High-Energy SAXS/WAXS: A Versatile Tool for Materials Analysis

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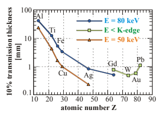
ABSTRACT

One of the primary tools for studying nanoscale inhomogeneities, such as pores and precipitates, is small-angle x-ray scattering (SAXS). Wide-angle scattering (WAXS), on the other hand, can be used to investigate amorphous and/or crystalline phases and their internal strain and texture states. Here we present a combined SAXS/WAXS probe which uses high-energy x-rays (HEX) from the sector 1-ID Advanced Photon Source beamline. Key camera features include and intense HEX brilliance, which enables spatial and temporal resolution, and the high penetrating power of HEX (several mm in most materials at 80 keV), which enables in situ experiments and samples bulk behavior. We illustrate the use of spatial and temporal modes with recent results on thermal barrier coatings and in situ annealing of bulk-metallic glasses, respectively.

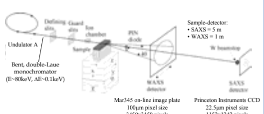
High Energy X-rays

Undulator beamlines at 3rd generation sources: high-brilliance and flux
I_o (1x1mm^2 @ 80keV @ 0.1%bw) ~ 10^{12} ph/sec



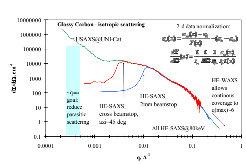
- penetration power ($\mu \propto E^{-3}$)
- small scattering angles
- transmission geometry
- kinematical diffraction

Measurement Geometry



Features
- *Direct* depth resolution to ~5 µm possible (without focussing)
- Perform WAXS,SAXS, and radiography with little or no change in setup
- Implementing Al and/or Si CRLs after HE mono to increase flux density (S. Shastri)

HE-SAXS performance



One-dimensional lineouts to Igor/Matlab for analysis

Spatially resolved measurements of TBCs

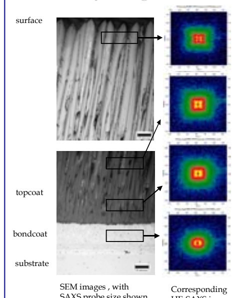
Collaborators:
J. Ilavsky, NIST, Gaithersburg, MA and UNI-CAT, APS, Argonne, IL
A. Kulkarni and H. Herman, SUNY Stonybrook, NY
S. Fang and P. Lawton, Chromalloy Gas Turbine Corp, Orangeburg, NY

Coatings grown by electron beam physical vapor deposition: Stainless steel substrate, 50 µm thick NiCoCrAlY bondcoat, 800 µm thick Y_2O_3 stabilized ZrO_2 topcoat

Goal: Resolve the local crystallography and porosity across the thickness of a thermal barrier coating.

Reference: A. Kulkarni et al, J. Am. Ceram. Soc., in press

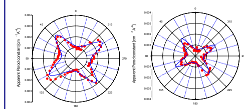
Porosity through thickness



SEM images , with SAXS probe size shown

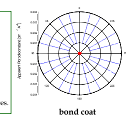
Corresponding HE-SAXS images

SAXS analysis: Porod constant versus orientation and depth



y=0.05 (~center of topcoat) y=0.75 mm (top surface)

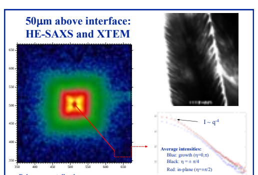
- Lineouts of I(η) vs q were evaluated using an anisotropic Porod scattering method **
- The maximum surface area is observed at 45-50 degrees
- Scattering magnitude varies strongly versus depth
- Directional dependence is attributed primarily to intra-columnar striations and nanopores.



bond coat

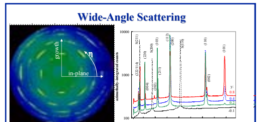
Reference: J. Ilavsky et al., Mat. Sci. Eng, A, A272, 215-221 (1999).

50µm above interface: HE-SAXS and XTEM



Primary contribution:
Porod scattering from intra-columnar pores

Wide-Angle Scattering

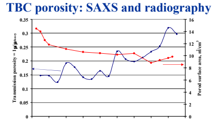


2-d image from center of coating (y=0.4)

Azimuthal integrations vs. depth (Δη=360deg: powder scans)

- Topcoat is identified as tetragonal $(Zr_{0.93}Y_{0.07})O_2$
- Topcoat is highly textured as [001&110] || growth direction (~constant with depth)
- Coating– substrate transition is clearly identified
- Technique can measure internal strain versus orientation (not shown here)

TBC porosity: SAXS and radiography



Interpretation: microstructural evolution during growth
Nucleation of many nano-scale (SAXS-sensitive) columns, which grow larger (Saxs-insensitive) with increasing thickness. Larger inter-columnar pores (higher total porosity) with thickness detected by radiography.
Combining the techniques allows hierarchy of pores to be distinguished.

Summary

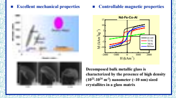
- The high-energy SAXS/WAXS instrument was used to track microstructural gradients with ~20 µm resolution.
- 2-d SAXS: orientation dependence of porosity distinguished.
- Radiography and SAXS: reveals a heirarchy of pores, with gradients across the topcoat thickness.
- Results can be used to tailor microstructure
- Future plans
  - WAXS resolution down to 1 µm through focusing
  - SAXS/WAXS resolution down to 5 µm through optimized slits
  - In-situ annealing to test microstructural stability

In-situ investigation of phase separation in bulk-metallic glasses

Collaborators:
X.L. Wang, Y.D. Wang, J.K. Zhao, A.D. Stoica and C.T. Liu, Oak Ridge National Lab
W. H. Wang, Chinese Academy of Science

Bulk Metallic Glass Containing Nanoprecipitates Exhibit Unconventional Properties

- Excellent mechanical properties
- Controllable magnetic properties



Decomposed bulk metallic glass is characterized by the presence of high density (10^{23}-10^{24} m^{-3}) nanometer (~10 nm) sized crystallites in a glass matrix

Several Mechanisms Have Been Proposed for the Nucleation of the Crystalline Phase

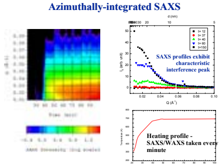
- Classical nucleation and growth

$$I_s = A \cdot D_{eff}(T) \cdot \exp\left(-\frac{\Delta G^*}{k_B T}\right)$$

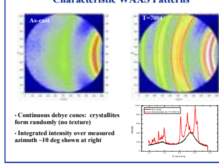
  - low density at T~ T_g
- Heterogenous nucleation on impurity sites
  - e.g., Zr_4Ni_2O in oxidized $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (Liu et al.)
  - density is dictated by the number of impurity sites
- Phase separation
  - spinodal decomposition?
  - kinetics holds the key to differentiate various mechanisms

Goal: conduct in-situ SAXS/WAXS annealing experiments to investigate BMG transformation mechanisms

Azimuthally-integrated SAXS

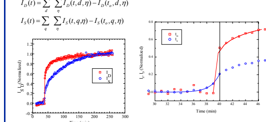


Characteristic WAXS Patterns



- Continuous debye cones: crystallites form randomly (no texture)
- Integrated intensity over measured azimuth ~10 deg shown at right

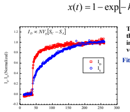
Combined SAXS and WAXS reveals kinetics



- Phase separation occurred first, setting stage for crystallization
- Rapid rise of small angle scattering intensity for t < 40 min
- Slow growth of diffraction intensity for t > 40 min.

Increase of Diffraction Intensity Is Well Described by JMA Transformation Theory

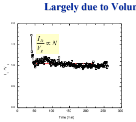
$$x(t) = 1 - \exp\left[-k(t - t_0)^n\right]$$



The excellent fit obtained with JMA theory indicates that the diffraction intensity is proportional to the volume fraction transformed.

Fitting parameters
- *n (kinetic exponent)* = 0.33±0.03, indicating overlapping of diffusion zones
- *k (growth constant)* = 0.26±0.03, giving τ = 1.6 min

Late Stage (t > 40 min) Intensity Increase Is Largely due to Volume Growth



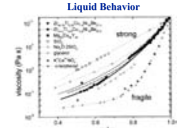
Corroborating evidence from SAXS:

I_S also grows but at a slower rate than I_D.

This is because $I_D \propto V_g$ whereas $I_S \propto V_g^2$

I_D/V_g is almost constant
- fixed number of particles
- on-site or instantaneous rather than continuous nucleation

Slow Volume Growth Is Attributed to Strong Liquid Behavior



References: 1. R. Busch, JOM (2000); 2. C. Agnell, Science (1995)

Summary

- Simultaneous SAXS/WAXS experiments on BMGs show two different kinds of kinetics operating in separate stages
  - Nucleation of the crystalline phase via phase separation
    - § fixed number of nuclei
  - Slow growth of the crystalline phase
- Experimental data suggest a new mechanism for nucleation - via the formation of clusters by short-range diffusion of the mobile atoms (e.g., Ni)
- Future experiments with better time resolution (~sec) will help to further clarify the proposed mechanism. In addition, diffraction peak widths will be quantified and compared with SAXS results.

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