

# Influence of plasma spray parameters on mechanical properties of yttria stabilized zirconia coatings. I: Four point bend test

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## Abstract

Yttria (8 wt.%) stabilized zirconia (YSZ) with a NiCrAlY bond coat was atmosphere plasma sprayed on mild steel substrates. The bond coat thickness (100–250  $\mu\text{m}$ ), YSZ coating thickness (300–500  $\mu\text{m}$ ), stand off distance (80–100 mm), and substrate temperature (273–393 K) were changed in a four by 17 experimental design matrix to investigate the influence of each spray parameter on the mechanical properties of coatings. Coatings were tested using a four point bend test arrangement. Coatings sprayed with thinner bond coat on a cold substrate exhibited higher yield strength and stiffness under bending. Change in the stand off distance and the top coat thickness did not statistically influence either yield strength or stiffness of the coatings. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Thermal barrier coatings; Mechanical properties; Plasma spray parameters

## 1. Introduction

Yttria stabilized zirconia (YSZ) plasma sprayed coatings are common thermal barrier coatings (TBCs) for applications such as gas turbines and diesel engines [1]. The TBC system allows conventional metals to be reliably used at high temperatures. At high temperatures, the ceramic layer provides thermal stability to the base metal due to insulation from the heat, while the bond coating (NiCrAlY) provides oxidation resistance [2].

Performance of the coating depends on the composition and characteristics (size and shape) of the feedstock powders [3,4], as well as the spraying condition such as plasma gun type, gun power, plasma gas composition and flow rate, and powder feeding rate [1,3–5]. The performance of TBCs has been determined by

measuring the physical properties such as thermal conductivity [1], thermal shock resistance [6,7], oxidation resistance [2], porosity amount and distribution [4], residual stresses [8–10], and mechanical properties such as tensile adhesion [10,11] and bending strength [12,13], hardness [14], and fatigue [15].

The common practice is to optimize spraying parameters to manufacture coatings with a desired performance. The mechanical performance of YSZ coatings involves brittle fracture by crack initiation and growth. Therefore, it is crucial to understand cracking in ceramic coatings under load. A variety of cracking mechanisms will evolve during loading, and arise from defects such as pores, splat boundaries, secondary phase interfaces, and pre-existing cracks within coatings. Acoustic emission (AE) analysis has also been used to monitor cracking in ceramic coatings during mechanical testing (three point bending [16], four point bending [12,13,17,18], tensile adhesion test [19], and indentation [20]) and during thermal cycling [21].

In the current study, the performance of plasma sprayed YSZ coatings on mild steel substrates with varying bond coat thickness and top coat thickness was

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Table 1  
Samples sprayed according to experimental design

| Samples | Bond coat ( $\mu\text{m}$ ) | Top coat ( $\mu\text{m}$ ) | Substrate temperature (K) | Stand off distance (mm) |
|---------|-----------------------------|----------------------------|---------------------------|-------------------------|
| G1      | 100                         | 300                        | 393                       | 80                      |
| G2      | 100                         | 300                        | 393                       | 100                     |
| G3      | 250                         | 300                        | 393                       | 80                      |
| G4      | 250                         | 500                        | 393                       | 100                     |
| G5      | 250                         | 500                        | 393                       | 80                      |
| G6      | 100                         | 500                        | 273                       | 80                      |
| G7      | 100                         | 500                        | 273                       | 100                     |
| G8      | 250                         | 300                        | 273                       | 80                      |
| G9      | 100                         | 500                        | 393                       | 80                      |
| G10     | 100                         | 300                        | 273                       | 80                      |
| G11     | 250                         | 300                        | 393                       | 100                     |
| G12     | 250                         | 300                        | 273                       | 100                     |
| G13     | 250                         | 500                        | 273                       | 80                      |
| G14     | 250                         | 500                        | 273                       | 100                     |
| G15     | 100                         | 300                        | 273                       | 100                     |
| G16     | 100                         | 500                        | 393                       | 100                     |
| G17     | 175                         | 400                        | 333                       | 90                      |

determined using four point bend tests. The influence of substrate temperature and spraying distance on the performance was also investigated. This study aimed to provide further understanding on the mechanical characteristics of thermally sprayed coatings and how the spray processing variables influence these characteristics. It is clear that such information on the mechanical characteristics of the thermally sprayed coatings leads coatings with a better performance.

Senturk et al. [12,13] showed that the in situ monitoring of samples using an AE transducer during a four point bend test could provide further understanding on the deformation of the plasma sprayed YSZ coatings. The same in situ monitoring of the AE activities was also followed during the four point tests in the current study, but will be reported in a separate publication [22].

## 2. Experimental procedure

### 2.1. Sample preparation

YSZ (8 wt.%) was sprayed onto mild-carbon steel substrates ( $90 \times 26.5 \times 2.6 \text{ mm}^3$ ) under spray parameters which were altered with respect to: (i) coating thickness (either 300 or 500  $\mu\text{m}$ ); (ii) the stand off distance (either 80 or 100 mm); and (iii) the substrate temperature (either at 273 or 393 K). The substrate temperature was measured using a hand held infrared temperature detector. The substrates were grit blasted and cleaned with ethyl alcohol before spraying. The average roughness of the grit blasted substrate was measured as  $4.0 \pm 0.5 \mu\text{m}$  using a Hommel T1000 mechanical profilometer (Hommel America, New Britain,

CT). A NiCrAlY bond coating of either 100 or 250  $\mu\text{m}$  thickness was atmospherically plasma sprayed before application of the YSZ top coat. Coatings were sprayed to dimensions of  $30 \times 26.5 \text{ mm}$ , leaving approximately 20 and 40 mm uncoated substrate on both sides since these areas made contact with the bend testing device. Air cooling on the back side of the substrates avoided overheating during the spray process.

A statistical experimental design procedure using StatGraph software (Statistical Graphics, Rockville, MD) was employed to determine the number of samples to be sprayed and the spray parameters necessary to determine relevant correlations. Table 1 lists the samples sprayed in the current study according to this experimental design. Six samples from each group in Table 1 were sprayed (the conditions given in Table 2) using a Metco 3 MB plasma gun (Sulzer-Metco, Westbury, NY) mounted on a six-axis articulated robot (Model S400, GMF Fanuc). Commercially available ceramic (YSZ) (Metco 204NS) and metal (NiCrAlY) (Praxair NI-346-1, Praxair Surface Technologies, Indianapolis, IN) feedstocks were used.

Table 2  
Spraying parameters

|  | YSZ       | NiCrAlY   |
|--|-----------|-----------|
| Gun Type   | Metco 3MB | Metco 3MB |
| Current (A)  | 600       | 500       |
| Voltage (V)  | 70        | 70        |
| Primary gas, Ar ( $\text{l min}^{-1}$ )                  | 40        | 40        |
| Secondary gas, $\text{H}_2$ ( $\text{l min}^{-1}$ )      | 11        | 8         |
| Powder carrier gas, $\text{N}_2$ ( $\text{l min}^{-1}$ ) | 3.5       | 3.65      |

## 2.2. Four point bend test

An Instron universal test machine (Model 8502, Instron, Canton, MA) was used to perform the four point bend tests at a crosshead displacement rate of  $10 \mu\text{m s}^{-1}$ . The length for inner and outer spans were 20 and 40 mm, respectively, and the samples were tested in a configuration to place the coating in tension. It was determined that six samples from each group would generate a 95% confidence limit. The sides of the samples were polished with 600 mesh abrasive before the tests to minimize artifacts from edge cracking. Six uncoated steel substrates were also tested to establish baseline criteria for the mechanical properties of uncoated samples. Load and displacement were recorded for each measurement. The displacement was corrected for the deformation in the support and the loading beam; i.e. the compliance of the test rig was measured and taken into account. The displacement was calibrated using an external LVDT (Model CD375-500, Macro Sensors, Pennsauken, NJ) that was placed close to the load actuator to enable more exact measurements.

## 3. Results

### 3.1. Four point bend tests

Fig. 1 illustrates the load–displacement curves obtained during the four point bend tests. In the figure, one representative curve is presented although there exists six load–displacement curves for each group. The load–displacement curve could be reproduced with a random 5–20% variation. Bending modulus was calculated from the slope of the load–displacement curve using the following equations:

$$(EI)^* = \frac{2D^3 \Delta P}{3 \Delta y} \quad (1)$$

where

$$(EI)^* = \frac{wE_{St}}{3}[(t_{St} - t_{NA})^3 + t_{NA}^3] + \frac{wE_C}{3}[(t_{St} + t_C - t_{NA})^3 - (t_{St} - t_{NA})^3] \quad (2)$$

where  $E$  is the bending modulus,  $I$  is moment of inertia, and  $t_{NA}$  is the distance of the neutral axis of the bar from the bottom of the substrate (Fig. 2) and is equal to

$$t_{NA} = \frac{E_{St}t_{St}^2 + E_Ct_C^2 + 2E_Ct_{St}t_C}{2(E_{St}t_{St} + E_Ct_C)} \quad (3)$$

where,  $P$  is the applied load,  $D$  is the distance between the loading and support bar (10 mm),  $y$  is the displacement,  $\Delta P/\Delta y$  is the slope of the load–displacement curve,  $w$  is the width of the bar,  $t_{St}$  and  $t_C$  are the

thickness of the substrate and coating layers including both top ( $t_{TC}$ ) and bond ( $t_{BC}$ ) coat layer, respectively. The terms  $E_{St}$  and  $E_C$  are, respectively, the bending modulus of the substrate and coating layer including both top and bond coatings; i.e. top and bond coat was considered as a whole assembly in the calculations. The bending modulus of steel substrate,  $E_{St}$  was calculated from the load–displacement curve for blank steel substrates using the equation:

$$E_{St} = \frac{8D^3 \Delta P}{wt_{St}^3 \Delta y} \quad (4)$$

where thicknesses were measured with an error of  $\pm 0.01$  mm. The bending modulus of the blank mild-steel substrate,  $E_{St}$  was measured as  $200 \pm 14$  GPa which is in agreement with the literature value of 204 GPa [23]. Bending modulus of coatings,  $E_C$  was calculated by solving Eqs. (1)–(3) simultaneously. A graphical solution routine was followed to determinate the  $E_C$  and  $t_{NA}$  from these three equations. In the solution, the bending modulus of the steel ( $E_{St}$ ) substrate was taken as 200 GPa. The bending modulus of some coatings ( $E_C$ ) calculated, such as those for group 14, was slightly negative and indicates a poor physical meaning. The reason for these negative values is that the bending modulus for these coatings are so small that a steel substrate with a coating and a blank steel substrate are indistinguishable in their bending properties within the limits of the experimental errors. One should note that when the  $E_{St}$  was taken as 186 GPa, the calculated  $E_C$  became slightly positive for those groups. The average  $E_C$  values for all the coatings are illustrated in Fig. 3 along with the average yield stress values at the outer surface of the coatings (One should note that stress values change throughout the coating as given in Fig. 2). The yield stress was calculated using the equation:

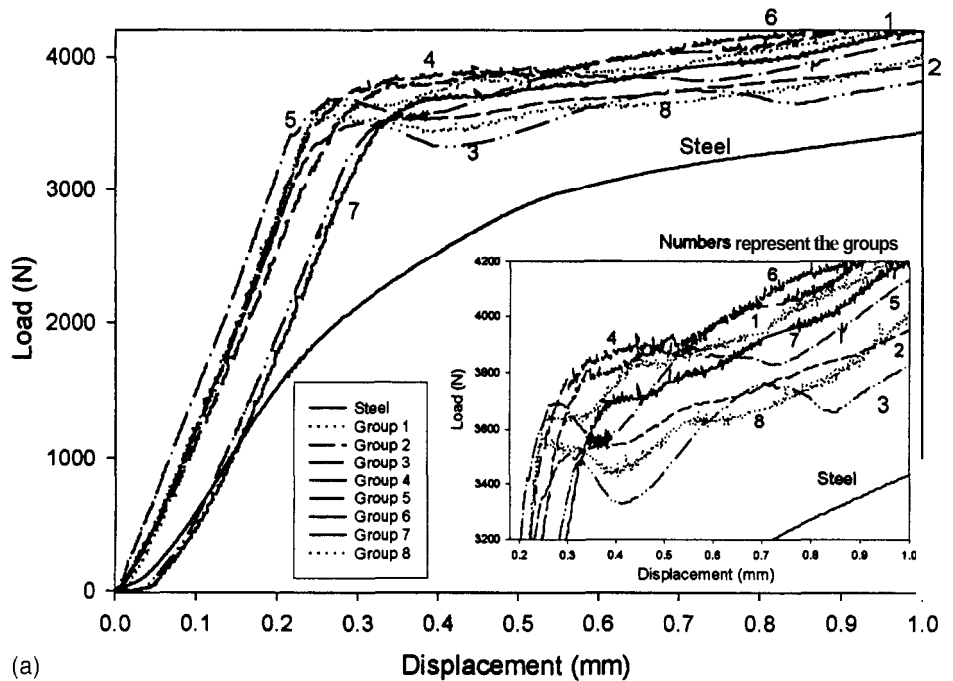
$$\sigma_{YC} = \frac{P_{YC}D(t_{St} + t_C - t_{NA})}{2(EI)^*} E_C \quad (5)$$

where  $P_{YC}$  is the yielding load and it was taken as the load for 0.01 mm permanent displacement where corresponding strain would be around 0.1%, and  $(EI)^*$  is as given in Eq. (2).

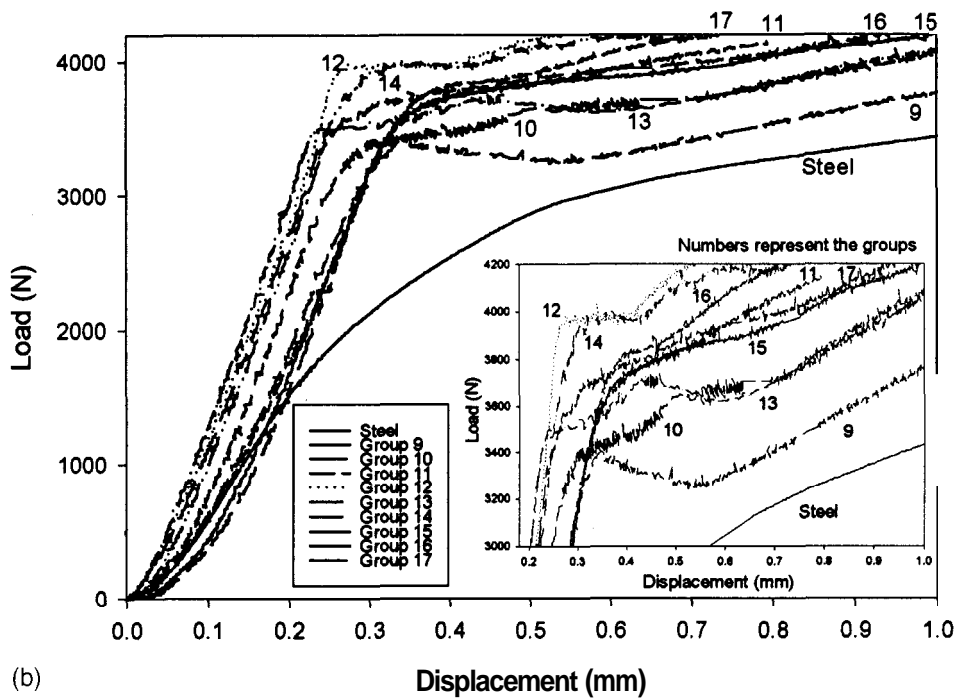
The comparison of bending modulus to yield stress is illustrated in Fig. 4 along with the inset showing yield strain for each group. Yield strain was calculated from Hooke's law by dividing  $\sigma_{YC}$  by  $E_C$ . Yield strain values are similar for the coatings, but it is smaller for the steel substrate.

### 3.2. Statistical analysis

To further understand the significance of the parameters on the properties of the coatings, all the results were statistically analyzed using the Statgraphics Plus 2.0 software.



(a)



(b)

Fig. 1. (a) Load–displacement curves for groups 1–8 along with that of steel substrate. Notice that only one representative curve of six is presented. Inset highlights the yielding load. (b) Load–displacement curves for groups 9–17 along with that of steel substrate. Notice that only one representative curve of six curves is presented. Inset highlights the yielding load.

### 3.2.1. Yield strength of coatings

To understand whether bending yield stresses ( $\sigma_{YC}$ ) significantly differ between the groups, the mean of the yield stress values for each group was compared statistically (Table 3). The numbers in Table 3 were calculated by subtracting the bending stress of the group in the column from the bending stress of the group in the row,

and then normalizing with respect to the bending stress of group in the row (i.e. (row – column)/row). The largest difference in means of the bending yield stress is between group 14 (being lowest) and group 15 (being highest), while many groups have statistically the same mean bending stresses as indicated by an 'N' in Table 3. Although the comparison in Table 3 indicates the dif-

Table 3  
Comparison of the mean of the bending yield stresses of coating layer ( $\sigma_{YC}$ ) for the groups<sup>a</sup>

|     | G1   | G2   | G3   | G4  | G5   | G6   | G7   | G8   | G9   | G10  | G11 | G12 | G13  | G14 | G15  | G16  | G17 |
|-----|------|------|------|-----|------|------|------|------|------|------|-----|-----|------|-----|------|------|-----|
| G1  |      | 0.4  | 0.7  | 1   | 0.3  | 0.5  | N    | N    | 0.8  | 0.3  | 0.9 | 0.8 | N    | 1   | -0.5 | -0.2 | 1   |
| G2  | -0.6 |      | 0.5  | 0.9 | N    | N    | -0.4 | -0.7 | 0.7  | N    | 0.9 | 0.6 | N    | 1   | -1.3 | -0.9 | 0.9 |
| G3  | -2.3 | -1.1 |      | 0.8 | -1.4 | -0.7 | -1.8 | -2.6 | N    | N    | N   | 0.2 | -1.7 | 1   | -3.8 | -3   | 0.9 |
| G4  | -21  | -13  | -5.6 |     | -15  | -10  | -17  | -22  | -3.4 | -14  | N   | N   | -17  | N   | -30  | -26  | N   |
| G5  | -0.3 | N    | 0.6  | 0.9 | 0.3  | 0.3  | N    | -0.5 | 0.7  | N    | 0.9 | 0.7 | N    | 1   | -1   | -0.6 | 1   |
| G6  | -0.9 | -0.2 | 0.4  | 0.9 | -0.4 | 0.4  | -0.6 | -1.1 | 0.6  | N    | 0.8 | 0.5 | -0.6 | 1   | -1.8 | -1.3 | 0.9 |
| G7  | N    | 0.3  | 0.6  | 0.9 | N    | 0.4  | 0.4  | -0.3 | 0.8  | N    | 0.9 | 0.7 | N    | 1   | -0.7 | -0.4 | 1   |
| G8  | N    | 0.4  | 0.7  | 1   | 0.3  | 0.5  | 0.2  | 0.8  | 0.8  | 0.4  | 0.9 | 0.8 | 0.2  | 1   | -0.3 | N    | 1   |
| G9  | -3.9 | -2.1 | N    | 0.8 | -2.6 | -1.6 | -3.2 | -4.3 | 0.7  | -2.3 | N   | N   | -3   | N   | -6.1 | -5   | N   |
| G10 | -0.5 | N    | 0.6  | 0.9 | -0.1 | N    | N    | -0.6 | 0.7  | N    | 0.9 | 0.6 | N    | 1   | -1.1 | -0.8 | N   |
| G11 | -10  | -6.1 | N    | N   | -7.3 | -4.9 | -8.6 | -11  | N    | -6.6 | N   | N   | -8.3 | 1   | -15  | -13  | N   |
| G12 | -3.1 | -1.6 | N    | N   | -2.1 | -1.2 | -2.6 | -3.5 | N    | -1.8 | N   | N   | -2.4 | N   | -5   | -4.1 | N   |
| G13 | N    | N    | 0.6  | 0.9 | N    | 0.4  | N    | -0.3 | 0.8  | N    | 0.9 | 0.7 | N    | 1   | -0.8 | -0.5 | 1   |
| G14 | -300 | -190 | -91  | N   | -224 | -159 | -259 | -327 | N    | -205 | -26 | N   | -249 | 1   | -439 | -370 | N   |
| G15 | 0.3  | 0.6  | 0.8  | 1   | 0.5  | 0.6  | 0.4  | 0.3  | 0.9  | 0.5  | 0.9 | 0.8 | 0.4  | 1   | 0.2  | 0.2  | 1   |
| G16 | 0.2  | 0.5  | 0.8  | 1   | 0.4  | 0.6  | 0.3  | N    | 0.8  | 0.4  | 0.9 | 0.8 | 0.3  | 1   | -0.2 | -33  | 1   |
| G17 | -26  | -16  | -7.4 | N   | -20  | -13  | -23  | -29  | N    | -18  | N   | N   | -22  | N   | -39  | -33  |     |

<sup>a</sup> N means the difference in the bending yield stresses of two groups are not statistically significant. Numbers (unitless) were found by subtracting the bending yield stress value of the group in the column from that of the group in the row, and dividing by that in the row (row-column)/row.

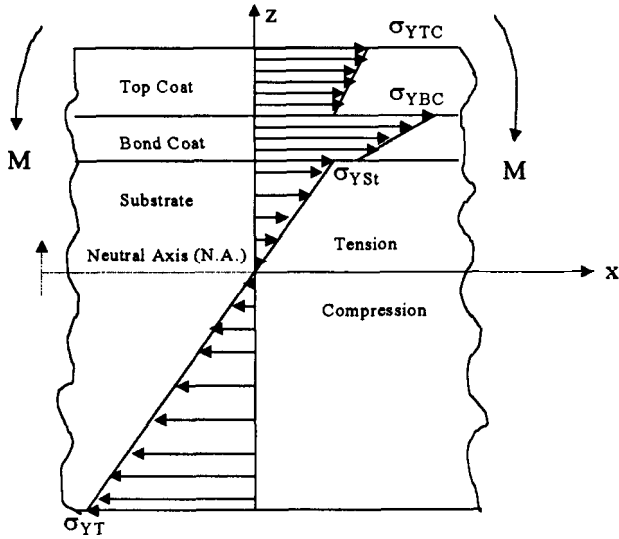


Fig. 2. Schematic illustration of the bending stress in the coating under four point bend test.

statistically significant relationship between the variables at the 99% confidence interval. A Student *t*-test,<sup>3</sup> which was used to determine the significance of each coating parameters, suggests that the bond coat thickness has a statistically significant influence on the bending yield stress ( $\sigma_{YC}$ ) at the 99% confidence interval while the substrate temperature affects the bending yield stress ( $\sigma_{YC}$ ) at the 95% confidence interval (Table 4). On the other hand, the top coat thickness and the stand off distance are not statistically significant parameters for the change in the bending yield stress ( $\sigma_{YC}$ ) of the coatings examined. The following equation from the fitted model indicates that the yield stress depends on the spray parameters; taking caution that this is only valid for the parameter range studied:

$$\sigma_{YC} \text{ (MPa)} = 461 - 0.71 \cdot t_b - 0.47 \cdot T_{St} \quad (6)$$

where  $t_b$  is the thickness of the bond coating (NiCrAlY) in  $\mu\text{m}$ , and  $T_{St}$  is the substrate temperature in K. The average value of residuals (mean absolute error) in the fit is 106 MPa; i.e.  $\sigma_{YC}$  can be calculated from Eq. (6) with a  $\pm 106$  MPa error. It is clear from this analysis that thinner bond coatings, and lower substrate temperature in the investigated interval result in a material with an overall higher yield strength. A 150  $\mu\text{m}$  decrease in bond coating (NiCrAlY) thickness causes a  $\sim 107 \pm 29$  MPa increase in the bending yield stress ( $\sigma_{YCL}$ ), while use of a pre-heated substrate decreases the bending yield stress by about  $56 \pm 28$  MPa

ferences for each pair, a more general analysis that might highlight trends was needed. This was achieved by a multi-linear regression analysis on the bending yield stress of coating ( $\sigma_{YC}$ ) values. Table 4 shows the results of fitting a multi-linear regression model to describe the relationship between yield stress and four independent variables (top coat thickness, bond coat thickness, the substrate temperature before coating, and stand off distance). An F-test<sup>2</sup> shows that there is a

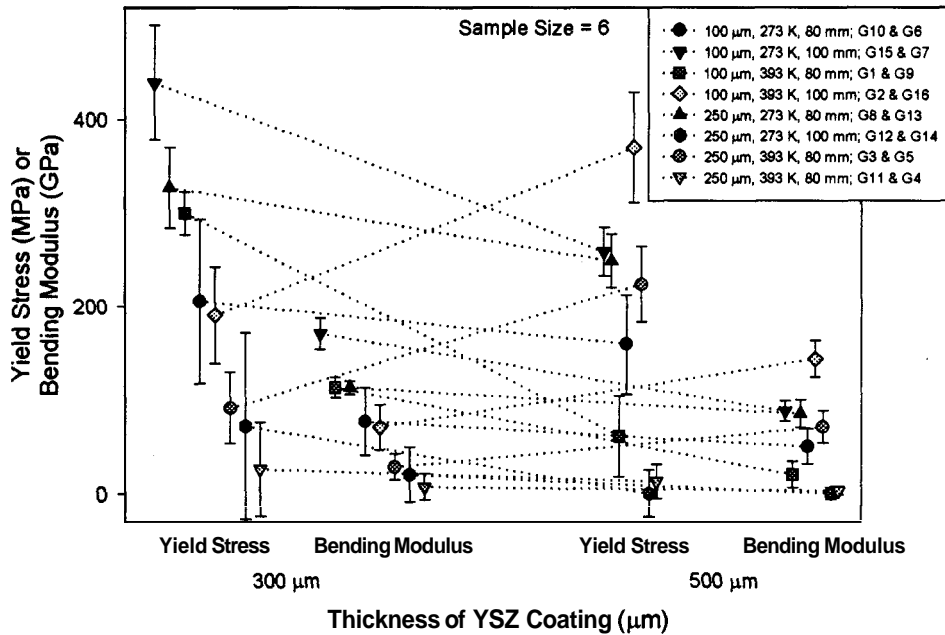


Fig. 3. Change of the bending yield stress ( $\sigma_{YC}$ ) and modulus ( $E_C$ ) of the coatings with spray parameters. The difference between the paired groups is the thickness of the yttria stabilized zirconia (YSZ) layer.

<sup>2</sup>F test is a statistical test to test the probability of a hypothesis being true. In this case the hypothesis is that there is a statistically significant correlation between the variables and the property.

<sup>3</sup> Student *t*-test is statistical test to test the probability of a hypothesis not being true. In this case, the hypothesis is that a variable does not statistically influence the property.

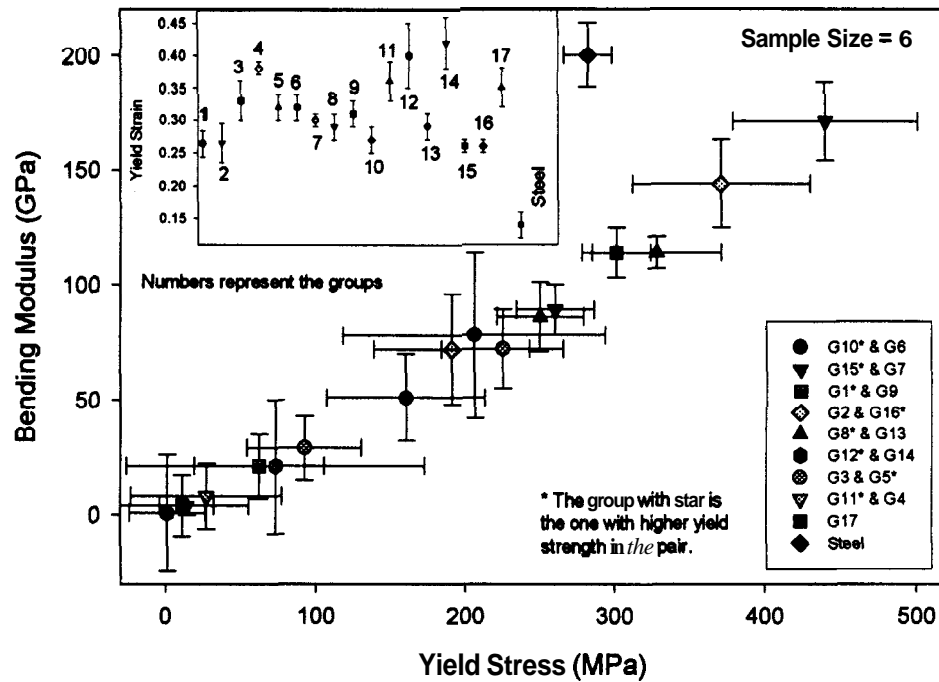


Fig. 4. Comparison of the bending modulus and yield stress for the coatings and the substrate. The yield strain calculated from Hooke's law represented in the inset.

Table 4

Results of the multi-linear regression analysis on the spray parameter dependence of the bending yield stress ( $\sigma_{YC}$ ) and modulus ( $E_C$ ) of the coating layers"

|                              | Estimated coefficient |             | S.E.                |             | t-test probability  |             |
|------------------------------|-----------------------|-------------|---------------------|-------------|---------------------|-------------|
|                              | $\sigma_{YC}$ (MPa)   | $E_C$ (GPa) | $\sigma_{YC}$ (MPa) | $E_C$ (GPa) | $\sigma_{YC}$ (MPa) | $E_C$ (GPa) |
| Constant                     | 461                   | 198         | 84                  | 37          | 0.00                | 0.00        |
| $t_{BC}$ ( $\mu\text{m}$ )   | -0.71                 | -0.31       | 0.19                | 0.07        | 0.00                | 0.00        |
| $T_{St}$ (K)                 | -0.47                 | -0.15       | 0.23                | 0.09        | 0.05                | 0.09        |
| $t_{TC}$ ( $\mu\text{m}$ )   |                       | -0.07       |                     | 0.05        |                     | 0.15 (?)    |
| Parameters with no influence |                       |             |                     |             |                     |             |
| $t_{TC}$ ( $\mu\text{m}$ )   | -0.15                 |             | 0.14                |             | 0.30                |             |
| $X_{sod}$ (mm)               | -0.61                 | -0.01       | 1.4                 | 0.5         | 0.66                | 0.98        |

"The t-test probability is the probability of each parameter not being statistically significantly influential. Note that t values are very high for those that are not statistically significantly influential. ( $t_{BC}$  is the thickness of the bond coating (NiCrAlY),  $t_{TC}$  is the thickness of the top coating (yttria stabilized zirconia, YSZ),  $T_{St}$  is the substrate temperature,  $X_{sod}$  is the stand off distance).

with respect to a cold substrate. Even though the multi-linear regression gave negative coefficients for the influence of top coat thickness and stand off distance on the yield stress indicating higher bending stress for lower top coat thickness and lower stand off distance, it should be cautioned that the statistical confidence according to the Student t-test is low (70 and 34%, respectively) as listed in Table 4. Therefore, top coating thickness and stand off distance were excluded as the parameters in Eq. (6).

### 3.2.2. Bending modulus of coatings

A similar comparison procedure was applied for the average bending modulus of each group as given in Table 5. The largest difference in means of the bending modulus is between group 14 (being lowest) and group 15 (being highest), while many groups have statistically the same mean bending modulus as indicated by an 'N' in Table 5. Similar to the bending yield stress analysis, a multi-linear regression procedure was also followed for determining the influence of spray parameters on

Table 5  
Comparison of the mean of the bending modulus of the coating layer ( $E_c$ ) for the groups"

|     | G1   | G2   | G3   | G4  | G5   | G6   | G7   | G8   | G9  | G10  | G11 | G12 | G13  | G14 | G15  | G16  | G17 |
|-----|------|------|------|-----|------|------|------|------|-----|------|-----|-----|------|-----|------|------|-----|
| G1  |      | 0.4  | 0.7  | 1   | 0.4  | 0.6  | 0.2  | N    | 0.8 | 0.3  | 0.9 | 0.8 | 0.2  | 1   | -0.5 | -0.3 | 1   |
| G2  | -0.6 |      | 0.6  | 0.9 | N    | N    | N    | -0.6 | 0.7 | N    | 0.9 | 0.7 | N    | 1   | -1.4 | -1   | 0.9 |
| G3  | -2.9 | -1.5 |      | 0.9 | -1.5 | -0.8 | -2.1 | -2.9 | N   | -1.7 | N   | N   | -2   | 1   | -4.9 | -4   | 0.9 |
| G4  | -28  | -17  | -6.3 |     | -17  | -12  | -21  | -28  | N   | -19  | N   | N   | -21  | N   | -42  | -35  | N   |
| G5  | -0.6 | N    | 0.6  | 0.9 |      | N    | N    | -0.6 | 0.7 | N    | 0.9 | 0.7 | N    | 1   | -1.4 | -1   | 0.9 |
| G6  | -1.2 | N    | 0.4  | 0.9 | N    |      | -0.7 | -1.2 | 0.6 | -0.5 | 0.8 | 0.6 | -0.7 | 1   | -2.4 | -1.8 | 0.9 |
| G7  | -0.3 | N    | 0.7  | 1   | N    | 0.4  |      | -0.3 | 0.8 | N    | 0.9 | 0.8 | N    | 1   | -0.9 | -0.6 | 1   |
| G8  | N    | 0.4  | 0.7  | 1   | 0.4  | 0.6  | 0.2  |      | 0.8 | 0.3  | 0.9 | 0.8 | 0.2  | 1   | -0.5 | -0.3 | 1   |
| G9  | -4.4 | -2.4 | N    | N   | -2.4 | -1.4 | -3.2 | -4.4 |     | -2.7 | N   | N   | -3.1 | N   | -7.1 | -5.9 | N   |
| G10 | -0.5 | N    | 0.6  | 0.9 | N    | 0.3  | N    | -0.5 | 0.7 |      | 0.9 | 0.7 | N    | 1   | -1.2 | -0.8 | 0.9 |
| G11 | -13  | -8   | N    | N   | -8   | -5.4 | -10  | -13  | N   | -8.8 |     | N   | -9.8 | N   | -20  | -17  | N   |
| G12 | -4.4 | -2.4 | N    | N   | -2.4 | -1.4 | -3.2 | -4.4 | N   | -2.7 | N   |     | -3.1 | N   | -7.1 | -5.9 | 0.8 |
| G13 | -0.3 | N    | 0.7  | 1   | N    | 0.4  | N    | -0.3 | 0.8 | N    | 0.9 | 0.8 |      | 1   | -1   | -0.7 | 1   |
| G14 | -113 | -71  | -28  | N   | -71  | -50  | -88  | -113 | N   | -77  | N   | N   | -85  |     | -170 | -143 | N   |
| G15 | 0.3  | 0.6  | 0.8  | 1   | 0.6  | 0.7  | 0.5  | 0.3  | 0.9 | 0.5  | 1   | 0.9 | 0.5  | 1   |      | 0.2  | 1   |
| G16 | 0.2  | 0.5  | 0.8  | 1   | 0.5  | 0.6  | 0.4  | 0.2  | 0.9 | 0.5  | 0.9 | 0.9 | 0.4  | 1   | -0.2 |      | 1   |
| G17 | -28  | -17  | -6.3 | N   | -17  | -12  | -21  | -28  | N   | -19  | N   | N   | -21  | N   | -42  | -35  |     |

<sup>a</sup> N means the difference in the bending modulus of the two groups are not statistically significant. Numbers (unitless) were found by subtracting the modulus value of the group in the column from that of the group in the row, and dividing by that in row ((row-column)/row).

the bending modulus ( $E_C$ ) of the coating layer to have a more complete understanding. An F-test shows that there is a statistically significant relationship between the variables at the 99% confidence interval. A Student t-test suggests that the bond coat thickness has a statistically significant influence on the bending modulus ( $E_C$ ) at the 99% confidence interval, while the substrate temperature affects the bending modulus ( $E_C$ ) at the 92% confidence interval (Table 4). The Student t-test also suggests that top coat thickness is influential on the bending modulus at the 85% confidence interval. On the other hand, the stand off distance does not have any statistically significant influence in the bending modulus of the coatings studied. According to the multi-linear regression analysis, the bending modulus ( $E_C$ ) in the range of parameters studied can be expressed as;

$$E_C \text{ (GPa)} = 198 - 0.31 \cdot t_{BC} - 0.15 \cdot T_{St} - 0.07 \cdot t_{TC} \quad (7)$$

The average value of residuals (mean absolute error) in the fit is 40 GPa, i.e.  $E_C$  can be calculated from Eq. (7) with a  $\pm 40$  GPa error. It is clear from this analysis that thinner bond and top coatings, and lower substrate temperature in the investigated interval result in materials with higher bending modulus. A 150  $\mu\text{m}$  increase in bond coating (NiCrAlY) thickness causes a  $47 \pm 10$  GPa drop in the bending modulus ( $E_C$ ), while use of a pre-heated substrate decreases the bending modulus by about  $19 \pm 11$  GPa with respect to a cold substrate. Similarly, a 200  $\mu\text{m}$  increase in the top coat thickness gives rise to a  $14 \pm 10$  GPa decrease in the bending modulus. The stand off distance as a parameter was excluded in Eq. (7) since the Student t-test indicated only a 3% confidence for the negative estimated coefficient calculated from the multi-linear regression analysis. One may also consider excluding the influence of

the top coating thickness since the t-test probability is less than 90%.

## 4. Discussion

### 4.1. Four point bend test

As indicated above, when stress and modulus were calculated from the load–displacement data recorded during the four point bend test, the bond and top coating layers were taken as a single layer since there is only one equation, that allows the determination of only one unknown, from the slope of the load–displacement curve. Therefore, the mechanical properties represented here are rather an average property of the bond and top coatings. One disadvantage of this assumption is that if one of the coating layers has superior properties with respect to the other, then it will not be possible to distinguish the influence of the latter layer on the coating properties.

The values of bending yield stress and elastic modulus for the coatings in the current study exhibit a wide range with a 20–30% average S.D. Table 6 summarizes the elastic modulus and yield strength values for YSZ and NiCrAlY coatings reported in the open literature. Elastic modulus varies from 0.1 to 70 GPa for YSZ coatings, and 100–200 GPa for NiCrAlY coatings, while yield stress is around 20–80 MPa for YSZ coatings, and 1.2 GPa for NiCrAlY coatings. Wallace and Ilavsky [24], for instance, measured the elastic modulus of a 5 mm thick free standing YSZ plasma sprayed coating to be  $29 \pm 1$  GPa on the surface using a Hertzian contact arrangement, while Siemers and Mehan [25] reported that vacuum plasma sprayed NiCrAlY alloy has elastic modulus of 200 GPa, and yield strength of 1.2 GPa under a tensile test. Taka-

Table 6  
Yield strength and elastic modulus of yttria stabilized zirconia (YSZ) and NiCrAlY coating reported in the literature

| Yield stress (MPa) | Elastic modulus (GPa) | Method/sample                                       | Ref.    |
|--------------------|-----------------------|---|---------|
| <i>7 wt.% YSZ</i>  |                       |   |         |
|                    | 51                    | Ultrasonic test on free standing plate, APS         | [33]    |
|                    | 45.5                  | Cantilever beam, coating assembly, APS              | [34]    |
|                    | 3040                  | Hertzian indentation, free standing plate, APS      | [24]    |
|                    | 65                    | Ultrasonic test, free standing plate, APS           | [35]    |
|                    | $44 \pm 6$            | Knoop indentation                                   | [14]    |
|                    | 0.115                 | Tensile test  | [36]    |
|                    | 70                    | Tensile test  | [37]    |
|                    | 40                    | Uniaxial tension                                    | [34]    |
| <i>NiCrAlY</i>     |                       |   |         |
|                    | $110 \pm 22$          | Knoop indentation, VPS                              | [14]    |
| 1200               | 200                   | Tensile test, VPS                                   | [25]    |
| <i>NiCrAlY/YSZ</i> |                       |   |         |
| 27–71              |                       | 4-point bend test on free standing NiCrAlY/YSZ, APS | [26]    |
| 1440               | 1–171                 | 4-point bend test on free standing NiCrAlY/YSZ, APS | Current |

hashi et al. [26] found that the yield strength of free standing YSZ/NiCrAlY coating depends on the porosity content and varies from 27 to 71 MPa for 18.6–5.0% porosity levels, respectively. Leigh et al. [14] using Knoop indentation measured elastic modulus as  $44 \pm 6$  and  $110 \pm 22$  GPa for YSZ and NiCrAlY coatings, respectively. In general, the variation within the measured properties in the current study is higher than the variation in the values measured using other techniques. The reason for the high deviation in the current study is the presence of a substrate (mild steel) with high elastic modulus and large thickness with respect to the coating layer. The thickness of the substrate is 5–7 times that of the coating layer. For a more accurate determination of bending modulus and yield stress from a four point bend test, it is necessary to produce coatings on a thinner steel substrate.

#### 4.2. Mechanical properties

To understand the observations on the deformation behavior of the coatings, it is necessary to consider the microstructure and the adhesion in coatings. The microstructure of a ceramic coating is rather complex with many cohered splats that consist of a mixture of different phases [1]. As received commercial YSZ powders are mixtures of monoclinic and tetragonal phases [27]. Upon spraying, the majority of the powder melts and forms a metastable tetragonal phase ( $t'$ ) due to rapid solidification, while some of the particles stay unmelted and form monoclinic phase [27]. In addition, micro- and macro-porosities and cracks (dominated by the stresses) exist within and between splats [14]. Stresses in the plasma sprayed coating result from the residual stresses due to tensile quenching stresses in lamella, and due to the cooling stresses (tensile or compressive) caused by the difference in thermal expansion coefficients of the substrate and coating. These residual stresses vary throughout the thickness of the coating [8]. Some of the stresses are released by the formation of micro-cracks in ceramic coatings [8,12,28]. The type and the quantity of the residual stresses also influence the adhesion at the substrate-bond coating, and bond coating-top coating interfaces [10]. It has been shown that the residual stresses in plasma sprayed YSZ coatings on a steel substrate are generally tensile, and increase with the coating thickness [8,9,28,29].

##### 4.2.1. Effect of bond coat thickness

As given in Eqs. (6) and (7), the bending yield stress and modulus of coatings are strongly controlled by the thickness of the bond coat layer. An increase in the bond coat thickness gives rise to a drop in the bending yield strength and bending modulus of the coating system. This is because a thicker bond coat layer introduces more residual stress which weakens both interface

binding strength and the coating body by increasing the amount of flaws in the structure.

##### 4.2.2. Effect of substrate temperature

Eqs. (6) and (7) also indicate that coatings sprayed on a pre-heated substrate exhibit lower bending strength and bending modulus. It has been reported that higher substrate temperature lowers the residual stresses [29]. Therefore, one would expect that coating on a pre-heated substrate should have exhibited higher bending strength. It is believed that adhesion strength between bond coat and substrate is lower for a pre-heated substrate because of weakening in the mechanical adhesion of the bond coat and substrate. It is possible that a locally over-heated area was created when the substrate was preheated. These locally over-heated areas may oxidize easily. It was reported that the oxidation on the substrate surface drastically weakens the adhesion [30]. Therefore, one possibility for the lower strength exhibited in the coatings deposited on pre-heated substrate would be the presence of an oxide layer.

##### 4.2.3. Effect of top coat thickness

As given in Table 6, the mechanical properties of NiCrAlY coatings are superior to that of a YSZ coatings. Therefore, the influence of the change in the top coat (YSZ) thickness on the mechanical properties of a TBC system was suppressed due to the nature of the test. As indicated above, in the calculation procedure the bond and top coat layers were considered as a single layer providing an average property. Nevertheless, as given in Table 4, the increase in top coat thickness decreases the bending modulus and bending yield stress at the 85 and 70% confidence interval, respectively. The confidence limit is lower for the yield stress analysis due to greater variation in this value. It is believed that a more accurate determination (for example using a thinner steel substrate) of the bending modulus would increase the confidence interval.

The reason that a coating with a thicker top coat mechanically weakens is further introduction of residual stresses and defects such as pores and cracks with increasing thickness.

##### 4.2.4. Effect of stand off distance

It was found that the stand off distance has no significant influence on the bending yield strength and bending modulus of the coating layers. The stand off distance mainly controls the cohesion between splats because the temperature and velocity of particles in the plasma flame significantly change with stand off distance [31]. It was reported that the temperature and velocity of particles in the plasma flame may vary by as much as approximately 1000 K, and  $50 \text{ m s}^{-1}$  in a 20 mm change in the stand off distance, respectively [32].

Therefore, better spreading and cohesion would be achieved with shorter spraying distances. However, one should bear in mind that residual stresses introduced are higher for shorter spraying distance since particle temperature is higher [28]. As a result, it is believed that these two competing factors; cohesion strength (positive influence) and residual stresses (negative influence), neutralize each other with respect to their influence on stand off distance and the performance of the coating. Although it was not possible to distinguish the influence of the stand off distance on the deformation characteristics of the plasma sprayed YSZ coatings using the four point bend test due to these two competing factors, the investigation of the AE activities during the four point tests of these samples clearly identified the influence of the stand off distance on the properties of these coatings. The AE studies, whose details will be discussed in the second part of this paper [22], showed that coatings plasma sprayed at shorter stand off distances exhibited higher cracking activities and reflect the presence of a higher amount of residual stresses.

#### 4.2.5. Yield strain

As given in Fig. 4, the yield strains of the coatings are similar, but higher than that of a steel substrate. One would expect that a steel substrate deforms more than a ceramic, however, it is believed that a coating with pores and cracks can deform more than the bulk counterparts before yielding. The yield strains of coatings with thicker bond coat such as coatings from groups 3, 4, 11, 12, and 14 are higher than other coatings. This may be because the coatings in the aforementioned groups have more defects such as pores, voids, and cracks.

## 5. Conclusions

All the coatings prepared with varying spray parameters were tested with four point bending. The bending yield stress and bending modulus were calculated from the load–displacement curves recorded during the bending tests by considering the top–bond coating system as a single assembly. The variation in the bending yield stress and modulus values calculated in the current study were generally higher than the previously reported values determined using other techniques such as Knoop indentation in the open literature.

A multi-linear statistical regression on the bending yield strength and bending modulus of the coating layers showed that coating layers with thinner bond and top coating sprayed on a cold steel substrate yield at higher stresses, and result in higher bending modulus. On the other hand, stand off distance was found to have no statistically significant influence on the bending yield strength and modulus.

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## Appendix A. Nomenclature

Throughout the text common engineering units of thermal spray field have been used.

|                     |   |
|---------------------|---|
| $D$                 | distance between loading and support bar (100 mm)   |
| $E$                 | bending modulus, GPa  |
| $E_{St}$            | bending modulus of steel substrate, GPa   |
| $E_C$               | bending modulus of coating system (top and bond coats), GPa   |
| $(EI)^*$            | elastic modulus times moment of inertia for the whole system including the substrate, bond coat and top coat layers |
| $I$                 | moment of inertia of the test specimen, $wt_c^3/12$ , mm <sup>4</sup>   |
| $P$                 | load, N   |
| $P_{YC}$            | yielding load of the coating system (top and bond coats), N   |
| $t_{St}$            | thickness of steel substrate, $\mu\text{m}$   |
| $t_{NA}$            | distance between the neutral axis of the test bar and the bottom of the substrate, $\mu\text{m}$                    |
| $t_C$               | thickness of the coating system (top and bond coats), $\mu\text{m}$   |
| $t_{TC}$            | thickness of top coat, $\mu\text{m}$  |
| $t_{BC}$            | thickness of bond coat, $\mu\text{m}$   |
| $T_{St}$            | temperature of steel substrate, K   |
| $X_{sod}$           | stand off distance, mm  |
| $w$                 | width of the testing bar, mm  |
| $y$                 | displacement at the cross-head, mm  |
| $\Delta P/\Delta y$ | slope of load displacement curve  |
| $\sigma_{YC}$       | bending yield stress of the coating system (top and bond coats), MPa  |

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