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Nano and Micro Hardness Testing of Aged EB-PVD TBCs

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Abstract

Previous studies on the erosion of EB PVD TBCs has shown that aging the coatings at between 1100°C and 1500°C before erosion increases the erosion rate. These changes in the erosion rate were attributed to a number of factors including changes to the nano porosity within the coatings as well as phase changes within the coatings. Such changes in the morphology of the coatings should be measurable as changes in their hardness. Thus it was decided to ascertain the effect that the aging had on the hardness of the coatings. Since, during erosion, the size of the interaction zone between the impacting particle and the coating is in the same range as the size of the individual columns of the coating it was decided to measure the change in the hardness of the columns as well as the coating as a whole.

It was found that the aging increased the hardness of both the coating as a whole and the individual columns of the coatings. The micro hardness of the coating was found to increase from 2.5-3.5 GPa in the as received condition to 4.5-6 GPa after 100hrs at 1100°C and to 7.5-8 GPa after 24hrs at 1500°C. The nano hardness of the individual columns on the other hand was found to increase from 18GPa in the as received condition to 35 GPa after aging. This paper discusses the increases in hardness due to aging in terms of the sintering and morphological changes that occur in the coating. The difference in the nano and micro hardness results are discussed in terms of the relative size of the indents and column size and the associated interactions that occur under the different indenter heads and loads

Keywords: Nano hardness, micro hardness, aging, EB PVD TBCs.

1. Introduction

The erosion of both electron beam physical vapour deposited (EB PVD) and plasma sprayed (PS) thermal barrier coatings (TBCs) has been well documented in the past [1-3] [4] and will not be covered here[5]. However, more recently the effects of aging on the erosion resistance and mechanical properties have also been studied [6-8]. Interestingly, where Janos et al [8] found that the aging increased the hardness and the erosion resistance of PS TBCs, due to improvements in the inter-splat bonding, Wellman and Nicholls [7] found that aging increased the erosion rate for EB PVD TBCs. 100hrs at 1100°C was found to double the erosion rate while 24hrs at 1500°C quadrupled it. The different response to sintering by the two different types of coating is directly related to the differences in erosion mechanism which results from the different structure of the coatings. In plasma sprayed coatings erosion rate is dependent on the strength of the inter-splat bonding and thus any strengthening of the bonds will improve the erosion resistance. While in EB PVD TBCs the increases in erosion rate where attributed to both changes in the porosity of the coatings and to the sintering together of the individual columns EB PVD TBCs are only about 80% dense. The sintering of the columns together resulted in the propagation of lateral cracks across neighbouring columns thus resulting in a greater mass loss per impact event. This adequately explains the increase in erosion rate at 1500°C where significant evidence of sintering was observed. However, since at 1100°C sintering was not as marked it was thought that there was something else affecting the erosion rate, possibly porosity and hardness.

These finding prompted the authors to investigate the effects of aging on the hardness of the coatings. However, in previous work [6] it was noted that there was a difference in the hardness between individual columns of an EB PVD TBC, 12-14GPa in the as received condition, and the coating as a whole, 2-3GPa. Thus it was necessary to use nano indentation techniques to assess the changes in the hardness of the columns of the EB PVD TBCs and micro hardness tests to determine the hardness of the coating as a whole. Since erosion contact areas are of a similar size to the area of the columns it is the columnar properties that are important and not the properties of the coating as a whole. Thus the main aim of this project was to determine the effect of aging on the measured hardness of both the individual columns and the coating as a whole for EB PVD TBCs.

2. Samples and Test Method

An 8wt% Y_2O_3 partially stabilised ZrO_2 was deposited, using EB PVD techniques, onto a number of different substrates which were then given two different heat treatments, namely 100hrs at 1100°C and 24hrs at 1500°C. The samples, including untreated ones, were then cut for the various aspects of the investigation. Cross sectioned samples were prepared for analysis and sections were prepared for nano and micro indentation. Due to the roughness of the coatings in the as deposited condition it was necessary to polish the samples in order to conduct the nano indentation studies. All the indentation tests were conducted on at Cranfield University using a Micro Materials NanoTest^{TM} 600, which uses a diamond Berkovich head. The Oliver and Pharr method was used to determine the hardness and Youngs Modulus of the coatings.

The following test conditions were used for the indentation studies.

Due to the size of the columns (10-17µm in diameter) nano indents, which are about 3-5µm in size, will be affected by edge effects and neighbouring columns unless positioned close to the centre of the column. Thus it was decided to do a number of indents, 49, and use statistical methods to de-convolute the results. Thus the nano indents where conducted on a 7 by 7 grid. A 10mN load was used for the microhardness tests, as this resulted in indents that could be contained within an individual column. In the case of micro indentation, since the indent size was expected to interact with a number of columns a 2N load was used and only 4 indents were done on each sample. Previous work on TBCs in the as received condition showed that at loads greater than 1-1.5N the coating hardness was assessed. Since the coatings were all in the region of 150µm thick (after preparation) it was assumed that the substrate had absolutely no effect on the measurements.

3. Results

3.1 Effects of Aging Treatments on Microstructure

The micrographs in Figures 1-3 show the effect of aging on the morphology of the coatings. Figure 1 is a reference sample and illustrates a typical EB PVD TBC with its pyramidal type tops to the columns. It was due to this morphology that it was necessary to polish the samples before indentation testing could be done. As can be seen from Figure 2 there is no visible change to the column morphology after only 100hrs at 1100°C. However, after 24hrs at 1500°C, as can be seen from Figure 3 there has been significant sintering of the columns, which have lost their pyramidal morphology and have started to sinter together. Further, as can be seen in Figure 3b, mud flat cracking has started to develop as a result of the sintering.

3.2 Micro Indentation

The results of the micro indentation studies are given in the graphs in Figure 4 and 5. These results showed that the hardness of the coating increased with aging condition for both the substrates tested.

The low hardness measured on the samples aged at 1500°C are a result of the measurement being taken on a porous section of the coating. This will be discussed further in a following section.

3.3 Nano Indentation

The graphs in Figure 6 and 7 are the results of the nano indentation tests performed on the coatings on the zirconia and the alumina substrates, plotting hardness against probability.

As can be seen from the results the hardness of the coatings was found to increase with an increase in aging condition except for the coating deposited on zirconia and aged at 1500°C. This anomaly will be explained in the Discussion.

4. Discussion

The micro indentation tests revealed that the hardness of the EB PVD TBC increased as a function of aging on both of the substrates, to similar levels, although the coating on the alumina substrate had a lower measured hardness in the as received condition. This was attributed to the fact that there was a greater degree of mismatch between the thermal expansion coefficient of the alumina and the coating than between the zirconia and the coating. Thus on cooling after deposition of the TBC (which occurs at 1000°C) there is less constraint between the individual columns on the alumina substrate and hence a lower measured hardness. The scatter in the results observed in the graph in Figure 5 was a result of some of the indents being positioned over cracked regions of the coating that was aged at 1500°C, as illustrated in Figure 8, consequently these results, the three lowest, can be disregarded. This was a result of sintering occurring in the samples aged at 1500°C for 24hrs and, in the case of the zirconia substrate, the formation of mud flat cracking.

Previous work on the micro indentation of EB PVD TBCs has shown that the load at which the tests are conducted is extremely important as can be seen form the graph in Figure 9. This graph shows the existence of a transition between measuring the properties of an individual column at low loads and the properties of the coating at high loads where the indented area interact with a number of different columns, hence a load of 2N was used for the micro indentation tests to ensure that the tests were conducted at loads greater than the transition loads.

As mentioned earlier it was decided to use a load of 10mN for the nano indentation tests and due to the fact that a statistical variation of the results was expected 49 indents were conducted on each of the test samples, this was in order to obtain a probability plot. It was hoped that the shape of the plot would be similar to that obtained for the nano indentation of bulk zirconia (from previous work [6]) as shown in Figure 10, i.e. the results would plateau indicating results un-affected by defect. Such a plot enables one to determine those results influenced by porosity or defects and the un-affected results. However, due to the columnar morphology of the EB PVD TBCs and the size of the columns, 10-17μm diameter, most of the nano indentation tests, which were performed on the tops of the columns, were influenced to some degree by either column boundaries or defects, resulting in the plots shown in Figure 6 and Figure 7. Thus, the hardness of the column was taken as the highest measured reading and it was assumed that all the other indents had been affected by interactions with defects and column boundaries. It was assumed that the highest result was the most probable correct reading of hardness. Ideally the results would have plateaued but this was unfortunately not the case.

Unfortunately due to the size of the indents and the low penetration depth it was not possible to find and photograph the indented areas and thus was not possible to ascertain the degree to which the indents interacted with the individual columns.

These changes in the hardness of the coating with aging are attributed to a number of different mechanisms which include: changes in the micro porosity of the columns, changes in the porosity of the coating as a whole due to sintering together of columns, indentation size effects and phase transformation at the higher aging temperature.

In all cases the measured increase in the hardness of the samples aged at 1100°C was attributed to changes in the morphology of the individual columns rather than changes to the coating as a whole.

For the samples aged at 1500°C the change in the hardness was attributed to a combination of the changes in the micro porosity within the columns the sintering together of the columns(although this would have a minor effect) and to phase transformations. The coating on the zirconia substrate, however, showed a decrease in the measured hardness; it is thought that this is not a true refection of the hardness of the columns but rather indicated that none of the indents centred on a column and hence all the measured results are low. The authors do not believe that these results represent the true hardness of the columns but rather that it is an effect as a result of the sintering and subsequent cooling of the sample and the resultant sinter cracks.

The hardness measured on the coating deposited onto the zirconia substrate and aged at 1500°C also needs to be discussed as it is significantly higher than expected. It was expected that the hardness of the columns would increase as a result of the aging process but not to such an extent. It is felt that there is an over estimation of the hardness due to ‘indentation size effect’. Bull [9] noted that a higher measured hardness would obtained when the material being tested did not reach full elastic-plastic behaviour during indentation, as a result of the tip of the indenter being blunt. The authors propose that this could also occur when testing hard materials (i.e. ceramics) at very low loads (possibly 10mN) thus resulting in an over estimation of the hardness measured. However, since the hardness of the aged samples are being compared to the results from as received samples, under identical testing conditions, one can still conclude that the 1500°C aging treatment resulted in a significant increase in the hardness of the columns.

Since this project was initiated to investigate the cause for the increase in the erosion rate of aged samples this should also be discussed. Since TBCs are ceramics and erode via a brittle mechanism it is expected that the erosion rate will be affected by changes in both hardness and fracture toughness of the ceramics. Since fracture toughness of the individual columns could not be measured it was decided to see how hardness changed with aging condition. This paper has clearly indicated that the hardness of the coating increases as a function of aging condition. Since TBCs are ceramic and brittle by nature it is reasonable to assume that as the hardness increases the coating will become more brittle, i.e. the fracture toughness of the coating and individual columns will decrease. Since a decrease in fracture toughness will result in an increase in erosion rate, the increase in hardness due to aging would account for part of the increase in the erosion rate of aged samples. As mentioned earlier, part of the increase in erosion rate of the samples aged at 1500°C is as a result of the sintering together of the columns enabling crack propagation across the columns, which prior to sintering would not occur, thus resulting in an increase in erosion rate.

The results of the micro hardness test conclusively show that the hardness of the coating as a whole increases with an increase in the aging conditions. The nano indentation results also show an increase in hardness with aging although more work is needed to be able to fully quantify the increase in hardness of the coatings with aging.

5. Conclusion

- It was found that the aging increased the hardness of both the coating as a whole and the individual columns of the coatings.

- The micro hardness of the coating was found to increase from 2.5-3.5 GPa in the as received condition to 4.5-6 GPa after 100hrs at 1100°C and to 7.5-8 GPa after 24hrs at 1500°C.

- The nano hardness of the individual columns on the other hand was found to increase from 18GPa in the as received condition to 35 GPa after aging.

- The observed increase in the erosion rate of EB PVD TBCs with aging condition can be partly attributed to the measured increase in hardness with aging conditions and the assumed decrease in fracture toughness.

6. Acknowledgements

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Table 1: Results of the micro indentation tests for the different substrates and aging conditions.

Table 2: Results of the nano indentation tests for the different substrates and aging conditions.

Figure 1: Micrographs of the top of an EB PVD TBC (a) as received and (b) polished.

Figure 2: Micrograph of aged samples after 100hrs @ 1100°C (a) and (b) Polished.

Figure 3: Micrograph of aged samples after 24hrs @ 1500°C (a) and (b) Polished.

Figure 4: Results of the micro hardness tests of the coatings on alumina tiles.

Figure 5: Results of the micro hardness tests of the coatings on zirconia tiles.

Figure 6: Probability plot of the nano indentation results for the different conditions on the zirconia substrate.

Figure 7: Probability plot of the nano indentation results for the different conditions on the alumina substrate.

Figure 8: Micrograph showing where two of the indents, circled, are interacting with the shrinkage cracks caused by the sintering.

Figure 9: Graph showing how the measured hardness of an EB PVD TBC changes with applied load [6].

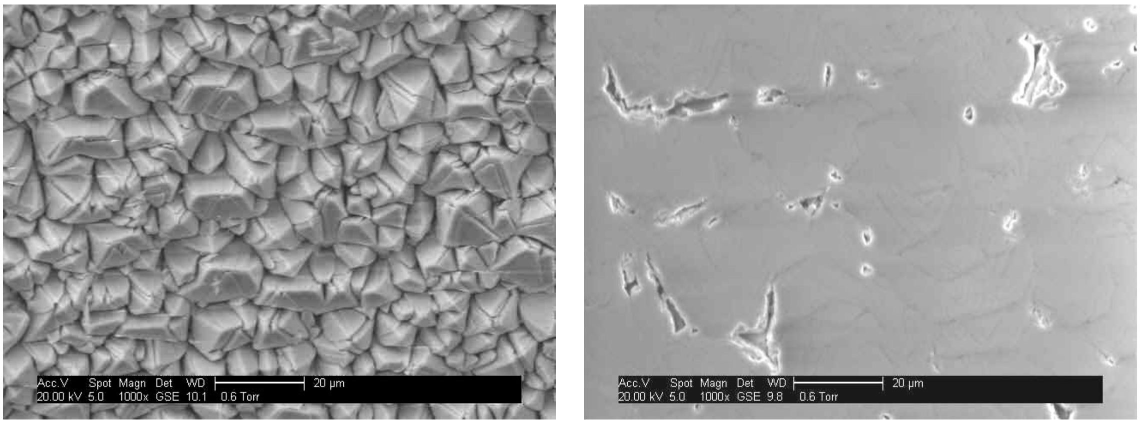
Figure 10: Probability plot of the results of the nano indentation tests on a bulk zirconia [6].

	As received	100 hours at 1100°C	24 hours at 1500°C
C263 substrate	1.98GPa (0.13)	-	-
Al_2O_3 substrate	2.17GPa (0.35)	5.04GPa (0.59)	7.85GPa (0.43)
ZrO_2 substrate	4.88GPa (0.42)	5.17GPa (0.42)	7.71GPa (1.78)

Table 1: Results of the micro indentation tests for the different substrates and aging conditions (Standard deviation in parenthesis).

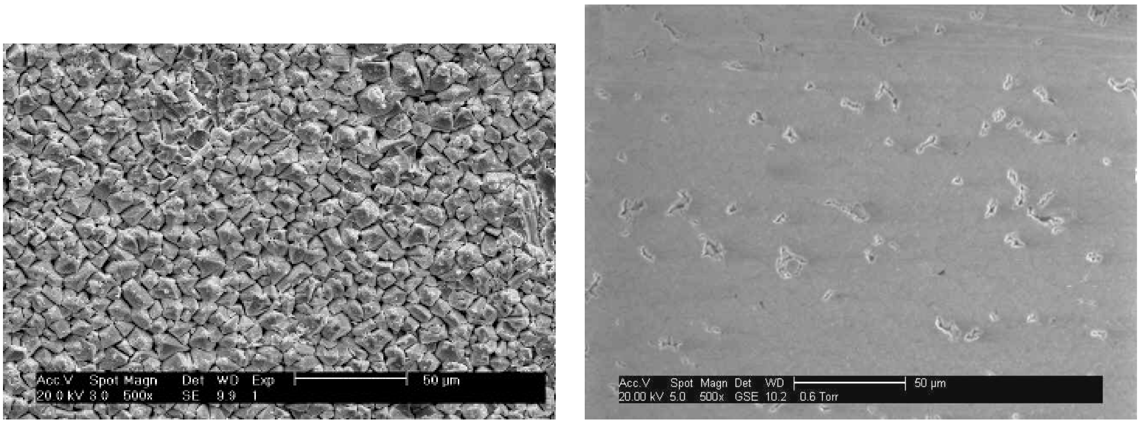
	As received	100 hours at 1100°C	24 hours at 1500°C
ZrO_2substrate	17.79GPa	19.45GPa	35.50GPa
Al_2O_3 substrate	20.23GPa	21.97GPa	16.36GPa

Table 2: Results of the nano indentation tests for the different substrates and aging conditions.



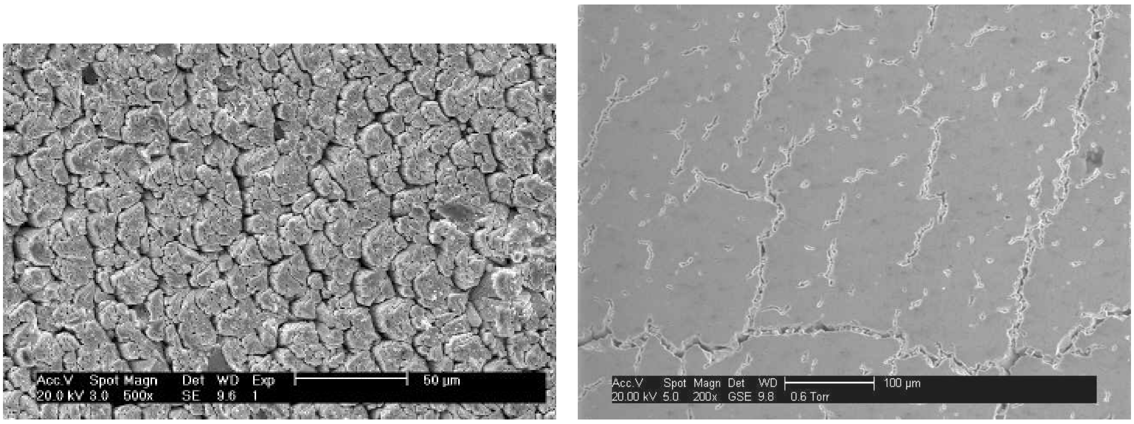
(a) (b)

Figure 1: Micrographs of the top of an EB PVD TBC (a) as received and (b) polished.



(a) (b)

Figure 2: Micrograph of aged samples after 100hrs @ 1100°C (a) and (b) Polished.



(a) (b)

Figure 3: Micrograph of aged samples after 24hrs @ 1500°C (a) and (b) Polished.

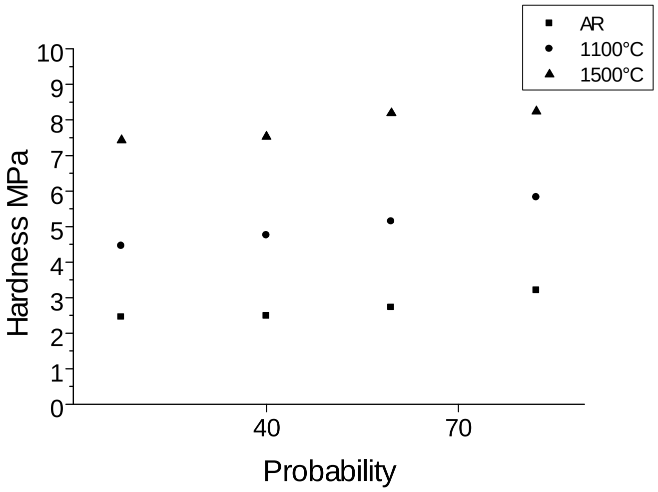


Figure 4: Results of the micro hardness tests of the coatings on alumina tiles.

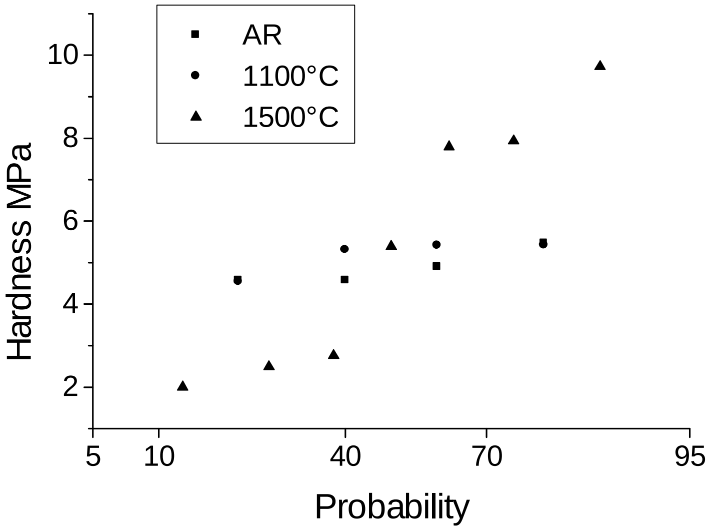


Figure 5: Results of the micro hardness tests of the coatings on zirconia tiles.

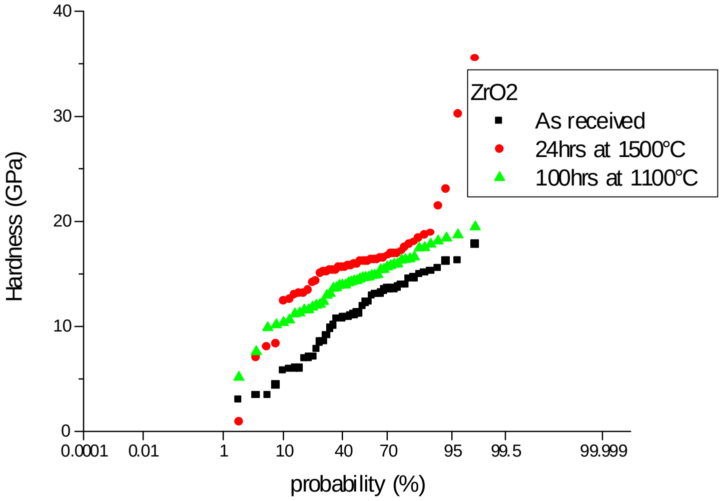


Figure 6: Probability plot of the nano indentation results for the different conditions on the zirconia substrate.

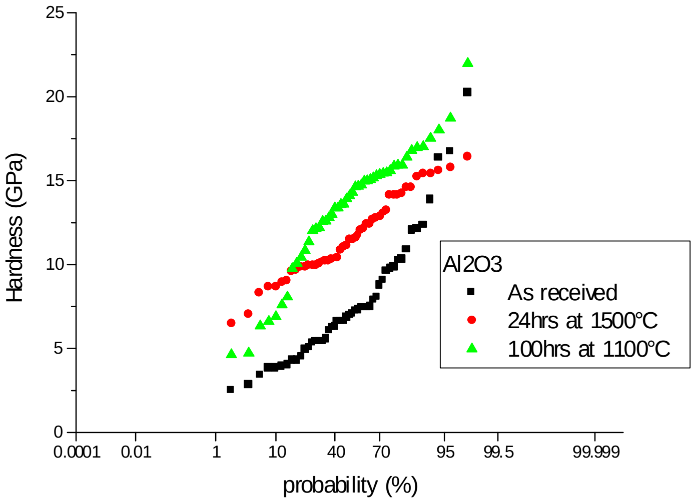
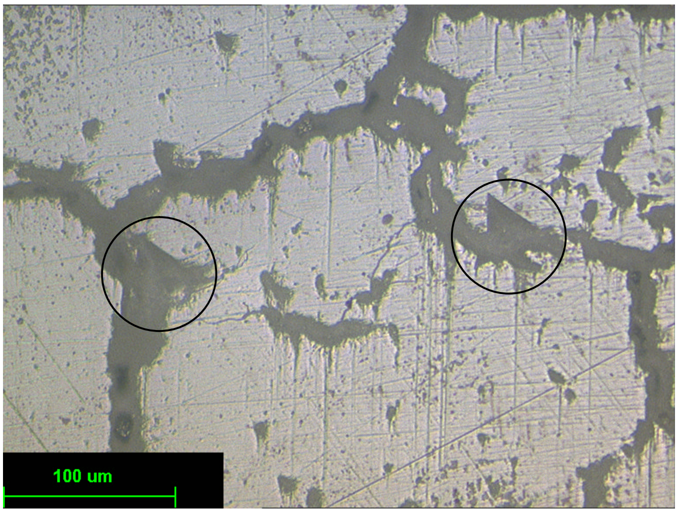


Figure 7: Probability plot of the nano indentation results for the different conditions on the alumina substrate.



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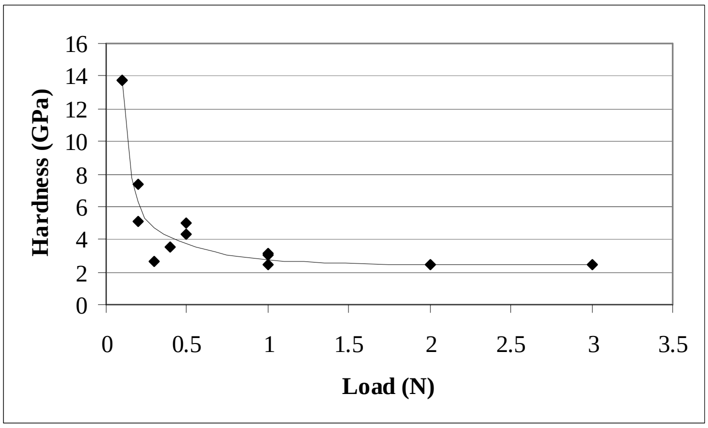
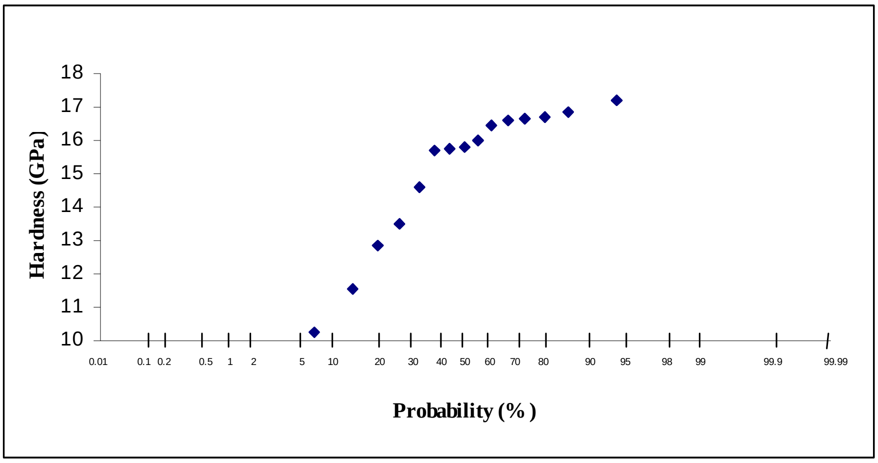


Figure 9: Graph showing how the measured hardness of an EB PVD TBC changes with applied load [6].



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