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PRESS RELEASE

ULTRA-HARD NANOCOMPOSITE COATINGS

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There has in recent years been much speculation and discussion about the existence and measurement of ultra-hardness in nanocomposite coatings, particularly in relation to the work of Professor S. Veprek of the Technical University Munich.

In 2006 the present author co-authored a publication which addressed some of these issues: A.C. Fischer-Cripps, P. Karvánková, S. Vepřek, Surf. Coat. Technol. 200 (2006) p.5645. In this paper we identified serious errors made in experimental work reported in past papers by S. Veprek and colleagues. The main findings were that previous workers:

- used $\epsilon = 1$ in the unloading analysis equations which is inappropriate for the type of materials and indenter used.
- used a constant Martens hardness H_M basis for the area function determination.
- used a book value of the Knoop value of H to determine H_M for use in the area function instead of the Meyer hardness which has more physical significance.
- used a fixed value of m for power law analysis of the unloading data rather than a fitted value.

The result of these, and other errors reported in the above reference, were that:

- Reasonable results for values of hardness H for the super-hard materials and diamond samples were obtained using previous incorrect methods of analysis due to a fortuitous combination of errors.
- Despite the above, incorrect values of elastic modulus E for all the samples were obtained when data were analysed using previous incorrect method of analysis.
- Previously published images from a calibrated SEM for impressions made on what were claimed to be ultra-hard coatings did not support values of $H > 100$ GPa.
- Correct values of E and H for both super-hard and diamond samples were obtained using proper equipment and analysis methods when these samples were independently tested.
- Values of H considerably lower than 100 GPa were obtained on data transcribed from previous measurements on what are claimed to be ultra-hard samples and analysed using correct methods.
- No firm conclusion could be reached at that time in relation to the claims for ultra-hardness due to the unknown quantity E/H for this material and the lack of an available sample to test directly.

Since then, it has now been established that the value for elastic modulus for both super-hard and what are claimed to be ultra-hard coatings is approximately 450 GPa. S. Veprek and coworkers also claim that the elastic modulus could reach as high as 645 GPa under the indenter due to a pressure-enhancement effect. This being so, then we now note the corresponding values of E/H :

	E/H
Sapphire	≈12-15
Super hard coatings:	≈10
Diamond:	≈10

If the claimed ultra-hard coatings had a hardness of 110 GPa, then E/H would be ≈ 4 for $E = 450$ GPa and ≈ 5.75 for $E = 645$ GPa. This being the case, it raises doubts that the calibration and analysis methods of previous works would provide a realistic estimate for the value of H for the claimed ultra-hard coatings since the ratio E/H for these coatings appears to be significantly different (lower) than that for the sapphire reference sample used to determine the tip shape.

The reason why apparently acceptable values for H for diamond and super-hard coatings were obtained using these previous incorrect methods is that the errors sometimes compounded and sometimes cancelled, with the result that due to the relatively high value of E/H for these materials, and its similarity to the sapphire reference sample, the error associated with the area function used by those workers was reduced in effect.

If the claimed ultra hardness coatings had a hardness of 55 GPa, then E/H would be approximately 8 or so (at $E=450$) and 12 for ($E=650$) and so the indentation curves would be fairly well represented and the associated analyses, with the proper application of the constants involved, would be a fair indication of the actual hardness. Indeed, proper analyses of previously published curves in comparison with theoretical models and finite element analyses indicates a consistency with E of about 450 GPa and hence H of about 55 GPa.

It is stated in Phil. Mag. Letters Vol. 87, No. 12, December 2007, 955–966 that the hardness measurements of Veprek et al. have been verified by Fisher-Cripps (sic) et al. (2006) for several typical superhard nanocomposites and for the reference bulk diamond, which Veprek et al. used for calibration. Although this is correct, the statement gives the impression that Fischer-Cripps et al. indirectly verified the claimed hardness of the ultra hard samples but fails to indicate that the values of elastic modulus were significantly in error when computed with these methods, nor does it convey the extent of the errors and their significance in determining a reliable value of hardness for what are claimed to be ultra hard samples.

It is further said in the above reference that Chen and Bull have recently shown that, for a material with a higher H/E-ratio than diamond, the automated indentation technique may underestimate its actual hardness and that this answers a question, which was left open in the 2006 paper, and confirms that the hardness measurements of Veprek et al. were correct. The present author disagrees. Chen and Bull made no such claim, and this contention appears to arise from their observation that the ratio of residual to maximum depth of penetration may diverge from that predicted upon the basis of conventional unloading analyses for $H/E > 0.1$. However, an examination of the work of Chen and Bull reveals that is the power law exponent m is allowed to vary in order to fit the data, this divergence is not significant. Further, calculations show that the ratio of these depths reported by Veprek and co-authors in various publications for what are claimed to be ultra-hard specimens are in accordance with those predicted on the basis of conventional unloading analyses where a much lower value of hardness than that claimed is obtained.

Since 2006, many papers have appeared in the literature from Veprek and co-workers in support of their original claims. Much of this work centres on theoretical and finite element computations to support the original experimental results. Recently, a new review of this work by Fischer-Cripps, Bull and Schwarzer has been accepted for publication in Philosophical Magazine. This new review provides a detailed analysis of these findings as well as a comprehensive literature review and re-analysis of the original data. The new review concludes that out of the issues examined, significant errors and inconsistencies have been identified in an examination of the primary literature sources, to the SEM images, experimental readings, Hertzian analysis, and

advanced finite element simulations. It is found that not one of the works examined supports the original claim of hardness for the nano composite coatings under consideration being in the vicinity of 100 GPa.

These findings are due to be presented at the ICMCTF conference in San Diego, April 2012.

The new review paper, and the contents of the presentation have been sent to Professor Veprek for comment and information. The response from S. Veprek has been (here quoted with permission) "Professor Stan Veprek expressed his fundamental disagreement and he shall justify it in due time". Professor Veprek is scheduled to make a rebuttal presentation at the above conference.

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