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Influence of Gradient Residual Stress and Tip Shape on Stress Fields Inside Indented TiN Hard Coating

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Nanoindentation of treated surfaces, thin films, and coatings is often used as a simple method to measure their hardness and stiffness. These quantities are technologically highly relevant and allow to qualitatively compare different material and surface treatments but fail to capture the entire extent of the highly complex mechanical interaction between indenter tip and the tested surface. Many studies have addressed this question by analytical or numerical modeling, but they must rely on verification by recalculating indentation curves or ex situ microscopy of surface deformation postexperiment. Herein, results from in situ measurements of the multiaxial stress distributions forming beneath an indenter tip while the tested sample is still under load are presented. A 9 μm-thick TiN hard coating is tested in 1) as-deposited state and 2) shot-peened by Al2O3 particles, using two diamond wedges as indenter tips, with 60° and 143° opening angle, respectively. The results reveal a strong influence of the tip shape on the deformation behavior and the main stress component developing inside the sample while under load. In addition, a crack-closing effect can be attributed to the exponentially declining near-surface compressive residual stress gradient that is present in the shot-peened sample.

1. Introduction

Nanoindentation is a facile method for assessing the technologically relevant properties of hardness and stiffness of treated surfaces, thin films, and coatings. Due to the complex mechanical interaction between the shape of the indenter tip pressing into the material, as well as the architecture and preexisting near-surface stress state of the tested material, it is, however, not trivial to understand the critical stress concentrations present during indentation in the material and which can result in different types of yielding or cracking behavior. For this reason, until recently, most research on the stress fields forming during nanoindentation has been performed by numerical modeling, calculation of the overall dependencies of indenter load versus indentation depth, and verification by classical nanoindentation experiments.[1–8] However, this approach is lacking in detailed experimental validation because it does not allow to specifically verify the calculated stress distributions that are present during indentation. To address this drawback, cross-sectional scanning X-ray nanodiffraction (CSnanoXRD) using synchrotron radiation and a dedicated in situ indentation setup has recently been used successfully for experiments on various ceramic thin film samples.[9–11] Another classical approach used in indentation modeling is the combination with electron microscopical examination of cross sections postmortem, that is, ex situ after the a nanoindentation experiment. Also in this case, CSnanoXRD has proved to be a useful tool, to properly understand deformation phenomena that took place under the indenter imprint and to properly attribute them to the stress levels present in different parts of the indented sample region.[12]

In this article, we want to exemplarily address the influence of 1) a preexisting residual stress gradient introduced through blasting the sample’s surface with a hard medium (shot-peening) and 2) the shape of the wedged diamond tip used for indentation on the mechanical response of the sample. For this purpose, we built on our previous work and investigated the same sample as in the study by Zeilinger et al.,[9] but added a blasting treatment before the in situ experiment and furthermore exchanged the comparatively sharp 60° wedge indenter tip for another with a more obtuse opening angle of 143°, which was chosen due to its similarity to a Vickers type diamond pyramid that is often used in nanoindentation testing. It is a common industrial practice to introduce near-surface compressive stresses by (shot) peening, rolling, or rapid heating by laser and the beneficial nature of this treatment is generally seen in the ability to make surfaces less prone to crack initiation and therefore enhancing a tool’s or component’s lifetime.[13,14] Some of these treatments

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have already been investigated by CSnanoXRD,[15,16] but the in situ stress response of a shot-peened coating subjected to indentation had not yet been studied.

2. Experimental Section

2.1. Sample Preparation

The ≈9 µm-thick TiN hard coating was deposited onto a ferritic steel substrate in an industrial-scale plasma-assisted chemical vapor deposition plant manufactured by Rübig (Wels, Austria) using the process gases TiCl4, H2, N2, and Ar, mixed by mass flow controllers. Direct current pulses were applied to the substrate to sustain the plasma, while the process pressure was set to 200 Pa. Approximately halfway through the deposition process, the substrate temperature was raised rapidly from 813 to 853 K, resulting in two sublayers with slightly differing film microstructures and residual stress levels. Up to this point, the sample is the same as described in the previous study by Zeilinger et al.,[9] but for this work, the TiN hard coating was additionally subjected to a shot-peening treatment using a pressure of 400 kPa and a spherical blasting medium of Al2O3 particles, 50 µm in size. This treatment resulted in compaction and smoothing of the coating’s surface, as well as the introduction of near-surface compressive residual stress.[17]

2.2. Synchrotron CSnanoXRD

The CSnanoXRD experiments were conducted on the beamline P03 “MiNaXS” at DESY in Hamburg, Germany, using a monochromatic X-ray beam with a photon energy of 15 keV and a cross section of ≈250 × 300 nm (V × H), achieved by Kirkpatrick-Baez elliptical focusing mirrors. The in situ indentation setup used for loading and scanning the stressed sample is described in detail in the study of Zeilinger et al.[9] and can also be seen in Figure 1. In essence, it features a lightweight load frame mounted on a piezo scanner, a piezo-driven hexapod used for alignment of the sample with respect to the indenter tip and force generation and, finally, a strain-gauge load cell with mN force resolution, onto which the wedged diamond tip is mounted with its edge parallel to the incident X-ray beam. Using the calibration procedure described by Ashiotis et al.,[18] the exact detector geometry with respect to the sample and the beam was determined, by measuring a NIST standard LaB6 powder. There were two indenter tip shapes used for this work, namely, a wedge of 50 µm length and an opening angle of 60°, as well as a wedge of 60 µm length and an opening angle of 143°, designed to closely resemble a typical Vickers type indenter tip.

2.3. Stress Evaluation

Strains and stresses inside the sample were determined by using the methodology presented in the study of Zeilinger et al.[9] It is composed of 1) integrating the 2D diffraction pattern into multiple cake-like sections, 2) peak fitting of the resulting orientation-dependent datasets containing the 111 and 200 TiN reflections, 3) the calculation of orientation-dependent strains using the strain-free lattice spacings of d0^TiN,111 = 0.245791 nm and d0^TiN,200 = 0.21280 nm, and 4) fitting the average stress state existing in the gauge volume to the observed orientation-dependent strains using the appropriate elastic constants of TiN.[9] Note that the slight difference in exact d0^TiN,hkl values used in this work and the study of Zeilinger et al. is due to experimental parameters and does not reflect an actual difference in the samples.

2.4. Microscopy

Images of the sample after indentation were acquired in a Zeiss LEO 1525 scanning electron microscope (SEM), using in-lens and secondary electron detectors for imaging. Cross sections showing the film’s deformation and possible cracking were prepared by milling with a focused ion beam (FIB) and imaging in SEM mode, using a Zeiss Auriga LaserFIB system, using an Orsay Physics Ga+ ion FIB column. Small beam currents were used in final polishing stages, to avoid damage to the sample and to provide an even surface for imaging.

3. Results and Discussion

3.1. Microstructure and Residual Stress before Indentation

The 9 µm-thick TiN thin film investigated in this work features a nanocrystalline microstructure with columnar grains (cf., Figure 2a) and a <100> fiber texture.[9] Prior to the shot-peening
treatment, residual stresses stemming from deposition are already compressive, ranging between $1.4$ and $0.8$ GPa and thereafter, a pronounced exponentially declining additional compressive stress gradient is present in the upper part of the film, reaching a maximum value of $3.3$ GPa at the surface (cf., Figure 2b). As this upper part was deposited at a slightly elevated temperature, compared with the lower part, it has a 1) a stronger preferred crystallite orientation, 2) a lower residual stress, and 3) a lower point defect density, as indicated by lower peak breadth (cf., Figure 2c). However, due to the surface deformation that is the characteristic mechanism of shot-peening, in the blasted film also a distinct increase in peak width can be seen in the film’s upper part, approximately inversely proportionate to the additionally introduced compressive stresses.

3.2. Stress Distributions during Indentation

In comparison with the indentation response of the as-deposited TiN film, indented with the 60° opening angle wedged tip and at a load of 1.4 N (discussed in detail in our previous study), the stress distributions in the shot-peened TiN film, indented with the 143° wedged tip and at a load of 1.6 N, show a number of differences. A slightly higher force was applied to the latter, due to force measurement offsets that were not considered during the experiment. However, it will become clear that this slight difference does not impact the conclusions drawn from this comparison.

The first and rather obvious observation is that the compressive stress gradient due to the blasting treatment is simply superimposed onto the in-plane stress field induced by the indentation process, as can be seen in Figure 3b at lateral coordinates...
≥ 5 μm. Yet, the highest in-plane stress in the blasted sample, at −6.2 GPa, is still much lower than in the other sample, where a compressive stress of −8.2 GPa was found (cf., Figure 3a). This can thus be attributed to the differing indenter tip shapes, where the one with the sharper opening angle clearly induces much stronger stresses acting in-plane. This even includes the formation of a region loaded very slightly in tension, directly beneath the sharper indenter tip, located at the interface between the lower and upper part of the film, which also played a role in eventual failure of this sample, as discussed by Zeilinger et al.[9] There, two vertical intergranular cracks formed close to this region, connecting a dense crack network surrounding the indenter imprint and two further inclined cracks reaching down to the substrate interface and finally resulting in delamination outside the indented region (cf. Figure 4a).

Looking at the out-of-plane direction, the situation is the opposite, as in the blasted sample the highest evaluated vertically acting stress reaches −11.3 GPa, while in the other sample it reaches only −7.3 GPa. However, also tensile out-of-plane stress was only found in the sample indented with the 60° wedge, at a maximum value of 0.4 GPa and furthermore located at the same position as the maximum in-plane compressive stress. This situation with tensile loading in the presence of a highly deviatoric stress state is most likely critical for the initiation and growth of cracks in TiN, which, as a ceramic material, has only very limited strength in tension, while it is able to bear very high compressive loads. Therefore, it is very likely that this region featuring a tensile out-of-plane stress peak and a compressive in-plane stress peak is also the initiation site of the catastrophic crack growth that was observed at even higher loads, as seen in our earlier study on the same sample and in Figure 4a.[9] The existence of out-of-plane tensile stress can be attributed to the formation of pileups next to the penetrating indenter tip, as commonly found in ductile materials after nanoindentation, but also in this case.

Concerning shear stress, the maximum measured values are very similar in magnitude, reaching ±2.7 GPa in the blasted sample and ±2.9 GPa in the other one, but they are more concentrated in close vicinity of the sharper tip and extend further downward from the more obtuse tip. As these shear stress distributions are generally rather similar, they probably do not have a significant influence on the observed differences in the two films’ deformation behavior.

3.3. Indentation-induced deformation

To assess this in more detail, cross sections beneath the indenter imprints were examined by means of electron microscopy. Both samples were loaded with comparable maximum indenter forces of nearly 1.8 N in the case of the as-deposited sample, loaded with the sharp indenter tip and 2.0 N in the case of the shot-peened sample, loaded with the much more obtuse diamond tip. As discussed by Zeilinger et al.[9] and as shown in Figure 4a, the former shows very pronounced cracks that grew through the entire thickness of the film, featuring 1) a dense crack network in close vicinity to the indentation imprint, 2) two symmetrical vertical cracks emanating from this region downward until the interface between the film’s upper and lower part, 3) two symmetrical cracks inclined outward and progressing to the film–substrate interface, and 4) two symmetrical cracks running along this interface outward from the indented region.

This is much in contrast to the latter, where the only cracks that formed beneath the indenter imprint are confined to a shallow region beneath the film’s surface, as shown in Figure 4b, although the applied load was even slightly higher. These cracks have a very different morphology and rather resemble those observed during indentation of a CrN multilayer coating using a very similar setup and methodology by Ecker et al.[10] as they only reach a limited depth and exhibit a step-like serrated shape. Furthermore, the vertical crack opening observed here is much larger than the horizontal one, which is so small that it is indeed difficult to see at all, as indicated by the arrows in Figure 4b. It is most likely due to the highly compressive near-surface residual stress gradient, introduced by the blasting treatment of this sample, that these cracks are held closed horizontally, which is also supported by the in-plane stress distributions measured after the indenter force had been relieved. As shown in Figure 5b, in the shot-peened sample the near-surface compressive stress gradient is still present after the experiment, whereas in the other sample (Figure 5a) only very low compressive stresses are present close to the surface.

In terms of residual stresses, postindentation, it can be observed, furthermore, that in the sample indented with the 60° wedged tip, their distribution resembles that of the in-plane stresses induced during indentation, but at a much lower magnitude (cf., Figure 3a and 5a), whereas in the sample indented with the 143° wedged tip, there is a certain amount of stress

![Image](aem-journal.com)
relaxation (approximately 0.5 – 0.6 GPa) present roughly in the same region, where out-of-plane stresses were induced during indentation (cf., Figure 3d and 5b). This indicates that, for the sharper wedged tip, most plastic deformation takes place in the in-plane direction and is also driven by in-plane stress, whereas, in the case of the obtuse wedged tip, deformation happens chiefly out-of-plane and is also driven mostly by out-of-plane stress. This is generally plausible because it corresponds also to the respective highest observed stress component.

4. Conclusions

In this study, we have compared the indentation response of a nanocrystalline TiN film, indented by a comparatively sharp wedged tip with an opening angle of 60°, with that of the same film, pretreated by shot-peening, and indented with a much more obtuse wedged tip with an opening angle of 143°. Our observations allow us to draw conclusions on the influence of both the shape of the used indenter tip and the blasting treatment.

Whereas the sharp tip induced mainly high in-plane stress during loading and resulted in the formation of large cracks and through-thickness crack growth, the obtuse tip induced mainly high out-of-plane stress during the experiment and could only form small cracks close to the surface, which were additionally counteracted by the highly compressive near-surface gradient stress field that is due to the blasting process.

This illustrates 1) the positive effect a surface treatment like shot-peening can have, not only in offsetting potential tensile stresses at a workpiece’s surface, but also in its ability to hinder the growth of already existing cracks and 2) the importance of geometrical aspects in indentation testing, as there can be considerable differences in terms of which stress components are relevant in the mechanical response of the tested material.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

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[1] S. Rezaei, M. Arghavani, S. Wulfinghoff, N. C. Kruppe, T. Brögelmann, S. Reese, K. Bobzin, *Mech. Mater.* **2018**, *117*, 192.
[2] D. R. Katti, K. S. Katti, J. M. Sopp, M. Sarikaya, *Comput. Theor. Polym. Sci.* **2001**, 11, 397.
[3] N. Yu, A. A. Polycarpou, T. F. Conry, *Thin Solid Films* **2004**, *450*, 295.
[4] H. Pelletier, *Tribol. Int.* **2006**, *39*, 593.
[5] M. Rodríguez, J. M. Molina-Aldeguila, C. González, J. Llorca, *Acta Mater.* **2012**, *60*, 3953.
[6] M. Liu, C. Lu, K. Tieu, H. Yu, *Mater. Sci. Eng. A Struct. Mater. Prop. Microstruct. Process.* **2014**, *619*, 57.
[7] Y. Liu, B. Wang, M. Yoshino, S. Roy, H. Lu, R. Komanduri, *J. Mech. Phys. Solids* **2005**, *53*, 2718.
[8] G. Tang, Y.-L. Shen, D. R. P. Singh, N. Chawla, *Acta Mater.* **2010**, *58*, 2033.
[9] A. Zeilinger, J. Todt, C. Krywka, M. Müller, W. Ecker, B. Sartory, M. Meindlhuber, M. Stefenelli, R. Daniel, C. Mitterer, J. Keckes, *Sci. Rep.* **2016**, *6*, 22670.
[10] W. Ecker, J. Keckes, M. Krobat, J. Zalesak, R. Daniel, M. Rosenthal, J. Todt, *Mater. Des.* **2020**, *195*, 108478.
[11] J. Todt, C. Krywka, Z. L. Zhang, P. H. Mayrhofer, J. Keckes, M. Bartosik, *Acta Mater.* **2020**, *195*, 425.
[12] M. Stefenelli, R. Daniel, W. Ecker, D. Kiener, J. Todt, A. Zeilinger, C. Mitterer, M. Burghammer, J. Keckes, *Acta Mater.* **2015**, *85*, 24.
[13] R. K. Nalla, I. Altenberger, U. Noster, G. Y. Liu, B. Scholtes, R. O. Ritchie, *Mater. Sci. Eng., A* **2003**, *355*, 216.
[14] L. Faksa, W. Daves, W. Ecker, T. Klünsner, M. Tkadletz, C. Czettl, *Int. J. Refract. Met. Hard Mater.* **2019**, *82*, 174.
[15] M. Tkadletz, J. Keckes, N. Schalk, I. Krajinnovic, M. Burghammer, C. Czettl, C. Mitterer, *Surf. Coatings Technol.* **2015**, *262*, 134.
[16] H. Meyer, J. Epp, *Quantum Beam Sci.* **2018**, *2*, 20.
[17] M. Bartosik, R. Pitonak, J. Keckes, *Adv. Eng. Mater.* **2011**, *13*, 705.
[18] G. Ashiotis, A. Deschildre, Z. Nawaz, J. P. Wright, D. Karkoulis, F. E. Picca, J. Kieffer, *J. Appl. Crystallogr.* **2015**, *48*, 510.