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Elastic Modulus Measurements in Plasma Sprayed Deposits

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A commercial hardness indenter has been modified to record load displacement as a spherical ball is elastically loaded onto the surface of the material to be measured. The resulting data are used to calculate the elastic modulus. This technique has been used to characterize the elastic modulus of zirconium oxide-8% yttrium oxide plasma sprayed deposits. Moduli were measured both on the cross section and on the plan section, and the differences were correlated with the microstructure. Since relatively small areas of the material were sampled by the indenter, local mapping of elastic modulus variations on the size scale of the microstructure was possible. A periodic variation in modulus with position in the cross section was found on a length scale that corresponded to the average plasma spray pass thickness. Elastic modulus variations also have been found on a macro scale through the thickness of freestanding plasma sprayed deposits. These large scale variations were probably a result of self annealing during the production of these thick samples. Finally, significant increases in elastic modulus have been found in samples annealed for a total of 2.5 h at 1100 °C. These changes have been correlated with small angle neutron scattering measurements of void surface area.

Keywords elastic properties, instrumented indentation, plasma spray, small-angle neutron scattering, YSZ

1. Introduction

Plasma sprayed deposits are increasingly being used in high performance applications. Such applications, however, require a degree of understanding of microstructure and mechanical properties that is currently not available. While strength is typically the first property considered, the elastic properties are also of considerable importance in determining the inservice behavior, particularly where thermal gradients or substrate/coating thermal expansion mismatch are present (Ref 1, 2).

Various techniques have been developed for evaluating the elastic properties of plasma sprayed deposits (Ref 3). However, each technique has its own limitations—mainly due to small sizes, fragility of deposits, and problems with fabricating the required sample sizes and shapes. Also, the results of different techniques may not be directly comparable since each technique probes the microstructure on different scales and in different ways. Indentation techniques probe microstructure on the size scale of the indenter used and usually under compression (Ref 4). The scale varies from nanometers, where mechanical properties of material within a single splat can be studied, through micrometers, as in the present work. Other macroscopic techniques usually involve manufacture of special samples and their bending, pulling, or compressing (Ref 3, 5, 6) or the use of ultrasonic techniques (Ref 7). All of the techniques, with exception of indentation, usually require freestanding samples. This complicates the sample manufacturing and can limit the relationship between results of measurements and the real engineering part.

The elastic modulus of the plasma sprayed deposits has been found to be significantly smaller that that of bulk materials with similar porosity (Ref 3, 5, 7). For yttria-stabilized zirconia (YSZ) materials, values vary between about 20 to 100 GPa. It is very difficult to compare the measured values and different techniques, since the elastic modulus of samples with similar porosity levels vary widely. A strong relationship of elastic modulus to microstructure character, which cannot be expressed as porosity volume, has been proposed (Ref 3, 6). No quantification of this character and relationship with elastic properties has been performed yet. Anisotropy of the elastic modulus was found and was linked to the microstructure anisotropy.

For this paper, the elastic modulus of ZrO_2–8% Y_2O_3 samples was measured by an indentation technique in which a spherical ball was elastically loaded onto the sample surface and the load displacement data were used to calculate the elastic modulus (Ref 8). The loads employed were relatively small, nominally 5 N, and the resulting contact dimensions were small, on the order of the thickness of layer deposited during one pass of the torch over the substrate. This allowed measurement of the local elastic properties of the deposit. Since the measured elastic modulus was sensitive to local microstructure and bonding, it appears to be useful for process development as well as quality control.

Understanding the elastic modulus data requires correlation with the microstructure. However, quantitative characterization of the microstructure using polished sections and microscopy is fraught with difficulties. Polishing damage (grain pull-outs), the existence of fine microstructural features, and difficulty in thresholding the features in the image can result in wide variations in the measurements. Mercury intrusion porosimetry (MIP) can quantify the size/volume of internal voids but is insensitive to surface area, orientation, and isolated pores. An alternate technique, small-angle neutron scattering, (SANS) overcomes many

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of these difficulties. The SANS technique uses Porod scattering from internal interfaces where materials across the interface differ in their neutron scattering length. Therefore, it is sensitive to the internal surface area of the features, which in this case are voids and crack-like features. It is also sensitive to the anisotropy of the features which allows different void systems to be distinguished. This measurement approach differs from MIP in that not only are anisotropic surface areas measured, but also that both open and closed internal defects are accessible (Ref 9-11). These SANS measurements have been combined with elastic modulus measurements to investigate the effect of microstructure on physical properties of a series of ZrO_2-8%Y_2O_3 materials, including sintered bodies and freestanding plasma sprayed deposits.

2. Experimental Procedure

Measurement of elastic modulus using instrumented indentation was performed on different ZrO_2-8%Y_2O_3 (mass fraction) materials, (sintered reference samples and freestanding plasma sprayed deposits). Reference samples were made from a commercial ZrO_2 powder (Magnesium Electron, grade XZO 709/3), which was isostatically pressed at 300 MPa and sintered in air. (Certain commercial materials are identified in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.) The densities of the sintered samples were changed by varying the sintering temperature between 1380 °C and 1500 °C and were determined by measurements of mass and dimensions of the sample.

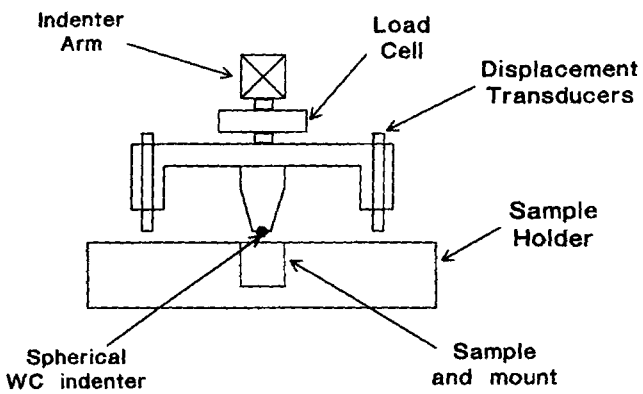


Fig. 1 Schematic of the modified indentation equipment used in this work

Plasma sprayed deposits were produced by the Plasma-Technik (Sulzer-Metzo AG, Wohlen, Switzerland) F4 spray system at the Thermal Spray Laboratory, State University of New York at Stony Brook. The spray nozzle diameter was 8 mm, the powder injector diameter was 1.8 mm, and the power was 500 A at 68 V. The powder feed rate was 26 g/min with argon primary gas at 40 L/min and 10 L/min hydrogen secondary gas, with 3 L/min argon carrier gas, all at standard temperature and pressure. To obtain the freestanding samples used in this study, deposits of about 5 mm thickness were sprayed onto an aluminum coated mild steel substrate of 50 mm by 25 mm by 2.5 mm dimensions. The Al layer was dissolved after deposition in 20% HCl to obtain freestanding deposits. The feedstock materials and spray distances for the freestanding deposits are listed in Table 1. A low-speed diamond saw was used for sectioning the samples to about 25 mm by 5 mm by 5 mm. The densities of the plasma sprayed samples were determined by mercury intrusion porosity. All of the ZrO_2 samples were prepared for indentation and scanning electron microscopy (SEM) by diamond sawing, followed by coarse grinding, polishing, then sputtering with approximately 15 nm Au-Pd.

The elastic modulus of the samples was measured using modified commercial indentation equipment to which load and displacement measuring sensors were added (Fig. 1). Indentation loading/unloading curves were recorded to 3 mN (0.3 g-force) and displacements to 10 nm. Polished surfaces of the samples were indented with a spherical 2.381 mm (3/32 in.) diameter WC sphere and a nominal 5 N load, resulting in a contact diameter between the WC sphere and the sample of approximately 50 μm and a peak elastic penetration depth of approximately 2.5 μm. The apparent elastic modulus of the sample, E^*, was calculated from the load-displacement curve using standard Hertzian contact theory (Ref 8):

$$E^* = \left(\frac{9}{16}\right)^{1/2} P h^{-3/2} R^{-1/2} \quad \text{(Eq 1)}$$

where h is the depth of elastic penetration of the spherical indenter, P is the load, and R is the indenter radius. The true modulus of the sample, E_s, can be calculated from the apparent modulus by taking into account the elastic properties of the spherical indenter:

$$E_s = \frac{1 - \nu_s^2}{(1/E^*) - \left[(1 - \nu_i^2)/E_i\right]} \quad \text{(Eq 2)}$$

where ν is Poisson's ratio, and the i and s subscripts refer to the indenter and sample, respectively. Poisson's ratio for the sample

Table 1 Feedstock materials parameters

Material	Composition, mass fraction, %	Size range, D_{10}, d_{90}(a), μm	Spray distance, mm	Process
Sulzer Metco Amdry 142	ZrO_2-8%Y_2O_3	41,113	90 and 115	Fused and crushed
Osram Sylvania SX233	ZrO_2-8%Y_2O_3	29,96	65 and 145	HOSP(b)

(a) d_{10} and d_{90} correspond to 10% and 90% cumulative powder particle diameters, respectively. (b) HOSP is a proprietary technique similar to plasma spheroidization and is equivalent to Metco 204.

was assumed to be 0.2 and the elastic properties of the WC indenter used in the calculations were E_i = 614 GPa and ν_i = 0.22.

The elastic modulus of the sample is calculated from a least squares fit of the $P^{2/3}$ versus h data from the loading curve, usually about 100 data points. Deviations from the expected elastic Hertzian contact behavior, such as yielding in metals or cracking or crushing in brittle ceramics, would result in deviations from the expected linear $P^{2/3}$ versus h relationship. For the load range examined here, the linear $P^{2/3}$ versus h relationship was obeyed for the materials investigated, indicating elastic behavior. Measurement of the elastic modulus of standard glass samples gave an average of 69.8 GPa, as compared to the expected value of 70 GPa, with a combined relative standard uncertainty of 0.5%.

3. Results and Discussion

3.1 Density-Elastic Modulus

The dependence of elastic modulus on sample density was determined for a series of sintered ZrO_2–8%Y_2O_3 samples. As expected, the modulus decreased with increasing porosity for these sintered samples, from a value of nearly 200 GPa for dense samples to 120 GPa for samples with 18% porosity. Comparison of these data to that for plasma sprayed samples of the same chemical composition shows a large deviation from the expected density-modulus relationship (Fig. 2), with a measured elastic modulus of 35 GPa for a plasma sprayed deposit with 7.5% porosity. Examination of the plasma sprayed deposit microstructure gives clues to this behavior. SEM photos (Fig. 3) show that there are globular isolated pores of approximately 1 to 5 μm in size and a high density of planar, crack-like defects on both the deposit cross section (Fig. 3a) as well as on the plan section (Fig. 3b). These two defect types, volumetric and planar, have different influences on the measured density and elastic modulus. The planar defects contribute little to the total volume of the sample and thus have little influence on the measured density. However, they can result in significant local compliance and reduction in the measured elastic modulus. On the other hand, the volumetric defects produce an isotropic reduction in the elastic modulus as well as a significant reduction in the density of the sample.

In the sintered samples where planar defects are absent, reduction in elastic modulus is produced only by the pores in the sample which also decrease the density. In the plasma sprayed samples where the voids are accompanied by a high density of

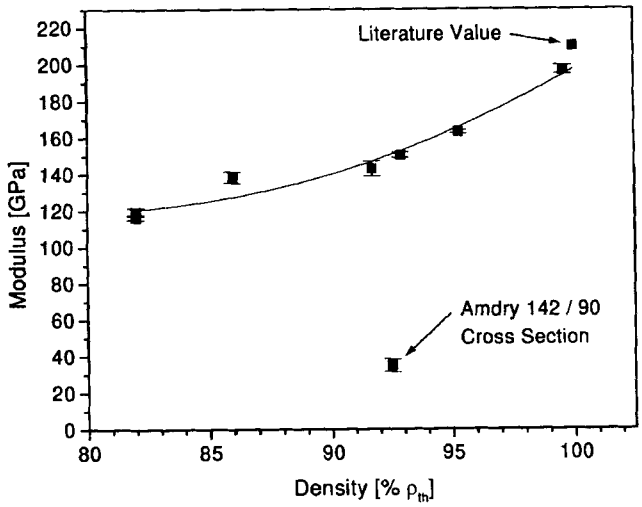
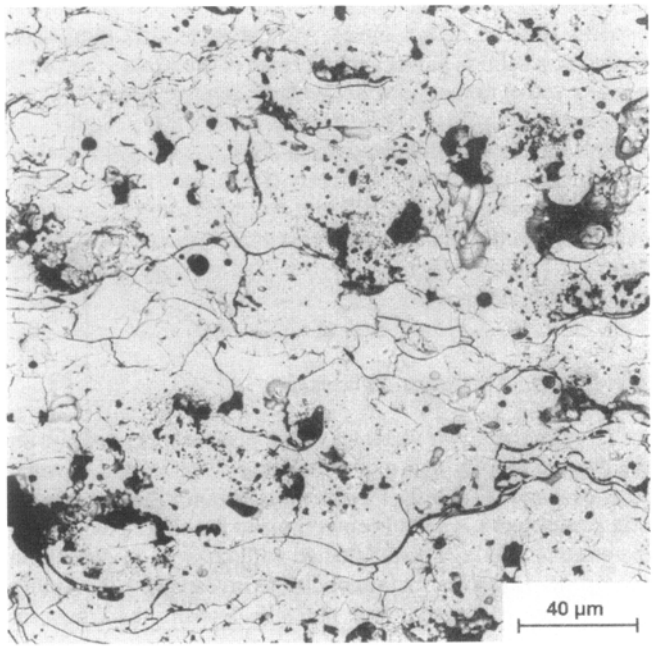
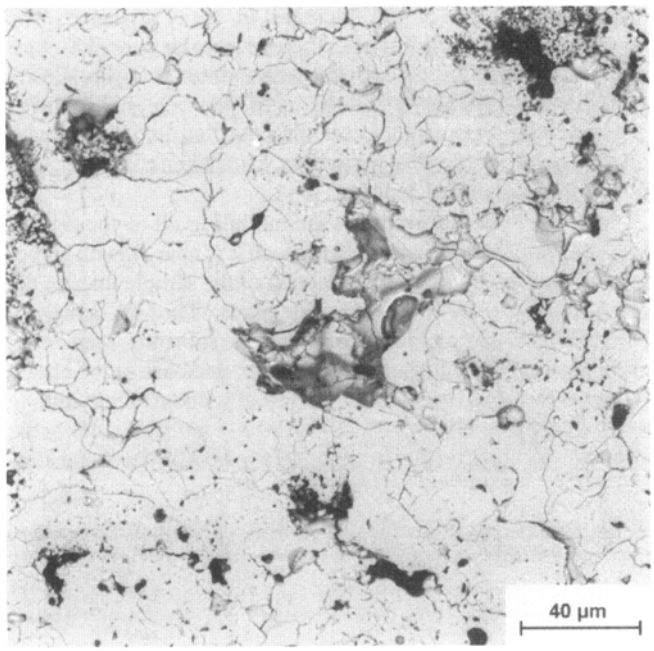


Fig. 2 Comparison of elastic modulus versus porosity dependence for sintered samples and Amdry 142 sample sprayed with 90 mm spray distance. Literature value is from Ref 12.



(a)



(b)

Fig. 3 (a) Microstructure of the cross section of an SX233 plasma sprayed deposit. The largest dark features are pull-outs from polishing damage. (b) Microstructure of the section parallel to the substrate, the plan section, of an SX233 plasma sprayed deposit

planar defects which have relatively little volume, there is a reduction in elastic modulus beyond that expected from pores alone. The combination of the effects from each of these defect types determines the elastic modulus.

The microstructures of the plasma sprayed deposits are inhomogeneous on the scale of the size of the contact area of the spherical indenter, particularly on the cross section (Fig. 3a). This microstructural inhomogeneity results in the relatively large standard deviation in the modulus measurements in comparison to those for homogeneous materials such as glass or the partially sintered ZrO_2 samples. Also, the crack-like flaws seen on the cross section have a strong degree of preferred orientation nearly parallel to the substrate, whereas the crack-like flaws on the plan section (Fig. 3b) have little preferred orientation. As will be shown, this preferred orientation is reflected in anisotropy in the elastic modulus. Clearly, if the elastic modulus is anisotropic, and large differences are found between sintered and plasma sprayed deposits of the same chemical composition and density, a bulk measurement, such as density, cannot adequately characterize material.

3.2 Elastic Modulus-Processing

The effects of two variables of the plasma spray process on the deposit density and modulus, spray distance and powder, were evaluated (Table 2). First, it must be noted that the deposition parameters have not been optimized for either powder and the relative rankings could change with changes in deposition conditions. However, for the conditions investigated, the Amdry 142 powder produced lower porosity deposits than those of SX233. For each of the powders, the porosity increases with increasing spray distance, with the largest increase in porosity corresponding to the largest increase in spray distance. The measured elastic modulus also showed powder specific trends (Table 2). Here, the SX233 deposits exhibited higher elastic moduli than the Amdry 142 deposits in spite of higher porosity. This behavior supports the contention that density is not an adequate measure of physical properties, even when comparing different plasma sprayed deposits.

Measurements showed that the moduli in all of the plasma sprayed deposits were orientation specific (Table 2), with higher moduli measured on the cross section of the sample than on the plan section (parallel to the substrate plane). The high density of planar defects that are nearly parallel to the substrate, seen on the cross section, is responsible for the large decrease in the elastic modulus measured on the plan section. It is this configuration in which the planar defect surfaces are nearly perpendicular to the indentation direction that produces the largest effect on the elastic modulus. Planar defects whose surfaces are nearly parallel to the indentation direction exhibit a much smaller effect. The more randomly oriented planar defects seen on the plan section have a much smaller density of defects with surfaces parallel to the cross section and, thus, have a smaller effect on the elastic modulus measured on the cross section.

As the processing conditions change, the elastic properties also change. The modulus measured on the plan section is 20 to 40% lower than on the cross section of the deposit, depending on the initial powder characteristics and the spray distance. The property anisotropy became more pronounced in the SX233 deposits for long spray distances, with the modulus measured on the plan section falling to relatively low values while the values on the cross section were nearly independent of spray distance. The low modulus values on the plan section for long spray distances may be the result of poor bonding between successive layers of splats and the formation of interlamellar voids.

3.3 SANS Measurements

Small angle neutron scattering (SANS) can be used to provide a quantitative measurement of the microstructure and to provide an explanation for the apparent inconsistencies in the porosity-modulus measurements. The SANS measurements are sensitive to internal surface area and can be evaluated as a total specific defect surface area, the total surface area of defects in the deposit normalized by the deposit volume. In both the Amdry 142 and SX233 deposits, high values of defect surface area correspond to low values of measured elastic modulus (Table 2). The data of the SX233 samples sprayed at 145 mm do not appear to be consistent, particularly for measurements on the plan section; the low value of the defect area would predict a relatively large value of the elastic modulus. The reason for this discrepancy is, at least in part, due to the incompleteness of the present SANS evaluation. Clearly the microstructure and the elastic properties are anisotropic while the SANS measurements are for the total surface areas in the sample, regardless of orientation. It is believed that a more complete analysis of the SANS data will yield directionally dependent values that will more closely describe the actual microstructural features and elastic modulus data.

3.4 Effect of Heat Treatments

The spatial variations in the elastic modulus of the thick (5 mm) plasma sprayed deposits were also investigated. For one Amdry 142 sample, the elastic modulus measured on the cross section 0.5 mm from the initial substrate interface was nearly 40% higher than that measured 0.5 mm from the top of the

Table 2 Porosity, elastic moduli, and SANS defect area for plasma sprayed deposits

			As sprayed			Thermally cycled		
			E, GPa		Defect area,	*E*, GPa		Defect area
Material	Spray distance, mm	Porosity, %	Cross section	Plan section	surface/volume, m^2/m^3	Cross section	Plan section	surface/volume, m^2/m^3
Amdry 142	90	7.5	34.8 ± 3.5	24.6 ± 1.5	2.8×10^6	40.0 ± 1.3	26.2 ± 1.5	1.8×10^6
Amdry 142	115	8.4	32.4 ± 1.5	22.3 ± 1.2	2.9×10^6	40.9 ± 2.4	27.6 ± 1.4	1.9×10^6
SX233	65	10.4	38.5 ± 2.5	31.1 ± 2.2	2.2×10^6	43.7 ± 1.7	40.5 ± 4.7	1.6×10^6
SX233	145	13.1	37.0 ± 4.5	21.9 ± 1.9	1.5×10^6	40.9 ± 2.6	30.0 ± 2.5	1.3×10^6

deposit (Fig. 4). It is believed that the higher modulus of the interior is the result of self annealing during the fabrication of these thick samples. Although care was taken to minimize the temperature increase of the deposit during repeated passes of the plasma torch, moderately elevated temperatures allowed some of the defects to be healed. Independent SANS measurements of the surface material and interior material could not be made to test this hypothesis due to a minimum thickness requirement for the measurement. However, SANS measurements were made on thick samples that were annealed. Plasma sprayed deposits were cycled 5 times for 0.5 h each time in and out of a furnace that was heated to 1100 °C. Although this thermal treatment did not significantly decrease the volume of porosity in the sample, there was a strong decrease in the defect area and an increase in the measured elastic modulus of all of the samples, both on the cross section as well as is on the plan section (Table 2). The degree of change depended not only on the powder used but also on the direction measured, with the largest increase in modulus found for the SX233 deposit on the plan section. Since the void volume stayed essentially constant, it appears that the defects that exhibited large surface to volume ratios, that is, the planar defects, were being removed during the thermal cycling treatment. These results support the arguments that the planar defects have a strong effect on the measured elastic modulus. While there was no apparent direct correlation between the modulus increase and the defect area decrease, this may be the result of the anisotropy of both the planar defects as well as anisotropy of the measurements themselves. Further work is needed to evaluate the contributions of each of the individual planar defect systems.

3.5 Periodic Microstructure Variations

In addition to the elastic modulus variations found between the outer surface and the interior, small-scale variations were also investigated. In order to remove any possible influence of neighboring indents on a given measurement, a minimum spacing between indents of 100 μm was maintained. When a line of indents with 100 μm spacing was made on the cross section with a very shallow angle with respect to the substrate surface, sampling of modulus variations can be made on a very fine scale through the deposit thickness, approximately 6.5 μm increments for a 3.7 ° angle. When these modulus data were smoothed and plotted, there was a clear periodic nature in the measurements (Fig. 5). Over the 320 μm depth measured, there were 5 apparent cyclic variations, corresponding to an average period of 64 μm. These 4.8 mm thick deposits were fabricated with 75 passes of the plasma torch, corresponding to an average pass thickness of 64 μm. The periodicity implied that factors in the deposition process were affecting the measured elastic properties.

Although the exact microstructural features that were responsible for the modulus maxima and minima could not be determined, the correlation between average pass thickness and modulus periodicity appears strong. The exact correspondence, however, is perhaps somewhat fortuitous considering the limited sophistication of the analysis. It should also be noted that the indenter size and load used resulted in a contact diameter on the surface of approximately 50 μm. The material within this entire contact circle contributed to the measured modulus value, suggesting that there was a strong degree of averaging over microstructural features. For this reason, it is believed that the true values of the periodic minima and maxima could be significantly lower and higher, respectively, than those measured here if a smaller contact circle is made and less microstructural averaging takes place. Since the performance of materials in many applications is dependent on the extremes in property values, rather than the mean value, these and similar measurements could have significant importance in determining the performance of plasma sprayed deposits.

4. Conclusions

Several techniques have been developed to analyze the microstructure and properties of plasma sprayed deposits. Using a combination of small angle neutron scattering and instru-

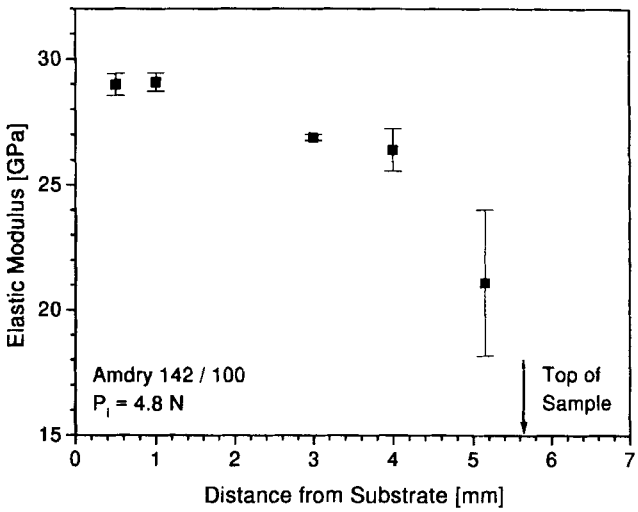


Fig. 4 The measured elastic modulus varied through the thickness of the sample (large scale variations, sample Amdry 142, sprayed with 100 mm spray distance). The variations are probably the result of self annealing.

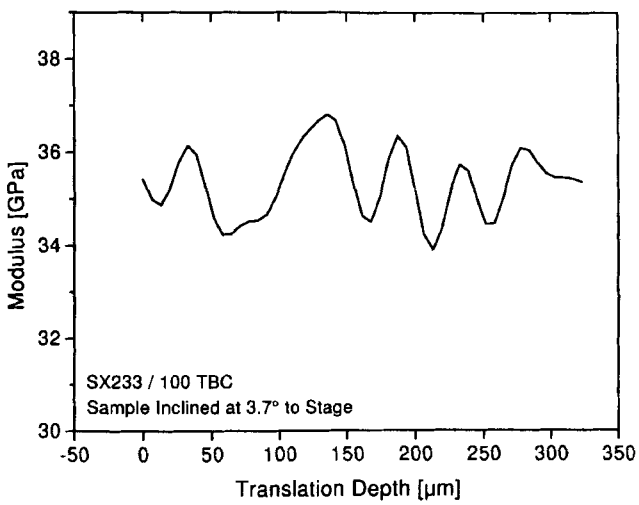


Fig. 5 Periodic variations in elastic modulus were found through the thickness of the plasma sprayed deposit on a size scale of the microstructure (small scale variations, sample SX 233 sprayed with 100 mm spray distance). The variations are probably the result of plasma sprayed layers.

mented Hertzian indentation, it has been found that planar defects, which contribute only insignificantly to the porosity of the material, have a very strong influence on the elastic modulus. It has been further shown that there are periodic variations in the elastic modulus throughout the thickness that are correlated with the spray parameters of the initial deposit.

Acknowledgments

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