

THE VARIABILITY IN STRENGTH OF THERMALLY SPRAYED COATINGS*

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Summary

There is a large variability in the bond strengths of coatings which are determined by the tensile adhesion test method. The primary intention of this work is to establish a suitable parameter which measures the strength variability of thermally sprayed coatings, as well as a meaningful parameter to index that strength. The Weibull modulus for metal (*e.g.* mild steel) and ceramic (*e.g.* zirconia, alumina) coatings has been found and then related to the defect nature of the coating.

This work has shown that the Weibull analysis method is a pertinent parameter to examine in the case of thermally sprayed coatings. The testing methods allow an "index of integrity" to be established for thermally sprayed coatings, involving both the Weibull modulus m and the characteristic value σ_0 so that interlaboratory tests or products from different manufacturers can be compared and contrasted.

1. Introduction

A common factor in many of the existing standard tensile adhesion tests (TATs) is the small number of samples required, typically five [1, 2]. This, combined with the relative simplicity of the test method itself, has doubtless made the TAT so popular. However, these very factors raise serious questions concerning the statistical validity of the TAT in its present form and to its applicability in assessing the strength of thermally sprayed coatings. "Strength" of coatings is rather illdefined and may be of lesser relevance to coating technology than shear strength or toughness. A related concern is that any property measurement should give some insight into the microstructural behaviour of coatings.

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Discontent with existing TAT standards is apparent in the literature where doubts concerning the procedure, analysis and accuracy of results are openly expressed [3, 4]. It is the purpose of this work to present the preliminary findings of an investigation into the significance of data obtained from a standard TAT (ASTM C633) when it is carried out on a statistically significant sample size. The suitability of an analysis based on the two-parameter Weibull function is also examined.

2. Theory

The Weibull modulus m is a measure of the amount of data scatter and, physically, reflects the flaw size distribution of the material [5]. It is convenient to express the two-parameter Weibull function in the form shown by the equation

$$\ln \left\{ \ln \left(\frac{1}{1 - P_f} \right) \right\} = m \ln \sigma + \ln \left(\frac{v}{\sigma_0^m} \right) \quad (1)$$

where P_f is the probability of failure for a brittle material, v is a constant which incorporates the volume of stressed material, σ_0 is the "characteristic value" and corresponds to that stress below which 63.2% of samples will fail and m is the Weibull modulus and is related to the data distribution.

A plot of $\ln[\ln\{1/(1 - P_f)\}]$ against $\ln \sigma$ produces a straight line of slope m . A least-squares fit or a maximum likelihood method are used to determine m , the choice depending on the sample size [6].

The value of P_f in eqn. (1) is found by using suitable estimators with the recommended estimator being [7, 8]

$$P_f = \frac{i - 0.5}{n} \quad (2)$$

where P_f is the probability of failure of the i th specimen in a batch of size n . The failure strengths are arranged in ascending order from the lowest ($i = 1$) to the highest ($i = n$). The inherent inaccuracy in m and σ_0 resulting purely from statistical sampling has been analysed [9, 10] and expressed in terms of the coefficient of variation CV where [9]

$$CV = \frac{\text{standard deviation}}{\text{mean}} \quad (3)$$

This analysis may be used to assess if scatter in m and σ_0 represent true differences between batches or merely inherent statistical scatter.

Investigations into the sample size required to give an accurate determination of m indicate that at least 35 specimens are needed to determine m to within approximately 10% of the true value [8, 11]. The true value of m in these studies was established for a very large sample size. The accuracy in a , is dependent on both the Weibull modulus and the sample size [9].

3. Experimental details

Approximately 35 TAT specimens of each coating were prepared in accordance with ASTM standard C 633. It should be noted that the coatings were not prepared with a view to optimizing the bond strength, and thus the bond strength values which are reported in this work are quite low. Mating surfaces were grit blasted with 30 · 36 mesh alumina grit at a pressure of approximately 0.40 · 0.55 MPa impacting perpendicular to the surface [12].

Surfaces to be coated were sprayed within 30 min of grit blasting with an 80 kW (Ar–Ar or Ar–He) plasma torch. An automated spraying table was used which allowed a coating thickness of 0.40 mm to be applied with an accuracy of ± 0.01 mm. Care was taken to ensure reproducible plasma-spraying deposition parameters since these may be a source of variance in the material properties of coatings. Following spraying, specimens were examined and those exhibiting damage (chipping, delamination etc.) were removed from the batch. The remaining specimens were kept desiccated until needed [13].

The TAT specimens were manufactured by using Cyanamid FM73 adhesive. Uniaxial alignment of the specimen and pull-off bar was maintained by assembling the specimen within a polymeric cylinder which could be removed after curing of the adhesive. Excess adhesive was polished off before testing the samples in a standard universal testing machine which was operated at a crosshead speed of 0.05 in min^{-1} (0.21 mm s^{-1}) in accordance with the ASTM standard.

The coatings investigated (with the sample size in parentheses) were alumina (42), alumina–2.5%titania (33), zirconia–5%calcia (32), zirconia–6% Y_2O_3 (34) and carbon steel (26). All compositions are stated as weight per cent.

4. Results

Figure 1 shows the frequency distribution of the failure stresses for the coatings tested. The ceramic coatings exhibit a monomodal distribution whereas the metallic coating did not.

Data analogous to that obtainable from ASTM C633 were generated by employing a random number method to select ten groups of five results from the parent data batch for each coating. Table 1 shows the arithmetic mean, mode and median values of the frequency distributions shown in Fig. 1. The last column in Table 1 gives the range of arithmetic means for the ten randomly selected data groups.

Figure 2 shows a Weibull plot of the TAT data. The Weibull modulus m , characteristic value σ_0 and coefficient of correlation (R) for that data appear in Table 2.

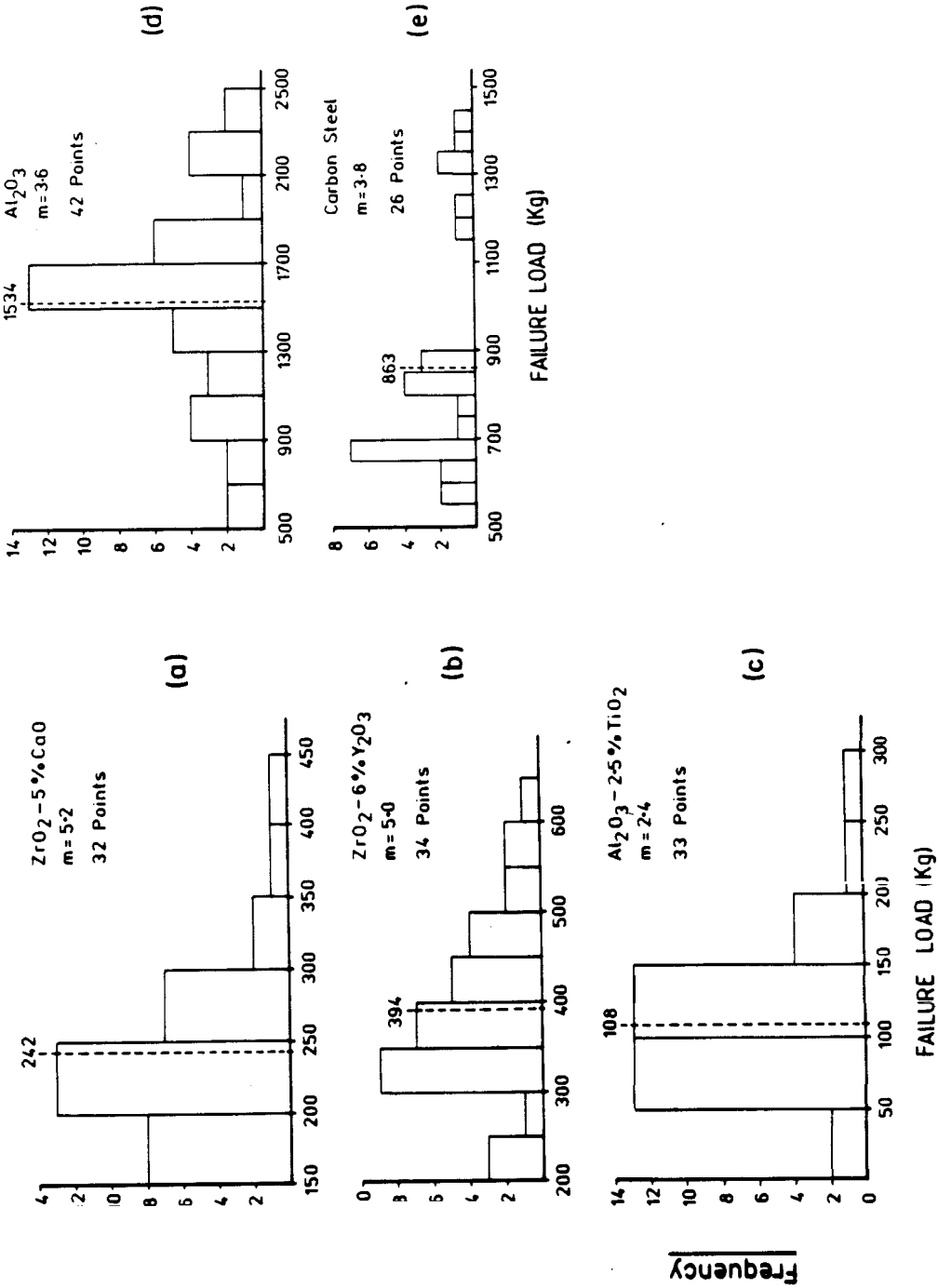


Fig. 1. Failure loads vs. frequency data for bond strength specimens. The dashed load values represent the arithmetic means for each set of data.

TABLE 1

Summary of statistical data

Coating	Mean (MPa)	Mode ^a (MPa)	Median (MPa)	Range of ten groups (MPa)
Al ₂ O ₃	29.7	30.9	30.8	25.4 · 33.4
Al ₂ O ₃ -2.5%TiO ₂	2.1	1.9	2.1	1.5 · 2.6
ZrO ₂ -5%CaO	4.7	4.4	4.5	3.8 · 5.8
ZrO ₂ -6%Y ₂ O ₃	7.6	6.3	7.4	6.1 · 9.5
Carbon steel	16.7	13.1	15.4	12.8 · 17.7

*Mid-point of range.

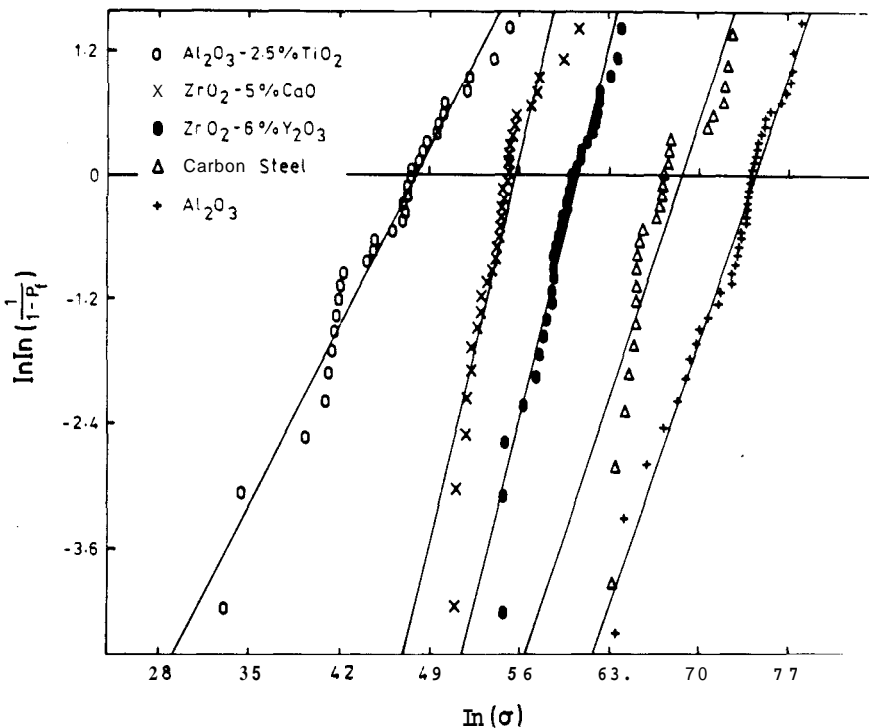
Fig. 2. Weibull distribution **plots** for ceramic and metallic **coatings**. +, data selected from ref. 3.

TABLE 2

Summary of **Weibull** data

Coating	<i>m</i>	σ_0 (MPa)	<i>R</i>
Al ₂ O ₃	3.6	33.6	0.98
Al ₂ O ₃ -2.5%TiO ₂	2.4	2.4	0.98
ZrO ₂ -5%CaO	5.9	4.9	0.94
ZrO ₂ -6%Y ₂ O ₃	5.1	8.3	0.97
Carbon steel	3.8	18.6	0.88

5. Discussion

The last column in Table 1 indicates that for a series of standard TATs the arithmetic mean of the five results may vary considerably between tests. This variation is of the order of 30% - 70% for Al_2O_3 and $\text{Al}_2\text{O}_3\text{-}2.5\%\text{TiO}_2$ coatings respectively. The usefulness of employing this standard to test batch lots and in comparing coatings must therefore be questioned.

One possible solution to improve the accuracy is to increase the sample size. The shape of the frequency distributions (Fig. 1), however, makes the choice of a meaningful measurement parameter difficult. Thus the arithmetic mean, the mode and median values of (relatively) large sample size TAT data are not good indicators of coating strength.

A possible alternative which has been used extensively in failure analysis of conventional brittle materials employs Weibull statistics. The application of this to thermally sprayed coatings has been limited but has proven to be promising [14, 15]. A Weibull plot of the TAT data is shown in Fig. 2 and the salient points summarized in Table 2. The figure indicates that, with the exception of carbon steel, the TAT data conforms to a Weibull distribution, with $R \geq 0.94$ (Table 2) for the ceramic coatings even though the $\text{ZrO}_2\text{-CaO}$ data shows significant deviations at high and low values. This then suggests that characterizing coatings in terms of the Weibull modulus m and characteristic values σ_0 may be useful in assessing coating properties.

The low Weibull modulus of the coatings examined is consistent with the observed microstructure of thermally sprayed coatings which typically exhibit 2% - 10% porosity in the form of interlamellar defects [16 - 18]. Further, the data in Table 2 show the $\text{Al}_2\text{O}_3\text{-}2.5\%\text{TiO}_2$ coatings to have the lowest Weibull modulus of those tested and hence the broadest flaw size distribution [5]. The toughness of this coating might then reasonably be expected to be similar to, or slightly below, that of a pure alumina coating. This has been observed [18].

Assigning a characteristic value σ_0 to the coatings indicates a threshold below which 63.2% of the samples will fail. It is therefore believed to be a better indicator of coating strength than the mean, mode or median of the frequency distributions which appear to underestimate or overestimate the failure load of the majority of samples. The characteristic stress is found from the constant term of eqn. (1) and thus the values reported in this work include a constant that is related to the volume of stressed material.

The poor Weibull fit ($R = 0.88$) of the carbon steel data may be a reflection of the non-brittle **behaviour** of this coating, as evidenced by fractographic investigations [19, 20]. Since the strength distribution is bimodal in character, separate Weibull **parameters** may be assigned to each **distribution**. In **fact**, distributions of this nature have been **observed** in the past and related to fracture morphologies [21].

6. Conclusions

The validity of using the arithmetic mean of five tensile adhesion test results (according to ASTM C633) as a meaningful indicator of coating adhesion or cohesion must be questioned. Such data may show a range of variation of up to 70%. Thus the average strength value (or the mode or median strength values of a larger sample size) may not be a suitable material property to use for comparing or assessing thermally sprayed coatings. The characteristic value σ_0 of the coatings, unlike the mean, mode or median values, does not underestimate or overestimate the failure load of the majority of samples.

The data from ceramic coatings (batch size approximately 30) fits a Weibull distribution well although some coatings display significant deviation at high and low strength values. The low Weibull modulus obtained for the coatings ($m < 6$) indicates a large flaw size distribution consistent with observed coating microstructure and may reflect information on coating toughness. Characterizing coatings in terms of their Weibull modulus and characteristic value appears to provide a meaningful measurement of coating adhesive or cohesive strength as well as giving insights into coating quality.

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