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ANALYSIS OF SHEAR BOND STRENGTH OF PLASMA-SPRAYED ALUMINA COATINGS ON STAINLESS STEEL

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SUMMARY

The effects of various surface roughness conditions and spray powders on the shear bond strength of plasma-sprayed alumina coatings on AISI 304 stainless steel were investigated. Substrate root-mean-square surface roughness values examined ranged from near 0 to 280 microinches with intermediate values at 115 and 225 microinches. Spray powders varied in particle size range, size distribution, median particle size, and purity.

Coatings on polished surfaces showed zero bond strength, which indicated that the coating-substrate bond was predominantly mechanical. Increased surface roughness resulted in increased bond strengths for all coatings. Increased median spray powder particle size and uniformity also contributed to higher bond strengths. The highest median bond strengths (380, 540, and 600 lb/sq in. at surface roughnesses of 115, 225, and 280 μin. on 0.301-sq in. specimens) were obtained with the highest purity spray powder and particle sizes ranging from 3.4 to 37.9 microns, a uniform particle size distribution, and a median particle size of 15.9 microns. For this material, as for the others, the highest bond strengths were obtained on 280-microinch surfaces.

The bond strength data were analyzed by Weibull statistical methods. The measured bond strengths decreased with increasing test areas (over the range from 0.05 to 0.43 sq in.). This decrease was approximated by curves based on probability theory calculations.

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*The material presented herein is included in the thesis submitted by the author to Case Institute of Technology in May 1964 in partial fulfillment of the requirements for the degree Master of Science.

TABLE I. - CHARACTERISTICS OF AS-RECEIVED ALUMINA SPRAY POWDERS

Powder[a]	Supplier's chemical analysis		Size range, μ	Median particle size, μ
	Concentration, weight percent	Compound		
A	97.5	Aluminum oxide	3.9 to 46.0	18.8
	2.5	Titanium oxide		
B	98.0	Aluminum oxide	3.7 to 38.9	8.6
	2.0	Silicon, ferrous, and sodium oxides		
C	99.49	Aluminum oxide	7.3 to 82.0	11.4
	.05	Silicon oxide		
	.1	Ferrous oxide		
	.1	Titanium oxide		
	.35	Sodium oxide		
D	99.49	Aluminum oxide	3.4 to 37.9	15.9
	.05	Silicon oxide		
	.1	Ferrous oxide		
	.1	Titanium oxide		
	.35	Sodium oxide		

[a]All powders determined to be 100 percent alpha alumina by X-ray diffraction analysis.

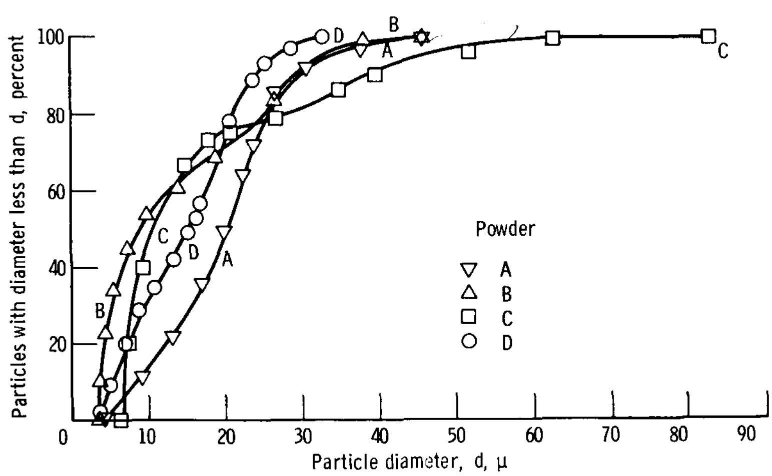

Figure 1. - Particle-size distribution of 500 particles of four alumina spray powders.

INTRODUCTION

Plasma-sprayed ceramic oxide coatings are used as thermal barriers on metallic structural materials in many aerospace applications. The inherent mismatch in the thermal expansion between coating and substrate materials has frequently caused the interfacial stress to exceed the bond strength. Under such conditions the coating spalls and the bare metal substrate is exposed to the adverse thermal environment. Thus, the stress at which the bond between an oxide coating and a metallic substrate fails and the factors which affect the failure stress have important significance in the design of coated parts.

Previous attempts to develop a test capable of providing reliable, quantitative data on the stress necessary to shear a thermal sprayed oxide coating from a substrate have not been entirely satisfactory. Such tests have usually involved shearing the coatings off cylindrical mandrels (ref. 1) or pulling a coated sheet through a set of rigid jaws (ref. 2). In these tests, the stress on the bond is extremely nonuniform. For this reason, a testing technique was developed at the NASA Lewis Research Center in which the stress distribution at the coating-substrate interface is more uniform (ref. 3).

The object of the present investigation was to evaluate, by means of this test, the effects of spray-powder particle-size distributions, powder purity, and substrate-surface roughness on the measured bond strength of alumina coatings plasma-sprayed onto stainless steel substrates. The resultant bond strength data were analyzed by Weibull statistical methods.

MATERIALS

Four commercial alumina spray powders, designated A, B, C, and D[1] were employed in this investigation. The chemical analysis, X-ray diffraction identification, particle-size range, and median particle size for each powder are presented in table I. Figure 1 represents the actual particle-size distribution summation for each of the four powders, as determined by optically measuring and counting 500 particles. Figure 1 shows that powders B and C contain a greater percentage of particles below 10 microns than do powders A and D. Furthermore, powder C also contains some very large particles. Powders A and D, on the other hand, have a high percentage of particles between 10 and 35 microns; that is, they have a more uniform particle-size distribution with low percentages of fine (less than 10μ) and coarse particles. The substrate material was 1/4-inch-thick AISI 304 stainless steel.

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[1]Suppliers designation and name available to qualified requesters from author.

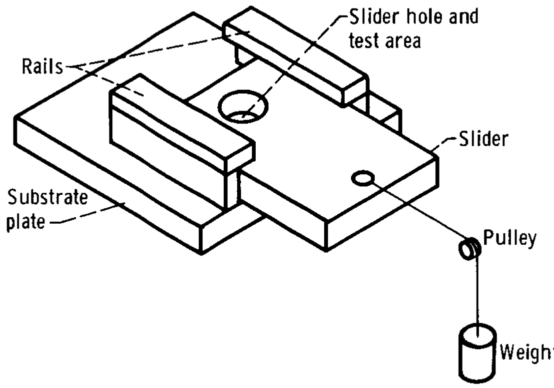

Figure 2. - Apparatus for bond shear-strength test.

APPARATUS AND PROCEDURE

The bond shear test apparatus, shown schematically in figure 2, consists of a 1/4-inch stainless-steel substrate plate to which is bolted a pair of steel rails. The rails act as guides for a movable slider (also 1/4-in. stainless steel). All mating clearances are approximately 0.002 inch.

In this test, the larger hole in the slider exposes a fixed area of the plate beneath it, which serves as the test area. Prior to coating, that portion of the substrate plate between the rails was polished to a measured root-mean-square surface roughness of less than 3 microinches. The test area was then, in most cases, roughened by sand or grit blasting (with the slider acting as a mask) to measured root-mean-square roughnesses of approximately 115, 225, or 280 microinches. After acetone cleaning, the slider was carefully replaced in its original position.

Coatings approximately 0.030 inch thick were deposited on the test areas through the hole in the slider by means of a commercial plasma torch under the following operating conditions (ref. 4):

Arc current, A	400
Arc voltage, V	70
Plasma gas flow, standard cu ft/hr	
High-purity dry nitrogen	100
Hydrogen	15
Nitrogen carrier gas flow, standard cu ft/hr	10
Powder feed rate, lb/hr	~2
Torch-to-substrate distance, in.	6

During deposition, the substrate was cooled by air blowing on the face opposite from that being coated. The substrate temperature (measured 0.030 in. below the surface being coated by an embedded thermocouple) was never greater than 360° F and usually averaged 330° F. This temperature was reached in a few seconds during coating deposition. After spray-coating for about 2 minutes, the torch was shut off and the test assembly cooled to room temperature under the continued application of the cooling airstream. Cooling to room temperature took approximately 10 minutes.

Although the front face of the assembly was covered with brass shim stock to prevent spray particles from reaching any place other than the test area, the cool assembly was vacuumed to remove any stray alumina powder. The assembly was then mounted horizontally on a test stand, a cable and a weight holder were attached to the slider, and the coating-substrate interface was deadweight-loaded in 1-pound increments until shear failure occurred. Failure was rapid as soon as a critical stress was reached.

The uniformity of interfacial loading can be inferred from the fact that the coating remained intact in the slider hole. Further indication of uniformity is provided by reference 5, which reports the results of photoelastic stress studies on a similar shear disk developed to evaluate structural adhesives.

In this study, the effects of surface roughness and spray powder on the shear bond strength were determined by a minimum of 10 trials per combination of powder and roughness. All final tests were conducted on 5/8-inch-diameter test areas, and bond strengths were calculated on the basis of this projected geometrical area[2], that is, $\pi(5/16)^2$. These data were analyzed by standard and statistical means. The effect of test area (i.e., different slider hole sizes) was also briefly investigated. Finally, selected coatings and substrates were examined microscopically, and representative as-sheared coatings were subjected to X-ray analysis.

RESULTS AND DISCUSSION

Weibull Analysis of Data

All the bond failures apparently occurred by brittle fracture; therefore, the use of Weibull analysis techniques, developed to examine brittle fracture data, appeared feasible.

The data for all the tests on the 5/8-inch-diameter test areas are displayed on Weibull plots in figure 3 (p. 6). In such plots, the log log of the reciprocal of the probability of survival (or 1 minus the failure probability), graduated in statistical percent of specimens failed, is plotted against the log of the bond strength. The slope of a Weibull plot is designated m. The value of m is an index of material homogeneity and failure reproducibility; that is, higher values of m indicate more predictable failure behavior. (A more detailed description of the Weibull analysis is presented in appendix A.)

Figure 3 shows how both the magnitude and the slopes of the bond strength distribu-

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[2]Some specimens were roughened by identical procedures, and true area calculations were made on the basis of surface profile traces. Values obtained ranged from approximately 3 percent greater than projected geometrical area for 115-μin. surfaces to approximately 11 percent greater for 280-μin. surfaces. Because of these small differences and the relative uncertainty of the evaluation technique, stress calculations were based on projected area.

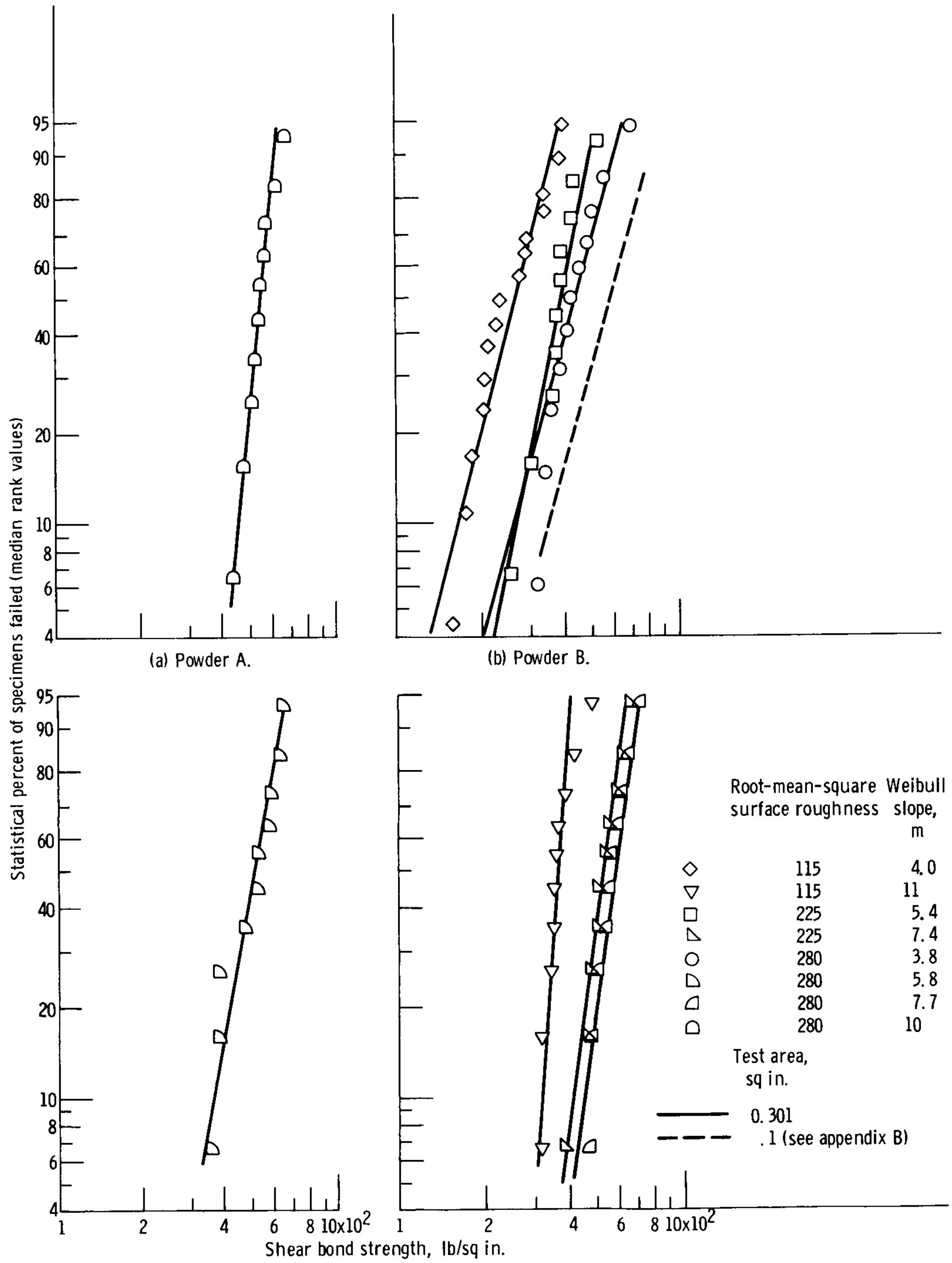

Figure 3. - Weibull plots of bond shear-strength data for coatings of four spray powders on surfaces of varying roughness.

TABLE II. - BOND STRENGTH DATA AND ANALYSIS SUMMARY FOR COATINGS OF ALUMINA POWDERS SPRAYED ONTO STAINLESS STEEL SUBSTRATES OF VARYING ROUGHNESS

Powder	Root-mean-square surface roughness, μin.	Median bond strength, lb/sq in.	Weibull slope[a]
A	280	545	10
B	<3	~0	-----
	115	270	[b]4.0
	225	390	5.4
	280	440	[b]3.8
C	280	510	5.8
D	<3	~0	-----
	115	380	11
	225	540	7.4
	280	600	7.7

[a]Assuming $X_u = 0$.
[b]Least mean square.

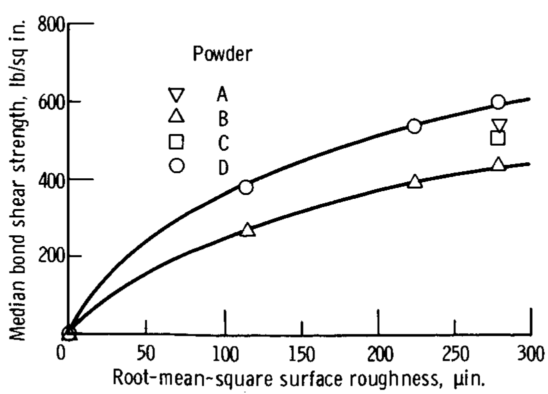

Figure 4. - Median bond shear strength (50 percent failed value) for four alumina spray powders on stainless steel substrates of varying roughness (see fig. 3).

tions vary with the different surface roughnesses and spray powders employed in this investigation. It also shows the way the experimental data fit the Weibull distribution. The important data from figure 3 are summarized in table II and will be discussed in the following sections.

Effect of substrate roughness. - The effect of substrate roughness on median bond strength (i.e., the bond strength on the Weibull plots (fig. 3) at which 50 statistical percent of the specimens failed) is graphically presented in figure 4. This figure shows that coatings deposited on polished surfaces with a measured root-mean-square surface roughness of less than 3 microinches (essentially zero) have zero bond strength. This indicates that there is no significant chemical or diffusional bond between stainless steel and alumina under the deposition conditions employed. Furthermore, figure 4 shows that with increasing surface roughness the bond strengths increase, but the effect becomes less pronounced at higher levels. Thus, it can be concluded that the bond is predominantly due to mechanical interlocking.

Effect of materials variables on bond strength. - Different spray powder sizes produce coatings with different median bond strengths at any given roughness level (fig. 4). At 280 microinches, the powders rank, according to median bond strength, D, A, C, and B. From the particle size distributions for the four powders (fig. 1), it appears that those powders with a higher percentage of

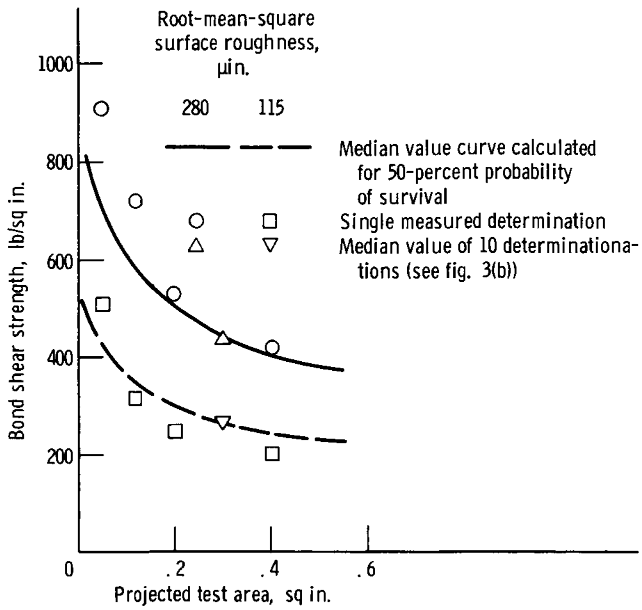

Figure 5. - Effect of projected test area on measured and calculated bond shear strength of powder-B coatings at two surface roughnesses.

intermediate-size particles (between 10 and 35μ) and with a more uniform particle size distribution produce coatings with higher bond strengths. Comparison of tables I and II indicates no correlation between total powder impurity content and median bond strength.

The fracture mode is also important, and the degree of interfacial failure can vary with coatings of different powders. In this investigation, coatings of powder D showed less interfacial failure than did coatings of powders A, B, and C; evidently the bond strengths of coatings sprayed from powder D were close to the shear strength of the deposited coating material. This may be associated with the smaller particle-size range of powder D.

Effect of area on bond strength. - Figure 5 shows the experimental bond strengths which were determined for coatings of powder B deposited on various sizes of test areas preroughened to two levels of root-mean-square-surface roughness (115 and 280 μin.). Figure 5 also includes curves representing the calculated relation between test area and bond strength, based on probability theory. The points necessary to plot the curves in figure 5 were obtained by a technique presented in reference 6 (see appendix B).

It can be seen that the calculated mean bond strengths are high for small test areas, but gradually decrease with increasing test area. The measured values of bond strength, representing only one experimental determination, approximate the calculated curves.

This size effect on strength is consistent with similar observations on the mechanical properties of ceramic oxides (ref. 7) and gives an insight into the wide differences in the bond-strength levels of coating-substrate systems (for an example, see ref. 8).

The influence of test area on bond strength was considered when the final test area was selected. The value of 0.301 square inch (5/8-in. diam.) was chosen since this area fell on the flatter portion of the curve of strength plotted against area and thus tended to eliminate unrealistically high measurements associated with smaller test areas.

Microscopic and X-ray Analyses

Metallographic examination of representative coating-substrate cross sections indicated few observable differences among the coatings of the four alumina powders. All

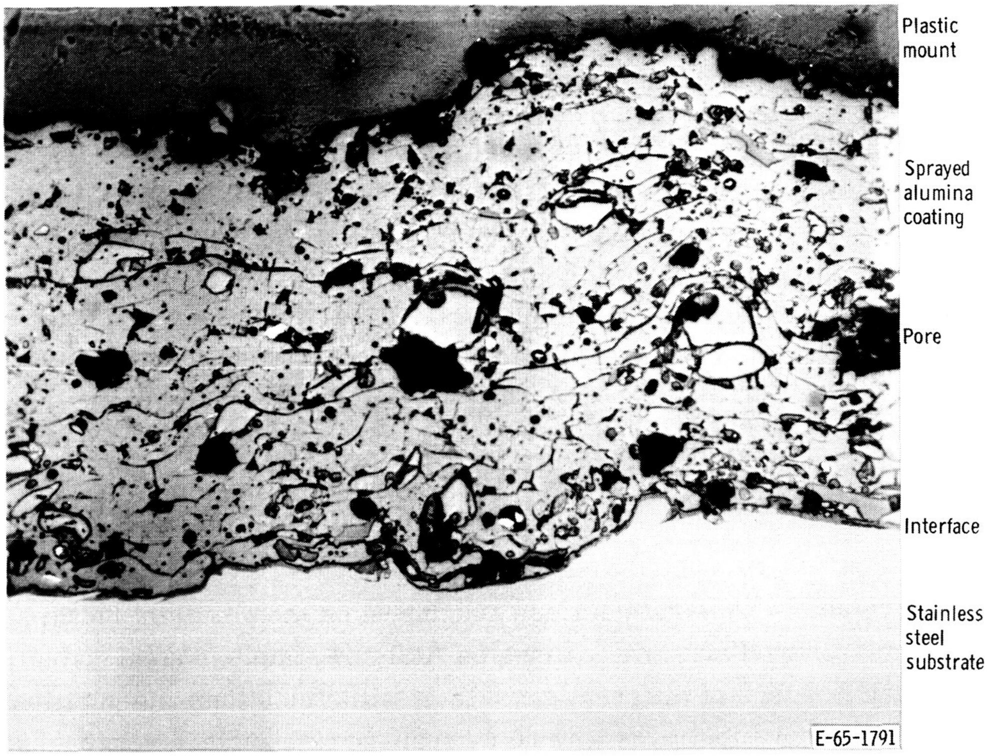

Figure 6. - Cross section of alumina coating of powder D on 304 stainless steel with a root-mean-square surface roughness of 280. Unetched. X250.

coatings showed good penetration into the depressions of the roughened substrate, but no evidence of any coating-substrate interaction was observed. A typical micrograph of a coating-substrate cross section is shown in figure 6 (This figure represents a small metallographic specimen, and the coating is thinner here than on those specimens normally tested). Some porosity is apparent, but a portion of it can be attributed to local loss of coating during polishing. The nonhomogeneous structure is typical of sprayed aluminum oxide coatings.

Substrates were examined after each shear test. Although coating separation occurred predominantly at the interface, some small fragments of coating remained randomly entrapped in the substrate depressions. Visual examination revealed that, for coatings of powders A, B, and C, about 10 percent of the substrate depressions contained entrapped coating fragments. For coatings of powder D, the amount of entrapped material was usually about 30 percent. Such residual fragments indicate that brittle fracture occurred partially through sections of the coating itself, rather than by total separation at the interface.

The as-sheared coatings were also examined. The face that was originally in contact with the substrate was rather rough, since it had conformed to the peaks and valleys of the substrate. In every case, some inclusions were detected at this interface. From the appearance of these inclusions on the metalloscope, they are believed to have been metallic. Since these inclusions were heavily concentrated on the face that was orginally in contact with the substrate, they appear to have been the result of the shearing-off of some substrate peaks.

X-ray diffraction analysis on the as-sheared coatings showed that those of powder C had approximately 50 percent alpha and 50 percent gamma alumina at the original substrate interface, while those of the other three powders consisted of 95 to 100 percent gamma alumina at the interface. The lower amount of gamma alumina in coatings of powder C (7.3 to 82μ) was expected, since the larger particles in this powder could not cool rapidly enough to transform to the gamma phase completely.

SUMMARY OF RESULTS

An investigation was conducted to determine the effects of variations in spray-powder size and chemistry and in substrate surface roughness on the resultant bond shear strength of plasma-sprayed alumina coatings on AISI 304 stainless steel. Coatings of four alumina spray powders of different particle-size distributions and purities were deposited on stainless steel substrates with root-mean-square surface roughnesses of approximately 3, 115, 225, and 280 microinches. Test areas ranged from 0.05 to 0.43 square inch with the majority of testing being conducted on an area of 0.301 square inch. The resultant data were analyzed by Weibull statistical methods. The following results were obtained:

1. A high-purity spray powder (powder D) having the narrowest particle size range (3.4 to 37.9μ), a moderately high median particle size (15.9μ), and a relatively uniform size distribution produced coatings having the highest median bond strength on all intentionally roughened surfaces. Coatings of this material failed less at the coating-substrate interface than did those of the other materials, which indicated that coating shear strength, as well as bond strength, is an important factor to be considered in future tests.

2. Powders A and D, with higher percentages of particles between 10 and 35 microns (lower percentages of coarse or fine particles) and higher median particle sizes, produced coatings with higher bond strengths, which indicated that particle-size uniformity contributed to better bonding in the range investigated. Furthermore, the Weibull plots for coatings of these materials had higher slopes and thus more reproducible data.

3. The bond strength of all coatings deposited on polished surfaces was zero, which indicated a predominantly mechanical bond. Increasing the surface roughness of the stainless steel substrates resulted in an increase in the bond shear strengths, but this effect became less pronounced at increasing roughness values. Median bond shear strengths for coatings of powders A, B, C, and D on 280-microinch surfaces (0.301-sq in. test area) were 545, 440, 510, and 600 pounds per square inch, respectively.

4. The measured bond strengths decreased with increasing test areas over the range investigated (from 0.05 to 0.43 sq in.). This decrease was approximated by curves based on probability theory calculations.

5. There was no apparent relation between the total impurity content of the four alumina spray powders and the bond strengths of the resultant plasma-sprayed coatings.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 16, 1965.

APPENDIX A

WEIBULL ANALYSIS TECHNIQUE

The Weibull distribution function is an empirical expression of the probability of occurrence of an event and approximates a wide variety of data distributions. In its simplest form, the Weibull distribution function (refs. 7 and 9) is expressed as

$$F_x = 1 - \exp\left[-\left(\frac{X - X_u}{X_o}\right)^m\right]$$

where the parameters, in terms of this investigation, are

F_x statistical fraction of specimens which, when tested at one set of conditions, failed at given stress or lower

X stress

X_u stress below which no specimens failed

X_o characteristic strength, stress at which 63.2 percent of specimens failed

m Weibull slope

The Weibull slope m is a measure of flaw distribution and size and an indication of material homogeneity; that is, a high value of m indicates that the material is homogeneous and has a uniform density of flaws. The value of m is also affected by the reproducibility of the testing technique. This analysis is most easily carried out by a rearrangement of the Weibull function as follows:

$$\log \log\left(\frac{1}{1 - F_x}\right) = m \log(X - X_u) - m \log X_o + \log \log e$$

In this form, a plot of the distribution function will be linear in a system where log log $[1/(1 - F_x)]$ is the ordinate and log $(X - X_u)$ is the abscissa.

Values of F_x are obtained by arranging each set of data in order of increasing failure stress. Each value, then, has a position in this list, that is, an order number. Then, from suitable tables (ref. 10), each order number is converted to a median rank, which is the value of F_x used for that particular observation.

The values of F_x and $X - X_u$ can be plotted directly on specially designed Weibull coordinate paper as the log log of the reciprocal of the probability of survival (or the reciprocal of 1 minus the failure probability), graduated in statistical percent of specimens failed, as a function of the log of strength. For the correct value of X_u, the plot will be linear.

If the original data plot is a straight line, then $X_u = 0$ (i.e., the lower limit of the failure stress is zero). If the original data plot is concave downward, then $X_u \neq 0$ (i.e., there is some finite stress below which no specimens ever fail). Trial and error approximations of X_u can then be substituted into $X - X_u$ until the plot becomes linear. (If the trial value chosen is greater than the correct X_u, the plot will be concave upward.) Once a linear plot is achieved, the slope m of the line can be measured directly.

APPENDIX B

FAILURE PROBABILITY AS FUNCTION OF TEST AREA SIZE

If S_1 is the probability of survival of a coating on an area A_1, the probability of survival S_2 of an identical coating on a test area A_2 tested under the same conditions is

$$S_2 = S_1^{(A_2/A_1)}$$

(For a similar approach, see ref. 6.) The failure probability is 1 minus the survival probability, or

$$F_{X,2} = 1 - S_2 = 1 - (S_1)^{A_2/A_1}$$

For example, in this investigation the test area for most of the tests was 0.301 square inch. For a similar coating on a test area of only 0.1 square inch, the area ratio A_2/A_1 would be 0.333. Consider the median bond strength value obtained for the larger test area as the starting point, although the comparison can be made at any level of failure probability. The 50 statistical percent probability of survival is

$$S_1 = 0.5$$

and the 50 statistical percent probability of failure is

$$F_1 = 0.5$$

Hence,

$$S_2 = (S_1)^{A_2/A_1} = (0.5)^{0.333} = 0.8$$

and

$$F_{X,2} = 1 - S_2 = 0.2$$

Thus, at the same bond strength at which the failure probability is 50 percent for a 0.301-square-inch test area, it is only 20 percent for a 0.1-square-inch test area. This operation can be illustrated for the data at 280 microinches in figure 3(b) (p. 6). The 50-percent value ($S_1 = F_{X,1} = 0.5$) is 440 pounds per square inch. The 20-percent value for the smaller area is found by moving vertically downward. This value is a point on the approximate Weibull plot for the smaller test specimens. If a line is drawn through this point parallel to the Weibull plot for the 280 surfaces with a test area of 0.301 square inch, the approximate Weibull distribution for similar coatings with a test area of 0.1 square inch is obtained.

Where this approximate Weibull plot intercepts the 50-percent failure level, the median strength is established. Median strengths obtained in this manner were employed to plot the curves in figure 5 (p. 8).

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