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Statistical analysis of microhardness variations in thermal spray coatings

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A thermal barrier coating system consisting of a NiCoCrAlY bond coat and cerium-stabilized zirconia ceramic coating was sprayed on to a metallic substrate. Ageing at 400 and 800 °C for 100, 500, and 1000 h was performed. Microhardness measurements of as-sprayed and heat-treated samples were used to evaluate microstructural variations throughout the thermally sprayed coating after different ageing conditions. Forty readings were taken at both the bond coat and ceramic coating positions within the thermal barrier coating (TBC) system and adjusted by subtracting the two largest and two smallest readings. Both data sets were statistically analysed to assess whether they belonged to Weibull or Gaussian (or "normal") distributions. This study has established that the homogeneity of coatings, at least as measured by a microhardness test, varies during service and, thus, may influence the lifetime.

Nomenclature

α Confidence limit
μ Mean value
σ Standard deviation
σ^2 Variance
$\tilde{m}$ Weibull modulus obtained from any method
$\tilde{x}_0$ Characteristic value obtained from any method
CV Coefficient of variation
$f(x)$ Probability density function
$F(x)$ Cumulative density function
i ith order in ascending data set
L Log-likelihood function
m Weibull modulus
n Total number of data points
x Microhardness data
x_i Microhardness data which is ith order in ascending data set
x_0 Characteristic value which gives 63.2% cumulative density

1. Introduction

Thermal barrier coatings consisting of a plasma-sprayed ceramic coating and a bond coat are used for protection of components which are subjected to elevated temperature environments [1, 2]. The performance of a coating system varies with many factors which are intrinsic properties of the bond coat and ceramic coating and these properties may change after thermal cycling [3–5]. Efforts to understand fully the failure mechanisms during operation have indicated that oxidation of the bond coat and residual stress changes within the ceramic coating play important roles in degradation of the coating system [6–8]. The evaluation of mechanical properties [9–10], especially by microhardness methods [10], before and after simulated operating conditions, may allow reliability assessment of the system. The microhardness studies employed in the present study imply that a statistically based evaluation of the bonding strength may account for the variations in material properties that are practically observed.

2. Experimental procedure

The coating system, consisting of 200 μm NiCoCrAlY bond coat (Metco 461) and 1400 μm cerium-stabilized zirconia (Metco 205), was thermally sprayed on to a metallic substrate and then aged at 400 and 800 °C for 100, 500, and 1000 h. The codes of these samples are listed in Table I.

A MICROMET II tester was employed at a load of 300 g for 15 s to find the Vickers hardness number (VHN). Microhardness data of the as-sprayed and aged specimens was measured at regions within the bond coat and the ceramic coating. The position of each series of indentations was precisely located with respect to the distance from the substrate interfacial region. Each measurement series comprised 40 readings which were randomly located along each region of interest. Data were then adjusted by subtracting the two largest and two smallest readings to discriminate against results that would be atypical of the overall material properties. Such data points may arise from high or low porosity regions of the microstructure that

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TABLE I Identification codes for heat treated and aged samples

Condition	As-sprayed	400 °C, 100 h	400 °C, 500h	400 °C, 1000 h	800 °C, 100 h	800 °C, 500 h	800 °C 1000 h
Sample code	AS	B1	B2	B3	C1	C2	C3

correspond to unrepresentative structures of the material. Both data sets (i.e. the complete data and the adjusted data set) were analysed by Gaussian and Weibull distributions, as well as by student's t-tests.

3. Theory of statistical analysis

3.1. Gaussian distribution

The Gaussian distribution is widely used by scientists and engineers to assess the degree of regularity of the data [11]. The mean value (or expected value), μ, and standard deviation (S.D.), σ, are commonly used to indicate the data scatter and are defined as:

$$\mu = \sum_{\text{all } x} x f(x) \quad (1)$$

$$\sigma = \left[\sum_{\text{all } x} (x - \mu)^2 f(x) \right]^{1/2} \quad (2)$$

where $f(x)$ is the probability density function of the distribution. The standard deviation and the variance, (σ^2), are measures of the absolute variation of data and depend on the scale of measurement. To compare several sets of data, it is more convenient to use the coefficient of variation (CV; where CV $= 100(\sigma/\mu)\%$), which gives a measure of relative variation. The student's t-test can be used to compare the hypothesis that the means of two data sets are equal. If the t-test value, t, is unity then the two data sets are identical. If the value is very small (less than, say, 0.001) then the means of the data sets are significantly different [12]. The strength distribution of brittle materials can be highly skewed or broadly distributed and it is difficult and inadequate to describe the variation by means of the Gaussian distribution. The Weibull distribution has merit in being simple to implement to accommodate this type of problem.

3.2. Weibull distribution

The Weibull distribution has been used successfully to describe a wide range of problems including the mechanical properties of brittle materials and lifetime testing [13, 14]. The Weibull function, in the two-parameter form, is given as

$$F(x) = 1 - \exp\left[-\left(\frac{x}{x_0} \right) \right]^m \quad (3)$$

where $F(x)$ is the cumulative density function of probability, x is the microhardness data, x_0 is the characteristic value below which 63.2% of the data lie, and m is the Weibull modulus.

The so-called Weibull parameters are the Weibull modulus, m (or shape factor), which reflects the data scatter within the distribution, and characteristic value, x_0 (or scale factor), which gives 63.2% of the cumulative density. Techniques to determine the desired Weibull parameters include the Weibull plot, maximum likelihood estimation (MLE), linear estimator, and direct non-linear curve fitting. The former two methods will be used in this study and addressed in the following paragraphs.

The Weibull plot is the most common and easiest way to obtain the Weibull parameters. A Weibull plot can be drawn by rearranging Equation 3 and taking natural logarithms twice. Thus x_0 and m can be determined by fitting the following equation

$$\ln\left\{ \ln\left[\frac{1}{1 - F(x)} \right] \right\} = m[\ln(x) - \ln(x_0)] \quad (4)$$

The method of determining $F(x)$, which is the cumulative density function of probability, in the above equation has been discussed [14, 15]. The mean value of $F(x)$ is obtained from placing the data in ascending order and letting

$$F(x) = \frac{i}{n + 1} \quad (5)$$

where n is the total number of data points, and i is the ith order in ascending data set. The mean value is commonly used because it represents the expected value of the probability density function within the distribution. However, in highly skewed distributions the median value, where $F(x) = (i - 0.3)/(n + 0.4)$, may be a better choice. Other estimators such as $F(x) = (i - 0.5)/n$ and $(i - 0.375)/(n + 0.25)$ have also been used [15].

The second approach to obtain the Weibull parameters is the maximum likelihood (ML) method [16]. The likelihood function, L, is the mathematical expression of the probability of obtaining the observed data. The log-likelihood function is obtained by taking the natural logarithm of the likelihood function, i.e.

$$\ln(L) = n\ln(m) - nm\ln(x_0) + \sum_{i=1}^{n} (m - 1)\ln(x_i) - \sum_{i=1}^{n} \left(\frac{x_i}{x_0} \right)^m \quad (6)$$

The values of m and x_0 which maximize the Weibull likelihood function are found by (i) differentiating the

TABLE II χ^2 values of various a confidence intervals

α%	90	95	97.5	99	99.5
χ^2	2.706	3.841	5.024	6.635	7.879

TABLE III Microhardness results

Sample Code	Bond coat $\mu^a \pm \sigma^b$ Orig.[d]	Adjus.[e]	CV. (%)[c] Orig.	Adjus.	Ceramic coating $\mu \pm \sigma$ Orig.	Adjus.	CV. (%) Orig.	Adjus.
AS	196 ± 24	196 ± 17	12.2	8.7	239 ± 61	236 ± 49	25.5	20.8
B1	225 ± 36	227 ± 30	16.0	13.2	203 ± 49	201 ± 38	24.1	18.9
B2	227 ± 45	229 ± 37	19.8	16.2	210 ± 66	206 ± 55	31.4	26.7
B3	237 ± 32	237 ± 24	13.5	10.1	207 ± 54	209 ± 45	26.1	21.5
C1	257 ± 48	260 ± 33	18.7	12.7	238 ± 56	239 ± 45	23.5	18.8
C2	269 ± 31	270 ± 24	11.5	8.9	208 ± 56	306 ± 55	18.2	18.0
C3	228 ± 37	228 ± 26	16.2	11.4	267 ± 75	364 ± 59	28.1	22.3

[a] μ, mean
[b] σ, standard deviation
[c] CV. (%), coefficient of variation
[d] Orig., original data set
[e] Adjus., adjusted data set

log-likelihood function with respect to m and x_0, (ii) equating the resulting expressions to zero, and (iii) simultaneously solving for m and x_0. On rearrangement, we can have

$$x_0 = \left[\frac{\sum_{i=1}^{n}(x_i)^m}{n}\right]^{\frac{1}{m}} \quad (7)$$

$$\frac{n}{m} + \sum_{i=1}^{n}\ln(x_i) - \sum_{i=1}^{n}[\ln(x_i)]\left(\frac{x_i}{x_0}\right)^m = 0 \quad (8)$$

The parameters obtained by the Weibull plot method can be used as seed values for an iterative procedure that allows the Weibull values to converge within a few steps. An approximation for the confidence limits, based on the ML method, utilized the χ^2 distribution [17]. Recall the log-likelihood equation, Equation 6, and the Weibull parameters are subject to the following conditions

$$-2\ln[L(x_0,\tilde{m})] + 2\ln[L(\tilde{x}_0,\tilde{m})] = \chi^2_{1,\alpha} \quad (9)$$

$$-2\ln[L(\tilde{x}_0,m)] + 2\ln[L(\tilde{x}_0,\tilde{m})] = \chi^2_{1,\alpha} \quad (10)$$

where $\tilde{m}$ and $\tilde{x}_0$ are a pair of Weibull parameters obtained from any methods.

An approximate α confidence interval is obtained by finding the set of x_0 (representing lower and higher bounds) and the set of m values by applying Equations 9 and 10, respectively. Some commonly used χ^2 values of various a confidence intervals are listed in Table II.

4. Results and discussion

4.1. Gaussian and student's t-test analysis

The mean values and standard deviations (indicated by the error bar) of both data sets indicate the data scatter, Fig. 1 and Table III. Examination of the adjusted data sets for the mean values of the bond coat indicate that, in general terms, heat treatment increased the hardness of the layer. The average increase of 5%, from 225 VHN to 237 VHN, is well within the experimental error expected for a Vickers hardness test. It is also observed (except for sample C3) that longer times and higher temperatures produced a more significant hardness increase. Sample C3 did not show this trend, possibly due to extensive cracking

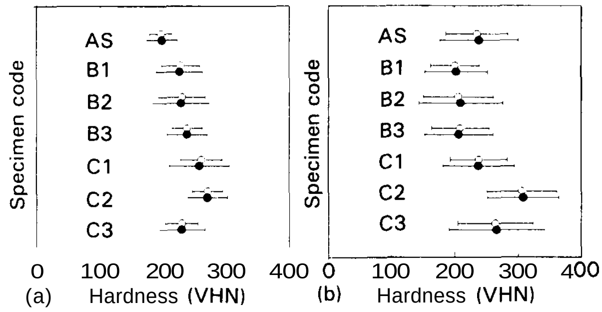

Figure 1 Gaussian statistics of (a) bond coat and (b) ceramic coating of samples, mean and standard deviation (represented by error bars). (●) Original data set, (O) adjusted data set.

from the excessive oxidation; but this postulate has not been confirmed. The hardness changes in the ceramic coating exhibit a decrease at the lower ageing temperature (400 °C) and a static (at 100 h) or significant increases (at 500 and 1000 h) at the 800 °C treatment. Hardness decreases may arise from stress relief at the lower temperature whereas the increase in ceramic coating hardness at high temperatures possibly arises from increased stresses due to bond coat oxidation. The Gaussian analysis indicates that discounting outliers decreases the variance by about 3%–5%; but it is still difficult to distinguish between the various samples.

The student's t-test is used to discriminate the means of two data sets; the results are shown in Table IV.

4.1.1. Bond coat

The student's t-test reveals that the mean hardness values of the aged samples belong to a different population distribution than the as-sprayed material. Ageing at 400 °C for various times does not significantly change this property; however, they differ from the 800 °C batch. These results may imply that the performance of these coatings may change according to distinct operating temperatures.

TABLE IV Student's t-test results for bond coat (BC) and ceramic coating (CC) components of the TBC[a]

		AS	B1	B2	B3	C1	C2	C3
BC	AS		0	0	0	0	0	0
	B1	0		0.85	0.13	0	0	0.87
	B2	0	0.84		0.26	0.01	0	0.92
	B3	0	0.14	0.27		0	0	0.14
	C1	0	0	0	0.03		0.15	0
	C2	0	0	0	0	0.18		0
	C3	0	0.75	0.95	0.25	0	0	
CC	AS		0	0.04	0.02	0.78	0	0.03
	B1	0		0.62	0.43	0	0	0
	B2	0.02	0.66		0.84	0.04	0	0
	B3	0.01	0.75	0.80		0	0	0
	C1	0.95	0	0.01	0.01		0	0.04
	C2	0	0	0	0	0		0
	C3	0.08	0	0	0	0.06	0.01	

[a]Upper triangle of data represents adjusted data set and lower triangle represent the original data set.

4.1.2. Ceramic coating

The t-test also shows differences between the as-sprayed and the aged samples; except for sample C1. Ageing at 400 °C does not result in a large change in hardness, whereas ageing at 800°C does result in significant differences. The plots presented in Fig. 2 better illustrate these findings. To summarize; the student's t-test indicates that material properties (at least as measured by hardness tests) of these coating systems change after operation and also change at different working temperatures.

4.2. Weibull distribution

Figure 3 shows the VHN distribution within the bond coat for the samples. Fig. 3a presents the original data set where outlier effects can be observed at the tails of the curve, and Fig. 3b shows the adjusted data sets without the outliers. Similarly, Fig. 4a and b show the VHN distributions for the ceramic coating. The characteristic value, x_0, and Weibull modulii, m, of all data

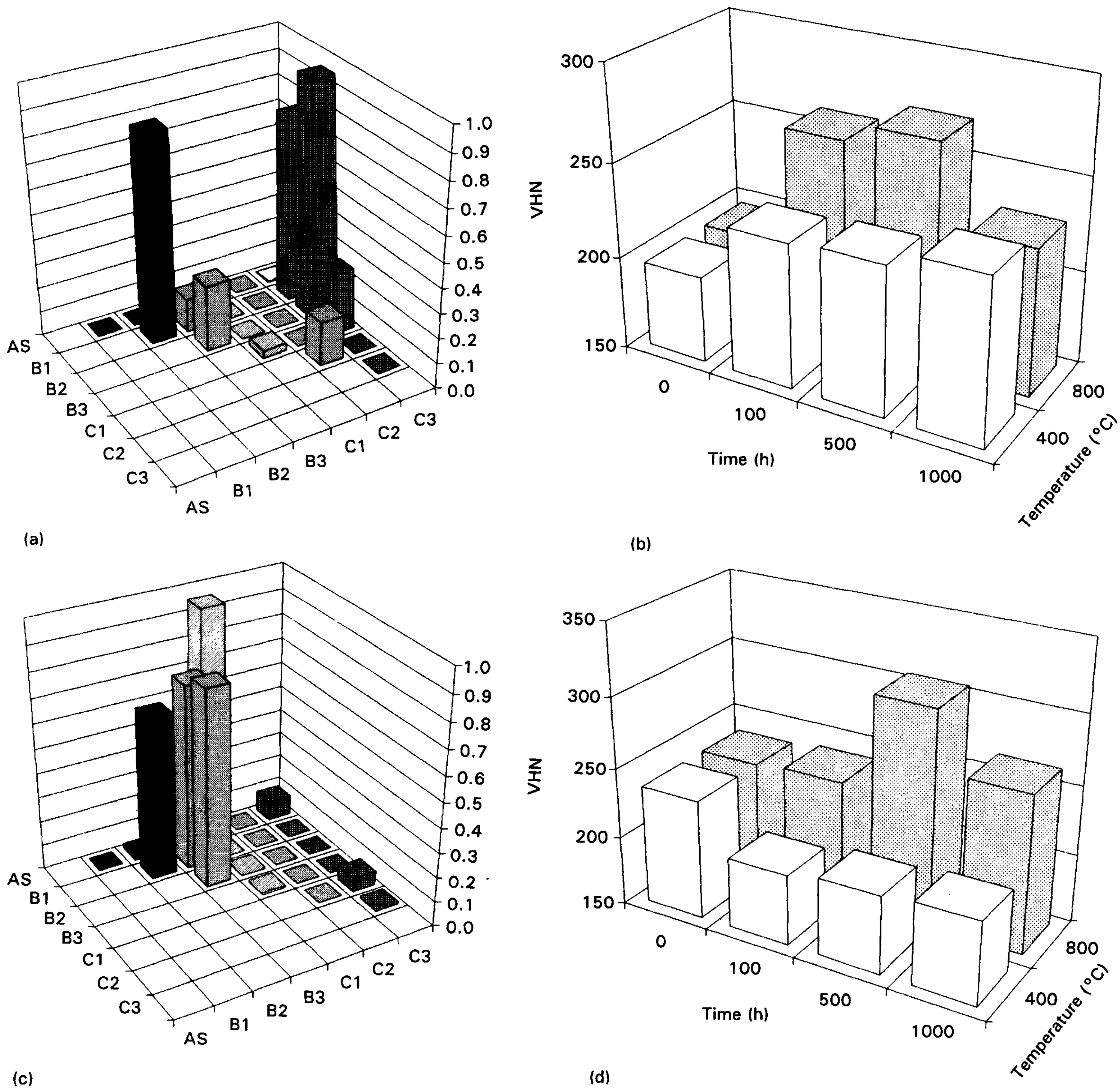

Figure 2 **Illustration of student's t-test results; only adjusted data are presented. (a, b) bond coat, (c, d) ceramic coating.**

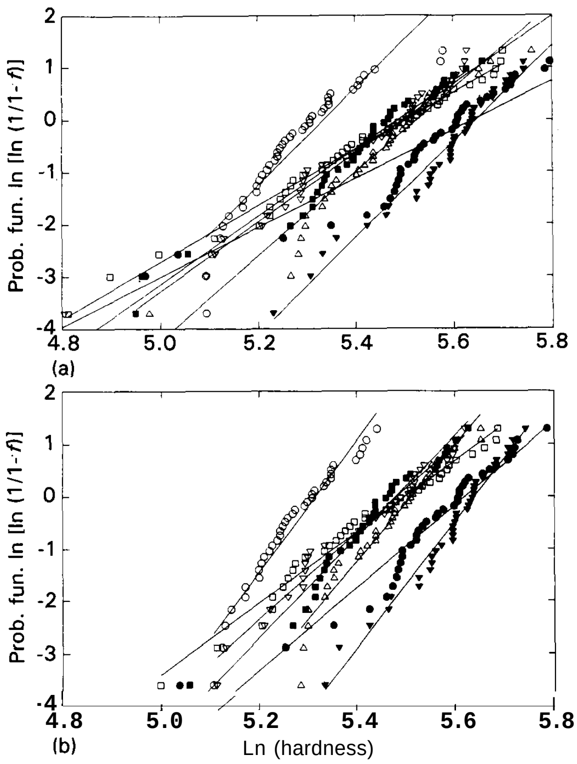

Figure 3 **Weibull plots for microhardness data within bond coat for as-sprayed and aged samples. (a) Original data set; (b) Adjusted data set with deletion of the two largest and two smallest data. (O) As, (▽) B1, (□) B2, (A) B3, (●) C1, (▼) C2, (■) C3.**

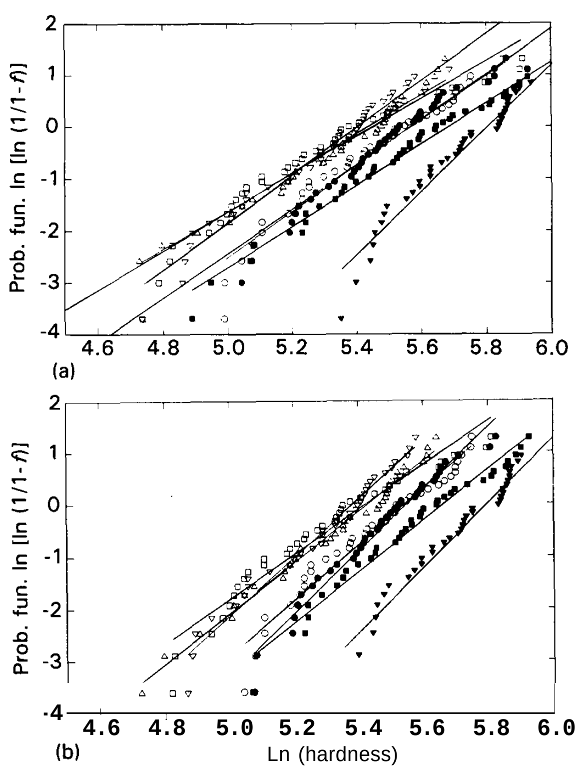

Figure 4 **Weibull plots for microhardness data within ceramic coating for as-sprayed and aged samples. (a) Original data set; (b) Adjusted data set with deletion of the two largest and two smallest data. For key, See Fig. 3.**

sets are summarized in Table V. Examination of the adjusted data sets for the x_0 values of the bond coat and ceramic coatings show similar trends as found by the Gaussian distribution. The Weibull modulus values can be classified as either high (between 6.8 and 12.5) for the bond coat material or low (i.e. between 4.3 and 6.2) for the ceramic coating. The low modulus corresponds to a higher variability in the hardness measurement and would be expected for the more brittle ceramic material. Weibull parameters with 90% and 95% confidence limits are listed in Table VI. Different from the single value (or "point") estimates discussed above, this method considers the interval estimates that will contain the parameter. Schematic illustration of these results are shown in Fig. 5.

More information can be obtained by the combination of results from the t-test and confidence interval estimation. For the bond coat, although ageing at 400 °C (i.e. the “B” series of specimens) does not significantly alter the mean of the distribution (from t-test results), the data distribution was skewed or broadened with respect to the as-sprayed sample because the Weibull modulus confidence intervals varied (confidence interval estimation), Fig. 5a. Ageing at 800 °C not only changes the mean but also the shape of the distribution. The Weibull modulus confidence intervals for the ceramic coatings did not show large variation after heat treatment, Fig. 5b. However, for the B2 specimen, distribution broadening of microhardness data was observed (i.e. m decreased) and this might be due to relaxation of residual stress. A significant difference was noticed from the t-test of the samples aged at 800 °C, although the shape of the data distribution did not have a large variation.

5. Conclusion

The microhardness measurement was used to characterize a thermally sprayed coating system consisting of a NiCoCrAlY intermetallic bond coat and a cerium-stabilized zirconia layer. Ageing at 400 and 800 °C for 100,500, and 1000 h was performed to simulate high-temperature conditions. The microhardness test evaluated variations throughout the coating system.

Data analysis according to Gaussian and Weibull distributions was performed to assess the engineering reliability of the coating system. It was found that this property varies according to ageing temperature, such that high variability operated at the higher temperature. The ageing time at higher temperature is important, but does not show any large effect at lower temperature. The student's t-test allows differences betwen two data sets to be characterized and Weibull confidence interval estimation gives the shape distribution of the data. Combination of the student's t-test and Weibull confidence estimation provides more detailed information about the variability within the coating systems.

A simplified model to explain the observed variations in coating systems is presented in Fig. 6. Fig. 6a shows a schematic drawing of a cross-section of an as-sprayed specimen where residual stresses and temperature effects may take place. Fig. 6b shows detail of a sample which has been heat treated and indicates areas (labelled a–d) which are focused on in Fig. 7. Fig. 7a shows how the adhesion strength at the bond coat–substrate interface change during ageing due to

TABLE V Weibull analysis of microhardness results

Sample	x_0 (BC)		x_0 (CC)		m (BC)		m (CC)	
	Orig.	Adjus.	Orig.	Adjus.	Orig.	Adjus.	Orig.	Adjus.
AS	208	203	262	256	9.3	12.5	4.4	5.3
B1	242	240	222	218	6.5	8.3	4.6	5.6
B2	246	244	232	226	5.4	6.8	3.6	4.3
B3	251	248	230	228	8.0	11.0	3.8	4.8
C1	282	276	262	257	4.7	7.9	4.3	5.9
C2	283	281	331	329	9.2	12.1	6.1	6.2
C3	244	240	294	288	6.6	9.6	4.0	4.9

TABLE VI Weibull parameters with 90% and 95% confidences estimated by maximum likelihood method (" − " indicates the lower bond of parameter, and " + " indicates the upper bond of parameter)

		$x_0 - 95$	$x_0 - 90$	x_0	$x_0 + 90$	$x_0 + 95$	m − 95	m − 90	m	$m + 90$	$m + 95$
Bond coat	AS	194	197	204	212	217	7.1	8.6	12.0	16.4	18.1
	B1	225	229	240	253	260	5.2	6.2	9.1	12.3	13.7
	B2	225	230	244	262	270	4.0	4.8	7.0	9.4	10.4
	B3	235	238	248	259	264	6.4	7.6	11.0	14.6	16.2
	C1	257	262	274	288	296	5.4	6.4	9.3	12.5	13.8
	C2	269	272	280	290	295	8.0	9.6	14.0	18.8	20.9
	C3	226	230	239	251	257	5.7	6.9	10.0	13.2	14.6
Ceramic coat	AS	230	237	256	279	290	3.2	3.8	5.6	7.6	8.4
	B1	198	203	217	234	243	3.6	4.3	6.3	8.6	9.6
	B2	196	204	227	256	272	2.3	2.8	4.0	5.3	5.8
	B3	204	210	227	247	258	3.1	3.8	5.6	7.7	8.6
	C1	233	239	257	280	291	3.4	4.0	5.8	7.7	8.5
	C2	299	307	329	356	370	3.6	4.3	6.1	8.1	8.9
	C3	257	265	288	318	332	2.9	3.4	5.0	6.7	7.4

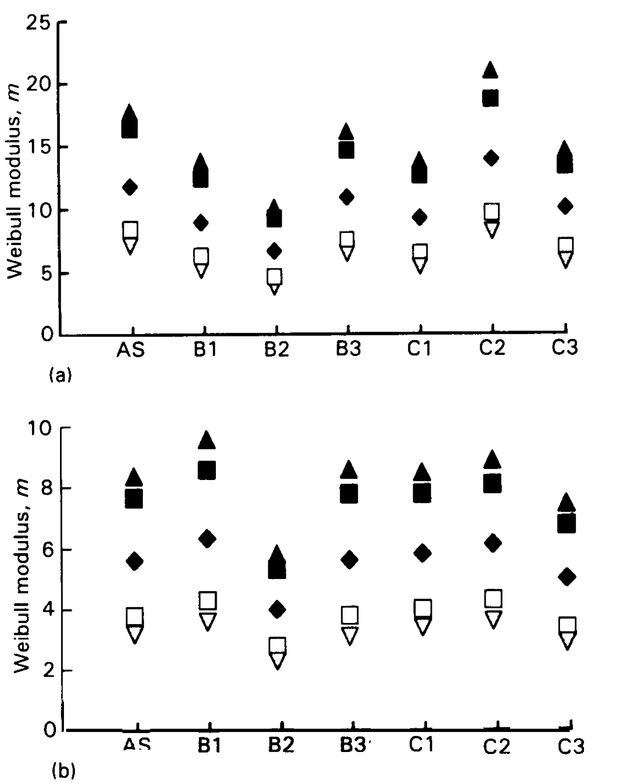

Figure 5 Confidence intervals for Weibull modulus obtained by maximum likelihood estimation. (a) Bond coat and (b) ceramic coating. (▲) 95% upper bound, (■) 90% upper bound, (▽) 95% lower bound, (□) 90% lower bound, (◆) estimators from maximum likelihood estimation.

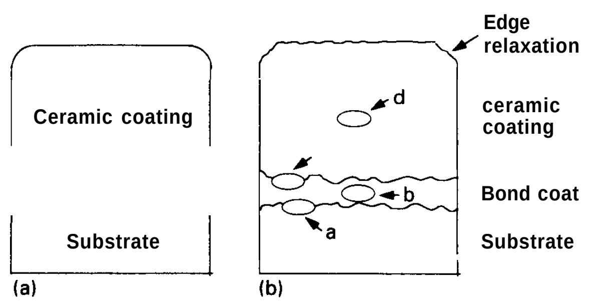

Figure 6 Schematic illustrations of (a) as-sprayed and (b) aged specimens.

the formation of oxides. These oxide films, though they may contribute to the increase of microhardness (Fig. 7b), may also decrease the adhesion strength and induce failure [6]. The thermal expansion mismatch between the bond coat and ceramic coating may cause degradation of the system as shown in Fig. 7c. And finally, micro- and macrocracks are induced within the ceramic coatings upon thermal ageing (Fig. 7d) and these are related to delamellation of the coatings. The precise nature of the oxidation and cracking mechanisms for coatings is still under investigation and Fig. 7 should only be considered as a preliminary physical model.

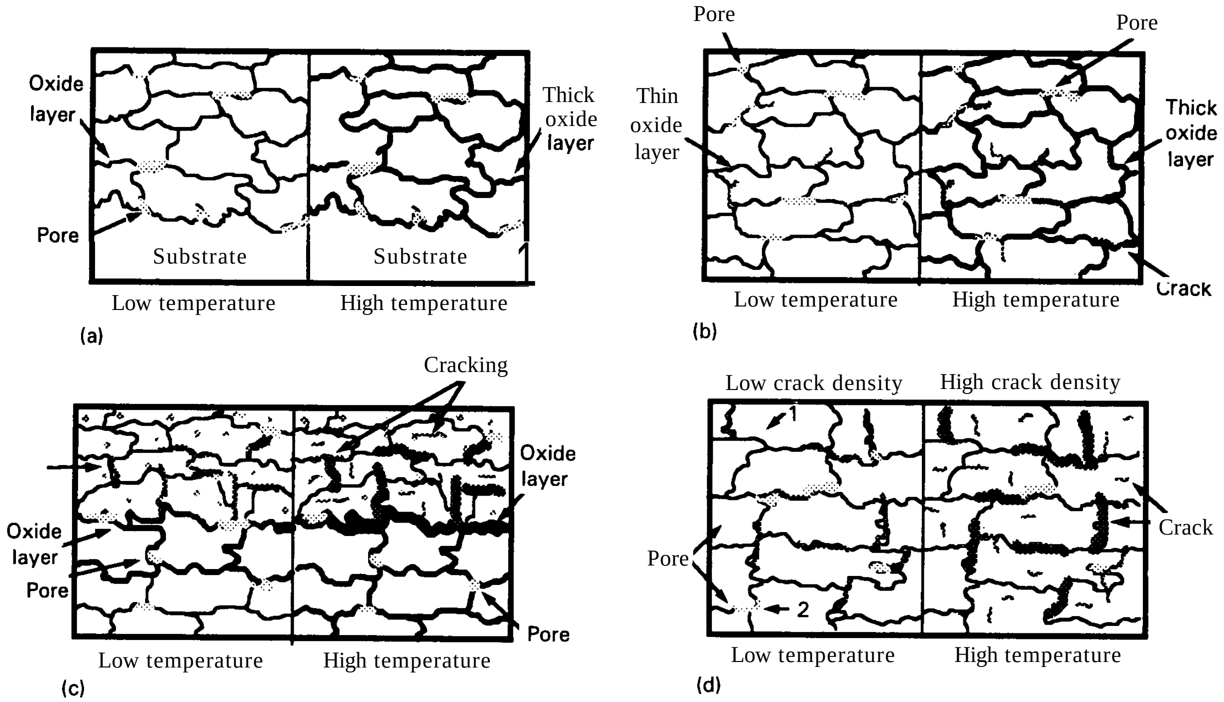

Figure 7 (a) Bond coat–substrate interface, (b) oxidation within the bond coat, (c) bond coat–ceramic coating interface, (d) cracking within the ceramic coating; 1, microcracking from pores, 2, macrocracking from splat boundaries.

The non-monotonic response between microhardness and the Weibull modulus infers that complex processes such as stress relaxation, growth of oxide layers within the bond coat, and phase changes occur. The variability of coatings during service may influence the lifetime of the materials. It is expected that microhardness measurements combined with other techniques will contribute to a better understanding of the performance of materials.

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