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NANO AND MICRO INDENTATION STUDIES OF BULK ZIRCONIA AND EB PVD TBCs

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ABSTRACT

In order to model the erosion of a material it is necessary to know the material properties of both the impacting particles as well as the target. In the case of electron beam (EB) physical vapour deposited (PVD) thermal barrier coatings (TBCs) the properties of the columns as opposed to the coating as a whole are important. This is due to the fact that discrete erosion events are on a similar scale as the size of the individual columns. Thus nano* and micro* indentation were used to determine the hardness and the Young's modulus of the columns. However, care had to be taken to ensure that it was the hardness of the columns that was being measured and not the coating as a whole. This paper discusses the differences in the results obtained when using the two different tests and relates them to the interactions between the indent and the columns of the EB PVD TBC microstructure. It was found that individual columns had a hardness of 14 GPa measured using nano indentation, while the hardness of the coating, using micro indentation decreased from 13 to 2.4 GPa as the indentation load increased from 0.1 to 3N. This decrease in hardness was attributed to the interaction between the indenter and a number of adjacent columns and the ability of the columns to move laterally under indentation.

Keywords: EB PVD TBCs, nanohardness, microhardness

INTRODUCTION

The nano indentation of electron beam (EB) physical vapour deposited (PVD) thermal barrier coatings (TBCs) reported here was part of a larger project involving modelling the erosion of EB PVD TBCs [1,2]. There were two main reasons for initiating the nano indentation tests; the first was to determine the

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* All the hardness tests were carried out using either the Nano Test 600 or the Micro Test 200.

material properties of the individual columns of the coating which were needed as input parameters for the erosion model - Figure 1 and 2 illustrate the columnar microstructure of EB PVD TB Cs-; the second was to assess the depth of the plastic zone due to solid particle impact, which proved unsuccessful because the boundary effects were too great. It was expected that by measuring the change in nano-hardness down a sectioned column it would be possible to determine the depth of the plastic zone. However, due to the scatter in the results obtained, it was not possible to determine any changes in hardness due to densification of the columns caused by impact. This scatter was attributed to the fact that the columns were only 10-15 μm in diameter and hence in sectioned samples there was not sufficient material underneath the indent to stop boundary effects influencing the results.

During solid particle erosion of EB PVD TBCs, where the impacting particles are typically less than 1 50μm in diameter and the contact footprints are 5-25 μm in diameter, the properties of the individual columnar grains are more important than those of the coating as a whole. This is due to the fact that discrete erosion events are of a similar scale (5-25μm) to the size of the individual columns, which are typically 10-1 5μm in diameter. The erosion tests were carried out using 1 00μm silica at typically 170 m/s, a full description of the erosion test rig used and the conditions under which the EB PVD TBCs were tested can be found in the literature [3]. Thus in modelling the erosion of EB PVD TBCs by particles of size 1 50μm or less, it is the hardness, Young's Modulus and the fracture toughness of the columns that needs to be known rather than those of the coating as a whole. The thinking was that nano indentation could provide the information on the first two, but in order to do this it was first necessary to determine how to obtain the hardness of a single column without the results being affected by microstructural features of the coating as a whole, i.e. porosity, boundaries or neighbouring columns.

In a sense this problem was similar to that of nano and micro indentation of thin film coatings, where it is difficult to separate effects of the coating and substrate interactions when determining the mechanical properties of continuous coatings [4]. To address this, other papers have concentrated on the cracking of the coatings and how this is affected by the substrate hardness [5]. In this project, it was necessary to separate the effects of lateral rather than vertical contributions to the constraint on indentation, since the EB PVD TBCs were of sufficient thickness not to be influenced by the substrate. As far as the authors are aware, only one other piece of work has been done on the nano and micro indentation of TBCs, by K.D Bouzakis et al [5]. However, the loads that were used, 200 to 1000 mN, which is on the border between nano and micro indentation, meant that they were not measuring the individual column properties but rather the coating properties.

2. METHOD

Two different hardness testers were used for this project a Nano Test 600 and a Micro Test 200. Three different samples were used for the testing. These included a bulk zirconia sample, and two 8wt% yttria stabilised zirconia thermal barrier coatings (TBC) which had been deposited using electron beam physical vapour deposition techniques onto a prepared aluminised substrate. One of the TBC samples had been eroded with one gram of 100 µm alumina at 140 m/s and was then sectioned and polished. Both the nano and the micro indentation tests were conducted on automated systems. All the samples tested were polished to a finish of less the 1 µm Ra, and the hardness and reduced Young's Modulus were determined by the instruments from the unloading curve from the load displacement curves obtained during nano-/micro-indentation. Three different forms of indentation test were used during the project; on the bulk zirconia sample each indent position on the bulk Zirconia sample was indented five times at increasing loads from 40 to 200mN; on the tops of the columns each indent position was indented five times at increasing loads from 20 to 100mN; all the other tests (both nano- and micro-) were single loading/unloading cycles.

The indentation test program will be discussed in 4 sections. The first section involves the nano-indentation of bulk zirconia, the second the nano- indentation of a sectioned EB PVD TBC. The large scatter in these results prompted the attempts to do nano indentation tests on the top of individual EB PVD TBC columns(section 3) and then it was decided to determine how an increase in load would affect the measured hardness and micro indentation tests, at loads from 0.1 -3N, carried out on the tops of the EB PVD TBCs columns (section 4).

2.1 NANO INDENTATION OF BULK ZIRCONIA

Initial nano indentation tests were conducted on a bulk zirconia sample in order to get baseline data against which to compare those of the EB PVD TBCs and to identify any possible problems. From the results in Table 1 and Figure 3, it can be seen that there was a fair degree of scatter. Each set of results was obtained from one position by indenting the same position at increasing loads from 40-200mN, thus the scatter represents variability in the zirconia properties at the micro-scale.

From figure 3, it can be seen that in a number of cases there is a reduction in the hardness as the load is increased. This was attributed to the indent being at or near a grain boundary or region of increased porosity. Thus as the load was increased the hardness decreased due to the increased interaction of the indent and the local defect. In order to determine which results were unaffected by defects and which results where low due to underlying porosity/defects the results of the hardness tests at 200mN were plotted on probability graph paper (Figure 4).

As can be seen from Figures 4a and 4b (diamond markers – represent a plot of all the results) it is apparent that there are two distinct sets of data (two Gaussian trends with different slopes – here each individual Gaussian trend plots a straight line against a normal probability ordinate). Thus it was possible to ascertain which readings were taken near underlying porosity and which represented the natural variation in the material hardness. The top eight results (those conforming to the linear trend with a shallow slope) were then re-plotted against a probability ordinate (Figure 4b - square markers); these results can be assumed to be true hardness readings of the bulk zirconia ceramic which have not been influenced by underlying or neighbouring porosity/defects. The bottom six results (those conforming to the linear trend with a steep slope, in Figure 4b – triangle markers) represent the results, which were taken above or near regions of porosity/defects, and were thus affected significantly by such defects resulting in a large scatter in the results. In this example some 40% of the hardness readings taken are affected by local surface defects.

2.2 NANO INDENTATION ON THE CROSS SECTION OF AN EB PVD TBC

Under solid particle impact conditions, a small degree of plastic deformation occurs in EB PVD TBCs. Since cracking occurs at the elastic plastic interface when indenting or impacting ceramics [6], then in order to model erosion, the depth of the plastic zone needs to be known [1,2]. The aim was that nano-indentation could be used to determine the degree / depth of plastic deformation occurring on impact.

To do this, it was necessary to nano-indent the cross section of an eroded specimen along the length of a column with the aim of seeing a hardness change at the plastic zone boundary. These measurements were achieved, however, there was a large scatter in the results obtained and it was not possible to determine the plastic zone boundary from the data. The scatter was thought to be due to the uncertainty in the proximity of column boundaries for the cross-sectioned samples, i.e it was not possible to determine the thickness of the column under the indent. Thus for the case where the column boundaries interacted with the indentation process the effective hardness reading was low and also cracking sometimes occurred. This resulted in a wide scatter of hardness readings, see Table 2, the average of which would under read the true hardness of a column.

From the wide scatter in the hardness results of the sectioned coating and from the probability graph, Figure 5, it can be deduced that the results were influenced by underlying porosity and column boundaries. Hence the hardness results from the cross section of the coating can not be used as a measure of the hardness of the columns. In reality the true hardness and elastic modulus is more likely to be estimated from the larger values in each of the measured parameters, vis 11.3 GPa for hardness and 168 GPa for the elastic modulus. Further, due to this scatter in the results nano hardness test could not be used to determine the extent of plastic deformation within the impacted region of EB PVD TBCs, since the change in the hardness due to particle impact may well be expected to be less than the scatter in the results of the nano hardness tests.

2.3 NANO INDENTATION ON TOP OF THE EB PVD TBC COLUMNS

Since it was not possible to unequivocally determine the column hardness from indentation results on a sectioned coating, it was decided to do nano indentation on the top of the columns. Indenting the top of the columns has the added advantage of being an effective 'infinite' thickness sample in the direction of loading. Thus, this method does not have the same problems as those associated with indenting the x - section of a coating, provided the indent is in the centre of the column and only interacts with that one column. In order to indent the top of the column it was necessary to lightly polish the specimen prior to-indentation in order to remove the pyramidal tops of the columns (see Figure 1 for a micrograph of an EB PVD TBC) to ensure that the sample was sufficiently flat for nano indentation. The main problem with nano indentation on the tops of the columns was ensuring that the indent was centred in the middle of a column and did not interact with neighbouring columns. The results, summarised in Table 3, were the only ones where the indent was contained within one column. It should be noted that these results are significantly higher than those measured along the sectioned sample and they agree fairly closely to the results from the bulk zirconia sample. They are thus assumed to be an accurate measure of the hardness of the columns in an EB PVD TBC.

2.4 MICRO HARDNESS TESTS ON THE TOP OF THE EB PVD TBC COLUMNS

A number of micro hardness tests were also conducted on the tops of the columns under different loads to determine what would happen when the load was spread across a number of different columns and how this would affect the apparent hardness. Figure 6 is a micrograph of these microhardness indents on the top of a polished EB PVD TBC; the arrows point to the indents corresponding to the different loads. The results of the microhardness tests are summarised in table 4. Note that as the load increased the measured hardness of the coating decreased, as shown in Figure 7. This decrease in the measured hardness was strongly dependent on the number of columns indented and the manner in which these columns interacted with the indenter. The largest of these hardness values, measured at the smallest load, approaches the value measured by nano-indentation on the top of the column.

3 DISCUSSION

The nano indentation of the bulk zirconia and the subsequent statistical analysis shows that an analysis of probability distributions could be used to separate results measured within grains from those which had been influenced by porosity. This analysis supplied a 'reference' distribution of hardness data for comparison against the results obtained from the X-sectioned sample, EB PVD TBC samples. It showed that all the hardness results from the sectioned EB PVD TBC sample had been affected by porosity and/or boundary defects, although the largest of these values approach those measured within grains on the bulk zirconia samples. Since the columns were only 15µm in diameter this result was not surprising as the sectioned columns were not sufficiently thick enough to contain the indent within the column, thus boundary affects were influencing the hardness readings.

The nano hardness testing of the tops of the EB PVD columns, however, was successful in determining the hardness of the columns. These measurements had to be used in conjunction with microscopy to determine whether the indent was contained within one column. This requirement was confirmed by a series of micro hardness tests conducted on the top of the EB PVD TBC columns under increasing loads where only the smallest load indents approached the hardness of the columns measured by nano-indentation. Figure 7 indicates that the apparent hardness of the coating decreased as the load increased until at a load of about 1N the hardness remained almost constant at about 2.4GPa. This can be explained in terms of the interaction of the indent with the columns and column boundary regions. As the load increased the number of columns, which interacted with the indent, increased. It should be noted that due to the columnar microstructure of EB PVD TBCs some lateral movement is possible between the columns. Hence some of the load can be adsorbed by the lateral movement of the columns and the measured hardness consequently is decreased. Further, as the load is increased, what one measures changes. At low indent loads, and provided that the indent was contained within one column, the hardness measured is that of the column. While at loads greater that 1 -2N, when the indent acts across a number of columns, it is the mean hardness of the coating that is measured. The interactions of the indents with the columns is illustrated in the micrographs in Figures 8a-d.

Figure 8a shows an example were the indent (3N) acts across a number of columns (possibly 16-20 in this example) with significant interaction between neighbouring columns. It is this interaction of the indent with a number of columns that accounts for the observed reduction in hardness, and is attributed to the high degree of lateral movement available to the columns. In contrast to this Figure 8b, a 0.5N indent, shows much less interaction between neighbouring columns, however the indent has still interacted with more than one column. In the first example it would appear that the hardness of the coating is being measured (neighbouring column interactions are observed), while in the second example it is questionable whether the hardness of the coating or the hardness of the column was measured. Figure 8c, a 0.3N indent, shows only a small degree on interaction with neighbouring columns, while the 0.1 N indents, Figure 8d, were centred within their respective columns, with minimal interaction, possibly with one neighbouring column, in both cases. These latter results are the ones, which gave the highest hardness readings (13.73 and 13.72) and are the closest to the results of the nano hardness tests. The reason that the hardness measured using 0.2 to 0.4 N loads were low is that the indents for these loads all spread across two or more grains and were not centred in one grain alone. Thus, referencing back to Figure 7, and with reference to the micrographs in figure 10, one can see that there is a transition between measuring the hardness of the individual columns to the hardness of the coating. This transition is dependent on the relative sizes of both the columns and the indents, which in turn determines the number of columns with which that indenter interacts.

4. CONCLUSIONS

This study has shown that there is a significant difference in the hardness between the individual columns of an EB PVD TBC (14 GPa) and the hardness of the bulk coating (2.4 GPa). This difference can be attributed to the ability of the coating to accommodate the indentation event by lateral movement of the individual columns. When measuring the microhardness of EB PVD TBCs the hardness of the coating decreased from 13.7 to 2.4 GPa as the indentation load increased from 0.1 to 3N.

Probability distribution functions have been used to identify which results, based on nano indentation, have been affected by porosity/boundary defects and what represent the natural scatter in hardness and elastic modulus readings of individual columns. Thus when using micro hardness to determine the hardness of an EB PVD TBC, a load of at least 2N should be used. However, in order to determine the properties (hardness, elastic modulus) of individual columns in an EB PVD TBC, nano indentation techniques in conjunction with microscopy and statistic analysis should be used.

5. Reference List

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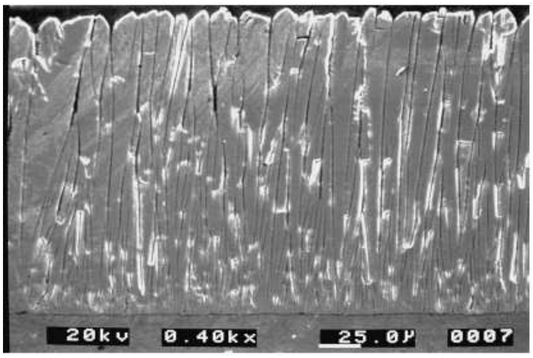


Figure 1: Scanning Electron Micrograph showing the columnar microstructure of EB TBCs.

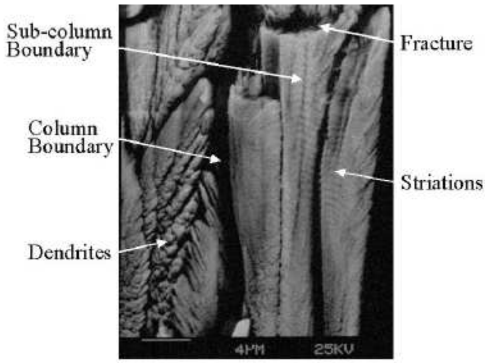


Figure 2: Scanning Electron Micrograph of an EB PVD coating showing various microstructural features [1].

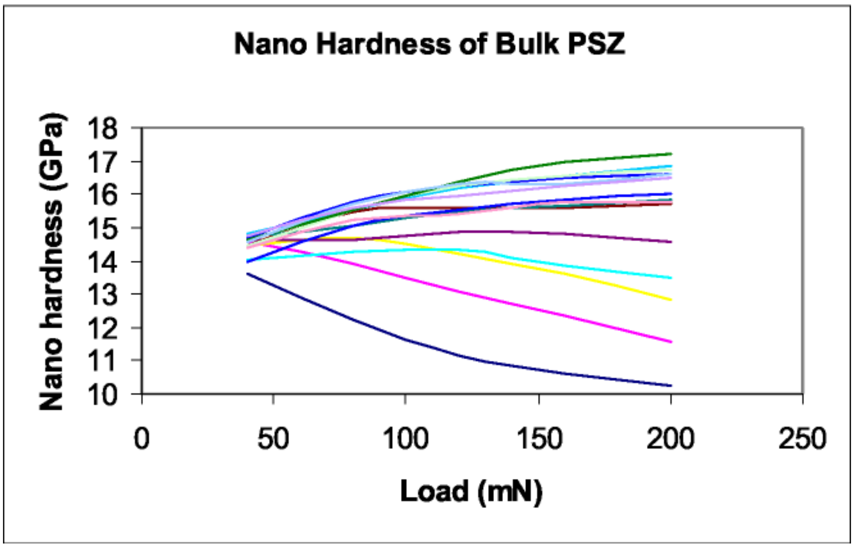
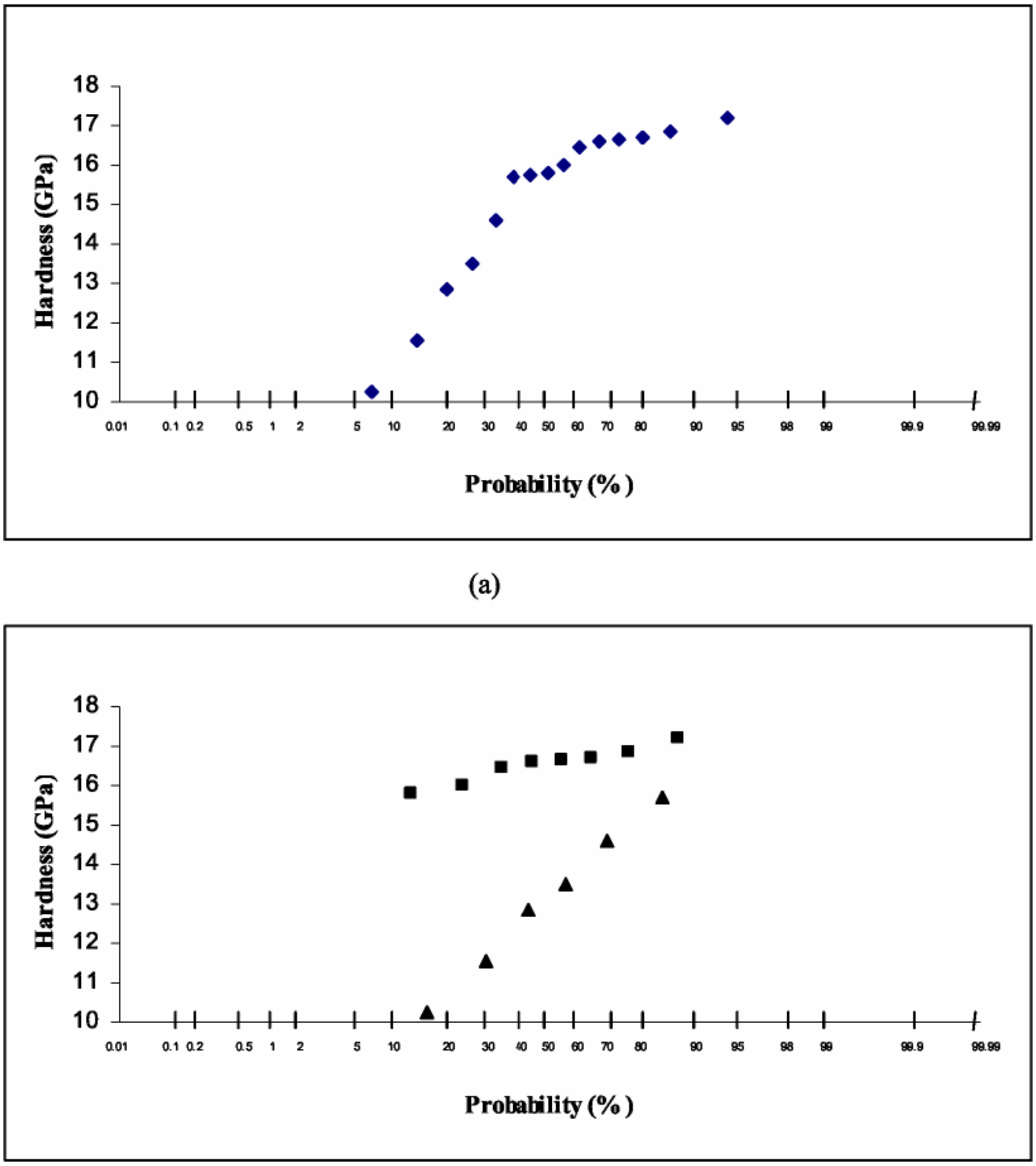


Figure 3: Graph of the nano hardness of bulk PSZ at a number of different positions under increasing loads.



(b)

Figure 4: Probability plot of nano-hardness of bulk PSZ.

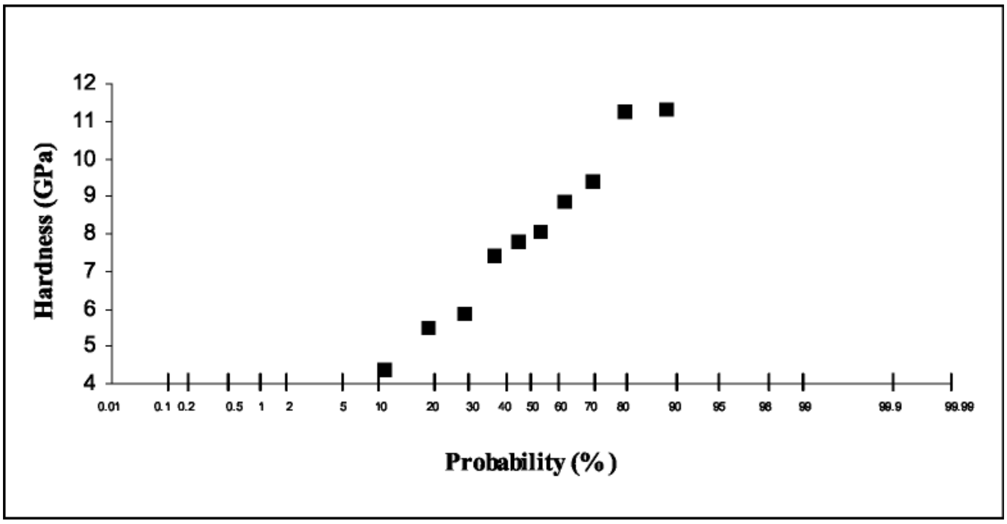


Figure 5: Hardness vs probability for the nano hardness tests on the cross section of the EB PVD TBC.

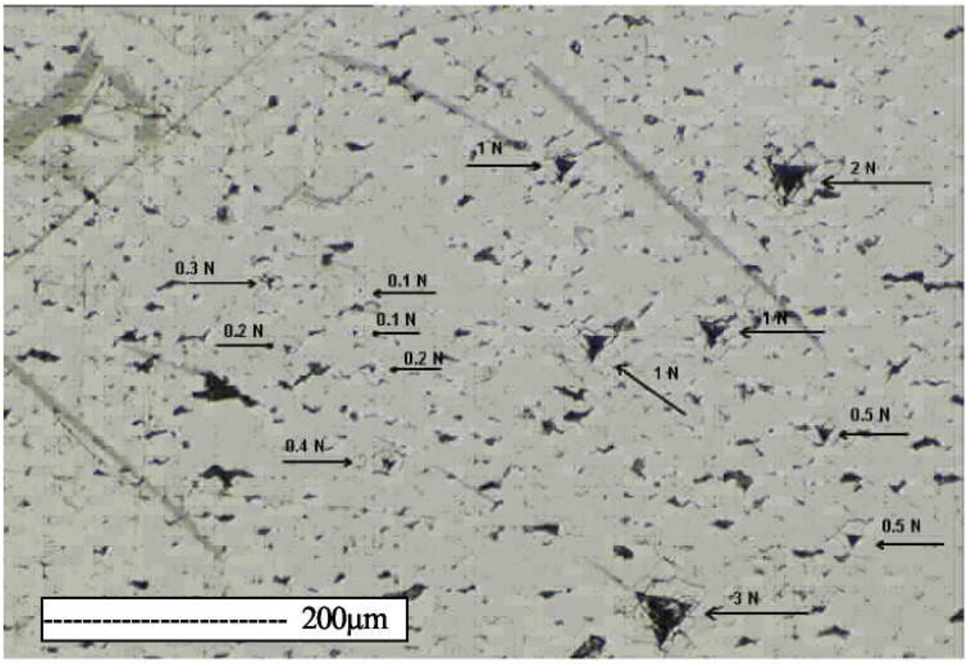


Figure 6: Micrograph of the micro indents on the top of the columns of an EB PVD TBC, arrows indicate the indents with load written above it.

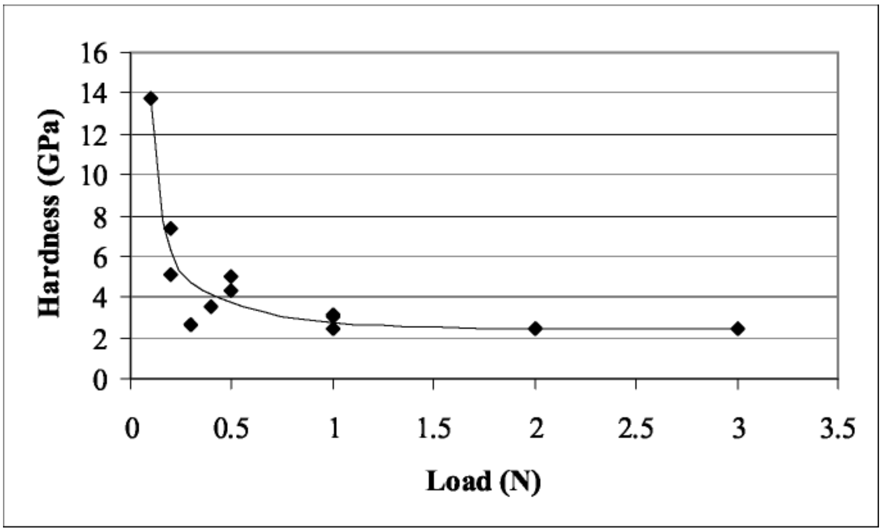


Figure 7: Graph of load vs hardness for the micro indentation tests on the tops of the columns of an EB PVD TBC, the curve through the points illustrates the trend.

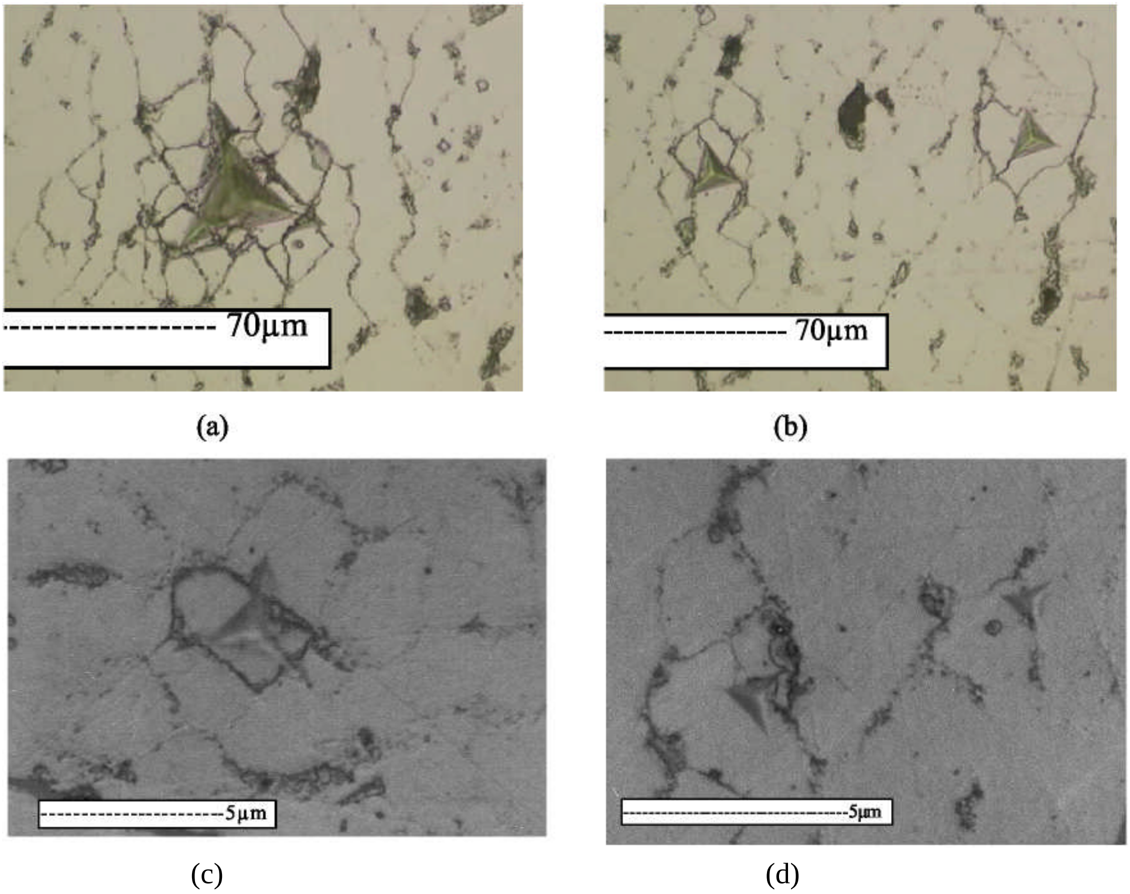


Figure 8: a) 3 N micro indent showing interaction with a number of columns. B) Two 0.5 N indents showing a much lower degree of interaction with neighbouring columns. c) The 0.3 N indent showing how in this case the column has been pushed down into the coating. d) The 0.1 N indents showing minimal interaction with column boundaries.

Load	ZR121	ZR122	ZR123	ZR124	ZR125	ZR131	ZR132	ZR133	ZR134	ZR135	ZR141	ZR142	ZR143	ZR144	ZR145
mN	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa
200	10.23	11.55	12.83	13.48	14.58	15.69	15.81	16.01	16.85	16.63	16.72	17.22	16.62	15.77	16.47
160	10.63	12.32	13.62	13.84	14.84	15.62	15.68	15.84	16.55	16.49	16.55	16.95	16.34	15.787	16.26
120	11.13	13.09	14.24	14.35	14.87	15.6	15.49	15.56	16.2	16.26	16.23	16.39	16.31	15.4	15.98
80	12.21	13.92	14.7	14.25	14.66	15.45	15.08	15.08	15.55	15.79	15.54	15.55	15.73	15.26	15.58
40	13.6	14.55	14.47	14.01	14.66	14.47	14.74	13.98	14.83	14.71	14.43	14.63	14.55	14.42	14.75

Table 1: Results of the nano-hardness tests on bulk PSZ.

Load	Hardness	Modulus
mN	GPa	GPa
100	7.42	104
100	9.37	144
100	8.06	124
100	5.5	120
100	8.84	132
100	11.24	145
100	7.81	142
100	5.87	110
100	4.38	109
100	11.32	168

Table 2: Results from the nano tests on a cross-sectioned EB PVD TBC.

Load	Sample ZR 28			Sample ZR 27		
mN	Hardness	Modulus	Reduced Mod	Hardness	Modulus	Reduced Mod
	GPa	GPa	GPa	GPa	GPa	GPa
100	15.82	218	191	16.32	198	176
80	15.86	216	190	14.62	197	175
60	15.18	226	197	13.35	187	168
40	14.67	223	195	11.68	180	162
20	13.67	214	188	10.02	173	157

Table 3: Nano hardness and Modulus measured from the top of a sample.

	Load N	Hardness GPa
1	0.1	13.73
2	0.1	13.72
3	0.2	7.4
4	0.2	5.13
5	0.3	2.67
6	0.4	3.51
7	0.5	4.31
8	0.5	4.98
9	1	2.41
10	1	3.07
11	1	3.18
12	2	2.45
13	3	2.47

Table 4: Table of hardness vs load for various micro hardness indents.