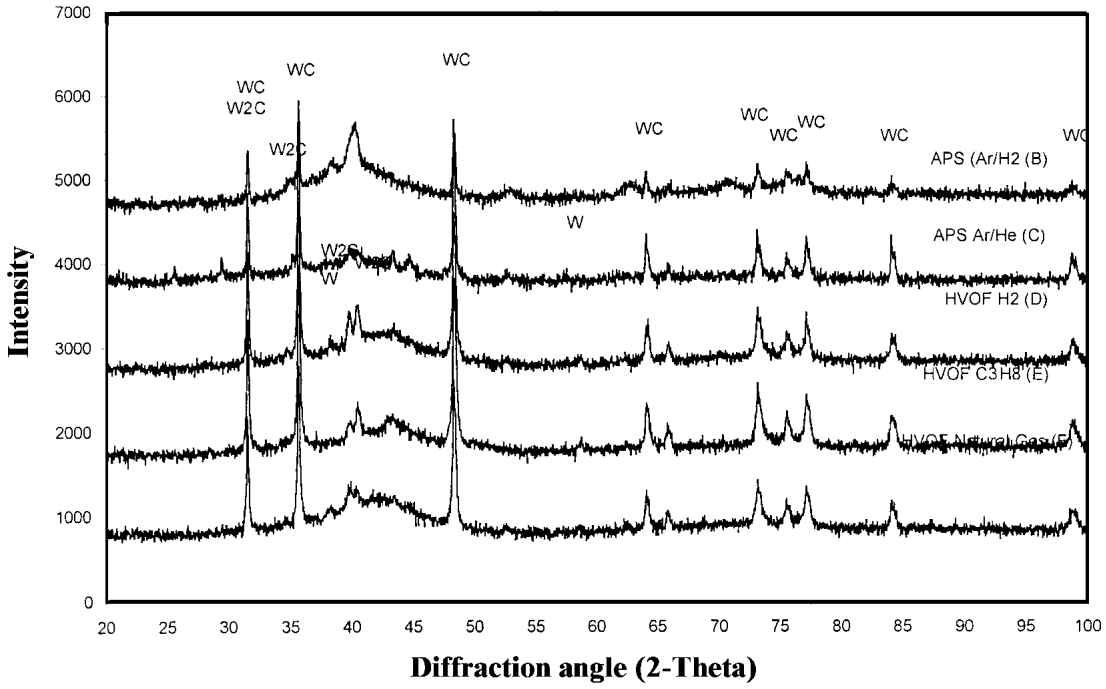

Fig. 4 XRD traces for WC-17%Co samples. Main peaks are identified.

sured, as was the extent of cracking. Both radial and circular cracks were seen, but most cracks were of mixed characteristics and were not easy to categorize. The outermost limits of surface-visible cracks in the directions parallel to the indentation diagonals were measured.

Because of the dimensions of the coating samples and the

Table 2 Microhardness Values (Rounded Up to Nearest Whole Number) and Brittleness Indications, Produced by Both Knoop and Vickers Indenting Procedures

	Vickers			True Average Knoop Correct Mean	Knoop Microhardness Testing; Statistics Generated From Individual Hardness Calculations			
Sample	Mean, HV_{300}	Standard Deviation	Vickers Brittleness Indicator, HV_{1-kg}		Mean of Hardness Values	Standard Deviation	Coefficient of Variation	Knoop Brittleness Indication
A	1231	85	0	1254	1096	261	0.24	0.13
B	937	87	0.40	949	821	213	0.26	0.26
C	930	69	0.15	965	838	221	0.26	0.13
D	959	54	0.04	1034	898	227	0.25	0.23
E	884	77	0.06	926	807	207	0.26	0.09
F	1154	66.4	0.04	1113	1115	52	0.05	0
G	543	46	0.13	458	401	97	0.24	0.29
H	524	43	0.12	497	433	107	0.25	0.39
I	680	67	0.13	617	522	142	0.27	0.53
J	629	33	0.001	652	578	145	0.25	0.2
K	866	44.4	0.03	765	768	56	0.07	0.17
L	952	44.5	0.22	847	737	203	0.27	0

load used, the standard methods for deriving indentation fracture toughness (K_c) from Palmquist cracks as specified in ISO 3878 were found to be unsuitable for thermal spray coatings. This is more fully explained in Section 4.2.2 below.

4. Results

4.1 Examination of the Microstructure

In Table 1, the main features of the microstructure are given. In general, the WC-Co coatings exhibited lower porosity than those formed from Cr_3C_2-25%NiCr. Examination of both the coating cross sections and a large area of polished surface for each coating sample revealed no coating delamination resulting from failure of the coating-substrate interface and no through-thickness cracks. The plasma sprayed coatings revealed a coarser microstructure, reflective of the grain sizes in the starting powders.

4.2.1 Microhardness. The Knoop microhardness values given in Table 2 are the arithmetic means of 20 indentations performed on the polished in-plane coating surfaces (10 each in orthogonal orientations) with an applied load of 500 g. Two average microhardness values are given for each coating. The first, tabulated in column 6, is the average of the 20 individual hardness tests, reflecting the universal but nevertheless erroneous averaging procedure of averaging individual hardness values, in accordance with Eq 1:

$$HK_1 = \frac{\sum_{d=1}^{n} \left(\frac{14229F}{d_1^2} \right)}{n} \quad \text{(Eq 1)}$$

where HK is Knoop microhardness number, d_1 is the long diagonal in micrometers, F is the applied force in gram force, and n is the number of measurements to be averaged.

As discussed elsewhere, for Vickers microhardness measurements,[12,14] this formula is the one almost exclusively applied in both industry and academia.

The second method is the Knoop hardness value (HK) calculated from the average of the indentation diagonal measurements according to the following formula:

$$HK_2 = \frac{14229F}{\left(\frac{\sum_{d=1}^{n} d_1}{n} \right)^2} \quad \text{(Eq 2)}$$

This is tabulated in column 5 of Table 2. Although rarely performed this way, the authors believe that this is the correct procedure to calculate representative values.

The Vickers microhardness values tabulated were determined for these coatings by Sulzer Metco using their standard procedure of averaging 10 microhardness measurements on the coating cross section made with an applied load of 300 g force (Table 1).

In Fig. 6, traditional Knoop microhardness values (Type 1) are compared with Vickers microhardness values as obtained by Sulzer Metco. The first method of calculation was used for consistency between the two sets of data and for comprehensibility.

Analysis of variance (ANOVA) was performed between the microhardness data measurements obtained for the different coating samples. The results demonstrated that the difference between the microhardness measurements for these coatings was significant at the 95% confidence level.

In Fig. 7, the correlation between Vickers cross section and Knoop surface microhardness data is shown graphically; both averaging procedures were used to calculate the Knoop microhardness statistics. In Fig. 7(a) the traditional Knoop (Type 1) microhardness values are compared with Vickers microhardness values, and in Fig. 7(b), the correct Knoop (Type 2) microhardness values are compared with Vickers microhardness values.

4.2.2 Assessing Brittleness. The generation of Palmquist cracks on the polished surface by microindentation with a 30 kg force load was attempted in accordance with standard procedures.[17] The crack patterns produced varied widely, and did not resemble radial, circumferential, or other ideal cracking patterns. Under these loading conditions, the cracks transverse the coating layer, and interact with and are deflected by the tougher substrate. The complex cracking patterns produced are not a result of the brittleness of the coating layer, but reflect its thickness, and the nature and position of the coating-substrate inter-

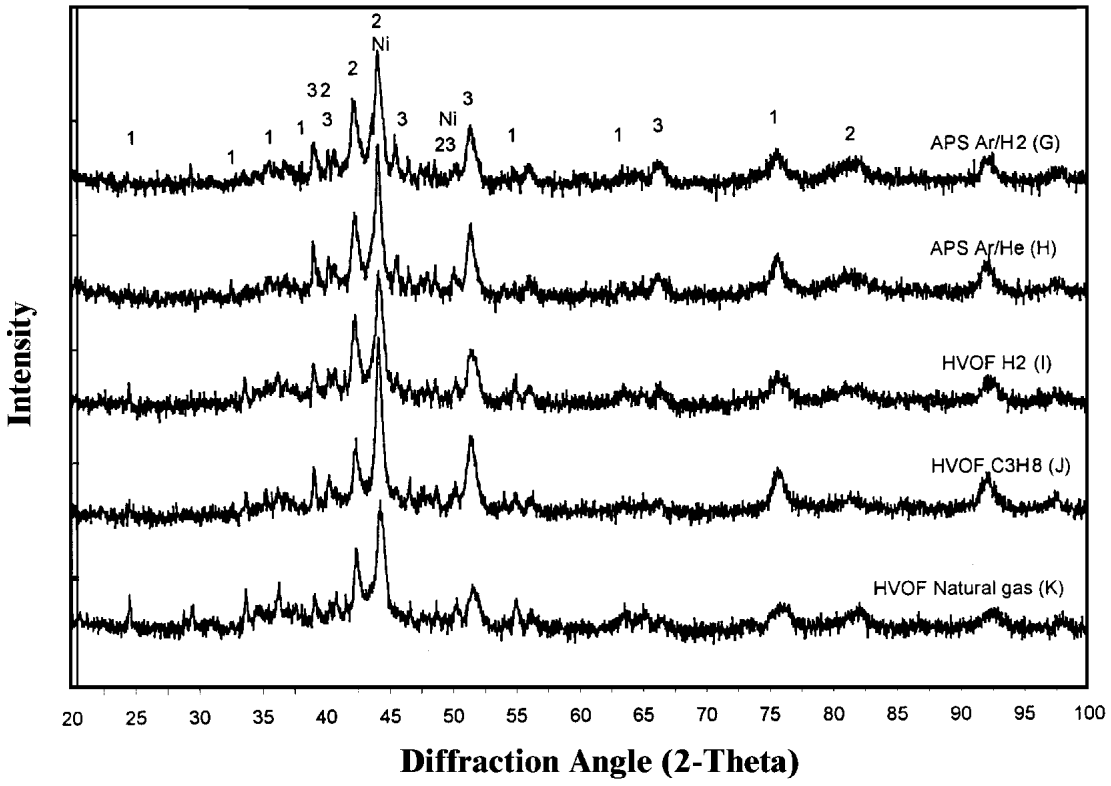

Fig. 5 XRD traces for Cr_3C_2-25%NiCr samples. Main peaks are identified.

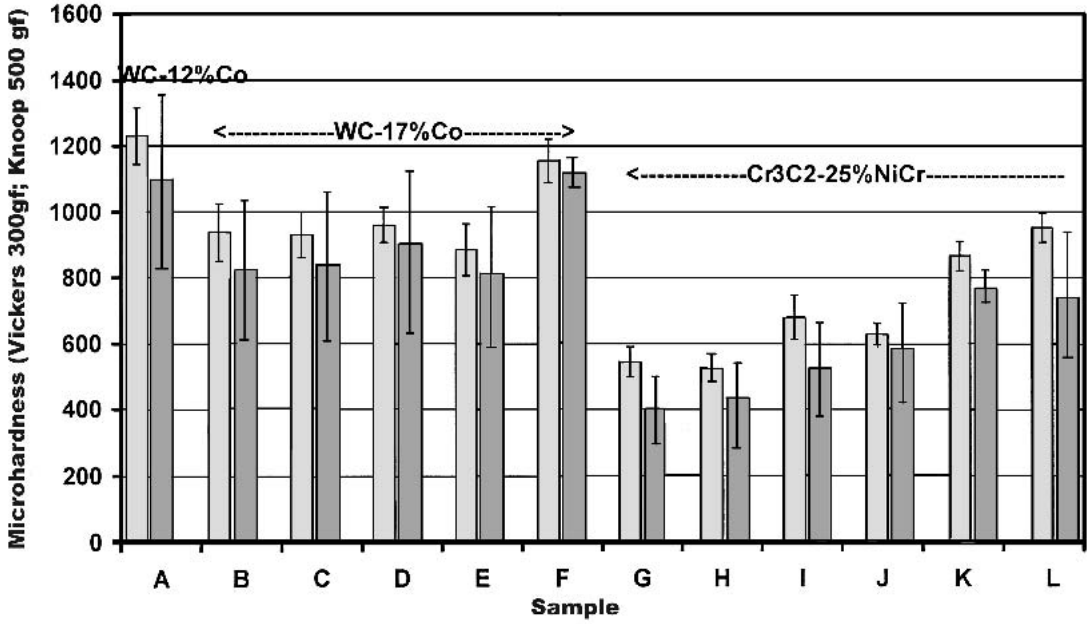

Fig. 6 Knoop and Vickers microhardness values for the thermal spray coatings used in this research

face. They are thus of no value for predicting the brittleness of the coating material, nor will they indicate the likelihood of brittle fracture mechanisms being initiated at the coating surface when subjected to tribological attack.

Two other procedures were used to assess the relative brittleness of the coatings. In the first procedure, the existence or otherwise of cracking or severe cracking around Knoop indentations was assessed. Multiple indentation procedures were

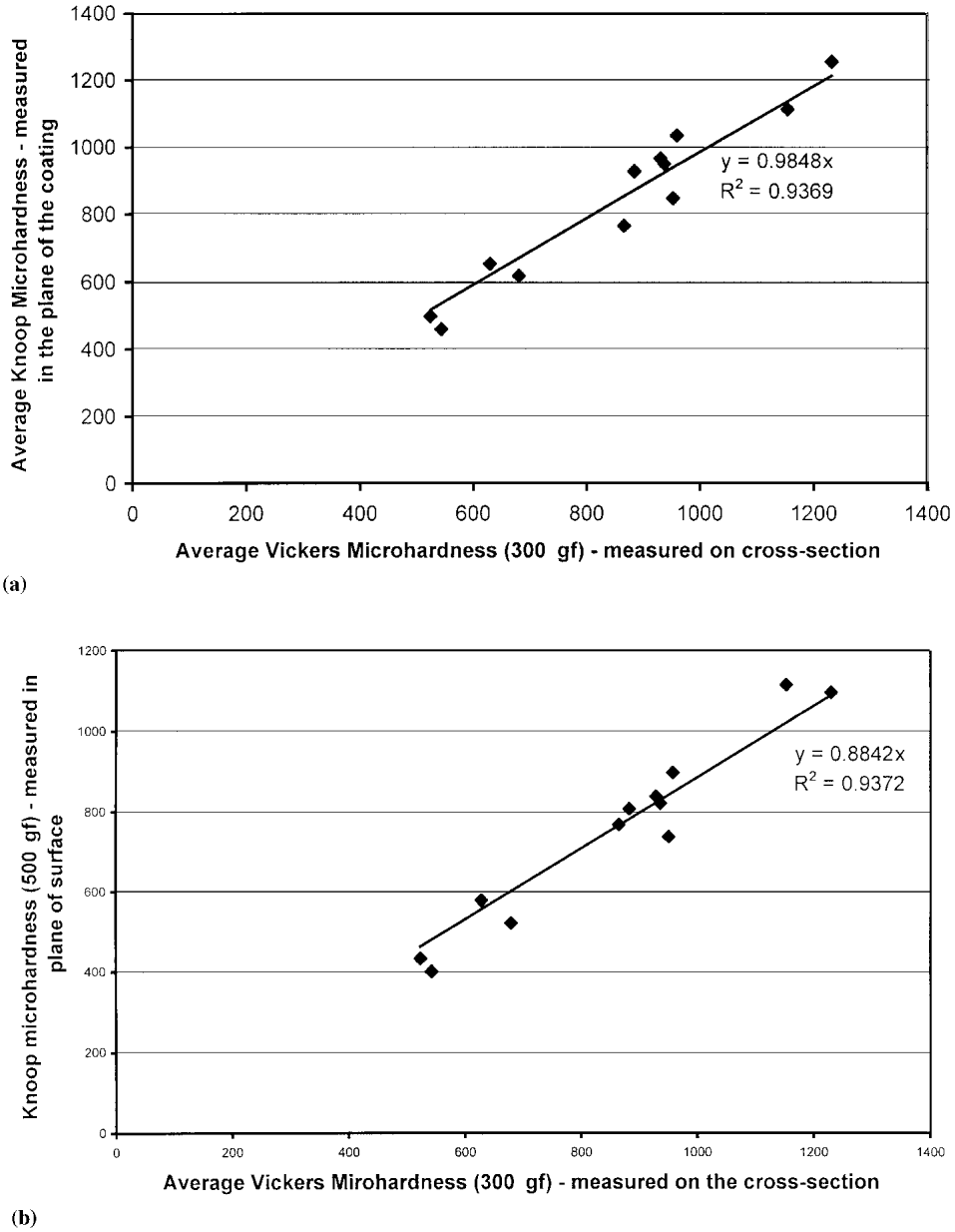

Fig. 7 The correlation between Vickers and Knoop microhardness values. **(a)** The traditional Knoop (Type 1) microhardness values compared with Vickers microhardness values. **(b)** The correct Knoop (Type 2) microhardness values compared with Vickers microhardness values.

performed, and the operator was required to either (1) make a yes or no decision about whether individual indentations showed signs of any cracking, or (2) decide whether significant cracking was in evidence.

In this work, the criterion of whether indentations could be measured in both directions was used. The Knoop indication of brittleness given in column 9 of Table 2 is thus simply the ratio of nonmeasurable to measurable indentations. Indenting continued until 20 clear indents were produced that were measurable in both directions. The number generated is the number of nonmeasurable indents (looking at both major and minor diagonals) divided by the total number of indents made to obtain 20 clearly defined indents, expressed as a ratio to two significant figures. The advantage of the technique is that it requires a simple "yes/no decision" concerning whether cracking is in evidence for each indent. There is no need to ascertain the extent of cracking, which is not trivial, and may be very time consuming. On the other hand, the extent of cracking per indent is not considered, although this might correlate better with wear processes. Although this type of procedure is to some extent load dependent, it was believed that for ranking purposes, as an indication of brittleness, the technique would have some utility.

In the second procedure, 10 indentations were made using a Vickers indenter under a 1 kg force, and both the diagonals of the indent and the extent of cracking were measured. Here, both radial and circular cracks were observed, but most indents featured

cracking of mixed characteristics, which were not easy to categorize. The outermost limits of surface-visible cracks in the directions parallel to the indentation diagonals were measured rather than the actual crack lengths. This procedure was used because the resulting cracks were sometimes branched, and rarely appeared as radial "textbook" cracks. For cemented carbides, Schubert et al.[18] used this modified crack length determination, but the cracks reported in his work are essentially radial cracks initiating at the corners of the Vickers indentation.

The present work followed the same procedure but did not differentiate between radial and median cracks, nor were multiple indentations performed until ideal cracking patterns were observed. By measuring the extent of *all* apparent cracking in tangential directions parallel to the two indentation diagonals for *all* indentations performed, it was hoped that results might better correlate with the microcracking that contributes to wear.

No attempt was made to derive fracture toughness after Shetty et al.[19] Their formulation of fracture toughness expresses K_{1c} as a function of $(H/c_{total})^{1/2}$. Because the cracking patterns varied so much between indents, it is clear that cracking was a local response and indicative of localized susceptibility of the surface to cracking, and cannot be considered to be a measurement of the bulk coating property.

A new, simpler empirical measure of toughness, "Vickers toughness," is defined as being the average of the indentation diagonals divided by the extent of cracking. The "Vickers brittleness," as given in Table 2, is defined by subtraction as 1 − Vickers toughness.

4.3 Microelasticity

The Young's modulus of a coating is a parameter often required by the mechanical engineer to design a coated machine element.[20] Because of dimensional complications, it is difficult to ascertain this property for coatings using conventional techniques.

It has been suggested that an estimation of Young's modulus for thermal spray coatings can be made from the ratio of the two diagonal lengths. The technique assumes that only the minor diagonal shows measurable elastic recovery, and thus the ratio of the indentation diagonals compared with the ratio of the Knoop diamond diagonals can be used to determine Young's modulus.

We implemented the technique using clearly defined indents on the coating surface. The indents were produced with the long diagonal both parallel and perpendicular to the direction of spray gun passes, and for some coatings, different results were obtained in the two directions.

Ten measurable indents were made in each of two perpendicular directions on the polished coating surface. The apparent Young's modulus in each direction and the average Young's modulus were calculated, in accordance with the theory given by Marshal et al.[21] These results are shown in Table 3.

It proved difficult to accurately measure the recovered indents in the plane of the coating, particularly because the indents were not clearly defined. For certain coatings, especially those showing a higher degree of porosity, the indent recovery was clearly affected by proximity of nearby pores and their location with regard to the indent diagonals. The combination of porosity and the tendency for the elastic recovery stresses to cause cracking rather than recovery cause wide scatter in measured indentation ratios.

In view of theoretical and reported values for WC-12%Co and WC-17%Co of around 570 and 550 GPa,[22] it is clear that some values such as that given for coating D, are anomalous. Similarly, the value calculated for coating J exceeds typical values of about 225 GPa for the sintered material.

Table 3 Average Young's Modulus Values for Coatings, Nearest GPa

		Young's Modulus, GPa		
Coating Type	Code	Direction, Low	Direction, High	Average
WC-12%Co HVOF	A	284	290	287
WC-17%Co PS	B	116	227	172
WC-17%Co PS	C	122	220	172
WC-17%Co HVOF	D	241	850!	546
WC-17%Co HVOF	E	243	426	335
WC-17%Co HVOF	F	354	375	365
Cr3C2-25%NiCr PS	G	65	121	93
Cr3C2-25%NiCr PS	H	57	201	129
Cr3C2-25%NiCr HVOF	I	71	119.8	95.5
Cr3C2-25%NiCr HVOF	J	205	1129!	666
Cr3C2-25%NiCr HVOF	K	201	217	209
Cr3C2-25%NiCr HVOF	L	123	214	169

5. Discussion

5.1 Difference Between Plasma Spray and High Velocity Oxygen Fuel (HVOF)

The plasma spray process occurs at high temperatures. The relatively low density of the spraying medium results in low particle accelerations during spraying, and thus results in low impact velocities. This leads to higher porosity levels in the coatings produced. The high temperature and comparatively long time for material interaction between particles and their spray environment lead to high levels of oxidization as particles travel through the air. Conversely, the HVOF[23] process employs high spray speeds and controlled temperatures which minimize materials degradation[24] and thus hard, dense coatings are formed.

In general, the plasma sprayed WC-Co samples are expected to suffer more chemical degradation during spraying, resulting in a brittle η phase (W_3Co_3C) and other mixed complex carbides being included within the microstructure. The HVOF processing occurs faster and at a lower temperature, so that η phase formation is suppressed. For phase diagrams of the WC-Co system, see Ref. 25-27.

Degradation of the WC to W_2C and sometimes to W occurs as a result of interaction between the spray particles and the oxidizing environment during spraying. This is difficult to minimize, because lowering the oxygen content when spraying with hydrocarbon can result in soot entrapment within the coating microstructure.

The degradation processes that occur in WC-Co particles during thermal spraying are well established; for example see Jarosinski et al.[28]

5.2 Plasma Spray Medium

Comparing the microstructures of coatings B and C using SEM indicates that greater dissolution of the carbide reinforcement into the matrix occurred during deposition of coating B. In both B and C, large carbide particles were retained, whereas

smaller particles (<10 μm), although common in coating C, were hardly in evidence in coating B.

Ar-He plasma spraying evolves faster speeds, but is a cooler process than Ar-H_2 spraying. Thus, one would expect that spraying with helium would produce lower porosity and also produce less material degradation as particles pass through air.

5.3 HVOF Coatings

SEM examination of the HVOF produced coatings that showed a decreasing retention of hard phases, in the order E < D < F, corresponding to spray medium C_3H_8 < H_2 < natural gas (which is mostly CH_4).

This shows an interesting correlation with microhardness, where in general, a decrease in porosity level and an increase in microhardness accompany a greater dissolution of the carbide particles into the matrix. Greater dissolution of hard phase particles is indicative of higher temperatures and greater plasticity of the sprayed material. This evidently allows for greater compaction, resulting in lower porosity. In general, retention of the hard phase and unalloyed matrix is considered desirable because crack propagation is impeded.

The thermal conductivity of the combustion products of methane is higher than that of propane. This explains the greater degree of carbide melting in coating F.

The specific fuel used affects the flame temperature, its density, and hence its accelerating power. The fuel also determines the type and density of the gaseous species and radicals present during spraying. The temperature and gaseous species present affect the rate of chemical degradation during spraying, and the accelerating power combined with the gun geometry determine the length of time the powder material is at elevated temperature and thus susceptible to decomposition reactions. The affect of fuel type on microhardness has been studied.[29]

Notably, Vuoristo et al.[30] also examined the affects that different fuels have on the processing environment, albeit using a different HVOF process. They found the reverse microhardness ranking for WC-12%Co when sprayed with C_3H_8, H_2, and natural gas, which is mostly CH_4. Although the microhardness of the coating samples examined here can be ranked, it is difficult to come to any definite general conclusions regarding the effect that different fuels have on microhardness.

The effect of the spray medium on the phases present in the coating is exceeded by the effect of the phases present in the starting powder and by the powder processing route.[31] Similarly, different spray parameters and the equipment used can significantly affect the coatings quality. This is seen when the very different properties of the two Cr_3C_2-25%NiCr sprayed with H_2 (I and L) are compared.

5.4 Choice of Microhardness Technique

Although it is the coating surface that is subjected to the stresses that result in wear, it appears to be the almost universal practice in the thermal spray industry to perform microhardness indentation on the polished cross section. This is because of (1) the difficulty and costs associated with polishing large areas of very hard materials, and (2) the difficulty with retaining planarity of the metallurgical sample. Although in previous work, these authors did not note significant variation in hardness as measured in the two directions,[13] the existence of such variation is noted by Pawlowski.[9]

Because Knoop indentations are much shallower than Vickers indentations, the requirement that sufficient coating thickness remains under the indent for the measurement to be valid is easily attained. When the long diagonal of the indent is parallel to the coating-substrate interface, variations of microhardness with depth have been noted, and correlated with residual stress in the coating.[8] For these reasons, it is preferred that microhardness indentation be performed on the polished coating surface.

To obtain Knoop microhardness values, only one dimension of the indentation is measured, whereas Vickers microhardness measurement requires the lengths of both diagonals of the indentation to be determined. Variability in the readings partly reflects the structure of these materials, but also partly reflects inaccuracies of the optical measuring procedures used,[14] and in general, the problems associated with measuring the indentations are more significant as the indentation becomes smaller. For these reasons, the authors prefer the Knoop microhardness determination.

The traditional microhardness values obtained by Sulzer Metco using the Vickers method are slightly (12%) higher than those obtained using the Knoop method. This accords well with Quinn,[32] who points out that at the higher microloads, HK values are often 10% lower than those obtained using the Vickers indenter. Although this general observation could explain the discrepancy between the two values, it may be noted that when measuring Vickers microhardness on the same sample and orientation with the same load as Sulzer Metco, the present authors consistently obtained lower hardness statistics. Thus, sample A was measured by Sulzer Metco as having a microhardness of 1231 ± 85 HV_{300}, but by the present authors as having a microhardness of 1158 ± 130.6 HV_{300}.[12] There is a poor between-person reproducibility, such that different operators, even when measuring the same indentations using the same equipment can certainly produce results that vary by at least this magnitude.[14]

Another possible explanation is that of the indentation size effect: It is noted that thermal spray materials generally exhibit lower hardness values for higher applied loads.[4] It has been argued that the indentation size effect can be linked to the dimensions of the indentations with respect to those of the individual splats, and this could be used to explain the lower microhardness as measured using Knoop than that obtained using the Vickers indenter. However, the present authors consider this argument spurious. After appropriate normalization procedures, the load versus microhardness curve (or indentation size effect) demonstrated by WC-Co thermal spray coatings has the same form as that demonstrated by other materials such as fully annealed high purity copper.[33] This shows that the indentation size effect is not linked to any particular structural features. As discussed elsewhere,[33] it is suggested that this phenomenon is generally the result of poor measurement and the erroneous averaging procedures as discussed in Section 4.2.1, and not a true materials effect. In Fig. 6(b), the true average (Type 2) Knoop microhardness is plotted against the average Vickers microhardness. Here a much better correlation is obtained with a discrepancy of only a couple of percent between the average microhardness values. The individual Sulzer Metco indentation measurements are not available, but in previous work[12,13] on materials of this type, we have established that the discrepancy

between the average Vickers microhardness calculated in the two ways, for 10 indents on WC-Co performed under a 300 gram force loading, is about 3%. It would seem, therefore, that the discrepancy between the two sets of readings is largely an artifact of the averaging error and not directly related to the microstructure of the material, although it reflects the range of microhardness values obtained.

Thus, in accordance with the results of a previous investigation,[14] the present authors believe that more consistent microhardness measurements are obtained with better reproducibility and repeatability if a Knoop indenter is used rather than the more widespread Vickers pyramid. For all the above-discussed reasons, and also because a larger sampling set was used, we have greater confidence in the microhardness ranking shown by the Knoop measurements than those produced at Sulzer Metco using Vickers. It is the correct Knoop (Type 2) measurements that are used in Part 2 of this article to examine the utility of microhardness as an indicator of wear resistance.

However, because of the layered, anisotropic structure of thermally sprayed coatings, different results are obtained as the orientation of the Knoop microhardness indenter with respect to the coating interface changes. Randomizing the orientation is problematic, however, because the indent is required to be an adequate distance from both the interface and coating surface such that the indent dimensions are a true coatings response. This severely restricts the geometrically allowable indent size when indenting on the coating cross section such that the long diagonal of the indenter is perpendicular to coating interface. For this reason, indenting on the polished surface is preferred to indenting on the cross section, especially since it is the polished surface that is subjected to wear stresses.

5.5 What Does Microhardness Measure?

The first scale for measuring indentation hardness was that devised by Brinell (1902) for measuring the hardness of metals, which are materials that deform plastically. As has been noted previously,[34] for porous and multiphase materials, only an effective hardness can be given. All indentation hardness scales are essentially measures of resistance to plastic deformation as the sample material is subjected to compressive forces.

When indenting thermal spray coatings, the material under the indenter experiences compaction facilitated by giving of the weakest link. This may be plastic deformation of the metal matrix, but is more likely to be failure of the matrix-reinforcement interface, and may involve cracking of the hard phase particles. For every indentation performed, several different mechanisms may work 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. Where present, the first and often biggest contributor to the indenter accommodation is porosity, which results in large indents and correspondingly low hardness values. During indentation, the total volume of pore in the stress field of indenter has zero hardness, and thus does not resist material plastic flow. The material between indenter and pore can be in tension, a requisite for cracking and other, brittle, indenter accommodation mechanisms. Conventional materials accommodate the indenter by plastic deformation along available slip planes in accordance with the Von Mises and Tresca criteria. Thermal spray coatings tend to deform plastically by splat sliding, with slip occurring along intersplat boundaries.

Perhaps the best way to conceptualize the hardness indentation of a material is that proposed by Gilman, i.e., it is considered as a strength microprobe.[35] The randomly distributed porosity and general heterogeneity of the microstructure is the reason that invariably a high degree of scatter is frequently reported for microhardness values measured on individual thermal spray coating samples. Further discussion may be found in Valente,[4] Lin and Berndt,[8] Leigh et al.,[36] and Factor and Roman.[13,14,33]

5.6 Determining a Measure of Coating Brittleness Using Indentation Techniques

The calculation of fracture toughness (K_{1c}) values from indentation crack lengths is based[37] on the classic derivation by Griffith.[38,39] Application of the model is only really legitimate for the cracks formed when indenting relatively homogeneous and isotropic materials such as glass and sintered ceramics. As summarized by Quinn,[32] even for bulk ceramic materials, the K_{1c} values calculated from Palmquist 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, many alternative equations for calculating K_{1c} values from indentation crack lengths are to be found in the literature. The appearance of cracking patterns obtained on thermally sprayed carbide coatings were very different from the patterns reported by Tanaka[40] for sintered carbides. The models are simply not appropriate.

De Palo et al.[41] performed the standard indentation procedure for measuring fracture toughness on the polished cross section of thermal spray coatings. The resultant cracks were very much longer in the direction parallel to the interface than perpendicular to it. The reasons for this observation are clear: perpendicular to the interface, the thin coating thickness is constrained by metallic substrate on one side and by mounting resin on the other. The cracks are not propagating in a continuum of material and the model is inappropriate. These workers ignored the perpendicular cracks and derived K_{1c} from the crack lengths along the interface. Thermal spray coatings have a layered structure. De Palo measured 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 the intersplat boundaries. We believe that to use results generated in this manner, as a true indication of coating brittleness, and to then attempt to correlate the statistic derived to surface wear degradation is unrealistic. Unless a wear mechanism is dominated by failure of the coating due to splats flaking off, any correlation between rate of wear and K_{1c} derived in this fashion will be coincidental. However, to measure specific phenomena such as intersplat cohesion or the apparent interface toughness,[42] the technique has some validity.

Table 2 shows the results of two attempts to derive brittleness indexes from microindentation. One technique used a Vickers indenter and the other used a Knoop indenter. The crudeness of the techniques resulted in the relative ranking for the various coatings being different in the two indexes. They are not without

value, however. Both rankings indicate that coating I is the most susceptible to cracking of the HVOF coatings, and coating B is similarly the most brittle of the plasma sprayed coatings.

Where wear can be expected to be heavily influenced by susceptibility to microcracking such as on components exposed to dry particle erosion, simple tests such as these might be used to reject poor contending coating types.

Indeed, in Part 2 of this article, we show that coating I performs the worst in both high and low angle particle erosion wear tests. In fact, if the rankings for both high and low angle impingement are considered together, the brittleness indexes calculated are reasonable indications of impact wear susceptibility.

The extent of cracking is indicative of the volume damaged by the indentation, reflecting the brittleness of surface regions. Although the technique measures extent of cracking and does not just record whether cracking occurred, the combination of (1) the various uncertainties in measuring crack lengths, (2) the dubious relevance of the statistic, (3) the probable influence of polishing technique, and (4) the selectivity in choosing areas away from surface pores, and their affect on crack blunting and termination, make this technique very unsatisfactory.

Because the problems discussed result from poor repeatability in the making and measuring of indentations and cracking patterns, quite apart from the subsequent data analysis, the authors are skeptical of the legitimacy of measuring the toughness of these coating materials from microindentation procedures.

5.7 Measurement of Local Elastic Response

The Knoop indenter also enables measurement of local elastic response, based on the assumption that only the short diagonal is susceptible to elastic recovery. From the very wide scatter in results obtained on these materials it is clear that this is not a good indication of Young's modulus for the coating as a whole (a macro property). The most probable reason for the significant variation between the average Young's modulus values in two orthogonal directions within the plane of the coating (which is demonstrated by many coatings) is the existence of directional residual stresses. These are most likely due to the direction of the spray gun motion relative to the substrate during spraying. For coating samples D and J, in one direction the elastically recovered indents actually had measured short diagonal values larger than that of the unrecovered indent. This would imply that the coating surface is in residual tensile stress, and that the Knoop indentation, if suitably oriented, allows local residual stress relaxation.

Using a different indentation procedure, Wallace and Illavsky[43] also found continuous variation in Young's modulus on the scale of the deposition gun passes throughout thermal sprayed deposits. From the values obtained, it would appear that the Knoop indentation technique, though perhaps suitable for fully densified ceramics, is not appropriate to generate bulk elasticity statistics for thermal spray coatings. Nevertheless, on examination of the data, several aspects may be noted, as discussed below.

Plasma sprayed coatings appear to have lower E values than the HVOF equivalents for both Cr_3C_2-25%NiCr and WC-17% Co. Coating I exhibited low E values, and also had a tendency to crack as indicated by both brittleness indexes. Coating J contained lakes of matrix material, which might partially explain the high elastic recovery in one direction, and also the large variability in both measured HK values and in the ratio of the two diagonals (D_1/D_2) as measured.

There is a subtle difference between the understanding of the purpose in measuring elasticity that is inherent to the work of Leigh et al.,[36] and the understanding that underlies this work. Leigh et al. regard the difficulty in obtaining "pure" elastic deformation using conventional stress-strain tests (because of cracking phenomena) as a reason to prefer the use of Knoop microhardness techniques when measuring thermal spray coatings. The present authors consider that the generation of highly localized elasticity information is of little value for characterizing the coating behavior, even if it is a "pure" materials response.

Brandt[10] claims that E values for Cr_3C_2-25%NiCr HVOF coatings derived using the three-point bending technique were 90 GPa for a wide variety of spray parameters and feedstock materials. Leigh et al.[36] measured 175 ± 34 GPa on the cross section and 93 ± 14 GPa in the plane of the coating. Similarly, the value determined by Brandt for WC-12%Co deposited by HVOF was about 230 GPa and for WC-17%Co HVOF his value was about 220 GPa. The values we obtained from the aspect ratio of Knoop microhardness indentations as reported herein are clearly inconsistent, and we conclude that although this technique might be very useful for research purposes into elastic variability and for following residual stresses and the like, they are not useful for generating Young's modulus statistics that characterize the coating as a whole. For this engineering purpose, it would appear that the three-point bending technique (and certainly the more accurate four-point bending technique) is more successful for generating repeatable measurements indicative of the continuum coating behavior. (The criterion for accepting individual Knoop indentations was whether both diagonals were measurable. Clearly, it is possible to develop other criteria such as rejecting extreme values, which would perhaps give results that are more reasonable. However, arbitrary correction factors instead force the data to generate preconceived "meaningful" results.)

6. Summary

In this first part of a two-part article, a series of six Cr3C2-25%NiCr and six WC-Co coatings produced by plasma spray and HVOF technologies with different fuel gases were characterized. Microhardness testing was performed on the coating surfaces using a Knoop indenter to give a measure of resistance to penetration.

Attempts to produce relevant coating brittleness and elasticity statistics were made. It was concluded that microindentation could not legitimately be used to measure K_{1c} for thermal spray coatings, but that examination of indent cracking could nevertheless be used to identify coatings having a particular susceptibility to microcracking. The Knoop indentation technique can be used to measure local elastic response, but accurate measurement of the short diagonal in the plane of the coating surface is not easy. For many coatings, the results obtained varied tremendously, and although the technique may be of value for mapping variations through the coating, it is not useful for generating characteristic properties that are representative of the coating as a whole.

Part 2 of this article assesses the correlation between microhardness and wear resistance for these coatings by subjecting them to a variety of wear tests.

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