

Reliability of the investigation of basic mechanical properties of PVD hard coatings

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Hard coatings deposited by physical vapour deposition are widely used for wear application. Therefore high quality analysis methods under standardized conditions have become more and more important. Primary objectives of examination are chemical composition, hardness and adhesion of the coatings. Especially the chemical composition can be analysed by a lot of methods like glow discharge optical spectroscopy (GDOS), photo electron spectroscopy (XPS), Auger electron spectroscopy (AES), energy dispersive X-ray spectroscopy (EDX), secondary ion und neutral mass spectrometry (SIMS, SNMS). On the other hand, the only possibility of hardness measurement is the use of a well defined indenter and optical inspection of the indentation or direct measurement of the load-indentation curve (depth sensing indentation method, DSI). The latter technique is now well established and is preferably used for hardness measurement of thin hard coatings. Another property of fundamental interest is the adhesion of the coating to the substrate. Here only a few methods exist and the most established one is the scratch test.

All these methods are widely used and the question of main interest is the comparability and reliability of the testing results. Taking up this topic PVD coatings with different chemical composition were produced under defined laboratory conditions. Their composition, hardness and adhesion was tested in round-robin experiments (participants in table 1).

Table 1 Participants on the round robin experiments

Participant	Investigated Properties
TU Bergakademie Freiberg; Institut für Werkstofftechnik	hardness, adhesion
Bundesanstalt für Materialprüfung und -forschung, Berlin	chemistry
Fraunhofer-Institut für Schicht- und Oberflächentechnik, Braunschweig	hardness, adhesion
Fraunhofer-Institut für Werkstoffmechanik, Freiburg	hardness, adhesion
Martin-Luther-Universität, Halle/Saale; FB Physik	hardness
Staatliches Materialprüfungsamt NRW, Dortmund	hardness
Ruhr Universität Bochum; Institut für Werkstoffe	hardness, adhesion
Institut für Oberflächen- und Schichtanalytik, Universität Kaiserslautern	chemistry
Stiftung Institut für Werkstofftechnik, Bremen	chemistry, hardness, adhesion, coating prod.
CSEM, Neuchâtel (associated)	adhesion

The coatings were deposited onto hardened and tempered M2 tool steel substrates by a reactive magnetron sputtering process. The surface roughness of the lapped and polished substrates was lower than $0,05 \mu\text{m}$ and the deviation from planarity was less than $1 \mu\text{m}$ over the total substrate area of $30 \times 30 \text{ mm}^2$. The coating thicknesses were fixed to $10 \mu\text{m}$ as a compromise between the needed volume for chemical analysis, hardness measure-

ment and usual application. The surface roughness of the coatings was 0,1 μm . X-ray stress measurements result in internal stresses in the coatings of around -2000 MPa. The indepth chemical compositions were homogeneous over the total coating thickness as qualitative analyses by GDOS have shown. Lateral homogeneity was investigated by EDX point analyses, revealing tolerances in the atomic composition of about 1%.

The intercomparison analyses were carried out using samples from the same batch in which uncertainties due to sample position with respect to the line in sight process can be neglected. For comparison with the results from the spectroscopical methods wet chemistry was employed as a neutral method with no need of standard samples using coatings removed from the substrates (table 2).

coating	Ti	N	C
$\text{TiN}_{0,994}$	49,52	49,21	
$\text{TiN}_{0,943}$	50,72	47,82	
$\text{TiN}_{0,935}$	51,13	47,80	
$\text{TiN}_{0,512}$	64,69	33,13	
$\text{Ti}(\text{C}_{0,32}\text{N}_{0,68})_{1,03}$	49,31	34,60	16,09
$\text{Ti}(\text{C}_{0,25}\text{N}_{0,75})_{1,01}$	49,71	37,80	12,49
$\text{Ti}(\text{C}_{0,17}\text{N}_{0,83})_{0,97}$	50,73	40,77	8,50
$\text{Ti}(\text{C}_{0,01}\text{N}_{0,99})_{0,91}$	52,35	46,96	0,68

coating	Ti	Al	N
$(\text{Ti}_{0,48}\text{Al}_{0,52})\text{N}_{0,91}$	24,99	27,43	47,58
$(\text{Ti}_{0,53}\text{Al}_{0,47})\text{N}_{0,54}$	30,55	26,56	30,79
$(\text{Ti}_{0,72}\text{Al}_{0,28})\text{N}_{1,00}$	35,70	13,81	49,60
$(\text{Ti}_{0,81}\text{Al}_{0,19})\text{N}_{0,55}$	52,09	12,23	35,68

Table 2 Results of wet chemical analysis

It was found that all the spectroscopical methods gave comparable results only in the area of the used calibration samples (usually stoichiometric TiN). In the substoichiometric region of titanium nitride GDOS shows little nitrogen and XPS too much nitrogen. Using a series of four TiN_x samples ($0,5 < x \leq 1$) for calibration leads to much more coincidence. For the other methods no statistical significant dependencies were found. For titanium carbonitride the C/N-ratio was analysed well by all methods and for titanium aluminium nitride it was found by all methods, including wet chemistry, that the Ti/Al-ratio (1 and 3 at the target) in the coatings depends on the nitrogen content or on the nitrogen partial pressure during the sputtering process, respectively. Because no well defined standards were at disposal there was a big scatter in the spectroscopical results. But the results from wet chemistry show mean values all the time. A more detailed paper on this topic was presented at the PSE'96 in Garmisch-Partenkirchen [H.-R. Stock et al., to be publ. in Surf. Coat. Technol.].

For hardness testing of the coatings the conventional Vickers hardness test was used at loads of 0.981 N and 1.961 N, respectively. For 10 μm hard coatings 0.981 N leads to an indentation depth less than 1/10 of the coating thickness. The DSI-measurements were carried out with maximum loads of 1 N, 0.25 N and 0.05 N. The uncertainties of 30 to 35 measurements (5 at each participant) are low (fig. 1 and 2), but especially for HV 0.2 no hardness dependence on composition is obvious because the composite hardness was

measured. For HV 0.1 details in hardness of different coatings can be seen. The comparability of the round robin results lie in a region smaller than 4%. Therefore both samples and measuring technique seem to be standardized quite well. For the DSI method much more details can be seen between the different coatings. However in this case not only plastic deformation but also elastic deformation is detected. For high loads scatter is comparable to Vickers indentation. For 0.05 N, that should be used for thin coatings, scatter of the values becomes much bigger. Two reasons must be discussed. First, the roughness of the analysed surface which is of the same magnitude as the penetration depth of about 50 nm, and second the nonideal geometry of the indenter tip, that affects low load results very much. To overcome this problem correction methods are under development, were the indenter geometry is directly measured by AFM or estimated by measurement of fused silica. By using those methods the results from single instruments become much more comparable (fig. 3).

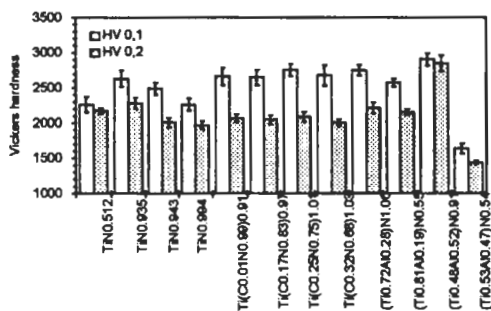


Fig. 1 Results of the Vickers hardness test

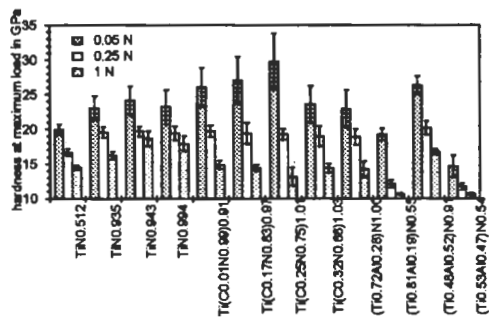


Fig. 2 Results of the DSI hardness test

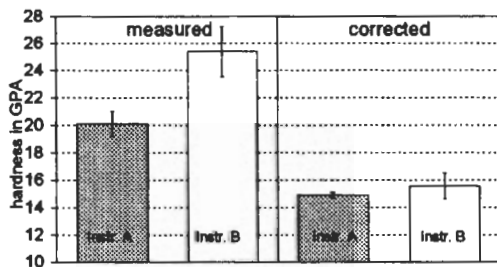


Fig. 3 Effect of correcting the DSI hardness measurement at 0.05 N

Scratch test round-robin experiments were carried out making five scratches at each participant under the instructions of the DIN V ENV 1071 Pt. 3. Acoustic emission and optical inspection were used to analyse the damage of the composites. The latter was based on the failure description from Burnett and Rickerby [Thin Solid Films 154(1987), 403].

Testing the well known titanium nitride on M2 show that acoustical emission and optical detection of coating flake lead to the same critical loads for most of the instruments. The

reproducibility of five measurements was better than 10 N. But it was found that the deviations between the instruments could be more than 30 N (fig. 4). For the other types of coatings the deviations were same or bigger, even if the coating thickness was thinner and tests were carried out on the same sample. For more detailed analysis the operators had to describe the appearance of the observed failure. More than 30 different failure descriptions were found at 310 scratches. Most of the descriptions were close to that of Burnett and Rickerby but other, like cracks or flaking only on one side of the scratch, indicate that there is a strong machine influence on the measurements. In addition, especially on coatings with metallic appearance, some observers had problems in separating adhesive failure (totally removed coating) from cohesive failure (partially brokenout coating). This indicates that for adhesion measurement with the scratch test one is far away from a standardized testing method. The first step was done by standardizing of the testing procedure. Neither the testing equipment nor observation and description of characteristic failure appearance is standardized until now. Therefore, scratch test results cannot be compared at all. It should also be realised that the gap between measured critical load and the property adhesion wanted is not filled yet.

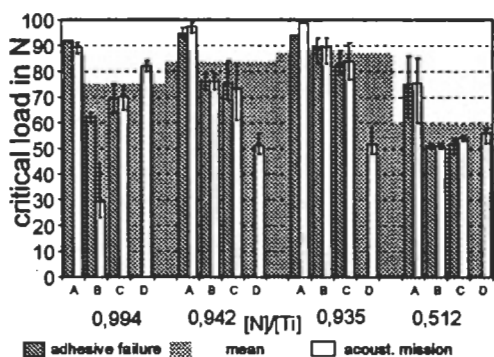


Fig. 4 Results of scratch tests at TiN_x

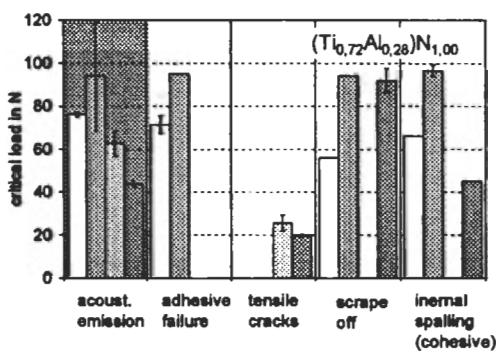


Fig. 5 Acoustic emission and optical inspection during scratch test

Summarizing, the presented samples were usable to investigate the reliability of testing hard coating basic properties. For chemical analysis, the uncertainties mostly depend on missing standards. For hardness testing, main restrictions come from physical limits. The possibility of adhesion testing shows many limits. At the moment the scratch test seems to be a technological test for errors in manufacturing and coating deposition more than for estimation of adhesion.

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