Residual Stress Measurements in Thin Coatings

Dileep Singh
Nuclear Engineering Division
June 10, 2010

Coworkers:
J. Routbort, K. Pappacena, O. Erylimaz, G. Chen, W. Liu

Project ID # PM031

Vehicle Technologies – Annual Review – June 7-11, 2010

Sponsored by ***Propulsion Systems Materials***

Argonne NATIONAL LABORATORY

... for a brighter future

U.S. Department of Energy

UChicago Argonne LLC

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Overview

Timeline

- Project start FY07
- Project end FY12
- 70% complete

Budget

- Total project – $700 K
- FY09 = $100 K (DOE)
- FY10 = $200 K (DOE)

Barriers

- Role of residual stresses in thin tribological coatings and its implications to the coating performance and reliability is not well characterized or understood

⇒ accurate stress/strain profiling not available
⇒ analysis and interpretation of data
⇒ adhesion energy measurements are not trivial
⇒ correlations of coating processing, stresses and performance is quite complex

Partners

- Borg Warner
- Galleon International
- Hauzer Techno Coatings, Inc.

This project complements the overall effort in the area of development of low friction high wear resistant coatings for vehicle applications

Relevance

- Minimizing friction and wear in vehicle drive trains and engine components can *significantly reduce parasitic energy losses, and consequently, will result in petroleum displacement*

- Performance (low friction and wear) of tribological coatings and its long-term durability is strongly dependent on the residual stress profiles in the coating and at the coating/substrate interface; thus, it is critical to understand residual stresses in the coatings *to extend component life and reduce life-cycle costs*

- No reliable technique(s) available to profile residual stresses in thin coatings

- Inter-relationships between processing, residual stresses, and coating performance not available

Develop and measure depth-resolved residual stress in thin coatings

Objectives

- Develop and refine high-energy x-ray and/or scanning electron microscopic techniques to profile residual strains/stresses in super-hard, low-friction coatings for vehicle applications

- Correlate residual stresses in coatings systems to processing technique and variables, material properties, adhesion energies, and tribological properties

- Develop a coating processing protocol to produce reliable coatings with engineered residual stresses for a specific coating system applicable for vehicles

- Transfer technology to industry

Approach

- Develop/refine high energy x-rays for profiling residual strains in thin coatings by measuring the change in the lattice parameter of the coating constituents
  - tribological coatings ≈2-5 μm so they require meso-scale techniques with high depth resolutions (<1 μm)
- Deposit low friction high wear resistance coatings and profile residual stresses
  - deposition power & rate
  - composition
- Develop scratch-based techniques to measure hardness, fracture toughness, and adhesion energy of thin coatings
- Relate residual stresses, mechanical & tribological properties, and processing to coating durability

processing ⟷ residual stresses ⟷ performance

Milestones

- FY09 *(all completed)*
  - Analyze the stress measurement data (ZrN, TiC coatings)
  - Correlate stresses and the processing conditions (MoCuN coated steel samples)
  - Explore measuring film mechanical behavior and adhesion energy using indentation techniques
  - Procure a scratch tester for adhesion energy measurements

- FY10
  - Characterize mechanical properties of MoN and MoCuN coatings using nanoindentation
  - Apply scratch testing to evaluate adhesion energy for MoCuN coatings fabricated at different processing conditions
  - Correlate measured adhesion energies to residual stresses and processing conditions (MoCuN)
  - Initiate tribological properties/performance of the MoCuN coatings
  - Develop collaborations with industry

Accomplishments

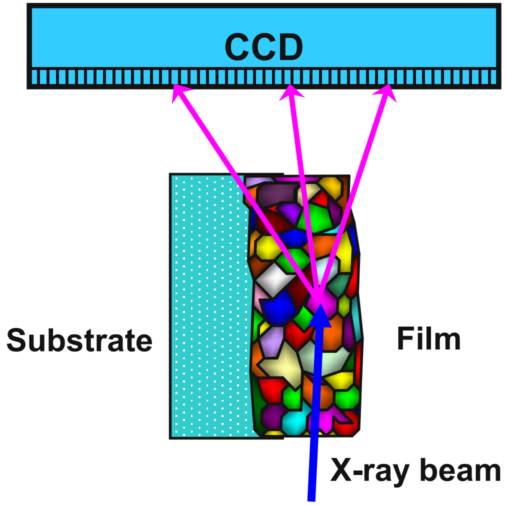
Strain measurement techniques

APS XOR/UNI
beamline 34-ID-E

Kirkpatrick-Baez mirrors
=> white or mono beam

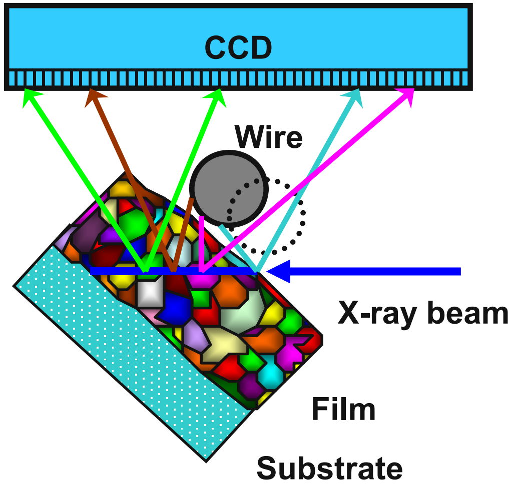
~ 0.5 X 0.5 μm^2

1. Cross-sectional microdiffraction



Scanning the cross section of a film using submicron mono x-ray beam.

2. Differential aperture x-ray microscopy (DAXM)

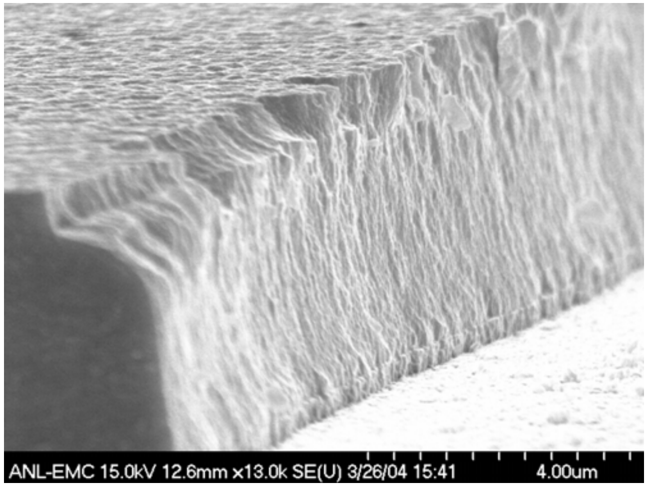


X-ray absorption wire acts as a differential aperture to separate information from different depths. (B.C. Larson et al. Nature **415**, 887 (2002)

Accomplishments

Coating systems investigated:

(A)



- MoCuN on H13 steel
- Fabricated in-house using PVD
- Mo bond coat
- Cu concentration
- deposition power & time varied

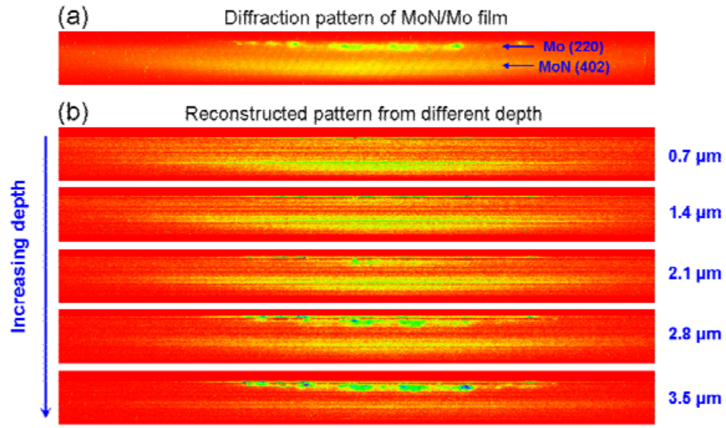
Sample ID	Mo & Cu Deposition Power (kW)	Deposition Time (s)
C70109	Mo:8; Cu: 0	7200
C70110	Mo: 8; Cu: 0.5	6600
C61215	Mo: 8; Cu: 0.8	7200

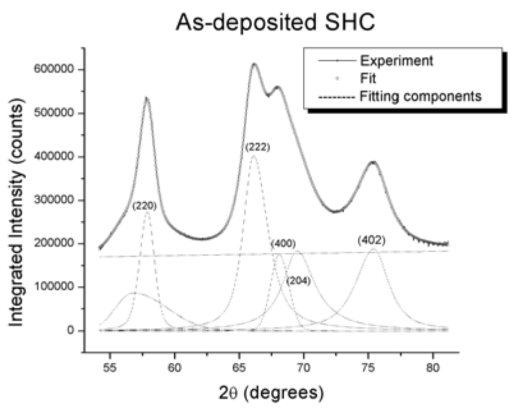
(B) TiC deposited on steel – high and low deposition rates

(C) ZrN deposited on steel – high and low deposition rates

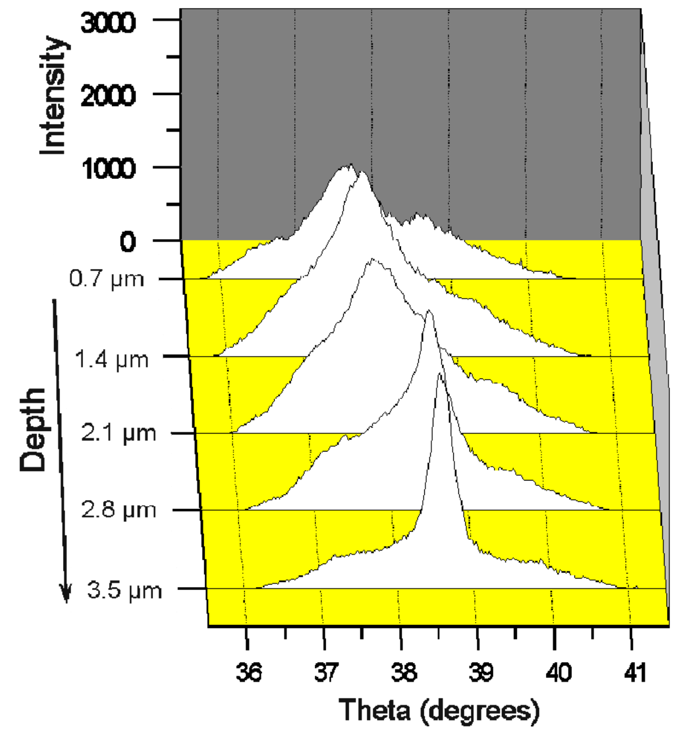
Accomplishments

Microdiffraction





Diffraction pattern of MoN/Mo coating

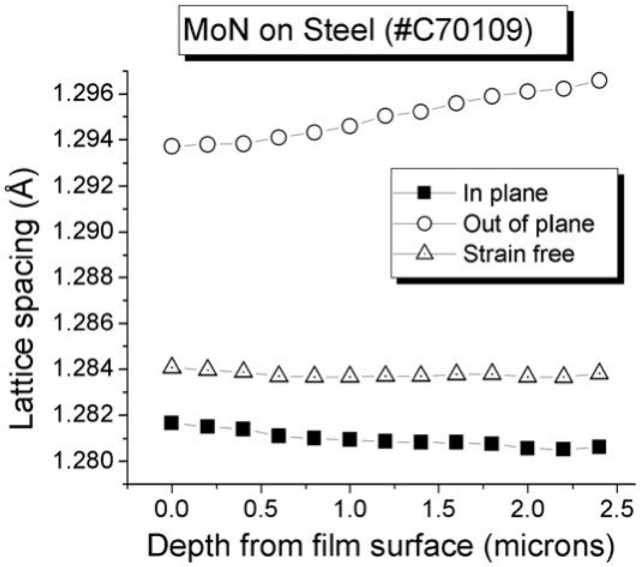


Shift in the diffraction peaks (MoN & Mo) as a function of depth indicative of variation of residual stresses as a function of depth

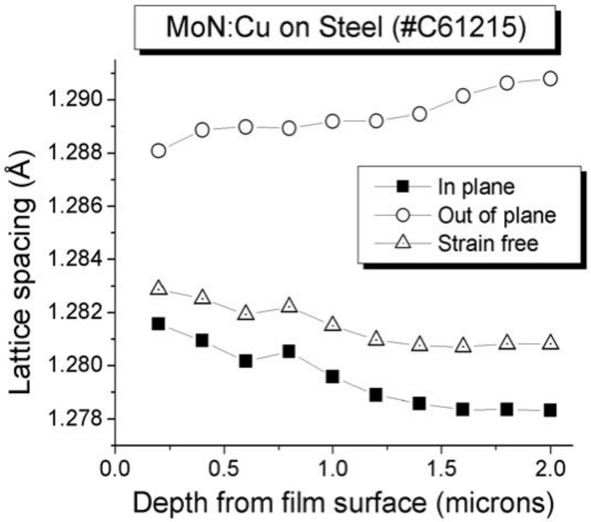
Accomplishments

Lattice Parameters of MoNCu Coatings

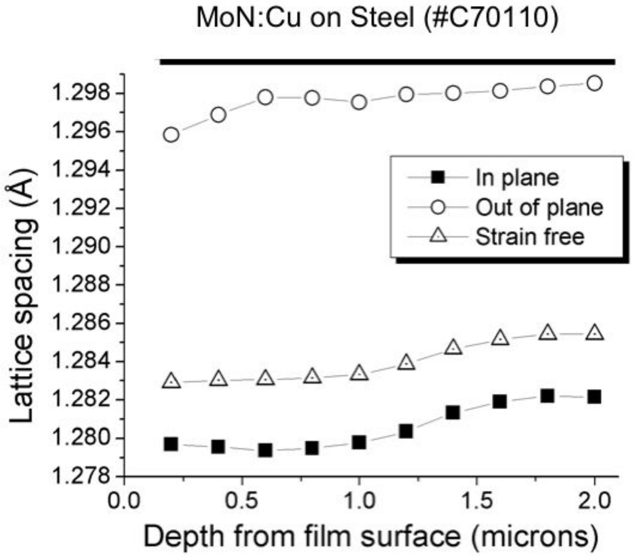
Mo: 8 kW, Cu: 0 kW, t = 7200 s



Mo: 8 kW, Cu: 0.8 kW, t = 7200 s



Mo: 8 kW, Cu: 0.5 kW, t = 6600 s



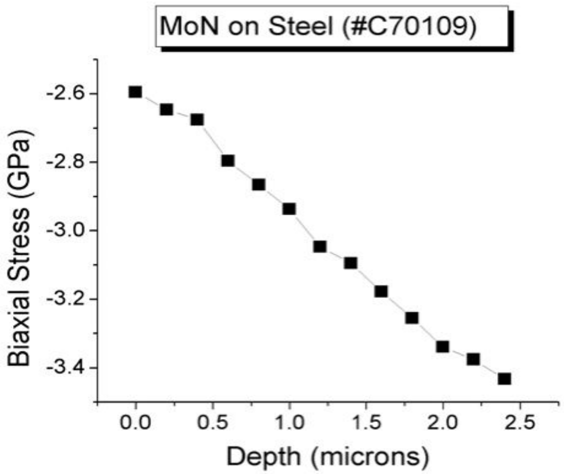
- Lattice parameters of MoN 222 reflections for various stress-states as a function of coating depth

- Strain free lattice parameters determined from $\sin^2\phi$ approach

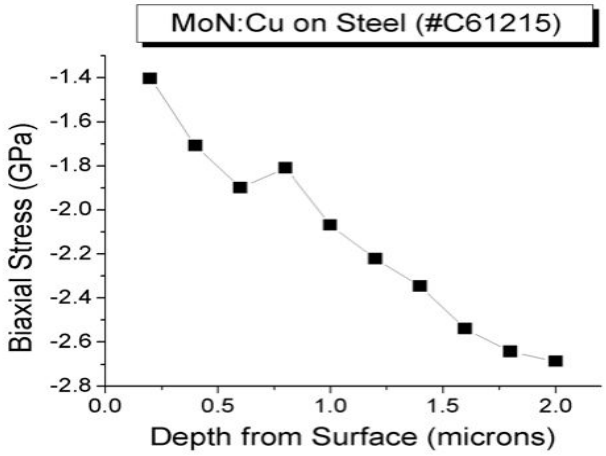
Accomplishments

Depth-resolved stresses in MoNCu films

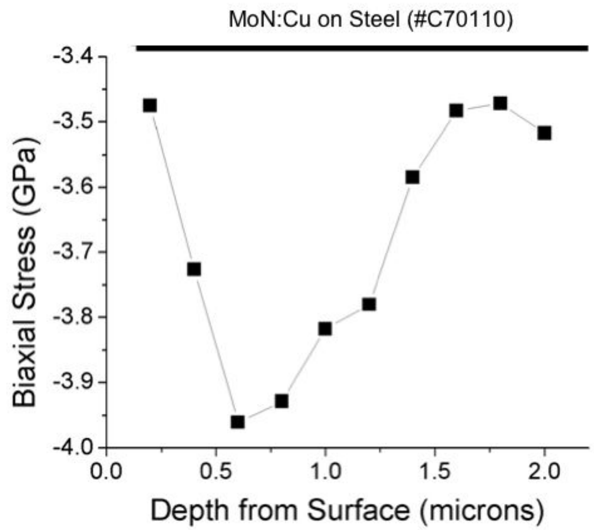
Mo: 8 kW, Cu: 0 kW, t = 7200 s



Mo: 8 kW, Cu: 0.8 kW, t = 7200 s



Mo: 8 kW, Cu: 0.5 kW, t = 6600 s

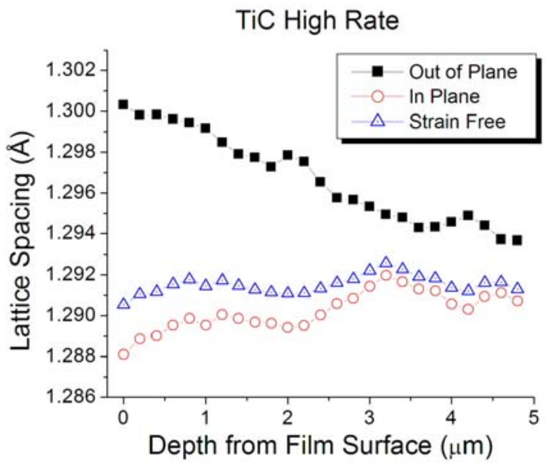


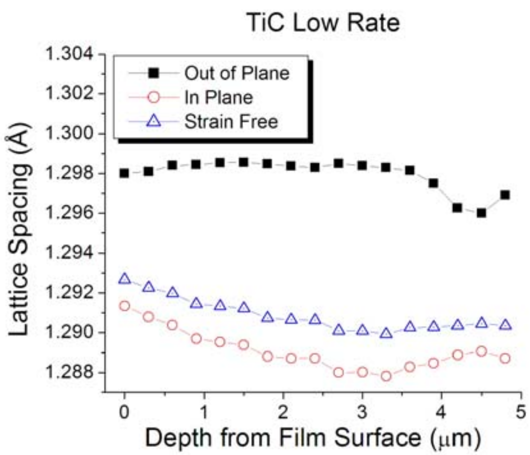
In-plane biaxial compressive stresses as a function of coating depth in the MoNCu coatings deposited on steel for various processing conditions

Accomplishments

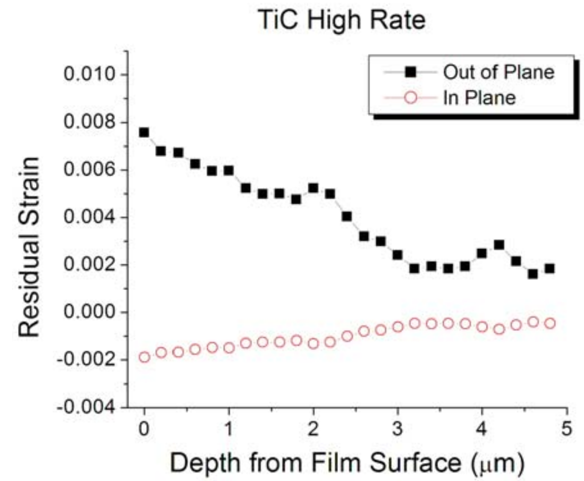
TiC Coating on Steel Results

Lattice Spacing

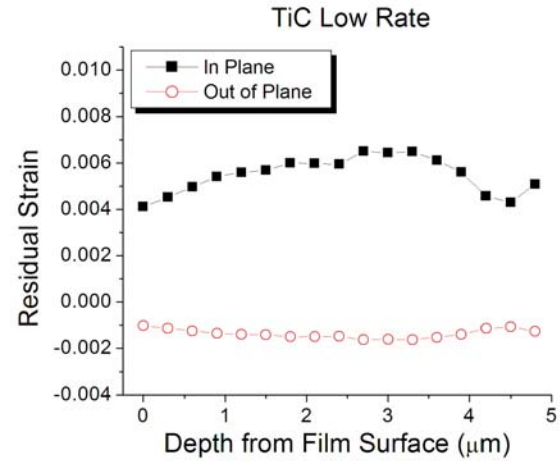




Residual Strain



HRRS process



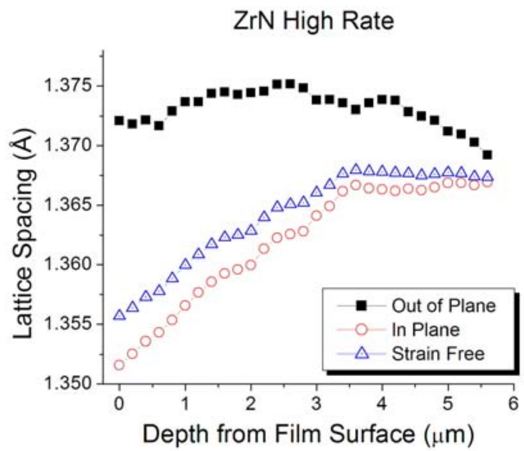
ARE process

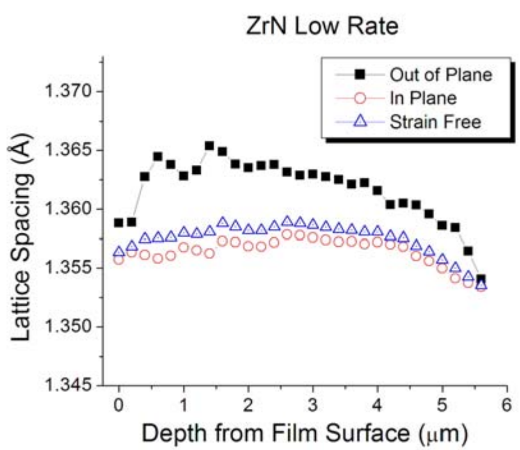
At high deposition rate, in-plane stresses are compressive as desired

Accomplishments

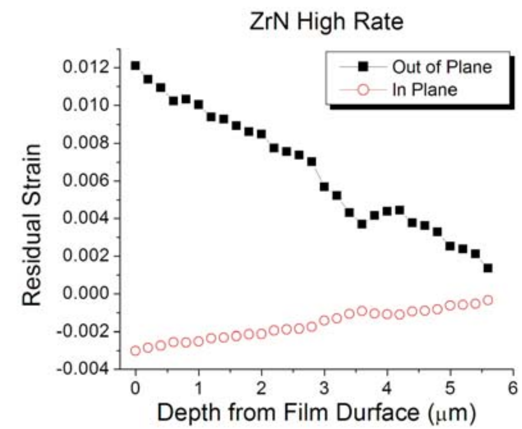
ZrN Coating on Steel Results

Lattice Spacing

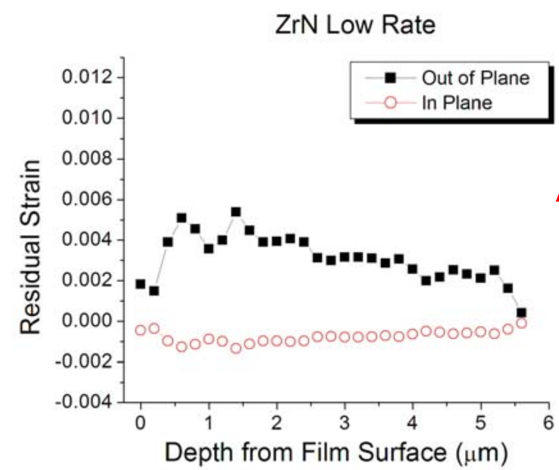




Residual Strain



HRRS process



ARE process

At high deposition rate, in-plane stresses are more compressive

Work of Adhesion Calculations

- Stress based Work of Adhesion calculation (Xie 2001)
  - Use scratch test to determine critical load (P) at which spallation occurs
  - Calculate compressive stress (σ_S) due to scratch test using P and other material properties

$$\sigma_S = \frac{0.15}{R}\left(\frac{PH_f}{H}\right)^{0.5} E_f^{0.3} E^{0.2}$$

  - Use scratch test stress σ_S along with the residual stress σ_R from deposition to determine work of adhesion

$$W = K_2 \sigma^2 t \frac{1-\nu_f^2}{E_f}$$

  - Choose appropriate K_2 value for deformation mode

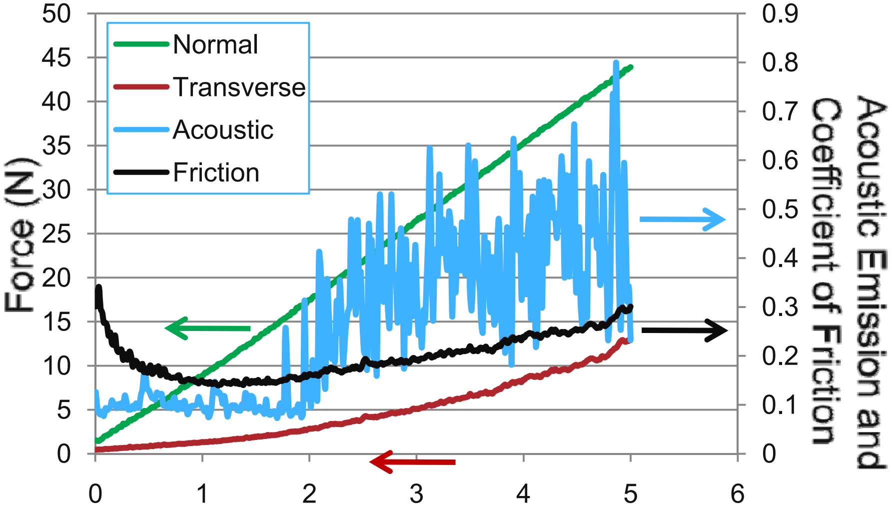
σ_S = scratch test stress
R = indenter radius
P = critical load
H_f = coating hardness
H = substrate hardness
E_f = coating modulus
E = substrate modulus
W = work of adhesion
K_2 = constant (for spallation = .343)
$\sigma = \sigma_R + \sigma_S$ = total stress
σ_R = residual stress
t = coating thickness
ν_f = coating Poisson's ratio

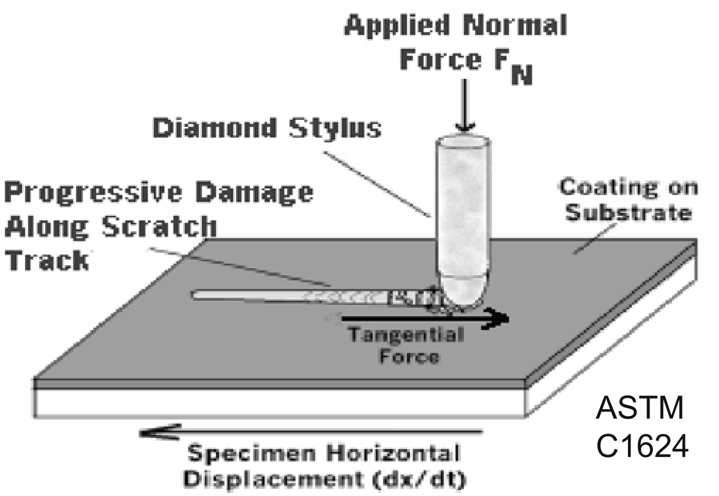
Xie, Y. and Hawthorne, H. M. *Surface and Coatings Technology* 141**:** 15-25 (2001)

Scratch Test Measurements

- Diamond stylus scratches coating with increasing applied normal force
- Acoustic events are recorded
- Microscopy is used to determine where spallation begins
- Coating spallation position is correlated with acoustic events to determine critical load

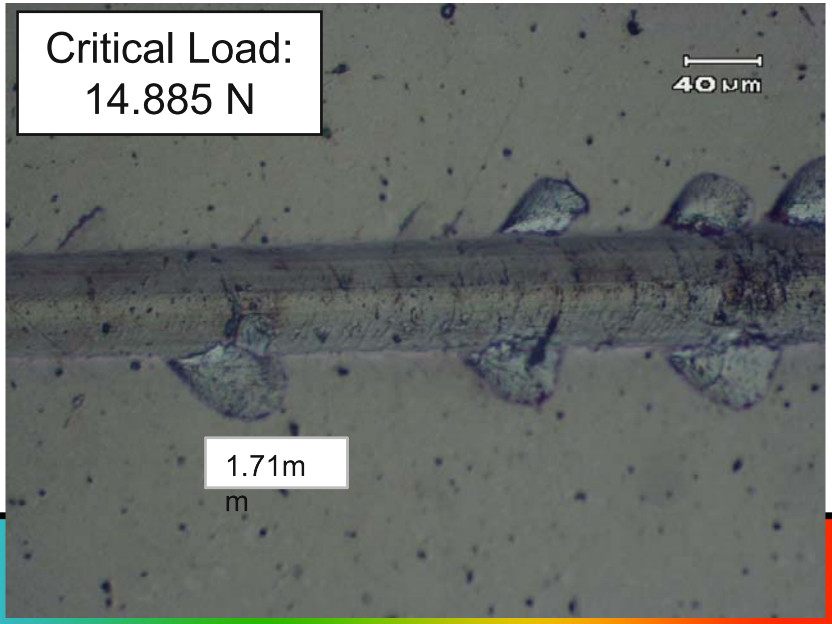
Typical scratch test data set





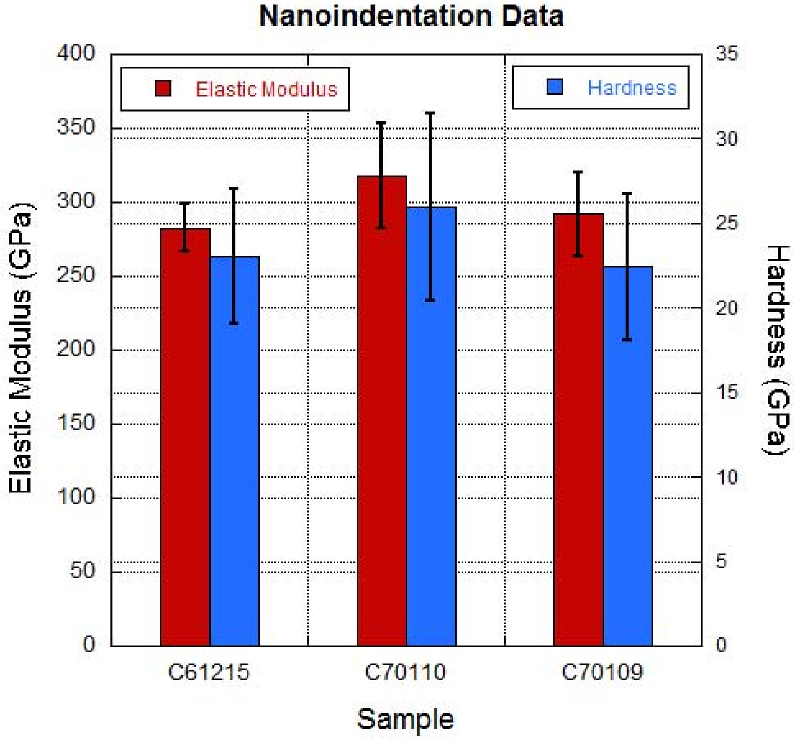
ASTM C1624

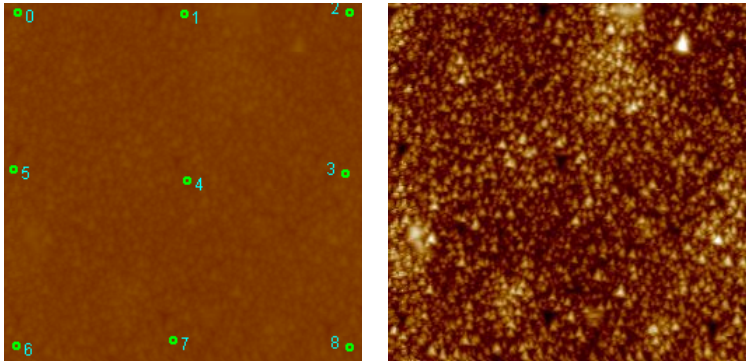
Example of spallation in the scratch track



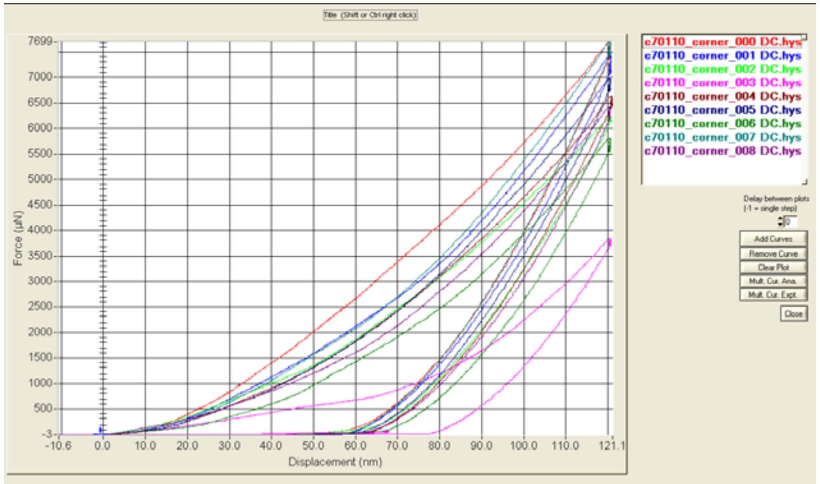
Nanoindentation Results

- Nanoindentation used to calculate the elastic modulus and hardness of each coating
- No significant differences in the elastic moduli or hardness values with copper content in MoCuN coatings





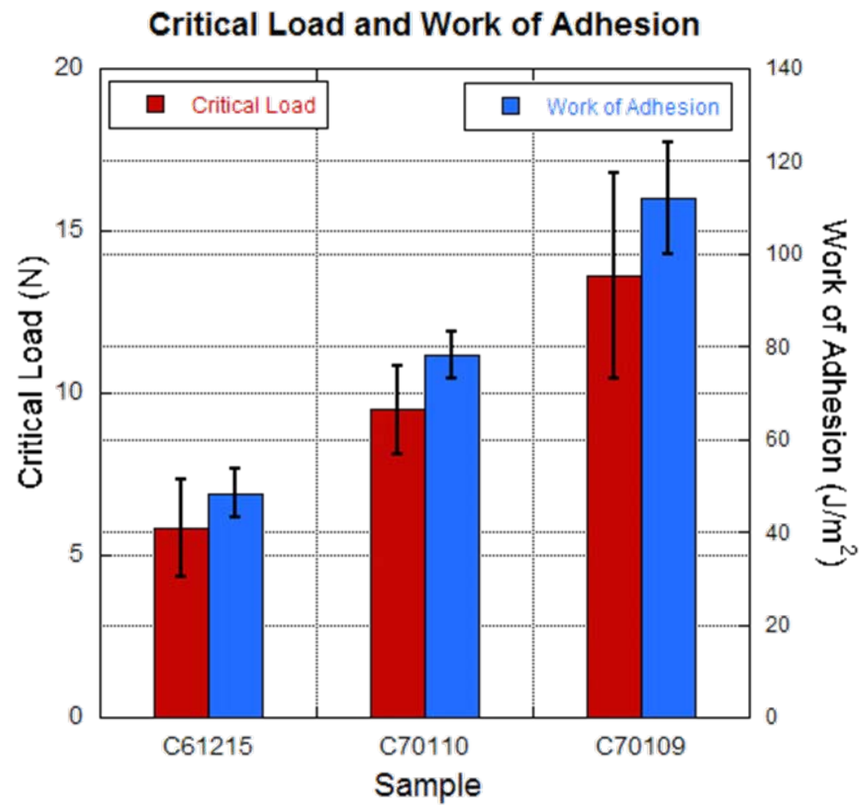
Positions and images of the 9 indentations



Force vs. displacement curves used to calculate elastic modulus and hardness

Work of Adhesion Results

- Critical loads ranged from 5-14 N using 125 μm stylus
- Calculated work of adhesion ranged from 48-112 J/m^2
  - (higher than DLC on WC-Co (Park 1997), and TiN on SS (Bull 1990), and SiCN on SS or Si (Mishra 2008), SiC on inconel, steel or titanium (Gruss 1999), lower or similar to ZrN on inconel, steel or titanium (Gruss 1999))
- Higher work of adhesion and critical load achieved with lower Cu content and higher in-plane compressive residual stresses



Sample ID	Mo & Cu Deposition Power (kW)	Deposition Time (s)
C70109	Mo:8; Cu: 0	7200
C70110	Mo: 8; Cu: 0.5	6600
C61215	Mo: 8; Cu: 0.8	7200

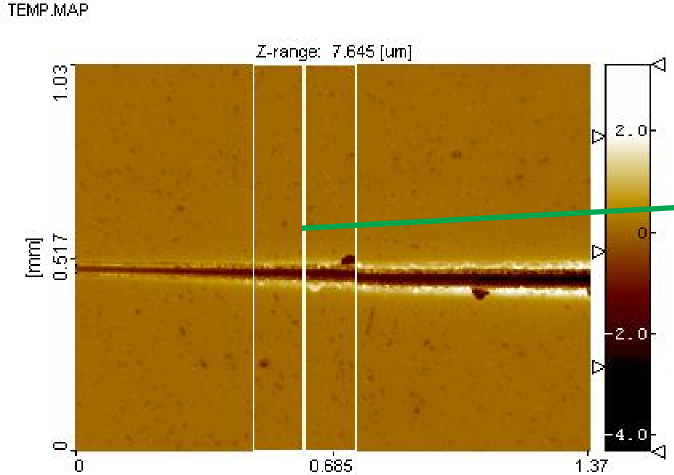
Park H.-S. and Kwon, D. *Thin Solid Films* 307: 156-162 (1997), Bull S. J. and Rickerby, D. S. *Surface Coatings and Technology* 42:149-164 (1990), Mishra S. K and Bhattacharyya, A. S. *Materials Letters* 62:398-402 (2008), Gruss K. A. and Davis, R. F. *Surface Coatings and Technology* 114:156-168 (1999)

Profilometer Results

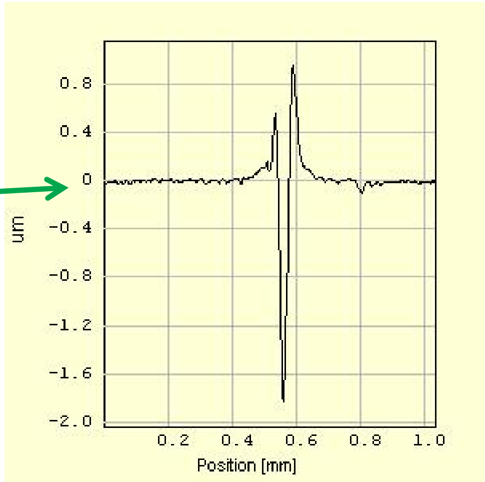
- Profilometer used to study the scratch track at the critical load
- Trench depth and pile up height were analyzed
- Samples with higher Cu content (and lower residual stress) exhibited lower trench depths and lower pile up heights

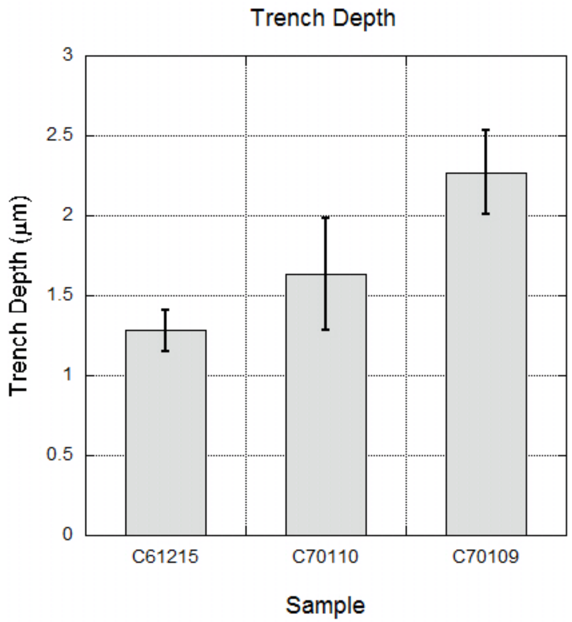
Sample ID	Mo & Cu Deposition Power (kW)	Deposition Time (s)
C70109	Mo:8; Cu: 0	7200
C70110	Mo: 8; Cu: 0.5	6600
C61215	Mo: 8; Cu: 0.8	7200

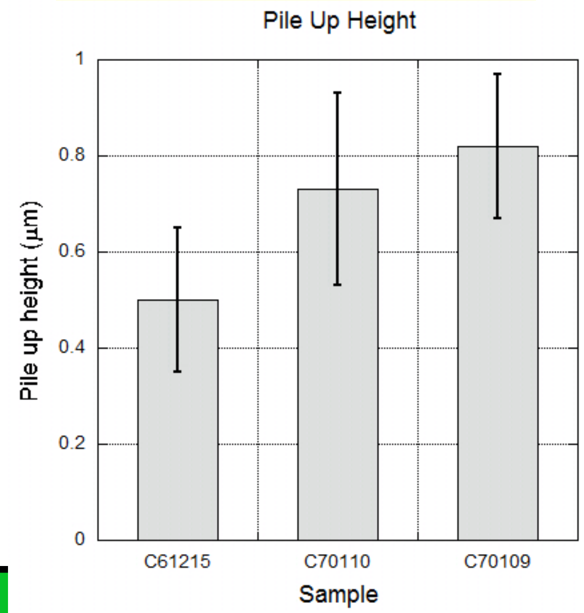
Map of material height along scratch track



Pile up height along center white line







Path Forward

- Complete adhesion energy evaluations for TiC and ZrN
- Complete mechanical properties of TiC and ZrN coated samples for varying processing conditions
- Measure tribological performance for MoCuN, TiC, and ZrN coated samples
- Correlate the measured residual stresses in MoCuN, ZrN, TiC coatings to tribological properties and processing
- Initiate discussions with coating manufacturers for collaboration

Conclusions

- X-ray based techniques developed and applied for residual stress measurements
- Stresses correlated to processing conditions (deposition rates, power and time) for MoCuN, TiC, and ZrN coatings
- Adhesion energy for MoCuN coated samples measured
- Nano-indentation technique has been demonstrated for characterization of coating