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Adhesion Evaluation of Plasma Sprayed Coatings Using Piecewise Linear Regression Analysis

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The critical load for adhesion of 75%WC-Co + 25%Ni alloy plasma sprayed coatings was evaluated by an interfacial indentation test. A statistical analysis—piecewise linear regression—was used to estimate the critical load P_C and its confidence interval. It was determined that a post heat treatment increases the practical adhesion load of plasma sprayed coatings. This increase was attributed to interdiffusion mechanisms verified at the interface between the coating and substrate.

Keywords interfacial adhesion testing, piecewise linear regression

1. Introduction

The coated surface must possess a suitable combination of properties to achieve tribological requirements, for example, good adhesion at the coating/substrate interface. Adhesion is defined by Holmberg and Matthews (Ref 1) as "the ability of a coating to remain attached to the substrate under required operating conditions." The definition of adhesion used by ASTM is "the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking forces or both" (Ref 2).

Demarecaux et al. (Ref 3) describes the process of basic adhesion (BA) of thermal sprayed coatings by three main components: physicochemistry adhesion, mechanical adhesion, and interdiffusion adhesion. On the other hand, the measurement of this adhesion or the measurement of the mechanical resistance achieved by application of an increasing force to separate the coating from the substrate is termed by Rickerby (Ref 4) as experimental or practical adhesion (EA). The relationship between EA and BA can be written as:

$$EA = BA - IS \pm SE \quad \text{(Eq 1)}$$

where *IS* is the internal stress and *SE* is the specific error of the method in measurement.

There are some mechanical tests to measure experimental adhesion. The goal of this work is to establish a critical load of adhesion with its confidence interval by a statistical analysis—piecewise linear regression—through the interface indentation test. In fact, because the critical load is not known, this is a nonlinear regression problem. This approach allowed estimation of the critical load P_C and its confidence interval.

Lesage (Ref 5) used the indentation test at the interface in hypersonic thermal sprayed coatings to determine the critical load of adhesion. Using logarithmic coordinates of crack, c, versus the indentation load, P, they obtained straight lines whose slopes were functions of the coating thickness. After annealing treatments at 873 K for 2 h, it was found that these straight lines intercepted at a single point corresponding to the apparent hardness of the coating and the substrate composite system. This apparent hardness could be represented by a straight line of slope 0,50 in a graph constructed by the relation between $\ln(d_r + d_s/4)$ and $\ln(P)$ (d_r and d_s being the diagonals of the indentations that would be obtained in the coating and substrate, respectively, under the action of load P).

The single point of intersection is called the critical load, P_C, and is the minimum value necessary to produce a crack at the interface. This value is close to that of basic adhesion since it was determined after removing residual stresses present in the coating (Eq 1).

The procedure that was carried out in this work is different from Lesage's (Ref 5). The apparent hardness has been obtained experimentally using a Vickers microhardness tester with increasing loads. Indentations were performed at the coating/substrate interface and the Vickers diagonals were considered precracks. According to brittle fracture mechanics, it is expected that the slope of the second linear spline will equal 0.67 (Ref 6) if the cracks produced are "half-penny" in morphology. A linear spline is a piecewise polynomial of order 1 (Ref 7). The authors have constructed a second linear spline for one coating thickness and have investigated the influence of heat treatment on the critical load adhesion of plasma sprayed coatings. The adhesion mechanisms as well as the residual stress effect have been changed by performing a post heat treatment. This procedure resulted in an increase of P_C. To ensure that the critical load was increased due to post heat treatment, the confidence intervals of the critical loads were estimated by statistical analysis. This analysis provided the standard asymptotic error related to the method specific error predicted in Eq 1.

2. Experimental Procedure

Three composite systems were produced for adhesion evaluation by changing either the substrate microstructure or the heat

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treatment. The coating system of 75%WC-Co + 25%Ni base alloy was kept constant. The substrates were sandblasted and the roughness, R_a, taken prior to coating.

The substrates used were of AISI E52100 steel. In the composite systems identified as CSI and CSIII, the steel substrates were used in the annealed condition. In the composite system CSII, the annealed steel was quenched and tempered prior to sandblasting. In the system CSIII, both coating and substrate were heat treated after plasma spraying.

Thermal spraying was performed with a Metco plasma gun, type 3MBII (Sulzer Metco, Westbury, NY), with the spray parameters recommended for the WC-Co: 71VF-NS Metco powder (Table 1) (Ref 8). The samples for interfacial indentation testing were prepared by taking cross sections that were mounted, grounded, and polished by conventional procedures (Ref 9), that is, cutting with an abrasive wheel; cold mounting under vacuum in low-viscosity epoxy resin; grinding with aluminum grinding paper in the sequence 60, 30, 15, and 9 µm; and polishing with diamond pastes 9, 3, and 1 µm, using alcohol as lubricant.

Surface observation and characterization were performed with a scanning electron microscope (SEM), which was used to take the composition profile along 20 µm across the coating/substrate interface (10 µm on each side, positioned 1 µm apart) and microprobe analysis of iron, tungsten, and cobalt, with an energy dispersive system. The microprobe analysis was performed at positions of 1 and 2 µm on each side of the coating/substrate interface.

After sample preparation, the Vickers indentation tests were performed under different loads. During testing, the indentations were produced to fall precisely at the coating/substrate interface, with its diagonals either perpendicular or parallel to it. For each composite system, five load values each were used in stages I and II.

The crack size c in stage I, according to Lima et al. (Ref 10), is given by:

$$c = \frac{a_h + a_v}{4} \quad \text{(Eq 2)}$$

where a_h is the size of the diagonal parallel to the interface and a_v is the diagonal size in the direction perpendicular to the interface.

Table 1 Plasma spraying parameters

Parameter	Value
Argon (Ar)	
Pressure, psi	100
Flux, L/min	46.7
Hydrogen (H_2)	
Pressure, psi	50
Flux, L/min Ar	4.7
Arc current, A	400
Arc voltage, V	61
Carrier gas flux, L/min Ar	6.3
Powder feed rate, g/min	60
Spray distance, mm	≅100

Source: Ref 8

For the indentations in stage II, the crack size c is given by the sum of the averages of the indentation diagonals and the left and right cracks parallel to the coating/substrate interface:

$$c = \left(\frac{a_h + a_v}{4}\right) + \left(\frac{c_d + c_e}{2}\right) \quad \text{(Eq 3)}$$

where c_d is the right-hand crack size and c_e is the left-hand crack size.

The crack dimensions in stage I were measured with a light microscope, and those in stage II were measured on SEM micrographs. In stage I five crack size values were reported for each load employed, and in stage II three crack size values were reported for each load value.

3. Statistical Procedure: Piecewise Linear Regression

An important case of practical interest involves the piecewise fitting of linear regression models of different groups of data. This can be treated using linear splines. Suppose that there is a single knot (the junction point of the pieces) at t and that there could be both a slope change and a discontinuity at the knot. Then the resulting model can be written as (Ref 7):

$$E(y) = S(x) = \beta_{00} + \beta_{01}x + \beta_{10}(x-t)_+^0 + \beta_{11}(x-t)_+^1$$

where the significance of $(x-t)_+^0$ and $(x-t)_+^1$ is:

$$(x-t)_+^0 = 1, \text{ if } x > t$$
$$= 0, \text{ if } x \le t$$

and

$$(x-t)_+^1 = (x-t), \text{ if } x > t$$
$$= 0, \text{ if } x \le t$$

Note that if $x \le t$, the straight-line model is:

$$E(y) = \beta_{00} + \beta_{01}x$$

and if $x > t$, the model is:

$$E(y) = \beta_{00} + \beta_{01}x + \beta_{10}(1) + \beta_{11}(x-t)$$
$$= (\beta_{00} + \beta_{10} - \beta_{11}t) + (\beta_{01} + \beta_{11})x$$

Therefore, if $x \le t$, the model has intercept β_{00} and slope β_{01}, while if $x > t$, the intercept is $(\beta_{00} + \beta_{10} - \beta_{11}t)$ and the slope is $(\beta_{01} + \beta_{11})$. This regression function is shown in Fig. 1. The parameter β_{10} represents the difference in mean response at the knot t.

However, in some cases of practical interest, the function must be continuous at the knot t. The estimation of critical loads is one of these cases. To determine the critical load P_C (i.e., at the knot t), both linear splines must be continuous so that a smooth function results. This is easily accomplished by deleting the term $\beta_{10}(x-t)_+^0$ from the original model (Ref 7):

$$E(y) = S(x) = \beta_{00} + \beta_{01}x + \beta_{11}(x - t)^1_+$$

In this case, if $x \le t$, the model is:

$$E(y) = \beta_{00} + \beta_{01}x$$

and if $x > t$, the model becomes:

$$E(y) = \beta_{00} + \beta_{01}x + \beta_{11}(x - t)$$

$$= (\beta_{00} - \beta_{11}t) + (\beta_{01} + \beta_{11})x$$

This piecewise regression function is shown in Fig. 2.

When the knot point t is unknown it becomes a parameter to be estimated, and the resulting problem is a nonlinear regression problem (Ref 7). Then the estimation of the critical adhesion load P_C (knot t) is a nonlinear regression problem.

A method widely used in computer algorithms (Ref 11) is linearization of the nonlinear function followed by the Gauss-Newton iteration method of parameter estimation. Linearization is accomplished by a Taylor series of the function around the point defined by the estimates of the unknown parameters. Only the linear terms are retained. The Gauss-Newton procedure may converge slowly in some cases, requiring many iterations. The fitting of a nonlinear regression model requires starting values to estimate parameters, and values that are close to the true parameters will minimize convergence difficulties.

The following model was proposed in the STATISTICA software, release 4.2 (StatSoft Inc., Tulsa, OK):

$$y = A + Bx + C(x - D)(x > D) + \varepsilon \qquad \text{(Eq 4)}$$

where $y = \ln(P)$; $x = \ln(c)$; A, B, C, and D are the parameters to be estimated by the STATISTICA program.

For $\ln(P) \le D$, the model is $\ln(c) = A + B \ln(P)$ and for $\ln(P) > D$, the model becomes $\ln(c) = (A - CD) + (B + C) \ln(P)$.

In this model the parameter D is the knot point and is equal to $\ln(P_C)$ of each composite system. This software was used to:

1. Estimate the parameters of the regression model
2. Estimate the confidence intervals for each parameter of the regression model
3. Evaluate statistically if the systems have different critical loads
4. Evaluate statistically the adequacy of the fitted model

In agreement with theoretical considerations already presented, it is expected that the slope of the linear spline, in stage I, be 0.50. In stage II, the theory of brittle fracture mechanics establishes that the slope of the linear spline must be 0.67.

Concerning the critical load P_C, it is known when there is a change from stage I to stage II. In agreement with the experimental data, it is expected that the critical loads of the composite systems range between the following load intervals:

- $14.7 \text{ N} \le P_C \le 17.7 \text{ N}$ for CSI
- $2.94 \text{ N} \le P_C \le 4.90 \text{ N}$ for CSII
- $34.3 \text{ N} \le P_C \le 39.2 \text{ N}$ for CSIII

The starting values of the estimated parameters were chosen according to these previous considerations. The starting value chosen for B (slope in stage I) in all systems was 0.50; the starting value chosen for C (see Eq 4) was 0.17, since $B + C$ (slope in stage II) should be 0.67. The starting value of the parameter A was chosen randomly. Finally the starting value of the parameter D (critical load), for each of the composite systems, was chosen in the load range mentioned above. These starting values were varied to verify whether the model converged to the same result. Several combinations of starting values were used for each system, and it was verified that in all sets the values estimated for A, B, C, and D were consistent.

Two different algorithms were used to estimate the parameters: the Quasi-Newton and the SIMPLEX. For each group of starting values, both algorithms provided the same results. However, it was noticed that convergence was slower when the SIMPLEX algorithm was used. The loss function used was (Observed value – Predicted value) (Ref 11).

The model adequacy was evaluated by the R^2 coefficient value, the percentage of explained variance, a test of p-value for each estimated parameter, and residual analysis.

4. Results and Discussion

Table 2 shows the R_a roughness values of AISI E52100 steel substrates after sandblasting.

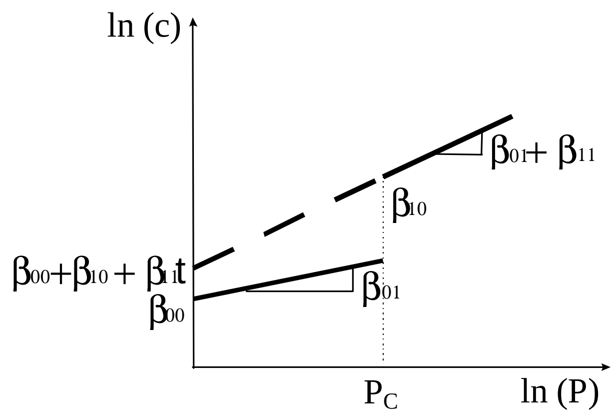

Fig. 1 Piecewise linear regression model: discontinuity at the knot t, that is P_C (Ref 7)

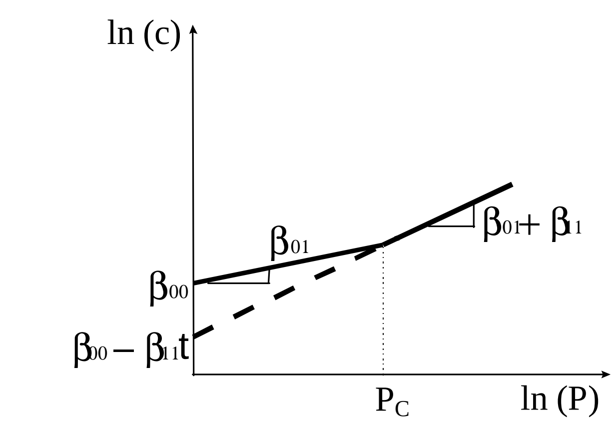

Fig. 2 Continuous piecewise linear regression model (Ref 7)

The iron, tungsten, and cobalt composition profiles obtained across the coating/substrate interface showed the presence of interdiffusion after heat treatment. These results were already published in a previous paper on this subject (Ref 12). The composition profiles in the CSI and CSII systems are very similar. This could be expected since neither one of them was heat treated after coating. The variation in composition among these coatings reflects the difference in composition of the distinct phases from which they were made. It should be pointed out that the high cobalt signal in the substrate is an artifact since the Co Kα energy level coincides with the one from Fe Kβ. The CSIII system, which was heat treated after coating, presents differences relative to the CSI and CSII. For example, its iron profile in the coating, up to 2 μm from the interface, slightly increased during heat treatment. The results also indicate that the cobalt content in the substrate increased. The tungsten profile, however, showed no significant change. The EDS microprobe spot analysis confirms the profile analysis since it shows no significant differences between the CSI and CSII systems. It also shows that in the CSIII system there was an increase in iron in the coating and an increase in cobalt in the substrate. No changes were noticed in tungsten content in the coating and in the substrate.

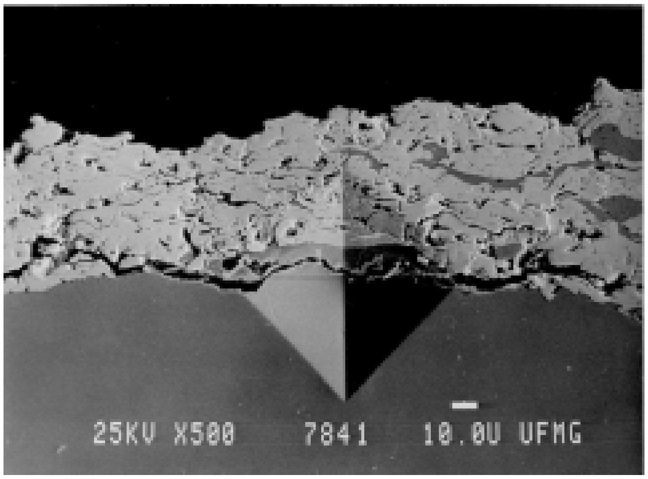

Fig. 3 Indentation in the CSII system with interface cracks. Load, 14.7 N. 500×. SEM

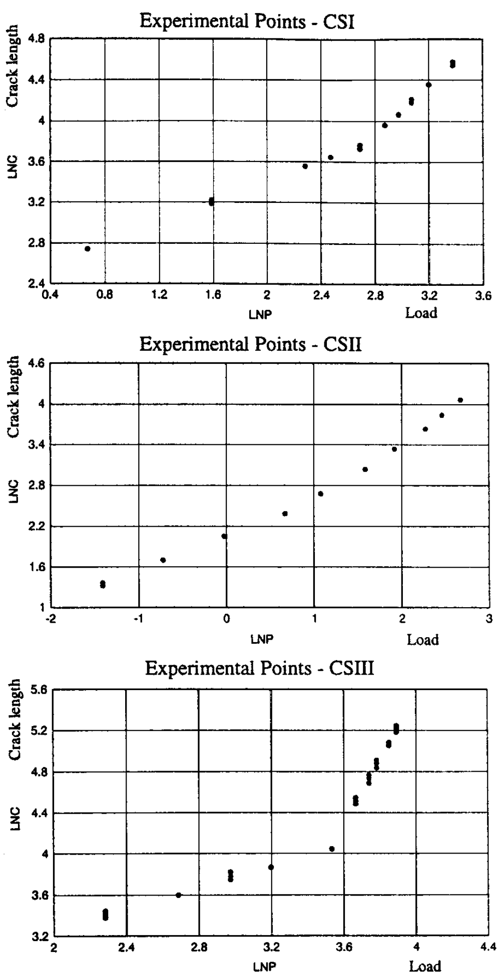

Fig. 4 ln(c) versus ln(P) plots of the composite systems CSI, CSII, and CSIII

These results indicate a significant interdiffusion of iron and cobalt during heat treatment. A minimum (x_{min}) and maximum (x_{max}) diffusion distance can be estimated by considering the austenitization time and temperature (Ref 12), since tempering was performed at 448 K. Since T/T_m (homologous temperature) is about 0.7, for both coating and substrate, it is expected that the diffusion coefficients of iron, cobalt, and tungsten are within the range 10^{-10} to 10^{-12} cm^2/s (Ref 13). Calculations considering this range indicate that $x_{min} = 0.42$ μm and $x_{max} = 4.2$ μm for iron and cobalt (Ref 12, 14). The interdiffusion distances of iron and cobalt that were detected by microprobe analysis and profile analysis (Ref 12, 14) ranged in this interval.

Table 2 Roughness values R_a of AISI E52100 steel substrates after sand blasting

	Heat treated	Annealed
R_a, μm	5.2 ± 0.4	10.0 ± 0.7

Table 3 Results from the nonlinear regression analysis

	CSI	CSII	CSIII
R^2	0.99945	0.99948	0.99928
Explained variance, %	99.890	99.896	99.856
Final loss	0.011940420	0.03320249	0.02597027
A	2.4001	2.0563	2.2522
B	0.50030	0.51956	0.50650
C	0.68619	0.40885	2.7372
D	2.7069	1.2744	3.5319
Standard error of A	0.01030	0.0059	0.04387
Standard error of B	0.00500	0.0065	0.01557
Standard error of C	0.25640	0.02047	0.05698
Standard error of D	0.01740	0.05393	0.00890
p-value of A	0.0000	0.0000	0.0000
p-value of B	0.0000	0.0000	0.0000
p-value of C	0.0000	0.0000	0.0000
p-value of D	0.0000	0.0000	0.0000
CI (95%) of A	[2.3826; 2.4176]	[2.0463; 2.0663]	[2.1778; 2.3267]
CI (95%) of B	[0.49182; 0.50879]	[0.50846; 0.53066]	[0.48008; 0.53292]
CI (95%) of C	[0.64268; 0.72970]	[0.37411; 0.44359]	[2.6405; 2.8339]
CI (95%) of D	[2.6774 ; 2.7364]	[1.1829; 1.3659]	[3.5230; 3.5408]

Figure 3 illustrates a typical indentation in the CSII system, where interface cracks can be noted.

The experimental points (crack size *c* versus load *P*) are shown in Fig. 4. The plots ln(*c*) versus ln(*P*) show that the CSIII system has the most significant slope change. In the CSII system this change is quite smooth.

The results from the nonlinear regression analysis, including the estimated values of parameters *A*, *B*, *C*, and *D* and their 95% confidence intervals (CI), are shown in Table 3. The normal probability plots of residuals and the residuals versus predicted values plots are shown, respectively, in Fig. 5 and 6. The high values of R^2 and percent of explained variance obtained in all composite systems indicate that the model is quite good. The four estimated parameters (*A*, *B*, *C*, and *D*) have also been successful in the *p*-value test. All of them have significant importance in the adjusted model.

The normal probability plots of residuals indicate that they have a normal distribution in all systems. The residuals versus predicted values plots show that CSI and CSIII systems have constant variance and confirm a good fit for the adjusted model. However, the residuals versus predicted values plot of CSII shows different behavior from the two other systems.

Although it has constant variance, the different behavior of CSII can be attributed to the load being a fixed variable. The microhardness tester equipment limits the choice of load values. Depending on the work range, large intervals between loads can be produced. As a consequence, there were large intervals in the space of the *x* variable (i.e., ln(*P*)).

The correlation matrices (Ref 12) indicated that the parameters *A* and *B* had strong correlation in the composite systems CSI and CSIII . However, such correlation between the parameters *A* and *B* could not avoid their estimation and the standard error associated with each of them.

Table 4 Slope and intercept values of the linear splines associated with stages I and II

	CSI		CSII		CSIII	
	Stage I	Stage II	Stage I	Stage II	Stage I	Stage II
Slope	0.500	1.187	0.520	0.928	0.507	3.244
Intercept	2.400	1.046	2.056	1.535	2.252	–7.415

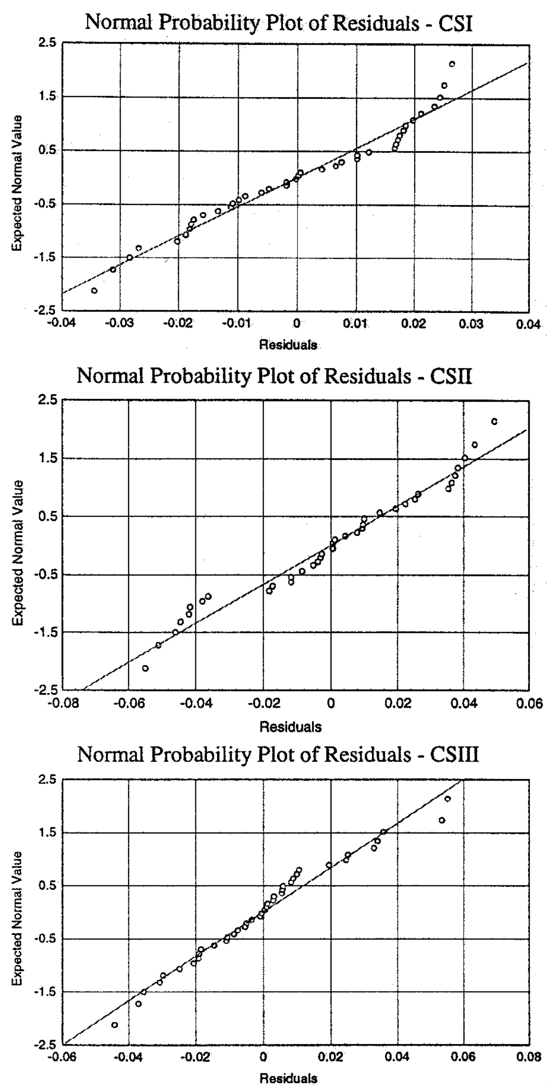

Fig. 5 Normal probability plots of residuals for CSI, CSII, and CSIII

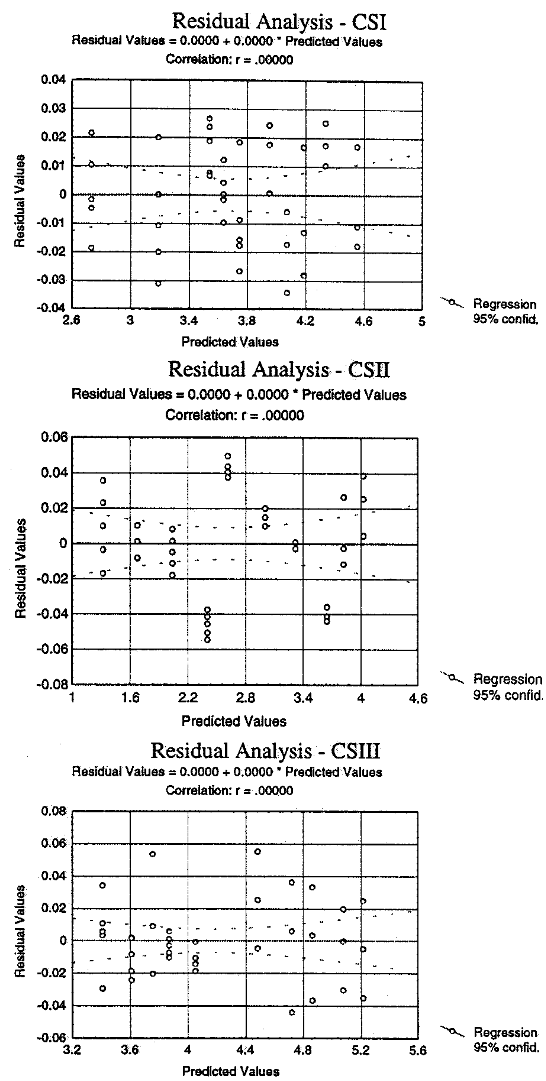

Fig. 6 Residuals versus predicted values plotted for CSI, CSII, and CSIII

Table 5 Critical load (P_C), critical crack size (c_C), and confidence interval (CI) (95%) of P_C

Composite system	P_C, N	CI (95%) of P_C	c_C, μm
CSI	14.98	[14.55; 15.43]	42.21
CSII	3.577	[3.264; 3.919]	15.16
CSIII	34.19	[33.89; 34.49]	56.89

The slope and intercept values provided by the nonlinear regression analysis are shown in Table 4.

The confidence interval of parameter B (CI (95%) of B in Table 3) shows that CSI and CSIII systems have slopes equal to 0.50 in stage I. However, the CSII system has a slightly different slope from 0.50 in stage I. The slopes obtained in stage II for all three composite systems are larger than the expected value 0.67, especially in system CSIII. Similar results have already been reported by Lesage (Ref 5).The critical load P_C, its CI, and the critical crack size c_C are shown in Table 5.

The CIs of the critical loads show statistically that the CSIII system has better adhesion at the substrate/coating interface and system CSII has poorer adhesion.

The estimated values of P_C in the nonlinear regression analysis are situated in the load range where it was experimentally observed to transition from stage I to stage II. The P_C value of CSIII system (34.19 N) is slightly smaller than the last load value in which cracks were not observed by SEM (34.3 N).

Table 5 indicates that post heat treatment increases the critical practical load, that is, EA.

This increase in the practical adhesion might be attributed to metallurgical bonds that were created at the coating/substrate interface during heat treatment.

The statistical model of piecewise linear regression with knot estimation is quite good for evaluating adhesion in coating/substrate interfaces of composite systems. This statistical approach makes possible estimation of both the critical load P_C and its CI. The CI estimation is the only way to ensure that critical load values were changed by heat treatment.

Quenching and tempering prior to sandblasting inhibited adhesion by limiting roughness and, therefore, decreasing mechanical interlocking between coating and substrate and is supported by the lower value of P_C for the CSII system.

The residual statistical analysis indicates a limitation in the equipment used to perform the interfacial adhesion test. The microhardness tester limits the load values, and the x variable ($\ln(P)$) becomes fixed. It would be better if the interval between load values were narrowed in order to prevent large intervals in the space of the variable $\ln(P)$. This procedure would result in a more reliable residual analysis.

5. Conclusions

- Post heat treatment increases the critical practical adhesion load of plasma sprayed 75%WC-Co + 25%Ni-base alloy coatings.
- The statistical model of piecewise linear regression with knot estimation is essential to estimate with good confidence changes in critical adhesion loads. This statistical approach has made it possible to estimate both the critical load P_C and its CI.
- Interdiffusion is an effective mechanism to increase the critical adhesion load in thermal sprayed coatings.

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