Deformation of Hard Coatings at Elevated Temperatures

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1. Introduction

Thin chromium aluminum nitride based hard tool coatings deposited by the cathodic arc PVD method represent the industrial state of the art for use in a wide range of metal machining applications, especially in high-performance, and interrupted cutting operations such as milling or hobbing [1–3]. These cubic ceramics offer a variety of attractive properties, such as a reasonable high temperature stability and a high resistance to abrasive wear and oxidation [4–11]. In the optimization of such coatings and the selection of candidate elements to be added, such as transition metals or silicon, one major goal is to optimize strength and fracture toughness at high temperatures, as those are crucial to improve wear resistance. A well-known fact is that the grain size, crystal textures, and nanolayer or nanocomposite nanostructure of these coatings significantly influence their mechanical properties.

In order to optimize the performance of these hard coating materials used in modern machining processes, it is necessary to investigate the material properties between at high temperatures generated in service, typically several hundreds of degrees above room temperature. However, the small length scale or thickness of the coatings limits the utility of conventional high temperature testing techniques. The recent extension of nanoscale techniques such as nanoindentation and nanoimpact to elevated temperatures has recently made this a possibility, and recent work using these techniques has demonstrated the utility of these techniques [3,12–16]. The development of vacuum techniques for high temperature nanoindentation [17–19] has recently also allowed measurement at temperatures where oxidation of the indenter or sample may be problematic.

The advent of focused ion beam (FIB) machining techniques for micro-scale specimen preparation [20] has enabled several novel test geometries to determine various properties of thin coatings. The most widely used of these geometries is the micropillar [21], which allows uniaxial compressive stress-strain behavior to be determined for micro-scale specimens. However, several other geometries have also been developed for testing tension [22], cantilever bending [23,24], and shear [25]. As toughness is a key parameter for hard coating performance, several studies have investigated micro-scale toughness tests using cantilevers [23,24,26], double cantilevered bridges [27], and double cantilevered beams [28]. However, the design of these test geometries requires prior knowledge of the yield strength to prevent plastic yielding from contributing to the apparent fracture energy, so high temperature compression testing is required before such test geometries can be implemented to determine high temperature fracture toughness of hard coatings.

Micropillar compression at high temperature offers several attractive advantages over hardness testing [21]. Indentation is highly dependent on tip geometry for accurate measurements, and indenter geometry variation due to erosion by oxidation and abrasive wear or plastic deformation of the tip is a serious concern at high temperatures [29]. Using a flat punch indenter avoids any such geometric variation. Also, the micropillar geometry offers a uniaxial stress state in contrast to the triaxial stress state of indentation. This provides a direct measurement of the compressive yield or failure stress, rather than an indirect method such as indentation where the relationship between the yield stress and hardness is complex [30]. Lastly, in situ micro-pillar compression allows direct visualization of the deformation mechanism changes at elevated temperature [31], so that buckling, fracture, or plastic deformation can be immediately observed. In this work, the benefits of in situ high temperature micro-compression testing are utilized to characterize the
uniaxial compressive strength of a range of chromium aluminum nitride coatings at near service temperatures.

2. Materials and methods

2.1. Sample production and characterization

All coating samples were produced at a coating temperature of 480 °C using a n°11 industrial PVD unit (PLATIT AG, Switzerland), using a combination of lateral (LARC®) and central (CERC®) cylindrical rotating arc cathodes, a process pressure of 3.5 to 4 Pa and a bias voltage during the main coating step of ~ 40 V. The targets were selected from highly pure Cr, Ti, AlCr, Al, and AlSi materials (PLANSEE AG, Germany) depending on the coating type. An overall coating thickness of approx. 7 μm was deposited on the substrates, which were either double side polished cemented carbide strips 5 × 40 × 0.5 mm (for micro-compression testing) or single side polished cemented carbide disks Ø 32 × 4 mm (for XRD and nanoindentation), both made from ultrafine grade CTU24L with 12% Co by mass (Ceratizit, Germany). In case of the CrN and AlCrN layers, the thick coatings were applied in two consequent batches with intermediate surfacing polishing. All samples were coated in triple rotation mode and were mechanically polished before FIB preparation.

Tescan Vela and Lyra dual-beam focused ion beam (FIB) stations were used to mill rectangular trenches using Ga+ at 30 kV and currents of ~6 nA to obtain cross sections of all the coatings. The cross sections were fine milled and polished using lower currents ranging from 1 nA to 300 pA and imaged using a Hitachi S4800 high-resolution scanning electron microscope (HRSEM).

Grazing incidence X-ray diffraction (Bruker AXS, D8 Discover) measurements were made by using CuKα (λ = 1.5418 Å) radiation to characterize the coatings. The excitation voltage and current were set at 40 kV and 40 mA, respectively, in the diffractometer. The angle of incidence was kept constant at 2°. The step size and the scan range used were 0.02° and from 20 to 90°, respectively. The grain size of the coatings was estimated from the Scherrer formula [32], as given in Eq. (1),

$$ t = \frac{0.9 \lambda}{B \cos(\theta)} $$

where B is the full width at half maximum (FWHM) of a Bragg peak, λ is the X-ray wavelength, and θ is the Bragg angle.

Micropillars were fabricated with equivalent diameters of ~1.5 μm with aspect ratios of ~3 using a Ga ion beam with an accelerating voltage of 30 kV in Tescan Vela and Lyra FIB instruments. Initially, coarse milling using high currents of ~6 nA was used to mill large craters around the micropillars to allow visualization during compression. Fine polishing to the desired micropillar dimensions was achieved using lower currents ranging from 1 nA to 300 pA, which in turn minimizes irradiation damage. The micropillars were imaged after FIB machining and after compression at elevated temperatures using a Hitachi S4800 high-resolution scanning electron microscope (HRSEM) and SEM of the Tescan Lyra FIB.

2.2. Micro-mechanical testing

Room temperature nanoindentation testing of the coatings was performed using a CSM Instruments NanoHardness Tester (NHT). This was calibrated using a fused silica reference with a calibrated modulus, E_p, of 73 ± 0.2 GPa immediately previous to testing due to the low indentation depths and high hardness and modulus of the coatings to be tested. A minimum of 20 indentations each was performed at maximum loads of 20, 30, 50 and 70 mN at loading rates of 20/30/50/70 mN/min, respectively, and a holding time at peak load of 1 s. The Young’s modulus was extracted from the load–displacement curves using the Oliver and Pharr method [33] assuming a Poisson’s ratio of ν = 0.3 for the coatings. The results for hardness and modulus were averaged from the four partial results.

Elevated temperature micro-compression was performed in situ in a Zeiss DSM 962 SEM using an Alemnis In-situ Indenter modified for high temperature operation [19]. This system allowed testing to be performed at precisely measured and calibrated surface temperatures [34] with near-negligible thermal drift. Micropillars were compressed using displacement control at a constant displacement rate appropriate to generate a 1 × 10⁻³ s⁻¹ strain rate for the heights of the pillars. At least 4 pillars were compressed for each test condition. The intrinsic displacement control of the system prevented the indenter tip from crushing the pillar samples upon a yield or fracture event, so that the pillars could be examined after failure.

3. Results and discussion

3.1. Microstructural characterization

In order to provide context to the mechanical testing measurements, the microstructures of the coating systems were characterized using several methods: HRSEM, XRD and FIB cross-sectioning.

X-ray diffraction was used to determine the crystal structure, crystallite size and texture of the coatings. The results from the various coatings, shown in Fig. 1, show broadly similar trends. Peak intensities and locations show slight differences between the different coatings, but the coatings all exhibit the typical peaks of the FCC phase occurring at 37.5°, 43.7°, 63.6° and 76.6°. No traces of soft hexagonal Al(Cr)N phase could be detected. The average crystallite size of the coatings, calculated from the half width of the three most intense peaks using Eq. 1, was determined to be ~16 nm for the CrN coating and ~11 nm for all of the aluminum-containing coatings. All of the coatings are only weakly textured with a slight preference for the (111) orientation.

XRD measurements can provide a general picture of the coating’s crystallographic structure, but this yields relatively little data about the coating’s morphology in terms of layer thicknesses, inclusions, and grain shape/orientation. Traditionally, this information was acquired using metallographic sectioning and polishing followed by HRSEM observation. Currently, cross-sections provided by FIB trench milling and polishing provide a more rapid alternative, which also reduces the risk of an abrasive alteration of the microstructure, such as removal of inclusions, and edge rounding typical of conventional polishing techniques. These FIB cross-sections are highly instructive for investigating coating microstructures, and they can be performed at specific locations without the need for mounting and polishing. Cross-sections of the various coating systems are shown in Fig. 2.

Fig. 1. Grazing incidence X-ray diffraction results for the investigated coatings.

![Fig. 1. Grazing incidence X-ray diffraction results for the investigated coatings.](image-url)
All of the coatings feature inclusions or defects on the order of up to several hundred nanometers in size as well as an adhesion layer to bond the hard coating to the WC-Cobalt hardmetal substrate. This bond layer is significantly thicker on the CrN and AlCrN coatings. The CrN coating displays larger columnar grains, which are slightly reduced in size in the AlCrN coating. However, most coatings show grains that appear to be significantly larger than XRD results suggest. The AlCrTiN coating shows significantly more grain refinement, but grain elongation in the columnar direction is still slightly observed. With the addition of Si instead of Ti, the grains become more equiaxed, but contrast between grains is reduced — possibly due to the formation of an amorphous Si-rich phase. Very little grain structure can be observed in the AlCrTiSiN coating, possibly due to this same amorphous phase or more significant grain refinement.

3.2. Stress–strain behavior

Engineering stress–strain relationships were determined for the various coating systems as a function of temperature from the micro-compression load–displacement data — Fig. 3. In general, all systems show an increase in failure strain or more ductile failure and a decrease in failure stress with increasing temperatures. The apparent modulus during loading in the engineering stress–strain curves is largely observed to remain constant with increasing temperature to within the measurement accuracy.

However, this additional apparent ductility at elevated temperatures was observed both in situ during testing and ex situ in the HRSEM (Fig. 4) to be accommodated through cracking and buckling of internal columnar grains. Some dislocation-based plasticity is expected to occur during the early stages of deformation and the nucleation of cracks. However, this is not straightforward to decouple from the fracture behavior due to the complex microstructures of the pillars. Fracture was frequently observed to be concentrated near microstructural defects in the coatings: columnar grain boundaries in the CrN coating at 25 °C or inclusions in the AlCrN coating at 500 °C — both shown in Fig. 4. Catastrophic brittle failure was not observed in most pillars. Instead, upon fracture, the stress dropped by ≥50%, and the test was halted.

The various coating systems display markedly differing behavior with increasing temperature. The CrN coating displays increased ductility at elevated temperatures, possibly due to the buckling columnar grains being able to accommodate increasing amounts of deformation through plasticity [35] at their bases. The finer grained AlCrN coating shows significant strengthening at low temperatures due to the reduced grain size, but this rapidly decreases with increasing temperature. The addition of titanium, forming AlCrTiN, appears to significantly moderate this temperature dependence strength, but at the cost of some ‘ductility’. The smaller grain size of the AlCrTiN does not add any apparent further strengthening over the AlCrN coating. This might be attributed to the effect of fractures at inclusions and voids putting a limit on the achievable strength, but the comparable hardness values seen between the coatings (Table 1) discount this. A more likely explanation for the upper limit in strength may be the equally fine crystallite sizes among all the aluminum containing coatings observed by XRD within the larger grain structures seen in FIB cross-sections.
The addition of silicon, however, appears to increase high temperature strength and promote graceful failure. Formation of a Si₃N₄ amorphous phase to create a nanocomposite around the harder CrN grains is known to promote toughness [28], which can create a petal-like morphology in pillars [36], rather than splitting fracture. The amorphous fraction in these AlCrSiN coatings appears to be relatively small in both HRSEM and XRD, so these pillars still fail by fracture (Fig. 4) even at elevated temperatures. The combination of adding both titanium and silicon to the coatings to form AlCrTiSiN appears to yield the best combination of high temperature strength and apparent ductility.

However, the absolute amount of strain attained in these tests is brought into question by the lower apparent moduli from the loading portion of the engineering stress–strain curves. These are observed to be significantly (30–60%) lower than the results from indentation – Table 1. Misalignment is not suspected to play a large role in this decreased stiffness, since the initial portions of the stress–strain curves are linear. Also identical stiffness values were obtained with different system configurations and indenter tips. Therefore, the reduced observed stiffness is primarily attributed to the geometry of the coating systems: error in pillar height measurement due to FIB undercutting and error from the pillar sink-in effect, where the pillar acts as a flat punch elastically deforming the substrate underneath. For pillars with a well-characterized geometry and known substrate modulus, the effect of pillar taper and sink-in can be successfully corrected for in the analysis [19,37]. However, in these tests, the pillars have been fabricated from industrially relevant coatings, which include an adhesion layer in between the hard coating and the cemented carbide substrate. This adhesion layer has varying thickness between the various coatings (Fig. 2), and the relative thickness of this layer compared to the thickness of the hard coating is observed to correlate with the stiffness of the engineering stress–strain curves.

### 3.3. Strength versus hardness

Since both the apparent ductility and the moduli demonstrate complex behavior, the main feature that can be directly extracted from the engineering stress–strain curves is the uniaxial compressive failure strength, \( f_c \), which is taken to be the maxima in the curves. In order to establish a context for these results in relation to previous measurements on hard coatings, industry standard nanoindentation testing was performed on the coatings at room temperature. Table 1 summarizes the extracted results from nanoindentation testing as well as the room temperature micro-compression failure stresses.

As Table 1 shows, the room temperature hardness of the aluminum-containing coatings ranges well above 30 GPa, where the silicon-containing coatings are slightly harder, compared to their Si-free counterparts. This effect is well-known and commonly attributed to the grain refinement brought upon by the silicon addition, the so-called nanocomposite structure [38]. CrN is a rather soft material in comparison, with a hardness of about half of that of the other coatings. The elastic moduli follow the same trend.

<table>
<thead>
<tr>
<th>Coating type</th>
<th>( H ) [GPa]</th>
<th>( E ) [GPa]</th>
<th>( H/E )</th>
<th>( \sigma_f ) [GPa]</th>
<th>( H/\sigma_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN</td>
<td>16.8 ± 0.9</td>
<td>360 ± 17</td>
<td>0.047</td>
<td>5.8 ± 0.8</td>
<td>2.90</td>
</tr>
<tr>
<td>AlCrN</td>
<td>33.5 ± 0.8</td>
<td>561 ± 15</td>
<td>0.060</td>
<td>11.8 ± 1.9</td>
<td>2.84</td>
</tr>
<tr>
<td>AlCrTiN</td>
<td>31.4 ± 0.8</td>
<td>540 ± 12</td>
<td>0.058</td>
<td>10.6 ± 1.5</td>
<td>2.96</td>
</tr>
<tr>
<td>AlCrSiN</td>
<td>34.3 ± 0.8</td>
<td>530 ± 14</td>
<td>0.065</td>
<td>11.1 ± 1.6</td>
<td>3.09</td>
</tr>
<tr>
<td>AlCrTiSiN</td>
<td>34.5 ± 1.0</td>
<td>538 ± 12</td>
<td>0.054</td>
<td>13.1 ± 1.0</td>
<td>2.63</td>
</tr>
</tbody>
</table>

Table 1

Summary of results of hardness and elastic modulus values from room temperature nanoindentation and compressive failure strength from micro-compression of the various coatings.

Fig. 4. Micropillar deformation and fracture for various coatings at different temperatures.
H/Y ratio is the equivalent cone angle of the indenter [42,45–47]. This has been related to an effective representative strain, ε_f, under the indenter such that sharper indenters give hardness values which are related to representative stress values at greater strains: Berkovich/Vickers indenters have an ε_f ≈ 8% and Cube Corner indenters have an ε_f ≈ 17%. However, for solids which do not display strain hardening, such as ceramics at small length scales [18,19,21,48], the yield stress is effectively identical to the peak flow stress of the material: H/Y ≈ H/σ_y.

For these materials, a more significant effect on the confinement parameter is caused by the elastic surface deflection during indentation due to their high H/E ratio [30,44]. Materials with relatively low yield strength to modulus ratio, such as metals, would behave nearly perfectly plastically with H/Y of ~ 3. However, materials with relatively high flow strength to their modulus, such as both brittle ceramics and non-brittle polymers, would approach H/Y values of 1. For the materials tested in this work, values of H/E of ~0.06 were measured (Table 1), which would produce H/Y values of ~2.7 [43]. This is in good agreement with most H/σ_y values observed in Table 1.

The exception is the AlCrSiN coating with an H/σ_y value of 3.09. This high value suggests that the average failure stress for the AlCrSiN coating at room temperature is lower than what might be a more general representative value due to flaws and inclusions in the micropillars. High values of H/σ_y (≫ 3) are expected if failure occurs prematurely due to brittle failure from crack nucleation from flaws, prior to the actual representative flow stress. Since the observed confinement parameters are mostly close to their ideal values, this suggests that the peak flow stress and failure of the pillars are significantly mediated by plastic or dislocation-controlled flow prior to the nucleation of cracks.

In general, the coatings are observed to show a decreasing confinement parameter, H/σ_y, with increasing H/E ratio, which follows from the increasing role of surface stiffness in hardness at high H/E ratios. At higher temperatures, the H/E ratios are expected to decrease, since the yield strength will decrease while the modulus remains roughly constant. This implies that the confinement parameter, H/σ_y, will likely approach the Tabor value of 3 at elevated temperatures [43]. This implies that high temperature nanoindentation testing should theoretically measure hardness values which correspond very well to micro-compression test values. However, the high strength/hardness of the coatings still makes blunting of the indenter at elevated temperatures a serious concern.

Micro-compression testing appears to be more sensitive to the coating flaws, since the scatter in σ_y is around three times greater than the scatter in H. This may be due to the confining pressure of the surrounding material under the indentation reducing the effect of cracking on failure. However, a much smaller statistical sampling was performed during micro-compression testing than in nanoindentation testing, so a direct statistical comparison of the scatter cannot be made.

3.4. Strength trends with temperature

The uniaxial compressive failure strength, σ_y, for the various coatings was also extracted from the stress–strain curves at elevated temperatures – Fig. 5. In general, the scatter in strength or the standard deviation of the failure stress is observed to decrease with increasing temperature, which implies an improvement in flaw/fracture tolerance. This is in agreement with the increases in apparent ductility in the stress–strain curves shown in Fig. 3. All the coatings also display a decrease in strength with increasing temperature, as expected. However, the coatings do not all show the same trend in temperature dependence.

The addition of Al to CrN-based coatings provided a significant increase in performance, but the AlCrN coating system still shows a very similar temperature dependence to the CrN coating. The addition of Ti or Si to the coatings changes this trend, suggesting that the new mechanism becomes controlling for intergranular fracture. AlCrSiN shows slightly better intermediate temperature performance, but it loses strength more rapidly at the higher temperatures than AlCrTiN. At temperatures ≥ 500 °C, AlCrTiN coating systems are expected to outperform AlCrSiN. By adding both Ti and Si to the AlCrN, the best performance was achieved; however, the decreasing trend in strength with temperature is more rapid than that observed in the AlCrTiN. Further variation of the Ti and Si contents in the AlCrTiSiN coating may yield even further improvement in the high-temperature mechanical properties.

One important observation to note from Fig. 5 is that the room temperature ranking of the coatings does not correlate to the ranking of coatings at high temperatures. For example, the AlCrN coating would be ranked second by the room temperature values, but at high temperature it would be ranked second to last. This highlights the necessity of high temperature measurements for determining coating performance for further coating development.

4. Conclusions

The elevated temperature strength of a wide range of chromium nitride-based hard coatings was evaluated using in situ micro-compression. This allowed the first direct measurement of the high temperature compressive strength, rather than the hardness, of such coatings. Room temperature comparisons between nanoindentation and micro-compression results for ranking coatings yielded good agreement. At elevated temperatures, the addition of Si and/or Ti to the coatings was found to be beneficial for decreasing the effect of temperature on coating strength; the addition of Ti is the more beneficial of the two. The addition of Si was found to be beneficial for increasing apparent ductility or retaining load via fracture tolerance. The addition of both Si and Ti was found to provide the highest coating strength at elevated temperature and the lowest temperature dependence. The variation in temperature dependence between the different coating compositions resulted in the high temperature coating rankings being different than those at room temperature. This highlights the necessity of high temperature measurements for determining coating performance for further coating development.

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