Residual stress evolution during decomposition of $\text{Ti}_{(1-x)}\text{Al}_{(x)}\text{N}$ coatings using high-energy x-rays

M.R.Terner^{1,a}, P.Hedström^{1,b}, J. Almer^{2,c}, J. Ilavsky^{2,d}, and M.Odén^{1,e}

¹Division of Engineering Materials, Luleå University of Technology, SE-971 87, Luleå, Sweden

²Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

^amark.terner@ltu.se, ^bpeter.hedstrom@ltu.se, ^calmer@aps.anl.gov,

^dilavsky@aps.anl.gov, ^emagnus.oden@ltu.se

Keywords: ceramic coatings, TiAlN, WAXS, SAXS, x-ray scattering, small-angle x-ray scattering, synchrotron radiation, x-ray diffraction

Abstract. Residual stresses and microstructural changes during phase separation in $\text{Ti}_{33}\text{Al}_{67}\text{N}$ coatings were examined using microfocused high energy x-rays from a synchrotron source. The transmission geometry allowed simultaneous acquisition of x-ray diffraction data over 360° and revealed that the decomposition at elevated temperatures occurred anisotropically, initiating preferentially along the film plane. The as-deposited compressive residual stress in the film plane first relaxed with annealing, before dramatically increasing concurrently with the initial stage of phase separation where metastable, nm-scale c-AlN platelets precipitated along the film direction. These findings were further supported from SAXS analyses.

Introduction

The performance of arc-evaporated TiN coatings on metal-cutting tools has been markedly improved by alloying with Al, where for Al contents up to $x=0.67$ it substitutes for Ti in the cubic lattice to form metastable $\text{Ti}_{(1-x)}\text{Al}_{(x)}\text{N}$. Studies have shown that at elevated temperatures the high compressive stress in the coating relaxes, and this is accompanied by decomposition of the metastable matrix into equilibrium c-TiN and h-AlN phases above 900°C [1]. Decomposition occurs via the precipitation of metastable, coherent, c-AlN nanoprecipitates, most probably via spinodal decomposition, on the (200) planes of c-TiN. There is also a concurrent macroscopic increase of coating hardness which is attributed to precipitation hardening arising from the coherency of the small precipitates, and as such this appears to be the first precipitation hardened ceramic material. The complexity of the microstructural and chemical changes during decomposition has limited the ability to determine residual stress changes in these coatings. This paper will report on the use of a combination of high energy x-ray diffraction and small-angle x-ray scattering to probe this material in greater detail.

Experimental Procedure

Materials and Methods. $\text{Ti}_{(1-x)}\text{Al}_{(x)}\text{N}$ arc-evaporated coatings with an Al content of $x=0.67$ were produced in a commercial deposition chamber onto WC-Co cutting tool substrates. The deposition temperature was $\sim 500^\circ\text{C}$, and the coatings were grown from TiAl targets in a N_2 reactive atmosphere to approximately $10\ \mu\text{m}$ thickness. The coatings undergo columnar growth and have $\langle 100 \rangle$ texture normal to the substrate-film interface, and are isotropic within the film plane (y-z). The samples were sectioned into 1mm slices and individual samples heat treated to 700, 800, 900 and 1000°C for 2 hours in argon. High energy synchrotron x-rays ($E = 80.72\ \text{keV}$) were used for

analysis at beam line 1-ID at the Advanced Photon Source (APS), in a transmission geometry as shown in Fig. 1. The beam was vertically focused using refractive lenses [2] to $\sim 3 \mu\text{m}$ (FWHM) while the horizontal size was defined to $120 \mu\text{m}$ using slits. For wide angle x-ray scattering (WAXS) diffraction patterns were collected for an exposure time of 60-200 s using a CCD area detector (Mar165, 165mm diameter, 2048x2048 pixels) concentric with the direct beam and placed 702 mm downstream of the sample. This allowed for the simultaneous collection of data over a 360° range of η , where $\eta = [90, 270]^\circ$ corresponds to the direction of film growth GD, i.e. normal to the plane of the film, and $\eta = [0, 180]^\circ$ corresponds the normal direction ND, i.e. the in-plane direction. Compared to the conventional $\sin^2\psi$ geometry, $\text{GD} = \psi = 0^\circ$ and $\text{ND} = \psi = \pm 90^\circ$. We note that, in contrast to conventional laboratory measurements, this technique negates the need for sample movement to access these different sample orientations.

For small-angle x-ray scattering (SAXS) measurements, the WAXS detector was horizontally translated out of the x-ray beam and the SAXS signal was collected with a smaller CCD ($26 \times 28 \text{ mm}^2$, 1152x1242 pixels) for an exposure time of 100-200 s. In contrast to WAXS, the SAXS detector was offset to the direct beam, such that only one of the four quadrants in azimuth was measured.

Figure 1. Experimental setup for high-energy SAXS/WAXS, with the coating growth and normal directions (GD,ND) and measured radius (r) and azimuth (η) for a single diffracted x-ray shown.

Data analysis. The 2-D WAXS data was transformed into 1-D linear plots using techniques detailed previously [3]. The data was divided into 5° η -bins and peaks were fit to pseudo-Voigt functions. The strain was determined by a linear least square fit of the peak positions as a function of $\sin^2\psi$ (with η - ψ conversion as noted above). As the elastic constants of $\text{Ti}_{33}\text{Al}_{67}\text{N}$ are unknown, we used the macroscopic constants $E = 450 \text{ GPa}$ and $\nu = 0.22$ for pure TiN to convert strain to estimated stress. Analysis of the SAXS data was performed using the Nika and Irena scripts developed for IGOR by Ilavsky et.al. [4].

Results and Discussion

WAXS. Fig. 2 shows the WAXS peak evolution averaged over the full 360° azimuth (η) for the four heat treatments. In the as-deposited state ($\sim 500^\circ\text{C}$) the coating is single phase NaCl-type ($c\text{-Ti}_{33}\text{Al}_{67}\text{N}$) and the first three peaks can be clearly identified, with some substrate signal due to finite vertical beam size and/or imperfect sample alignment. These peaks are shifted to lower d -spacings than in stoichiometric $c\text{-TiN}$, largely due to the compositional effect on lattice parameter of the smaller size of Al compared to Ti [1]. Note that the peak at $2.02 \text{ \AA}$ has been identified as a Co

reflection from the substrate and has been unambiguously eliminated as a possible source of the signal in samples where c-AlN is indicated.

After heat treatment to 700°C no new phases have been produced, but stress relaxation has occurred as evidenced by changes to the FWHM and peak positions; the FWHM of the all peaks decreased by ~20%, due to defect annihilation as frequently observed for arc-evaporated coatings [5]. At 800°C the peaks broaden to become comparable in width to the as-deposited state. In addition, peak asymmetry on the higher-d side of these peaks indicates the formation the c-TiN phase. Further, a low intensity, broad peak is also developing at $d \sim 2.69 \text{ \AA}$, which corresponds to the h-AlN phase. Despite the equilibrium decomposition products of c-TiN and h-AlN being detected at 800°C, it is also clear that broadening occurs towards lower-d spacing side which is consistent with formation of c-AlN. After annealing at 900°C the decomposition of the coating has progressed considerably, with the equilibrium product phases c-TiN and h-AlN dominating the phase assembly. At 1000°C the decomposition has further proceeded, with no distinct evidence of the original c-Ti₃₃Al₆₇N peaks remaining, nor of the intermediate c-AlN.

Figure 2. WAXS plots averaged over 360° η for the Ti₃₃Al₆₇N coatings heat treated at various temperatures. The positions of equilibrium c-TiN are marked.

Key:

c = c-AlN

h = h-AlN

s = substrate

A comparison of the WAXS intensities from the ND and GD orientations for (200) is shown in Fig. 3, averaged over $\delta\eta = 4^\circ$ wide sectors centered at $\eta = 0^\circ$ and 90° respectively. The data from ND, i.e. $\psi = 90^\circ$, is usually difficult to obtain from standard laboratory equipment. It reveals distinct anisotropy in the early stages of decomposition. The (200) peak positions, representing directional strains, are seen to shift considerably from as-deposited values along GD but negligibly along ND at 700°C. At 800°C however the trend is reversed. This shows that the strain evolution is clearly anisotropic (non-hydrostatic) during the early stages of phase separation. In other studies only the formation of a c-TiN shoulder on (200) was detected (measured along GD) and used as evidence of the start of phase separation (at 900°C [1]). Results here show that the shoulders on the peaks corresponding to the Al-free c-TiN product phase are more pronounced than c-AlN at the start of decomposition and are more pronounced along ND than GD (these results are also valid for other coating peaks, not shown). Also, a slight bump due to c-AlN can be seen along ND at 800°C, which is absent (within experimental error) along GD. This is the first x-ray evidence of the phase separation occurring preferentially along ND.

Figure 3. WAXS showing anisotropy of peak evolution in a) growth direction and b) normal direction. Key: T = c-Ti₃₃Al₆₇N, c = c-AlN

Residual Stress. A plot of d versus $\sin^2\psi$ (with the fit lines shown), is given in Fig. 4 for (200) which is representative of the other peaks, and Fig. 5 is a plot of the in-plane stress σ_{11} determined from the $\sin^2\psi$ data for all three coating peaks. The plots in Fig. 4 deviate from linearity at the ends corresponding to $\psi = 0$ and 90° , i.e. GD and ND. Such deviations have also been seen in other arc-evaporated TiN and CrN coatings by Almer et.al. [3] and attributed to highly directional defect populations created in the coating during deposition via ion bombardment. Such effects are not included in existing micromechanical models linking strains to stresses; despite this, they found that reliable estimates of in-plane (macro stresses) could be derived from x-ray strain data via both Reuss and Vook-Witt models. The jump in d -spacing after heat treatment at 900°C for 2 hours shows that the as-deposited cubic phase has significantly changed composition, being depleted of Al and is now close to the equilibrium c-TiN phase. The x-ray data and SAXS results show that the composition at 900°C has become reasonably isotropic, hence the peak used in this analysis at all azimuths represents the same phase, but of indeterminate composition.

The plot of σ_{11} (Fig. 5) shows that initially there is a high compressive stress followed by stress relaxation after annealing at 700°C , and then a dramatic increase in compressive stress after annealing at 800°C . This is associated with the early stages of phase separation, i.e. a precipitation hardening effect. Indeed, Hörling et.al. [6] have found the as-deposited coating hardness to be slightly increased at these temperatures, which would not be expected in the absence of precipitation hardening. The difference in stress values is attributed to use of macroscopic rather than (unknown) hkl-dependent elastic moduli for cubic Ti₃₃Al₆₇N, which is likely to be highly elastically anisotropic as are other metal-nitride systems [3]. The trend for all planes is, however, the same. Beyond 800°C there is a further stress relaxation. Only data for (220) appears to be reliable due to the shift in composition from c-Ti₃₃Al₆₇N to c-TiN. Additionally, at these temperatures the system is essentially two-phase and contains a large amount of h-AlN, so a consideration of the stress state in this phase is also included in Fig. 5. This was estimated by using the d -spacing of (100) at GD and ND as the endpoints of the straight line for the $\sin^2\psi$ method, with $E = 310$ GPa, $\nu = 0.24$ [7]. The stress in the h-AlN precipitates is also seen to be relaxing as the annealing temperature increases.

Hörling et.al [6] analysed essentially the same material processed and heat treated under the same conditions, and using the $\sin^2\psi$ method on the 422 peak in a laboratory setting determined the as-deposited stress to be -3.1 GPa, which is within the range determined from the analysis above. However they report a monotonic decrease in compressive stress with annealing up to 800°C , down

to a value of -0.7 GPa. No x-ray microstructural data was provided at 800°C, however at 900°C their data showed that the coating decomposition has barely started, whereas in our work it was well advanced. Given the strong correlation between microstructure (specifically, the size and phase fraction of the precipitates) and residual stress, the differences in stress values are therefore not unexpected.

Figure 4. d vs. $\sin^2\psi$ for (200), averaged over four quadrants with fit lines shown. Marker size indicates scatter of the data

Figure 5. Calculated in-plane residual stress σ_{11} vs. annealing temperature. $T = \text{Ti}_{33}\text{Al}_{67}\text{N}$ $N \leq 800^\circ\text{C}$ or $\text{TiN} \geq 900^\circ\text{C}$, $h = \text{h-AlN}$

SAXS. For the as-deposited samples, the SAXS patterns exhibited considerable anisotropy, with increased general scatter and a well-defined small-angle diffraction peak along the growth direction at $q = 0.051 \text{ \AA}^{-1}$. This corresponds to a spacing of $d = 2\pi/q = 123 \text{ \AA}$, which matches the period of rotation of the sample during deposition. We surmise that as the sample passes the two source targets and IR heater during deposition, the coating undergoes a characteristic densification and/or composition modulation, leading to a periodic layered structure. Such layered structures have been seen in these coatings only as contrast variations in high-resolution TEM [8] but this is the first quantitative evidence of these features seen using SAXS.

Figure 6. SAXS curves for coatings annealed at a) 900°C, 1 hour, showing distinct anisotropy in scattering, b) 1000°C 2 hours, generally isotropic with shift of shoulder to lower q ($d = 2\pi/q$)

Upon annealing, no significant particle scattering in the SAXS patterns was detected for temperatures up to 800°C. This may be due to the fact that the size of the early c-AlN particle nuclei (found to be $\sim 20\text{\AA}$ [1]) was near the size-detection limit of these experiments; for small particles, this limit is dictated by the signal/noise ratio at large $q > \sim 0.1\text{ \AA}^{-1}$, which as seen in Fig. 6 is limited. Above 800°C, decomposition was observed and found to be anisotropic, first occurring along ND. This is shown in Fig. 6(a) for a sample heat treated at 900°C for 1 hr (note that this is shorter than the 2 hour anneals discussed above). The signal from the ND has developed a “shoulder” around $q \sim 0.09\text{ \AA}^{-1}$ which is indicative of particle scattering, however the GD signal shows no particle scatter and is almost featureless, except for the peak discussed above at $q = 0.051$. Longer heat treatment at 900°C (2 hours) or even higher temperatures reveal that the later stages of decomposition are associated with reasonably isotropic scatter from all directions (Fig. 6(b)), and that the scatterer sizes are significantly larger as indicated by move of the shoulder to smaller q , where $d = 2\pi/q$. This indicates major structural changes have occurred, associated with growth of the precipitates to form an isotropic grain distribution, and removal of the as-deposited layered structure.

Conclusions

The application of both wide- and small-angle scattering with microfocused high-energy synchrotron x-rays has given unique insight into the decomposition of $\text{Ti}_{(1-x)}\text{Al}_{(x)}\text{N}$ coatings. It was shown that the early stage of decomposition is anisotropic, and that after a relaxation of the as-deposited compressive residual stresses there is a significant increase in compressive stress in the film plane. This is associated with the very early stage of decomposition, where the metastable c-AlN particles only several nm or less in thickness, are first formed along the in-plane direction.

Acknowledgments

The author would like to acknowledge the contribution of B. Harder at the APS for his assistance with technical issues, and J. Sjölen and T. Larsson from Seco Tools AB, Sweden, for producing the coatings used in this work. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

- [1] A. Hörling, L. Hultman, M. Odén, *et.al.*: J. Vac. Sci. Technol. Vol. 20(5) (2002), p.1815
- [2] J. Almer and S. Shastri: manuscript in preparation
- [3] J. Almer, U. Lienert, R. L. Peng, and M. Odén: J. Appl. Phys. Vol. 94(1) (2003), p. 697
- [4] <http://www.uni.aps.anl.gov/~ilavsky/nika.html>; <http://www.uni.aps.anl.gov/~ilavsky/irena.html>
- [5] J. Almer, M. Odén, L. Hultman, and G. Håkansson: J. Vac. Sci. Tech. Vol. 18(1) (2000), p. 121
- [6] A. Hörling, L. Hultman, M. Odén, J. Sjölen, *et.al.*: Surf. Coat. Technol. Vol. 191 (2005), p.384
- [7] W.D. Kingery, H.K. Bowen, D.R. Uhlmann: *Introduction to Ceramics* (J. Wiley & Sons, NY 1976)
- [8] J. Sjölen: manuscript in preparation

Residual Stresses VII

doi:10.4028/www.scientific.net/MSF.524-525

Residual Stress Evolution during Decomposition of $\text{Ti}_{(1-x)}\text{Al}_x\text{N}$ Coatings Using High-Energy X-Rays

doi:10.4028/www.scientific.net/MSF.524-525.619