3D-Quantitative Phase Analysis & Strain Mapping of Nanostructured Coatings by Synchrotron Energy Dispersive X-ray Diffraction:

A New Approach to Materials Characterization

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The Nano-Structured Materials Quartet @Rutgers

Act I:
3D Quantitative Phase Analysis and Strain Mapping of Nano-structured Coatings by Synchrotron EDXRD (*E. Koray Akdoğan)*….This presentation

Act II:
An Eigenstrain Analysis of Mechanical Properties in Nano-structured Ceramic Coatings By Synchrotron Probe (*Thomas Tsakalakos*)….Today 10:55

Act III:
Microscopic Strain Mapping in Nano-structured and Micro-structured Alumina Titania Under 4-Point Compressive and Tensile Bending
(*Alex Ignatov*)….Wednesday 10:55

Interlude: *(The Nano-Structured Materials Choir)*
Luigi Balarinni, Nazia Ahmedi, Michael McNeley, Julie Gimenez
(*4 Poster Presentations*)…..Thursday 16:00

Act IV:
Chemical Phase And Valence Studies of Plasma Sprayed Coating: X-ray Absorption Spectroscopy Results (*Mark Croft*)….Friday 8:15

Outline

- **Introduction**
  - Thermal Spray Coating: Fundamental Considerations
  - Rutgers-NSMG EDXRD Set-up at NSLS X17-B1
  - Comparison of Diffraction Geometries
  - Evolution of Nanostructured Materials Analysis by EDXRD

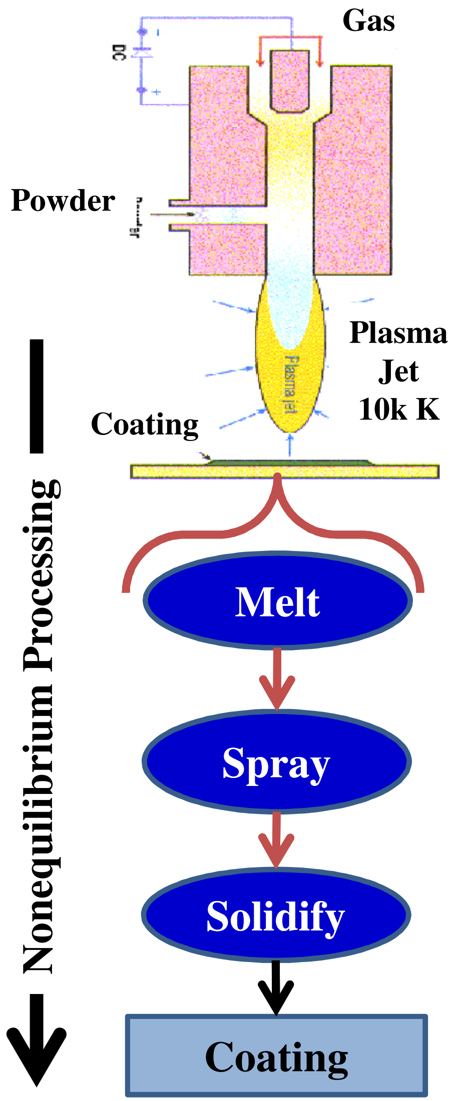
- **Simultaneous 3D Strain and Phase Mapping In TiO_2 Thermal Spray Coatings**
  - 3D Phase Mapping of TiO_2 Coating
  - EDXRD Quantitative Phase Analysis Results:
  - Lattice Parameters & Cell Volume of Rutile & Anatase in Precursor Powder & TSC
  - Comparison with X-ray Absorption Data
  - Variation of strain in the coating with depth

- **3D Phase Mapping In Thermal Spray Coatings "Interfacial Phenomena"**

- **Simultaneous 3D Strain and Phase Mapping In (Semi)-Amorphous Fe Thermal Spray Coatings By Combined Bragg-Brentano & EDXRD (Time permitting)**

- **Concluding Remarks**

Thermal Spraying of Coatings: A Brief Overview



Main Characteristics

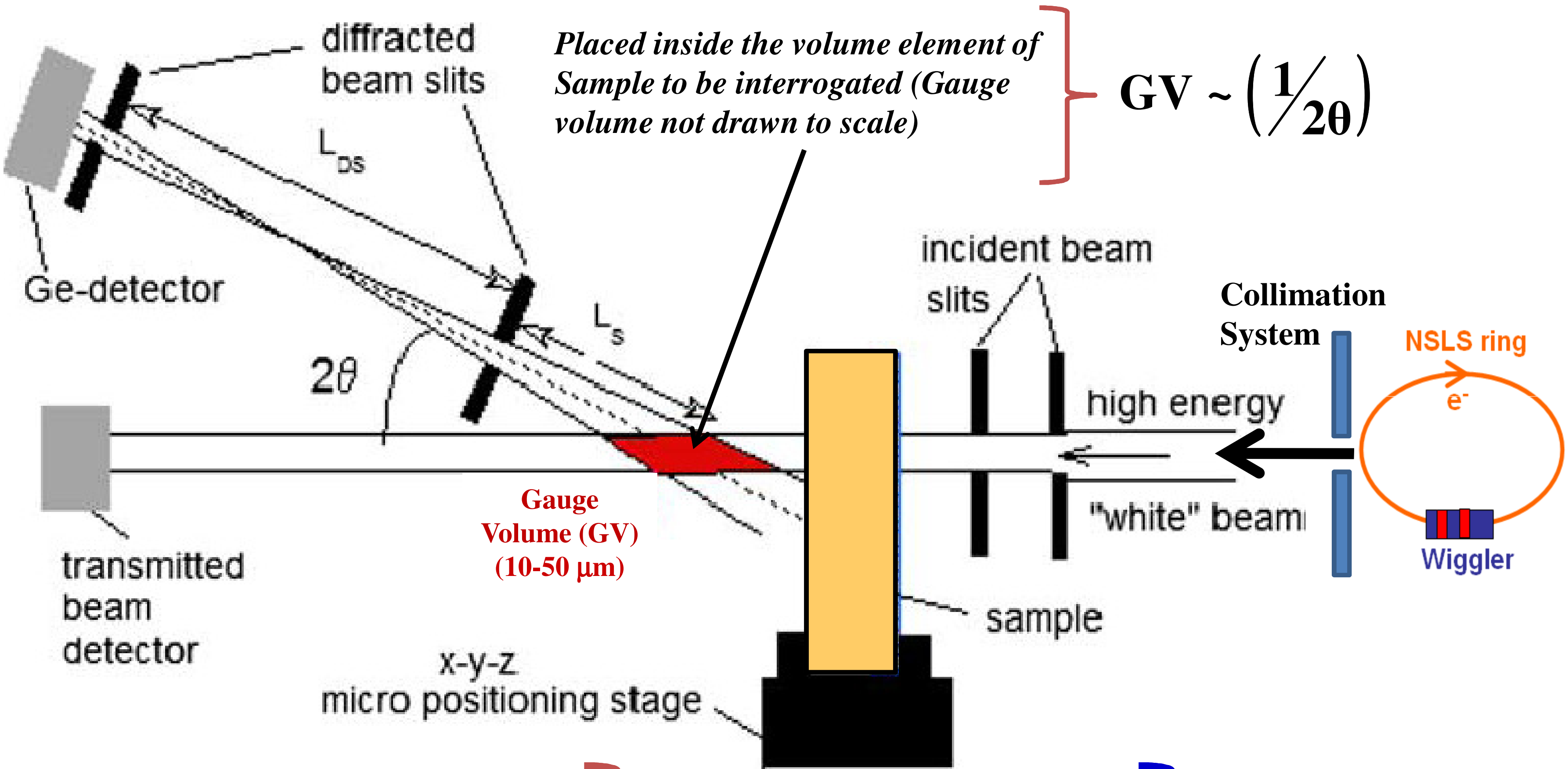
- Essentially an nonequilibrium processing method as it involves superheating enabling supersolubility whenever applicable.
- Able to form thermodynamically metastable but kinetically stabilized materials (single or multiphase)

Characteristic Phenomena in Deposited Layers

- Compositional fluctuations: partial melting, differential solidification, rapid solidification (coring)
- Residual stresses (Thermal expansion, rapid solid'n)
- Phase decomposition, oxidation, polymorphic transitions, strain-driven (stress-induced) transitions
- Porosity & Microcracking

Rutgers-NSMG EDXRD Set-up at NSLS X17-B1

(M. Croft, V. Shukla, E. K. Akdoğan, N. Jisrawi, Z. Zhong, R. Sadangi, A. Ignatov, L. Balarinni, K. Horvath, T. Tsakalakos)
J. Appl. Phys. 105, 093505 (2009)



- ✓Beamline X17-B1 at NSLS in BNL.
- ✓White radiation up to 200 keV
- ✓Fixed 2θ (4-12°; typically 4°)

High energy diffraction with a fixed gauge volume in space (determined by fixing 2θ)

EDXRD à la Rutgers-NSMG

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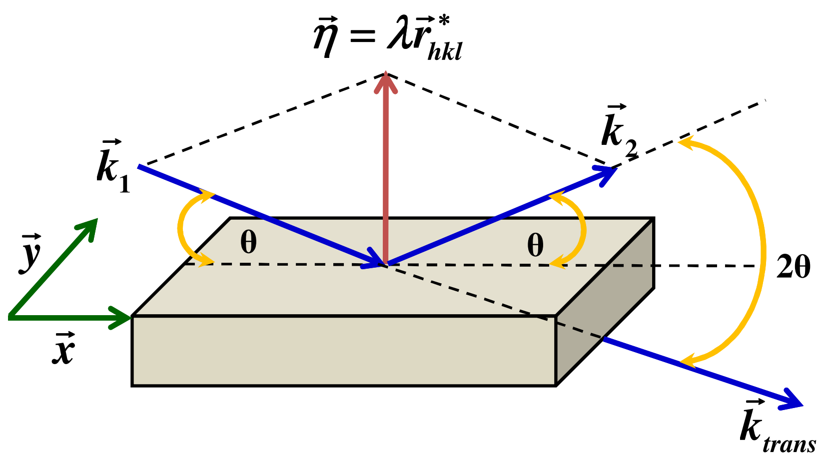
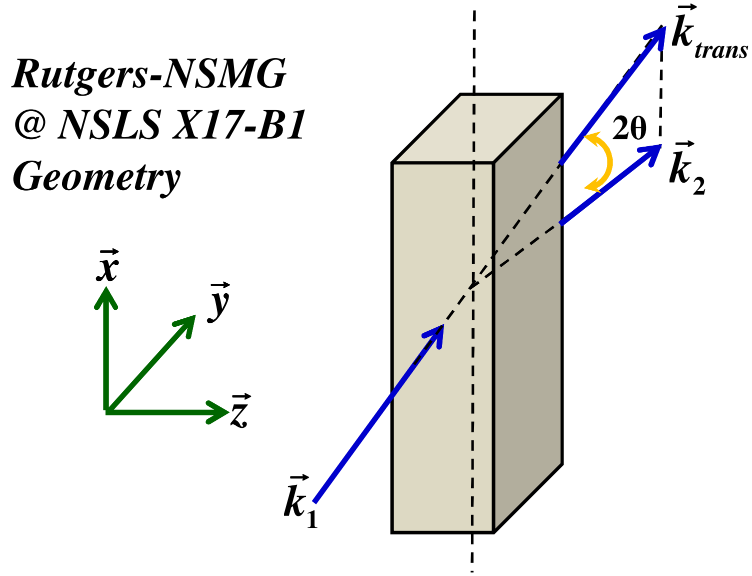
Comparison of Diffraction Geometries





$$\left(\left|\vec{k}_2-\vec{k}_1\right|\right)=\lambda\left|\vec{r}^*_{hkl}\right| \ \& \ \left|\vec{r}^*_{hkl}\right| = 1 / \left|\vec{d}^*_{hkl}\right|$$

$$\left|\vec{r}^*_{hkl}\right| = 2 \ \boxed{\sin\theta} \rightarrow$$ What's measured!

$$\left(\left|\vec{k}_2-\vec{k}_1\right|\right)=\lambda\left|\vec{r}^*_{hkl}\right| \ \& \ \left|\vec{r}^*_{hkl}\right|=\left|\vec{d}^*_{hkl}\right|^{-1} \ \& \ E=(hc)\lambda^{-1}$$

$$\left|\vec{r}^*_{hkl}\right|=\left[(hc)^{-1}\sin\theta\right]\boxed{E_{hkl}} \rightarrow$$ What's measured!

- ✓Surface & sub-surface limited
- ✓Degrees of freedom limited to 2D
- ✓Higher line resolution (diffraction)
- ✓Essentially a reflection method

- ✓Bulk Analysis capability limited by attenuation
- ✓Degrees of freedom is 3(D)
- ✓Lower line resolution (diffraction)
- ✓Essentially a transmission method

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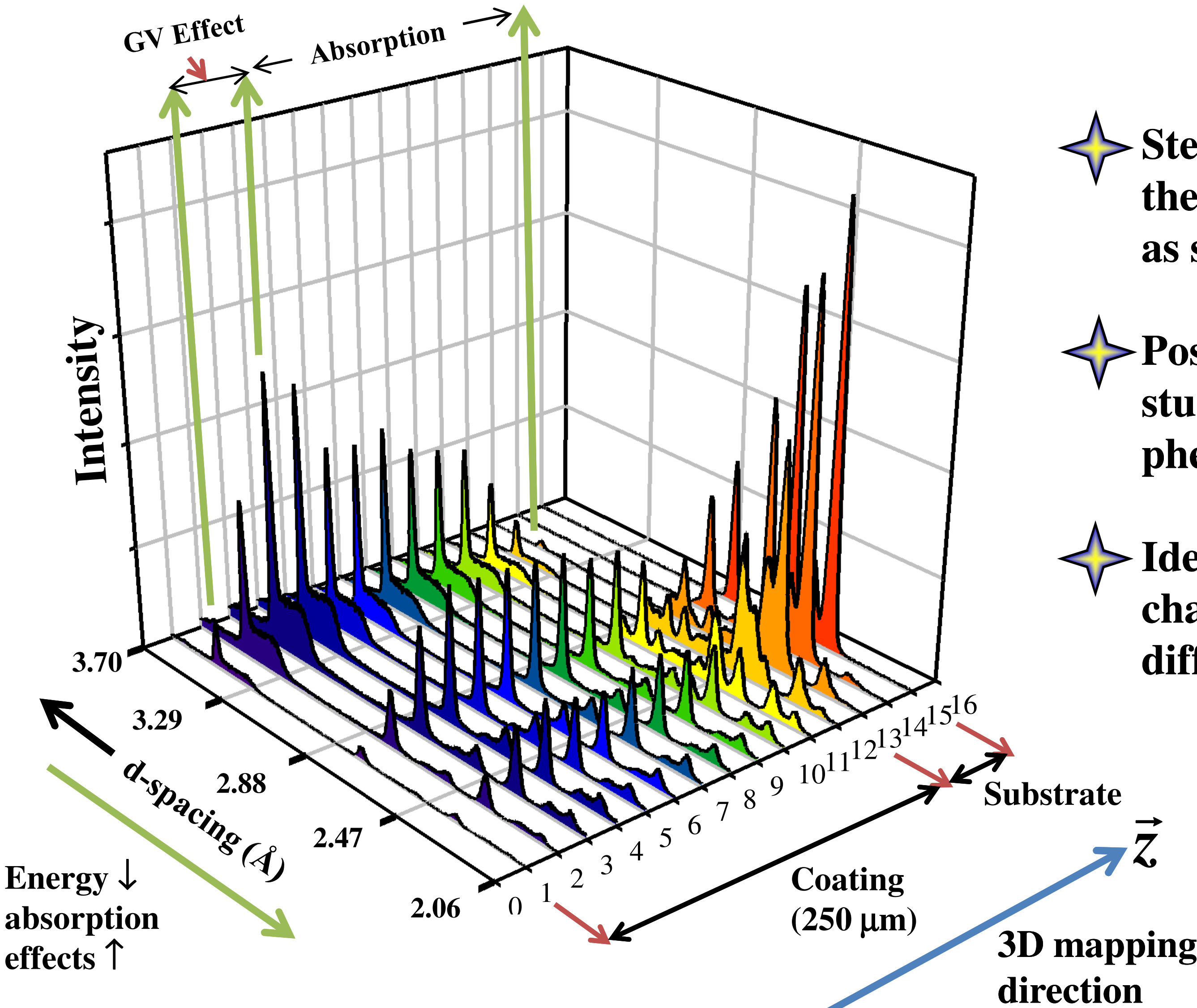
3D Phase Mapping (TiO_2 Coating)



- Step size in the $\vec{z}$ can be as small as ~1 µm.
- Possibility for studying interfacial phenomena.
- Ideally suited for characterizing diffuse interfaces.

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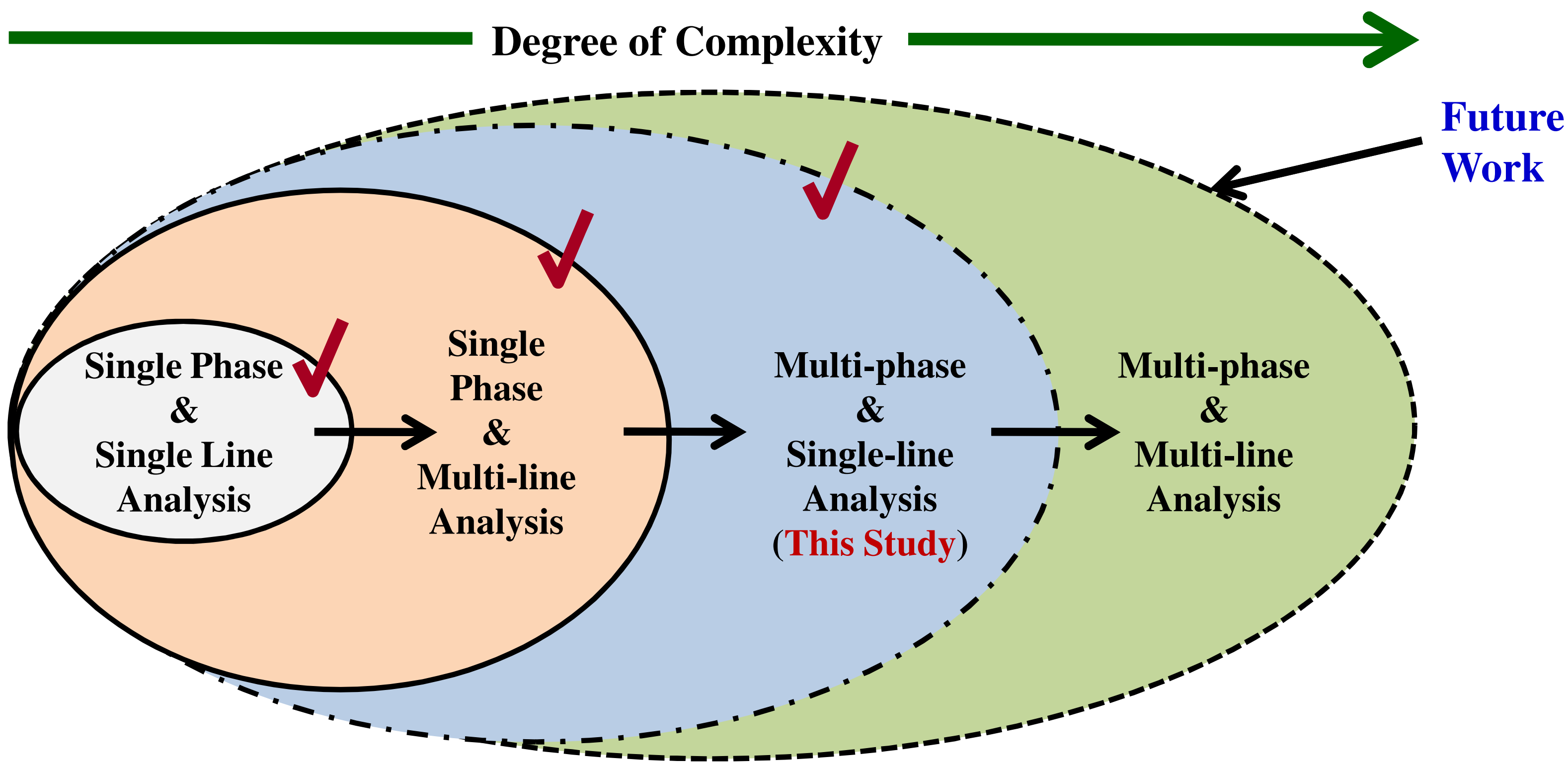
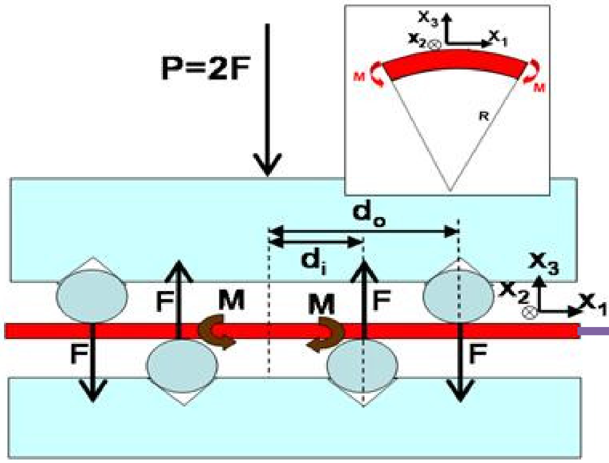
Evolution of Nanostructured Materials Analysis by EDXRD:

The Rutgers-NSMG Approach

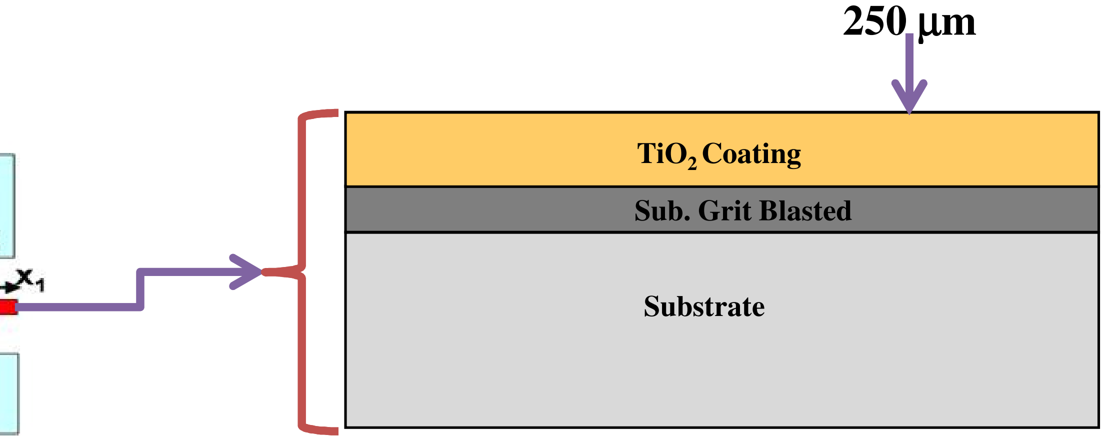


- Most engineering materials are multiphase with disparate mechanical properties, making (at least) multi-phase single-line analysis a necessity.
- EXRD is the only experimental method giving access to concomitant measurement of phase composition and strain in (nanostructured) coatings due to its 3D-mapping ability.

Simultaneous 3D Strain and Phase Mapping In TiO_2 Thermal Spray Coatings



4-Point Bending



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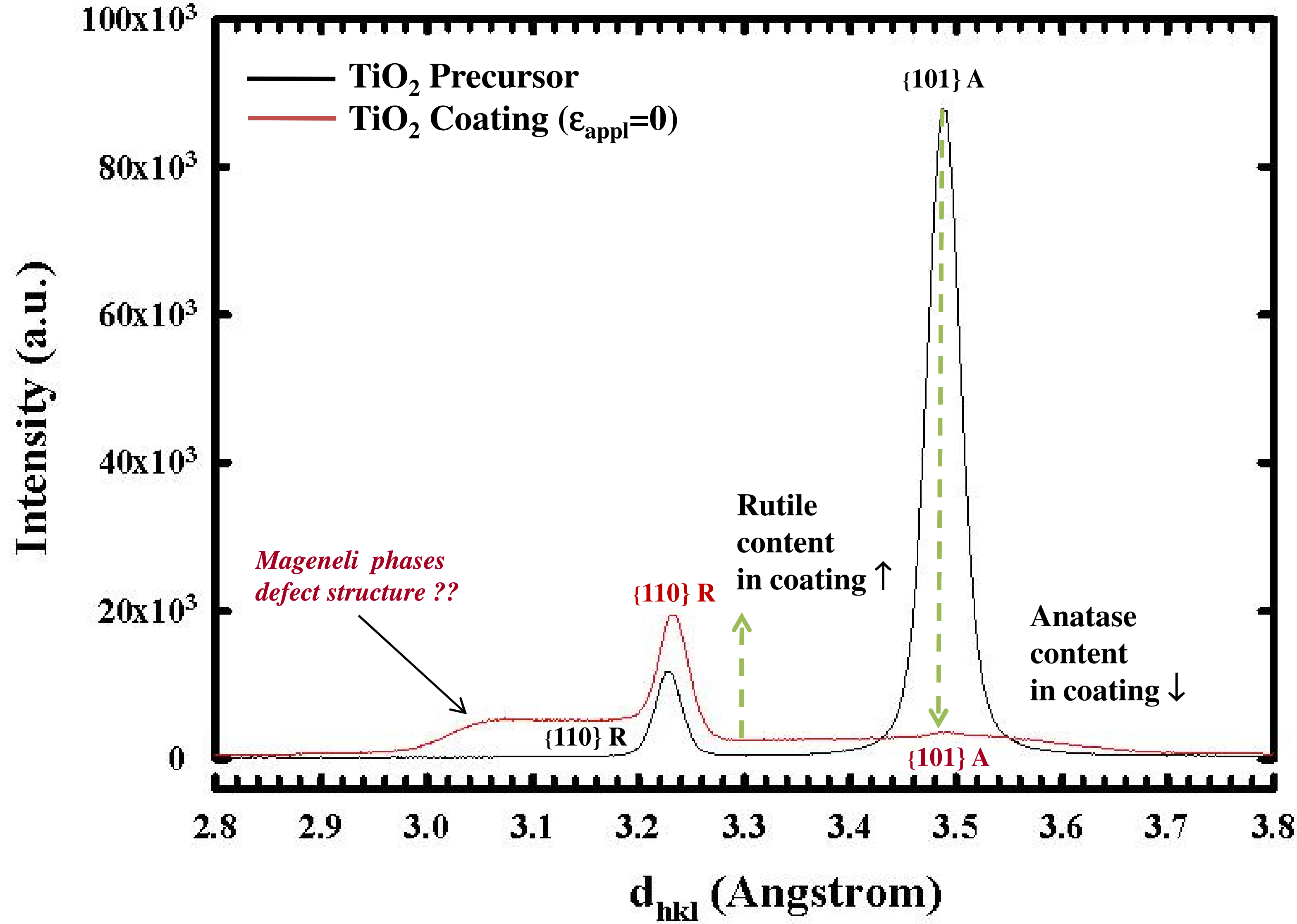
Comparison of Diffraction Spectra for Powder & Coating: 2.8-3.8 Å



EDXRD Quantitative Phase Analysis Results: TiO_2 Precursor vs. TSC ($\varepsilon_{appl} = 0$)

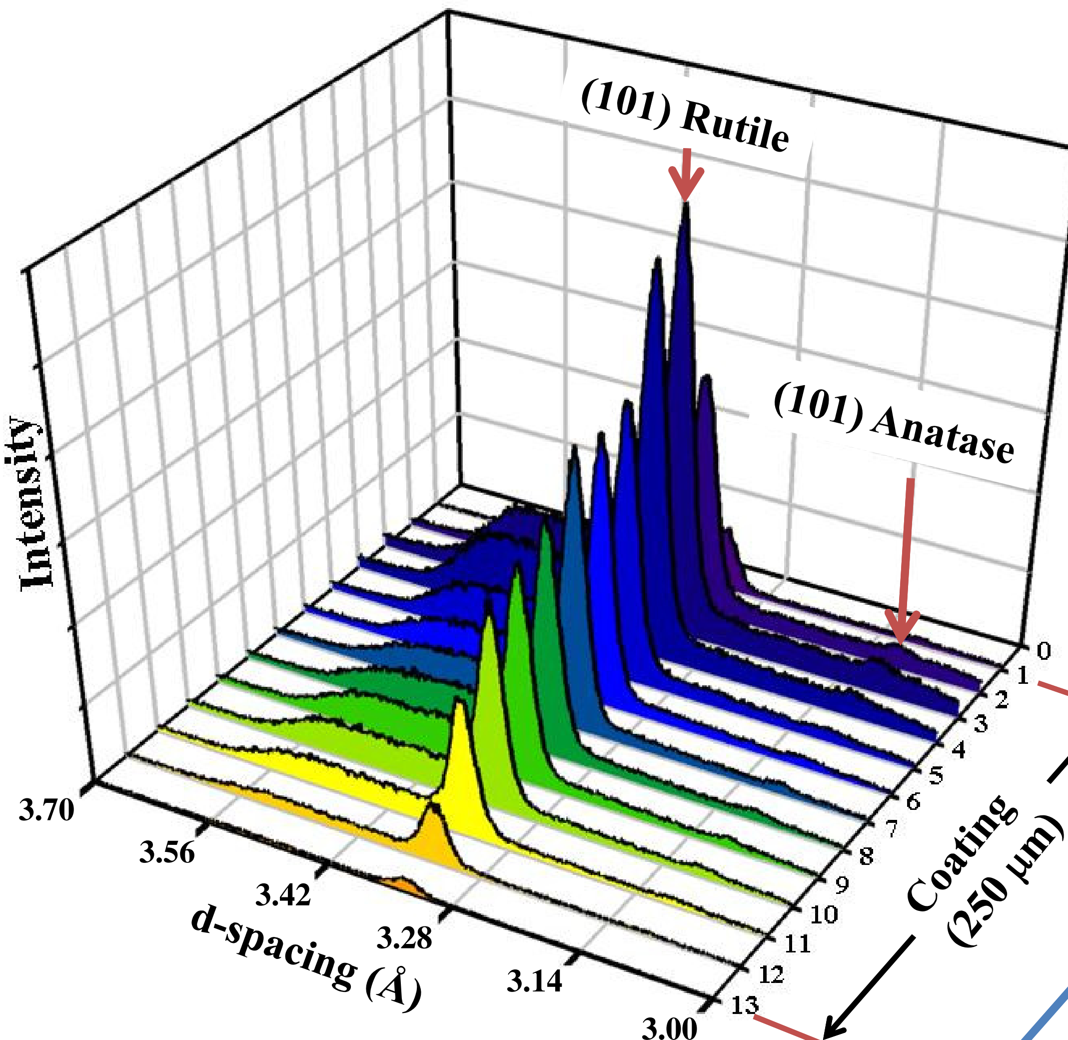
$$\%\,\text{Rutile} = \left[\frac{I_{(110)}^{\text{Rutile}} \left(RIR_{Rutile} \right)^{-1}}{\left(I_{(110)}^{\text{Rutile}} \left(RIR_{Rutile} \right)^{-1} + I_{(101)}^{\text{Anatase}} \left(RIR_{Anatase} \right)^{-1} \right)} \right] \times 100;$$

RIR: Reference Intensity Ratio

Material	Phase	hkl	d-spacing (Å)	Intensity (a.u.)	Phase composition (%)
TiO_2 powder	Rutile	(110)	3.2276	11854	*11.9*
	Anatase	(101)	3.4884	87711	*88.1*
TiO_2 Coating	Rutile	(110)	2.2326	19500	*84.3*
	Anatase	(101)	3.4906	3642	*15.7*

- **Coating mostly Rutile. A polymorphic Anatase→Rutile transition takes place in the coating. The transition is not complete; i.e. di-phasic coating.**

(101) Anatase & (110) Rutile Peaks vs. TiO_2 Coating Thickness



- 3D Phase mapping only possible with EDXRD.
- Variation across coating thickness shows no appreciable change in phase composition.
- The only thickness dependent variation is strain in TiO_2 TSCs.

$\vec{z}$ 3D mapping direction

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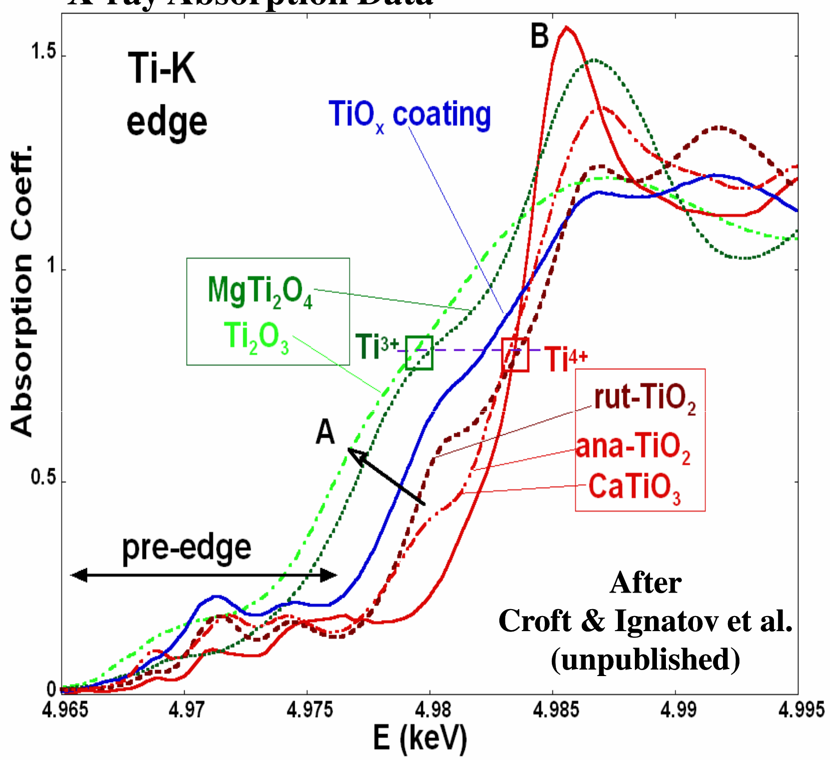
Lattice Parameters & Cell Volume of Rutile & Anatase in Precursor Powder & TSC

	TiO$_2$ Phase	a (Å)	c (Å)	Cell Volume (Å^3)
Powder	Rutile	4.5645 (4.5937)	2.9660 (2.9587)	61.8 (62.4)
	Anatase	3.7499 (3.7842)	9.5086 (9.5146)	133.7 (136.3)
Coating	Rutile	4.5716 (4.5937)	2.9657 (2.9587)	62.0 (62.4)
	Anatase	3.7524 (3.7842)	9.5121 (9.5146)	133.9 (136.3)

Numbers in parantheses are tabulated data from the respective PDF, which were included herein for comparison.

X-ray Absorption Data



After Croft & Ignatov et al. (unpublished)

The powder and the coating are deficient in oxygen in both phases!

$$(Ti^{4+}_{1-x}, Ti^{3+}_{x})O_{2-x/2}$$

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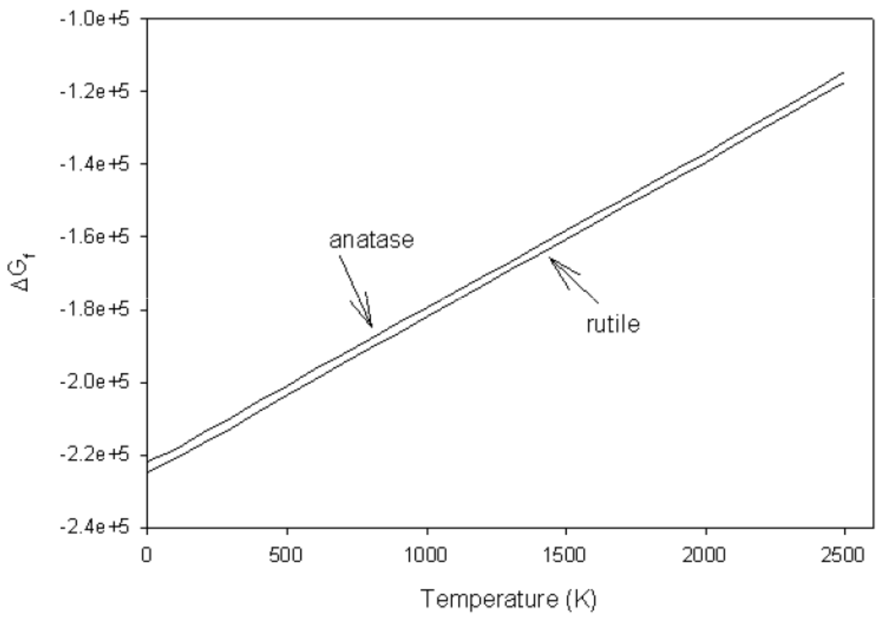
Gibbs Free Energy of Formation for Anatase and Rutile

(Courtesy of Kimberly A. Farrell; M. Sc. Thesis, Worcester Polytech. Inst. (2001))



Stall, D.R., "JANAF Thermochemical Tables," Joint Army-Navy-Air Force-ARPA; -NASA Thermochemical Working Group. (1996)

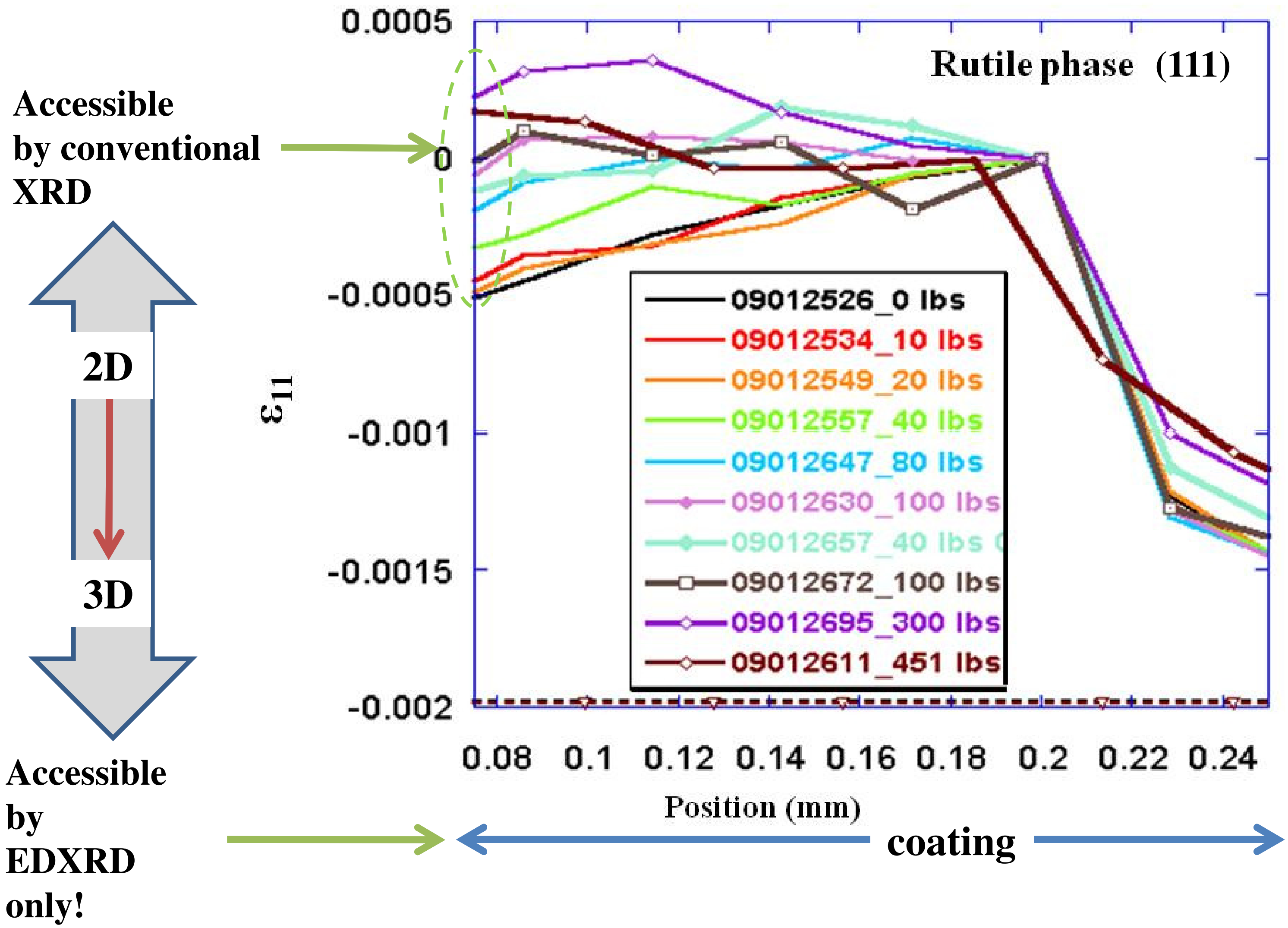
$$\left|\Delta G_f^{Rutile}\right| < \left|\Delta G_f^{Anatase}\right|$$

for 298K <T< 2500 K

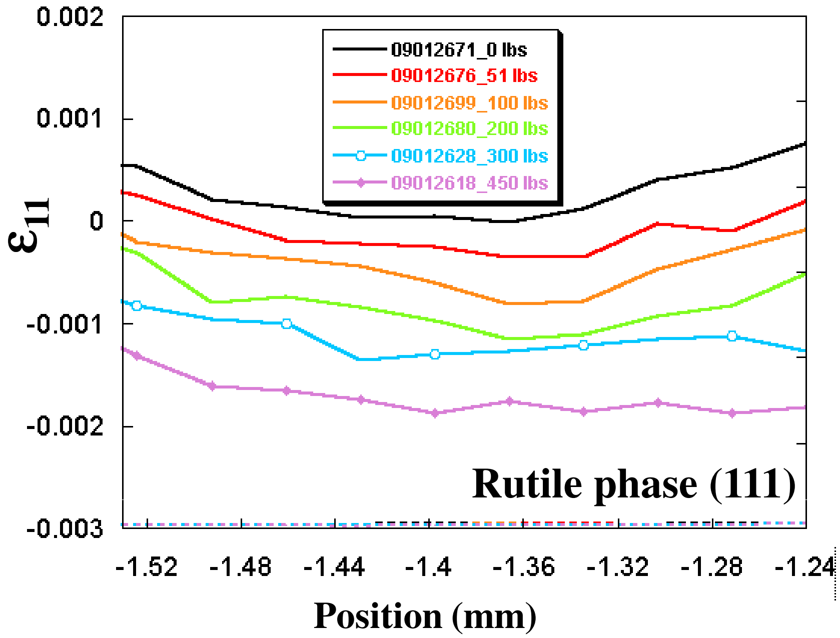
- **Even if the precursor powder is partially melted, the unmolten during Thermal spraying Anatase should transform to Rutile at RT (polymorphic transition)**

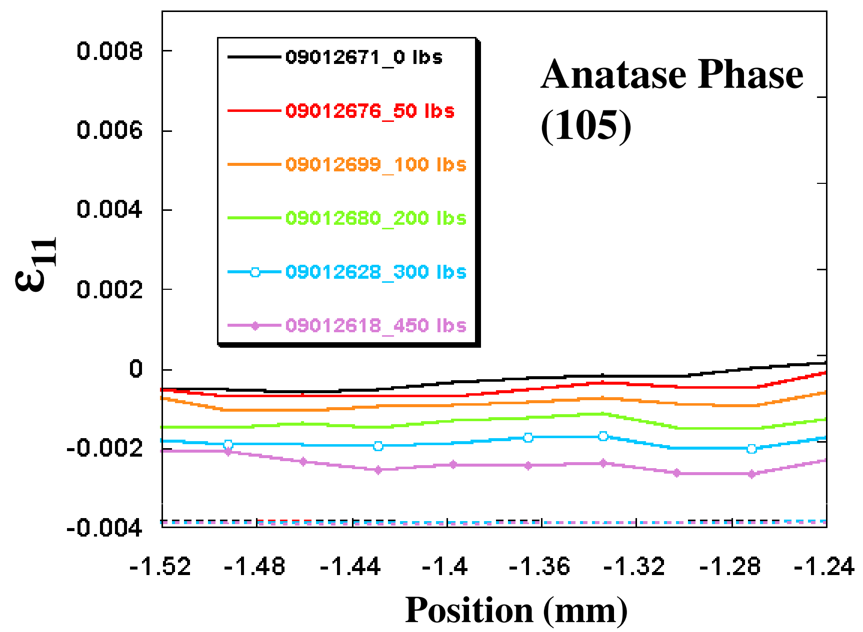
- **Residual Anatase in coating attributed to defect stabilization (oxygen vacancies) as residual strains are low.**

Multiphase Analysis of Strain in Di-phasic TiO_2 Coatings in Tension



TiO_2 Coating Under Compression





- Systemic variation of strain in each phase is observed. The magnitude of strain in the Rutile phase (matrix) varies over a broader range, while the same of Anatase is narrower.
- Difference in mechanical response in each phase is attributed to differences in Elastic moduli:

$$\sigma_{rutile} = \sigma_{anatase} \Rightarrow \tilde{E}_{rutile}\varepsilon_{rutile} = \tilde{E}_{anatase}\varepsilon_{anatase}$$

$$\therefore \quad \frac{\tilde{E}_{rutile}}{\tilde{E}_{anatase}} = \frac{\varepsilon_{anatase}}{\varepsilon_{rutile}}$$

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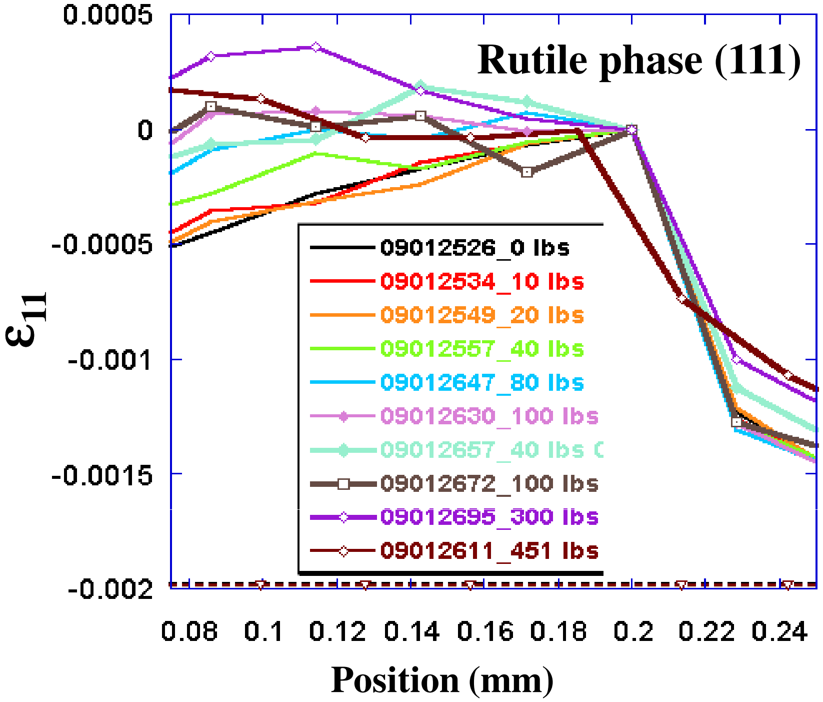
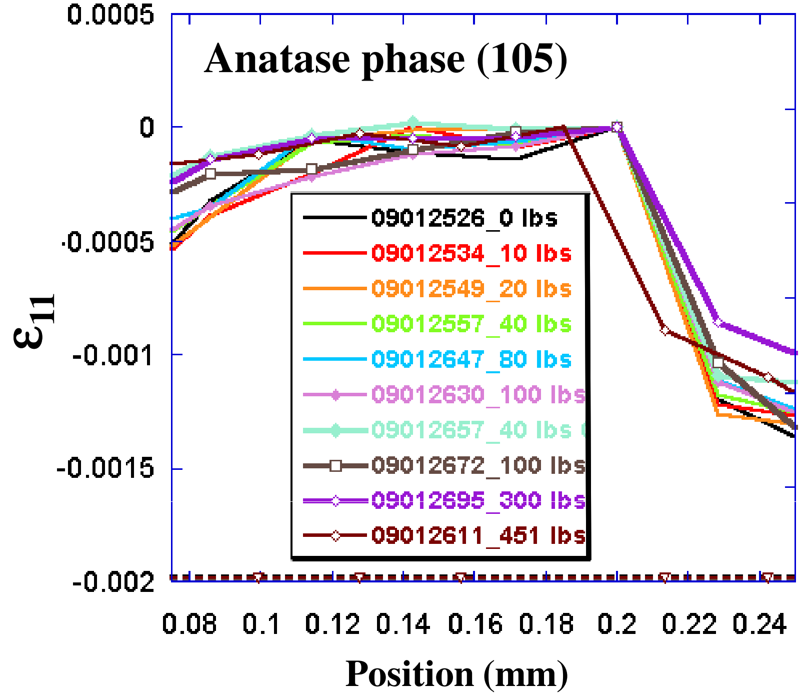
TiO_2 Coating Under Tension





- Systemic variation of strain in each phase is observed. The magnitude of strain in the Rutile phase (matrix) varies over a broader range, while the same of Anatase is narrower. Difference in mechanical response in each phase is attributed to differences in Elastic moduli as in the case of compression.

- Strains in tension are smaller than in compression (at low loads as well) which indicates ***micro-cracking*** upon thermal spraying.

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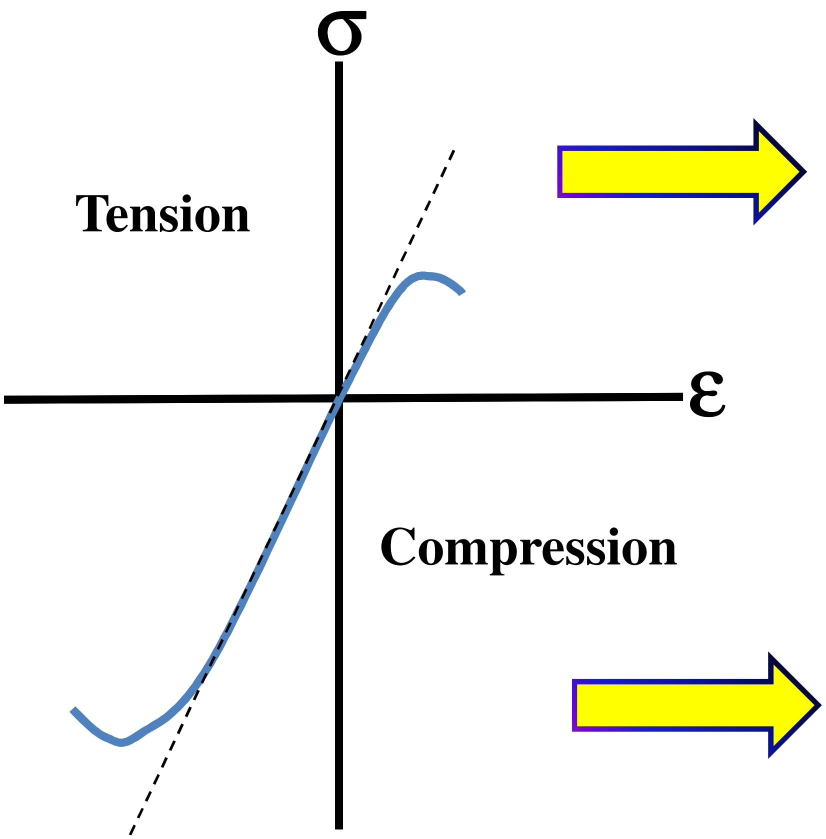
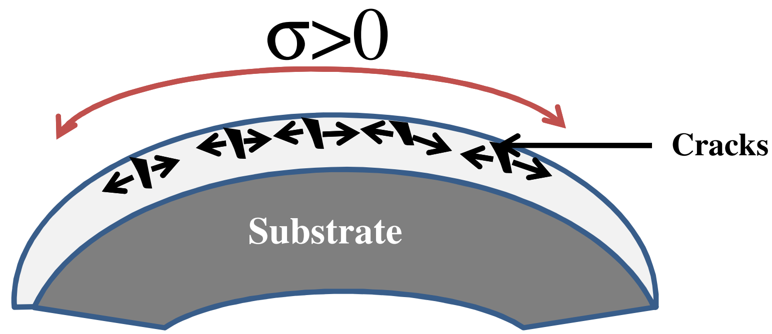
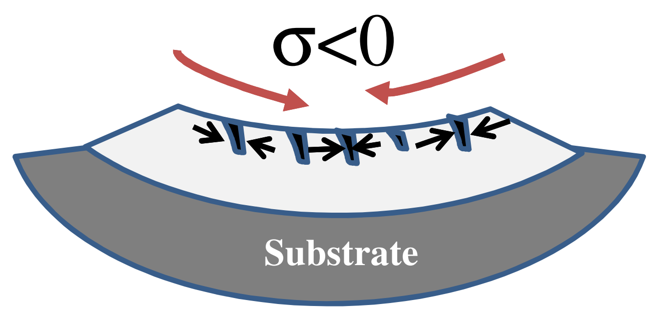
Origin of Strain response in Tension & Compression





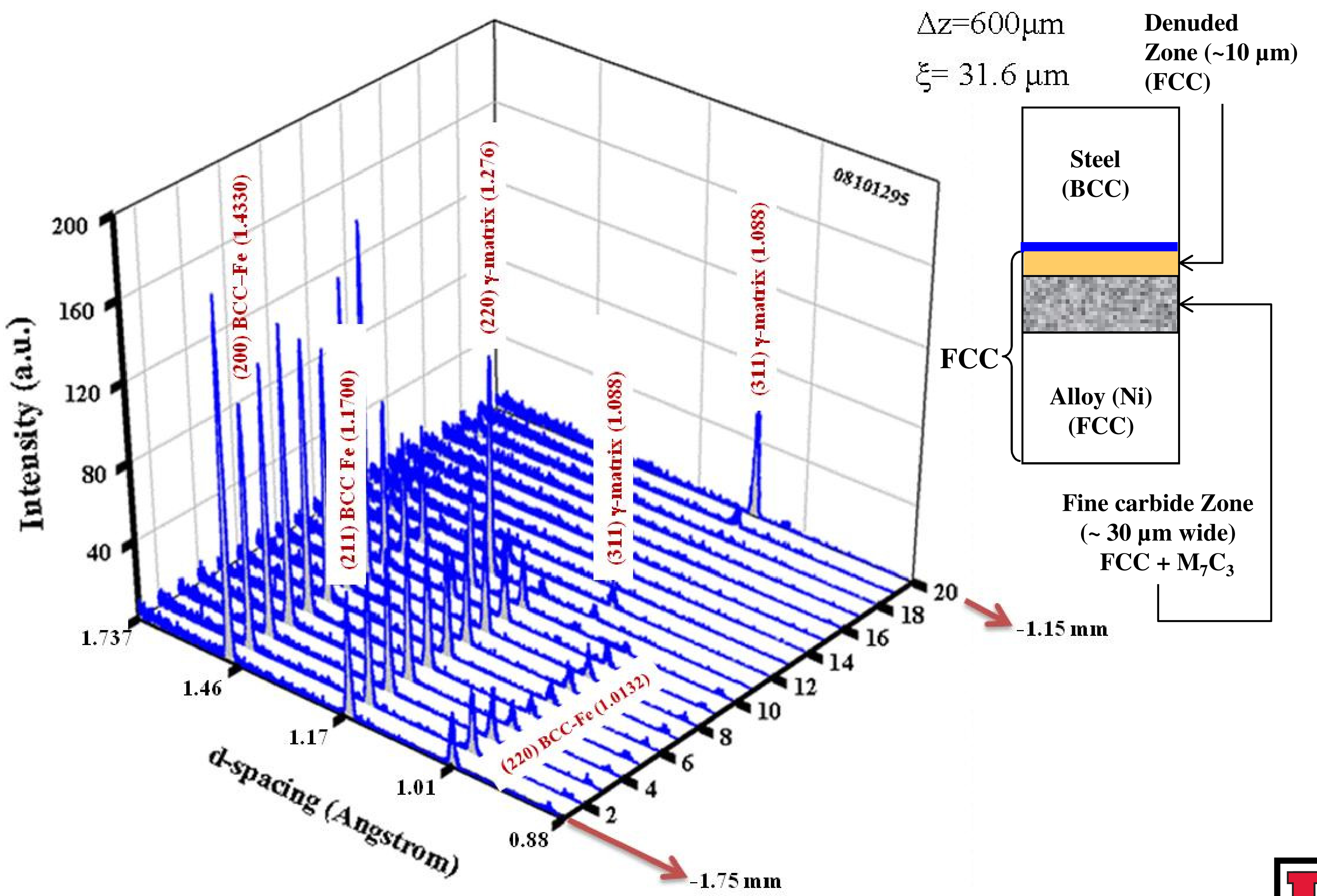
Tension promotes crack growth in a micro-cracked coating. Hence, less load-baring capability, less strain.



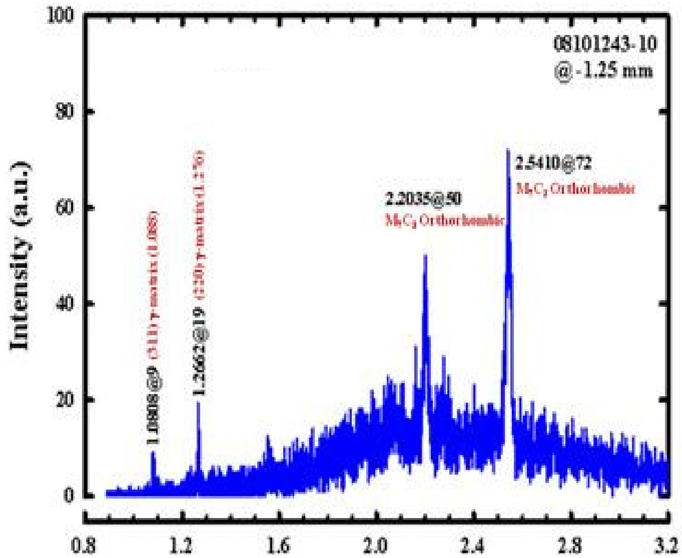
Compression promotes crack closure in a micro-cracked coating. Hence, more load-baring capability, more strain.

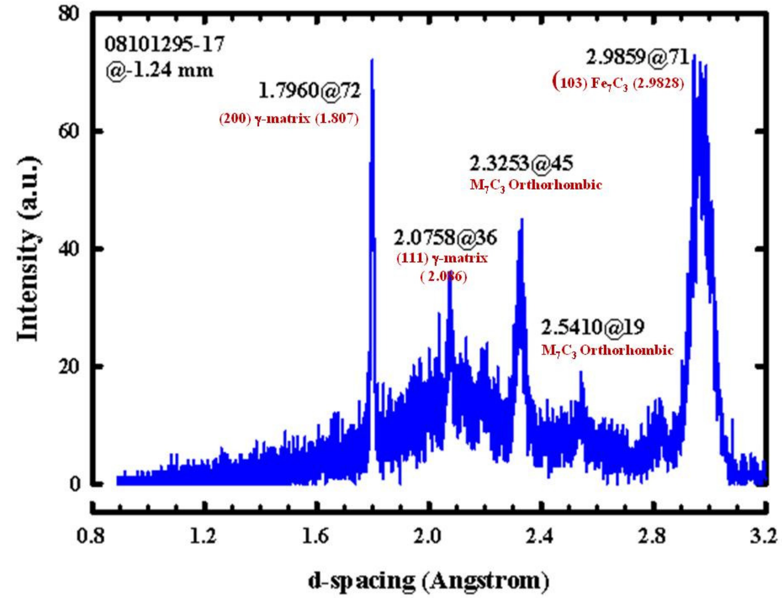
3D Phase Mapping
In
Thermal Spray Coatings
“Interfacial Phenomena”

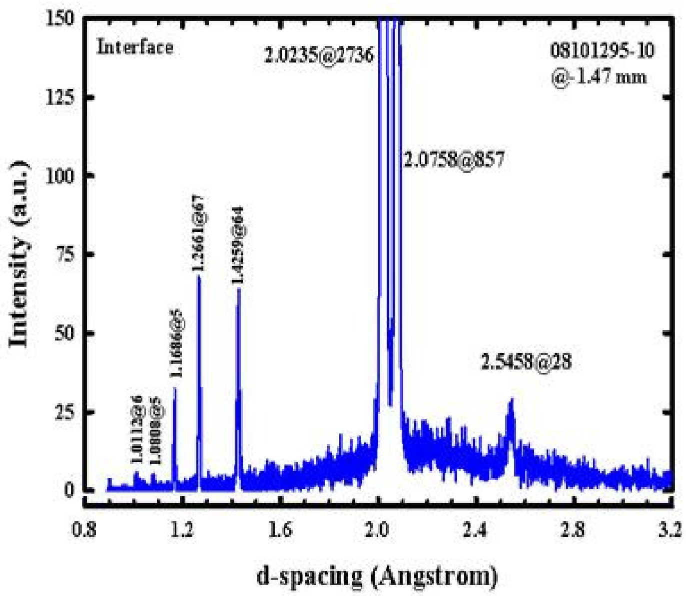
Steel-Ni Alloy Interfacial Phenomena

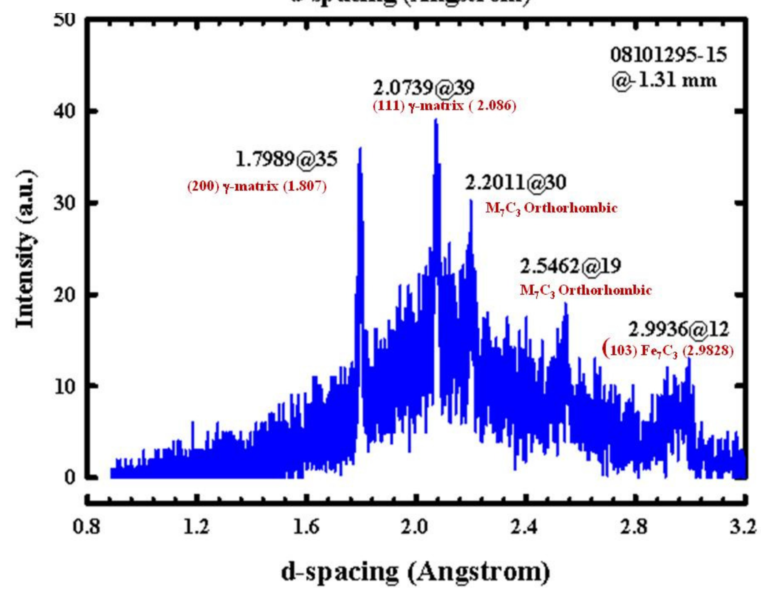


Steel/Ni Alloy Interfacial Phenomena









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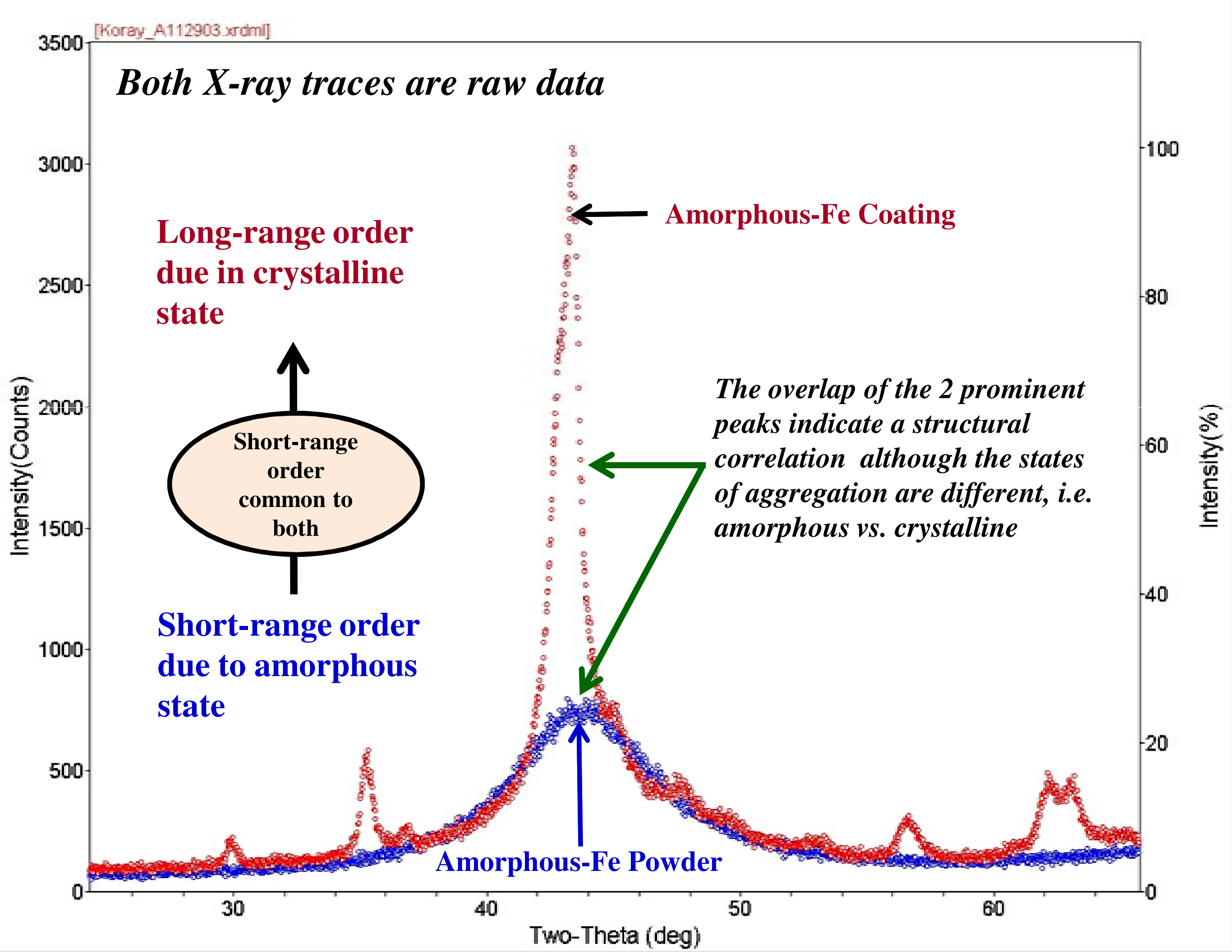
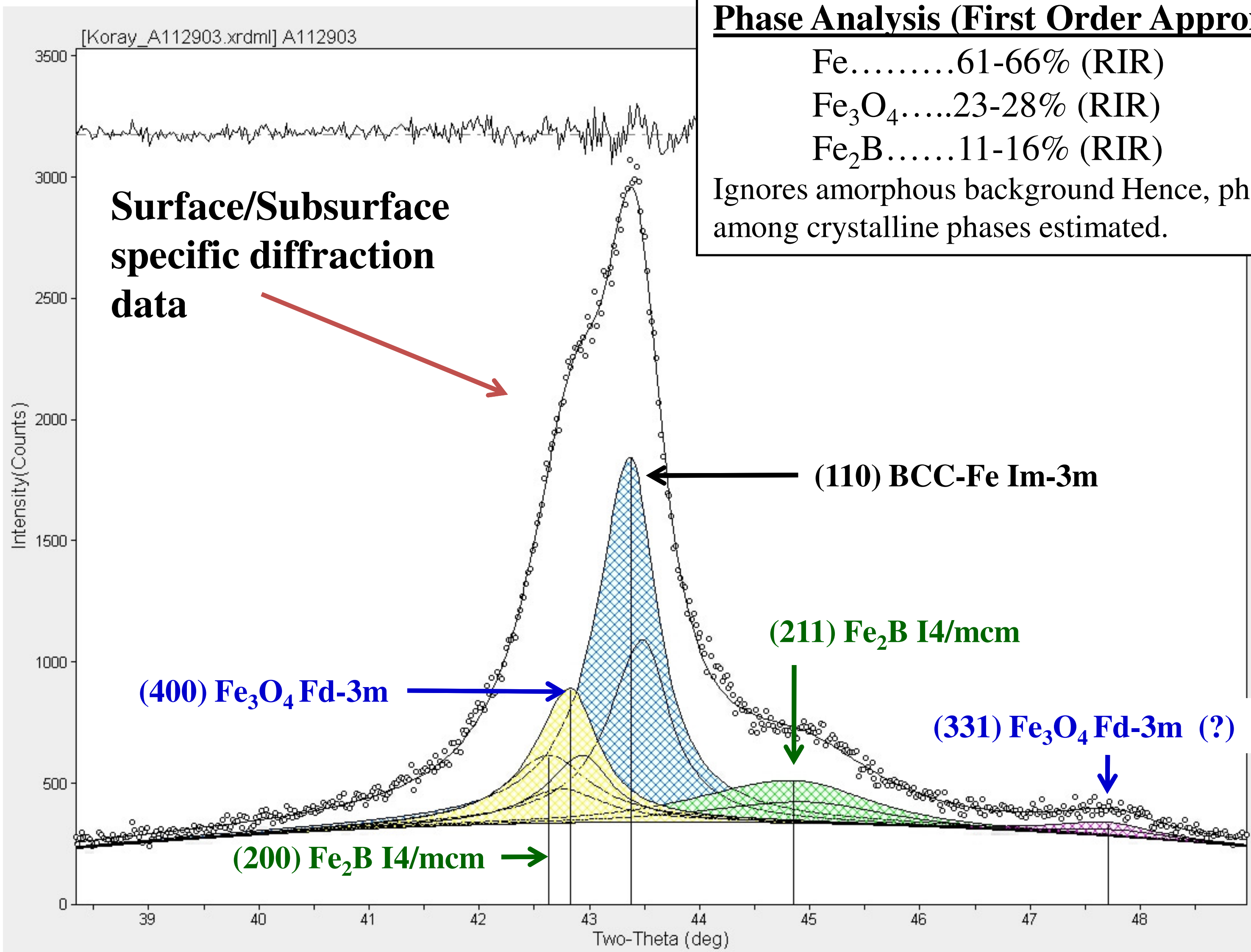
Simultaneous 3D Strain and Phase Mapping
In
(Semi)-Amorphous Fe
Thermal Spray Coatings
By
Combined Bragg-Brentano & EDXRD

Comparison of Bragg-Brentano Diffraction Patterns of Amorphous Fe Powder & Thermal Spray



Qualitative & Semi-Quantitative Phase Analysis



<u>Phase Analysis (First Order Approx'n)</u>

Fe………61-66% (RIR)

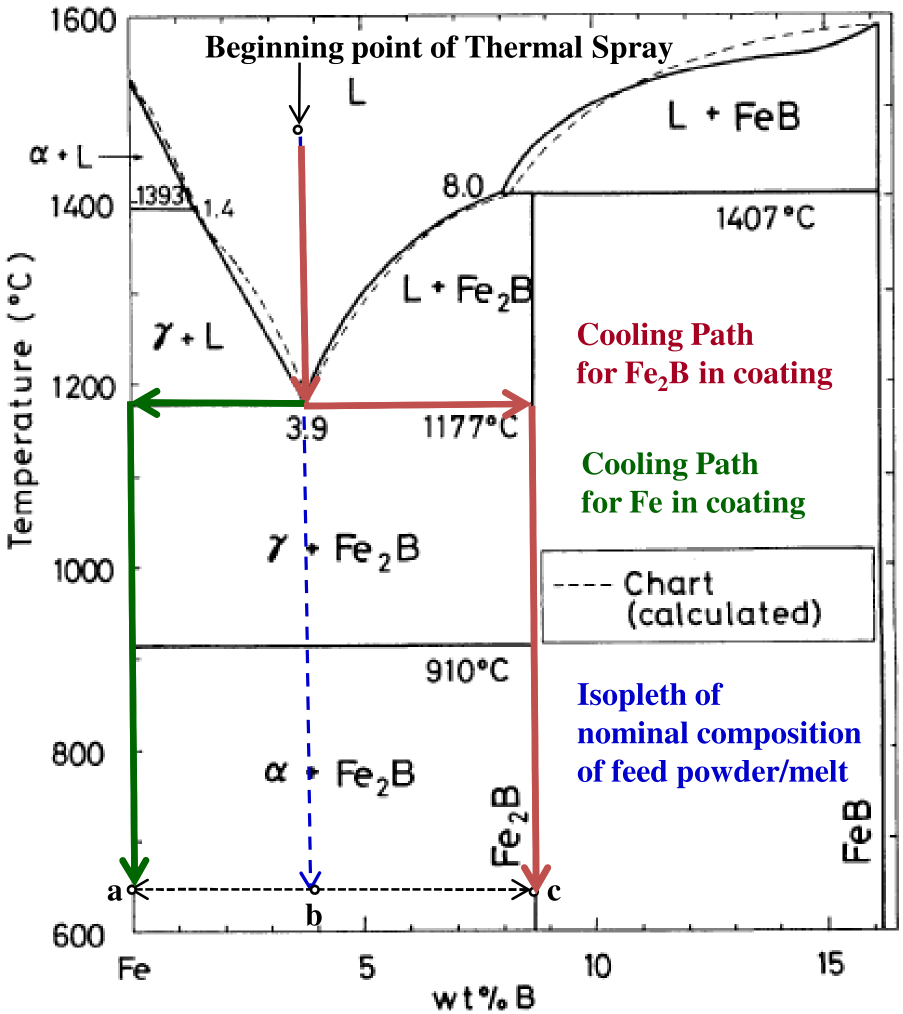
Fe_3O_4…..23-28% (RIR)

Fe_2B……11-16% (RIR)

Ignores amorphous background Hence, phase % among crystalline phases estimated.

Thermal History of the Coating

Assume Fe-B for simplicity. Same line of reasoning applies for Fe-B-C ternary & more complicated multi-component systems.



H. Ohtani, M. Nishizawa, T. Mishizawa; Trans. Of Iron & Steel Inst. of Jpn. P. 1043, Vol. 28 (1988)

$$\text{wt\% } Fe_2B = \frac{|ab|}{|ac|}\times 100$$

$$\text{wt\% } \alpha\text{-}Fe = \frac{|bc|}{|ac|}\times 100$$ → ***Prior to oxidation***

$$\text{wt\% } \alpha\text{-}Fe = \left[\left(\frac{|bc|}{|ac|}\right) - \psi\right]\times 100$$

Upon oxidation; ψ: weight fraction of Fe_3O_4

$$3Fe(s) + 2O_2(g) = Fe_3O_4(s)$$

$$K = \frac{a_{Fe_3O_4}}{P_{O_2}^2 a_{Fe}^3};\ a_{Fe_3O_4} \approx 1;$$

$$a_{Fe} < 1;\ P_{O_2}^{Air} = 0.21 \text{ atm}$$

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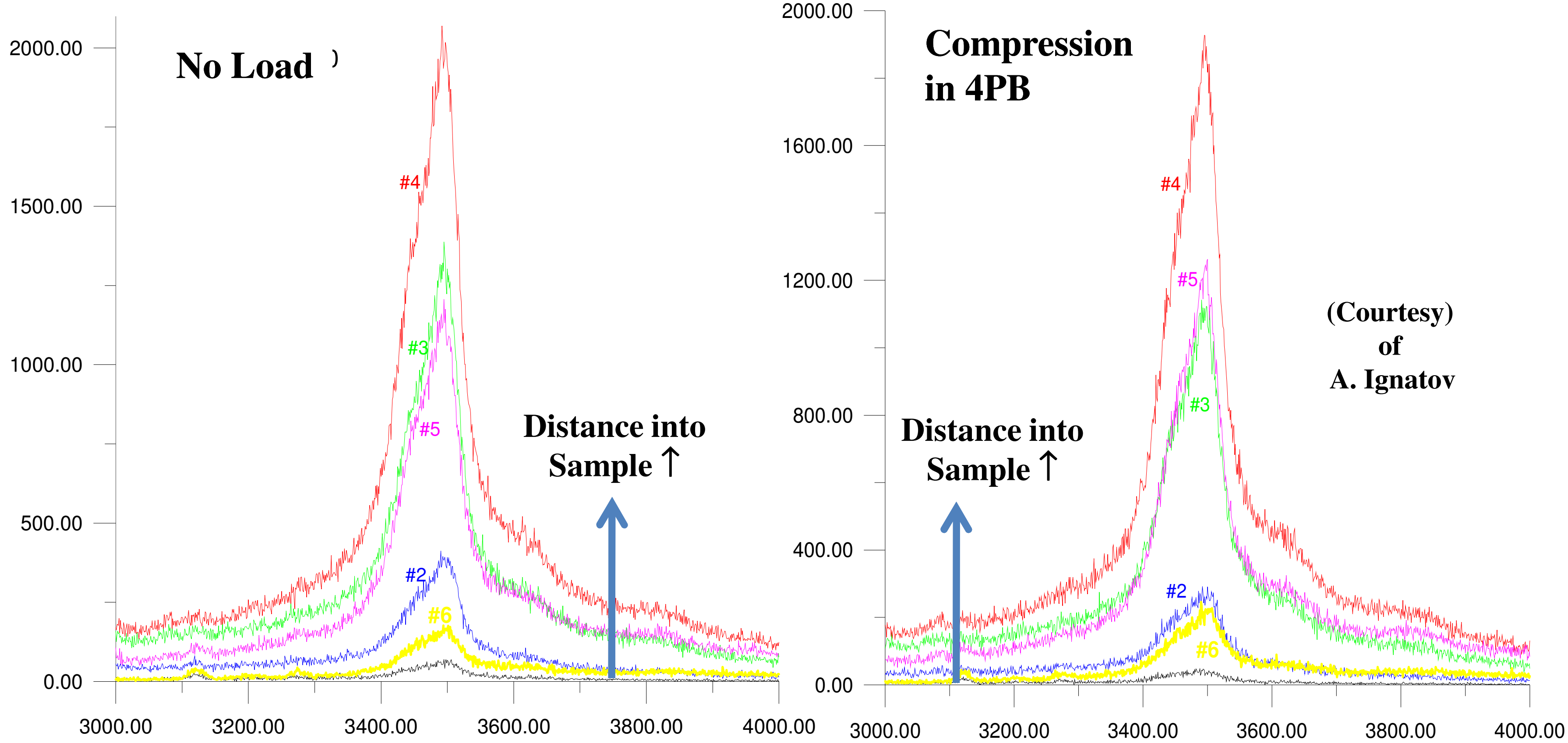
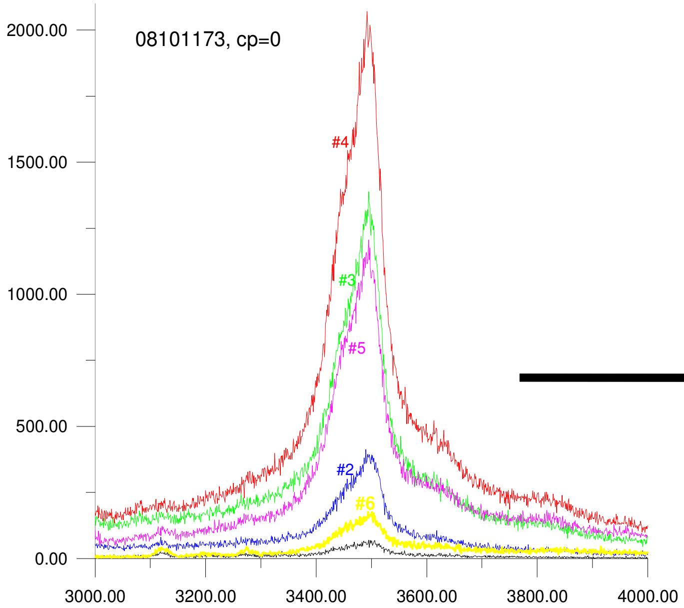
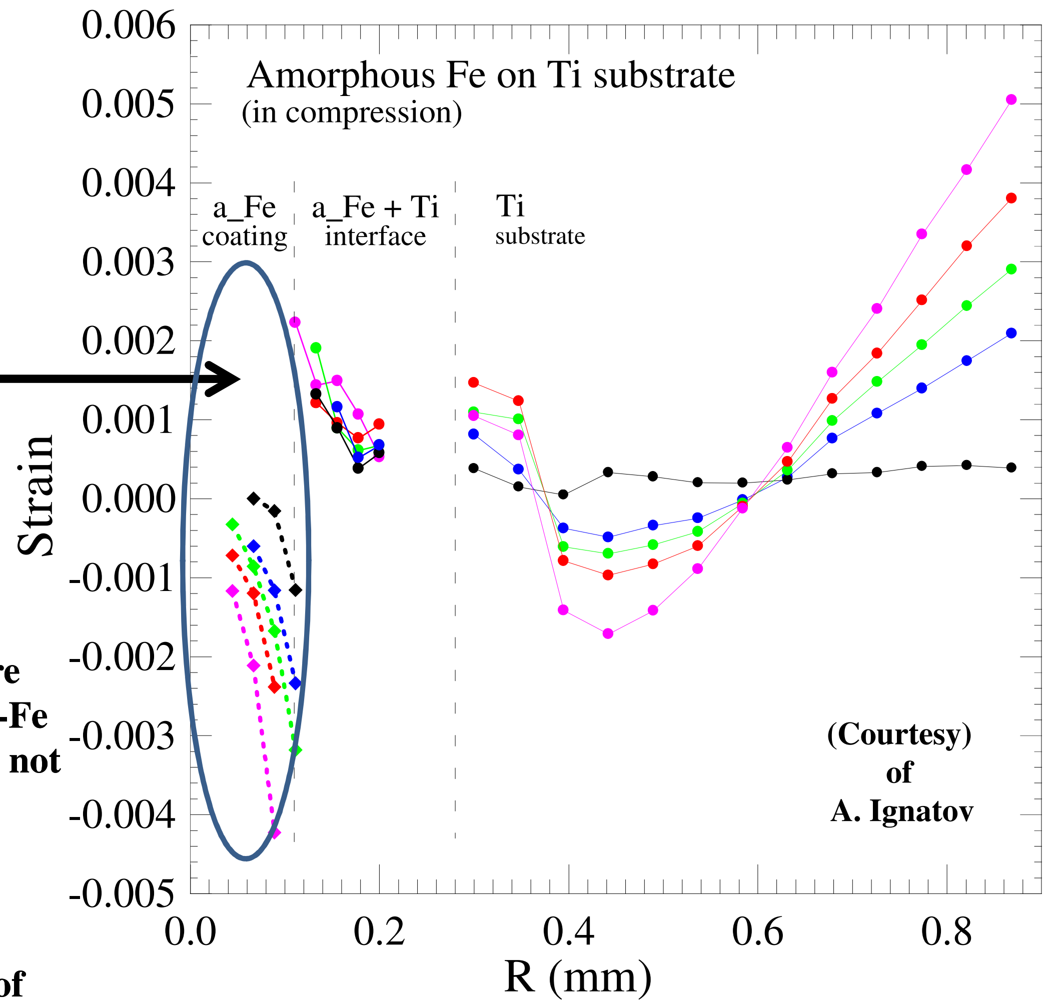
Comparison with 3D-EDXRD Diffraction Data



- **3D phase mapping by EDXRD shows that the phase decomposition and oxidation induced multiphase phase assemblage in the "alleged" amorphous coating is throughout the thickness of the coating as can be verified by the similarity of peak profiles between Bragg-Brentano and EDXRD data.**

Comparison with 3D-EDXRD Diffraction Data





- **EDXRD confirms the multiphase nature of the partially crystallized amorphous-Fe is throughout the coating thickness; i.e. not phase decomposition & oxidation not confined to surface.**
- **Preliminary analysis of strain without Peak decomposition provides estimate of "global" strain in the coating.**
- **Future work: Thickness dependent, multi-phase & multi-peak analysis by peak deconvolution**

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Concluding Remarks

- Introduced 3D-Phase and Strain Mapping of polycrystalline multiphase materials by Synchrotron EDXRD (S-EDXRD) as a new integrated approach of materials characterization.
- Analyzed TiO_2; Steel-Ni and amorphous-Fe coatings and shown the versatility of the proposed approach.
- Showed that 3D-phase mapping is essential in providing a full description of mechanical behavior of multiphase alloys.
- Showed that S-EDXRD can be used to study interfacial phenomena in due to small step scan size capability in phase mapping.
- Showed combined use of S-EDXRD with conventional (Bragg-Brentano) diffractometry is a viable approach for phase and strain mapping of complex multiphase materials. Combined with X-ray Absorption Spectrometry analysis capabilities are unmatched.