09/20/2022

BRUKER XRD ANWENDERTREFFEN 2022

MEASUREMENT OF COATING THICKNESS WITH X-RAY DIFFRACTION

M. Witte

SALZGITTER MANNESMANN FORSCHUNG

A Member of the Salzgitter Group

Introduction

- Salzgitter AG

XRD Thickness Measurement

- Motivation & Method
- Zn Coating on Steel
- Fe/Ni/Cr Standard
- Fe Nitride and Oxide Layers on Steel

- Messung von Zink-Texturen

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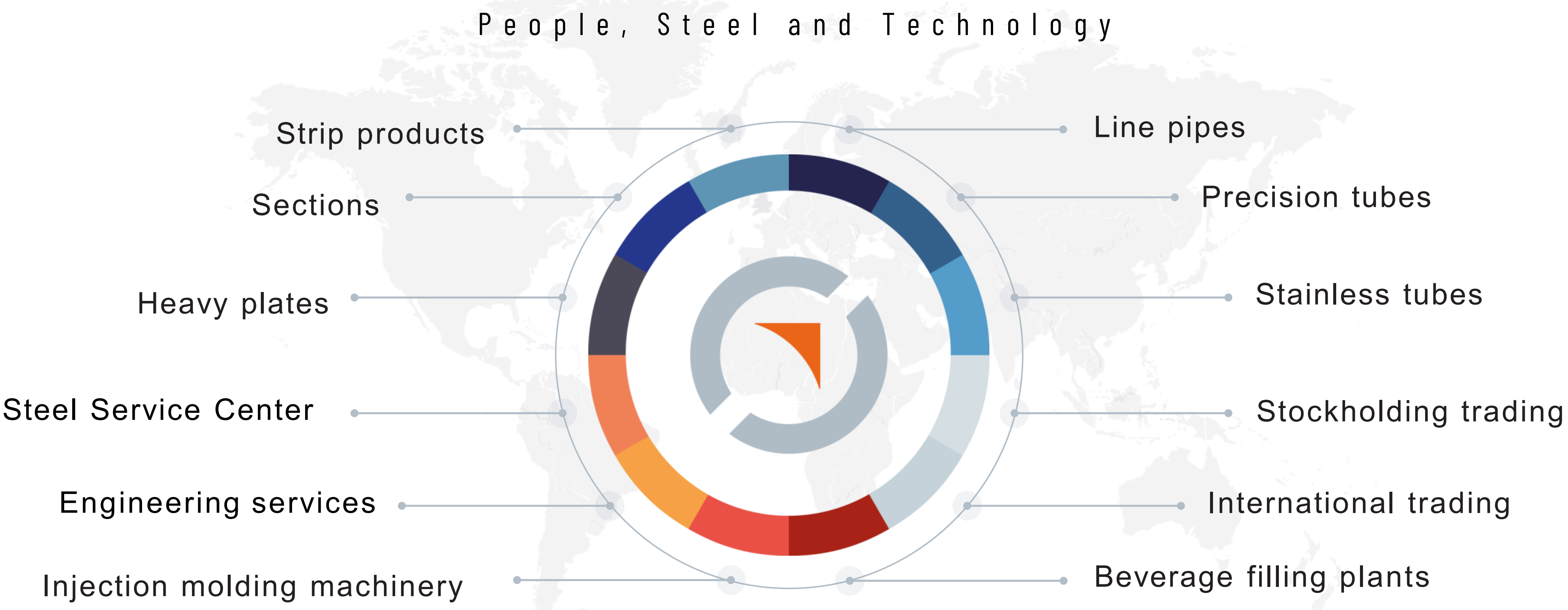
DIVERSIFIED PRODUCT PORTFOLIO
Salzgitter Group



GROUP STRUCTURE AND KEY DATA FY 2021

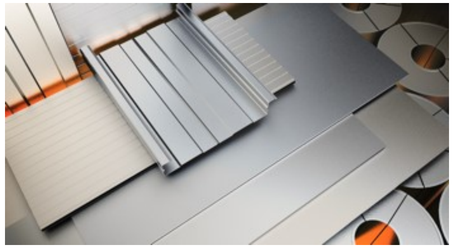
Salzgitter Group

Salzgitter Group

External Sales cons.: € 9.8 billion / **EBT:** € 706 million / **Employees:** 22,356

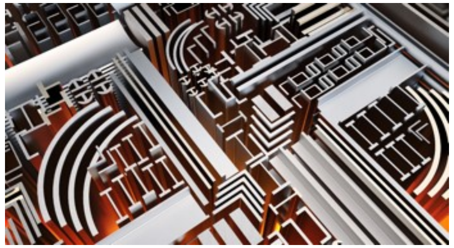
Steel Production

/ **External Sales:** € 3.1 billion
/ **Employees:** 7,158
/ **EBT:** € 495 million



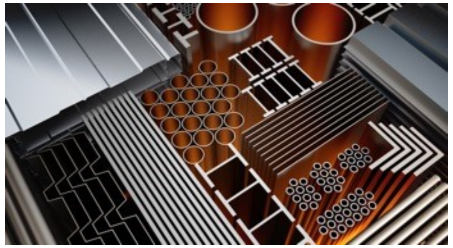
Steel Processing

/ **External Sales:** € 1.5 billion
/ **Employees:** 5,341
/ **EBT:** € -309 million



Trading

/ **External Sales:** € 3.6 billion
/ **Employees:** 1,934
/ **EBT:** € 353 million



Technology

/ **External Sales:** € 1.4 billion
/ **Employees:** 5,298
/ **EBT:** € 59 million

All data about employees as per 12/31

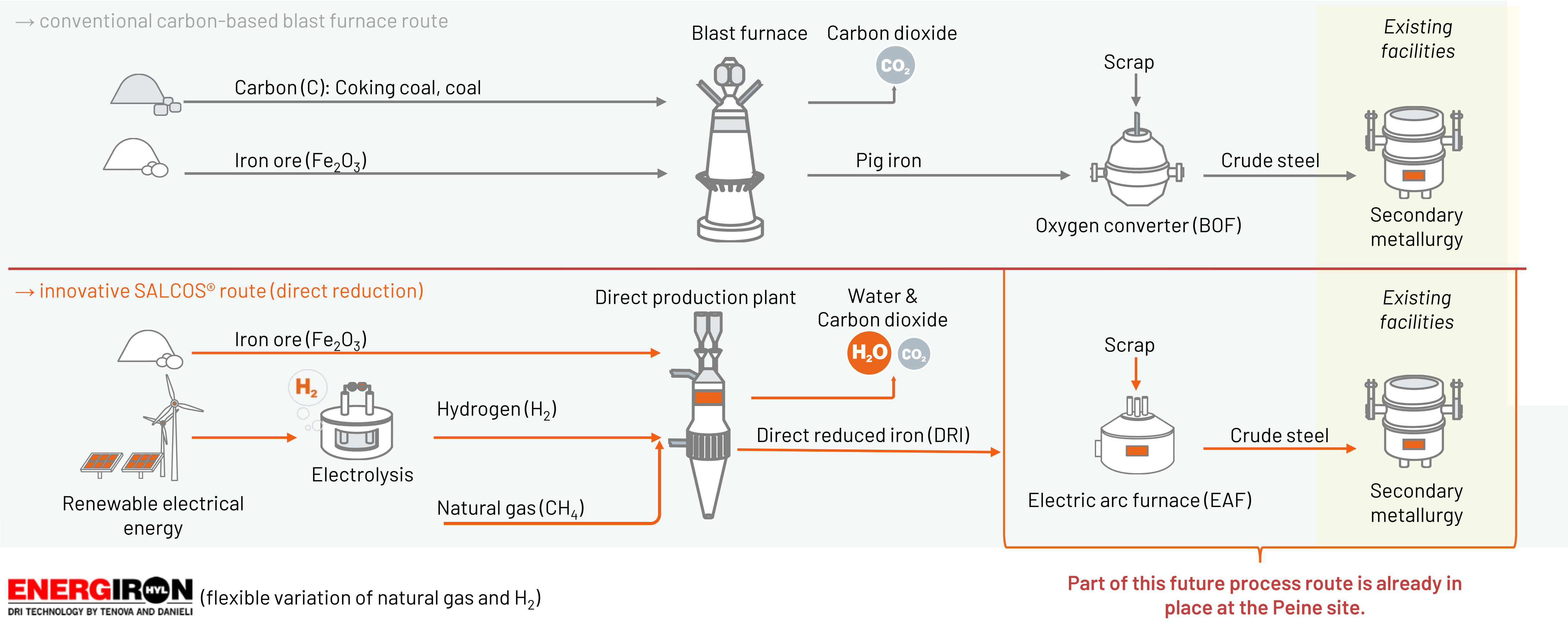
THE IDEA BEHIND SALCOS®

Salzgitter **L**ow **CO_2** **S**teelmaking

- Our approach: **Carbon Direct Avoidance** (CDA)
- **SALCOS®** maps out the route to **virtually carbon neutral** steel production
- **Hydrogen** as a **reduction agent** will replace carbon
- Transformation process is planned **in three stages**
- **Integration** of the new facilities **in the existing steelworks**
- **Same production capacity**
- By **2033: reduction of more than 95 % targeted in carbon emissions**

PART OF THE SALCOS® ROUTE ALREADY EXISTS

Comparison of the conventional and the future production technology



ENERGIRON DRI TECHNOLOGY BY TENOVA AND DANIELI (flexible variation of natural gas and H_2)

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XRD – THICKNESS MEASUREMENT
Motivation

Nano scale
- X-ray Reflectivty (XRR), Grazing Incidence X-ray Diffraction (GIXRD) Grazing-incidence Small-Angle X-ray Scattering (GISAXS)
  - Highly collimated beams, high intensity
  - layer thickness < 1 µm

Micro scale
- X-ray Fluoresence (XRF 0.01-75 µm)
  - Cannot differenciate polymorphs (e.g. Fe_2O_3 or Fe_3O_4)

Macro scale
- X-ray Transmission
  - High energy radiation, precision ± 500 nm

→ **How to measure coatings of 3-15 µm without XRF non-destructively?**

Available Equipment
- Bruker D8 Discover
- Vantec2000 area detector
- PolyCap with $Fe_{K\alpha}$-radiation, no monochromator

XRD – THICKNESS MEASUREMENT

Method

- Intensity of Fe-reflex is reduced by absorption from Zn layer.

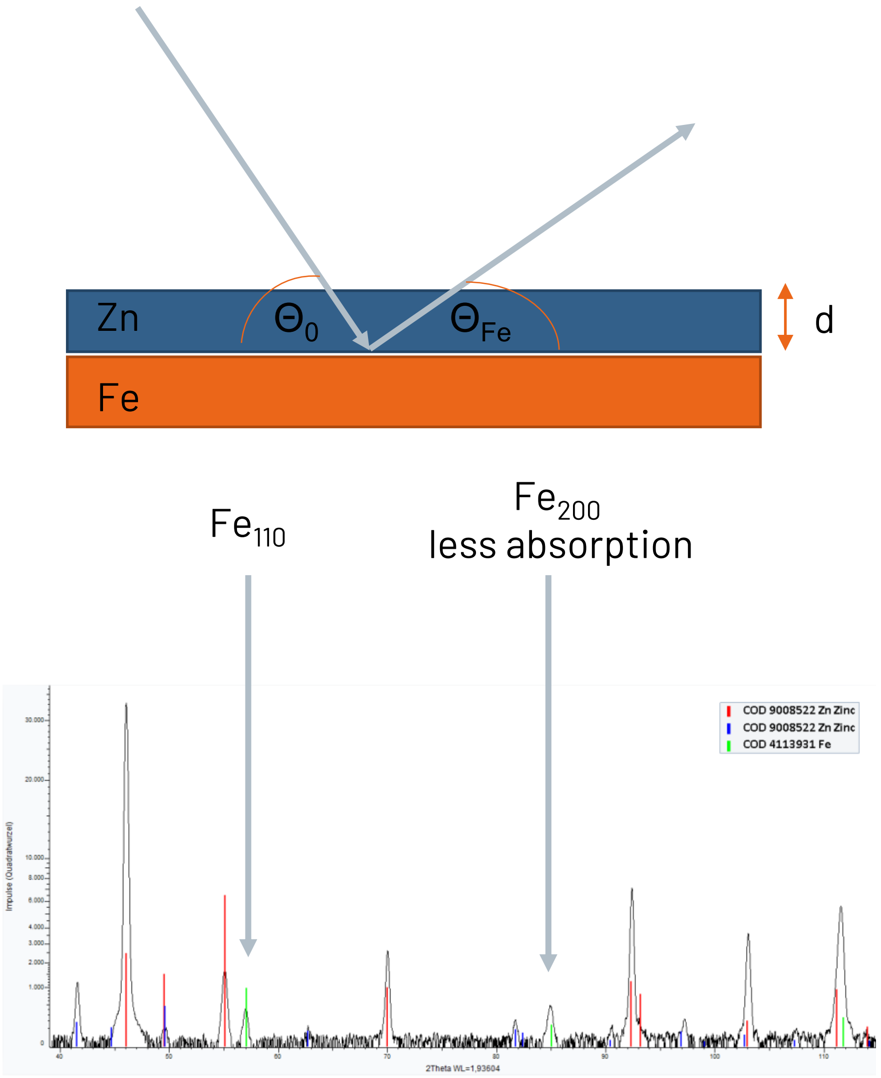
- From the Fe intensity with $I_{Fe,Zn}$ and without $I_{Fe,0}$ Zn the layer thickness can be determined:

$$I_{Fe,Zn} = I_{Fe,0} \cdot \exp(-\mu_{Zn} x_{Zn})$$

- The length of the x-ray path trough the Zn layer is:

$$x_{Zn} = d \cdot \left(\frac{1}{\sin(\theta_0)} + \frac{1}{\sin(\theta_{Fe} - \theta_0)}\right)$$

$$\rightarrow d = \frac{-\ln\left(\frac{I_{Fe,Zn}}{I_{Fe,0}}\right)}{\mu_{Zn}\left(\frac{1}{\sin(\theta_0)} + \frac{1}{\sin(\theta_{Fe} - \theta_0)}\right)}$$



Fe-Kα radiation, $\mu_{Zn} = 770\ cm^{-1}$

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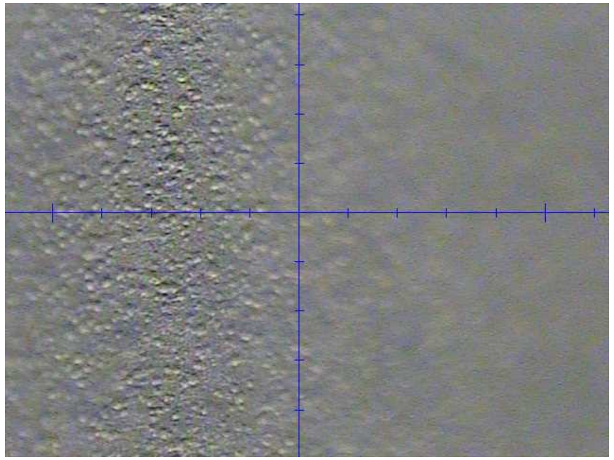
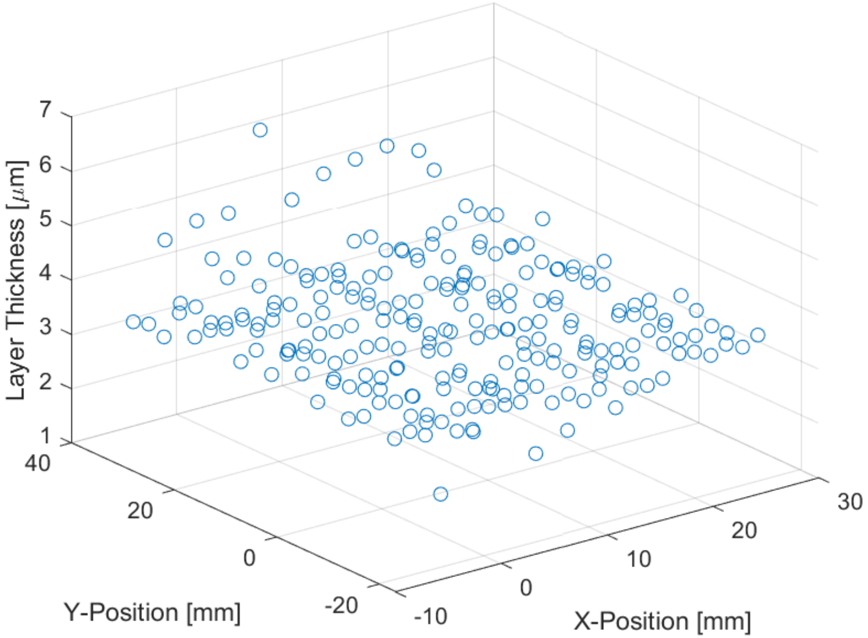
XRD- THICKNESS MAP
Zn Layer Mapping

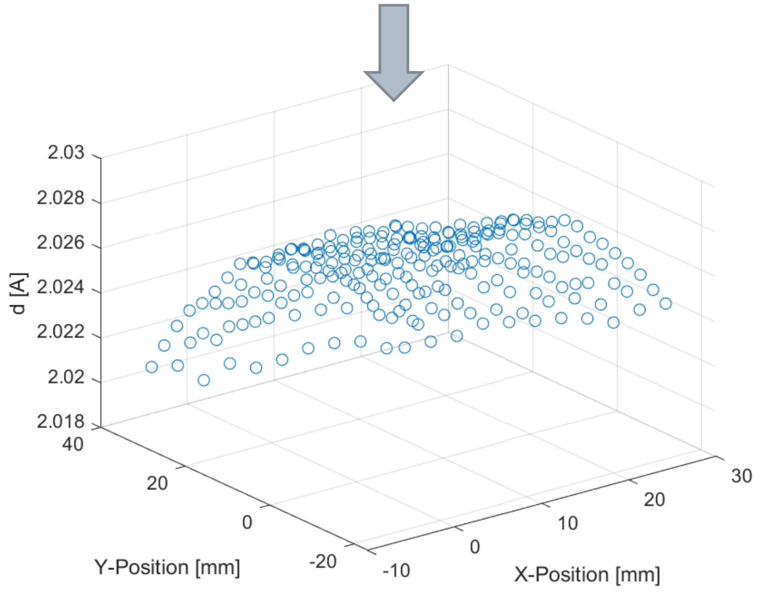
- Steel is coated with 2.5-20 µm Zn for corrosion protection.
- With a suitable sample stage and beam size the thickness distribution of an area can be mapped.
- Measurement of 231 points on 40 mm x 60 mm with 3 mm steps
- Reference thickness = 3 µm (weight)
- Scatter due to curvature



Video-Alignment out of focus



Thickness distribution



Deviation of Fe_{110} peak position

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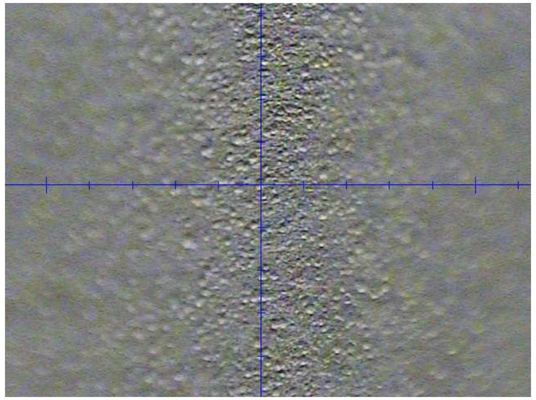
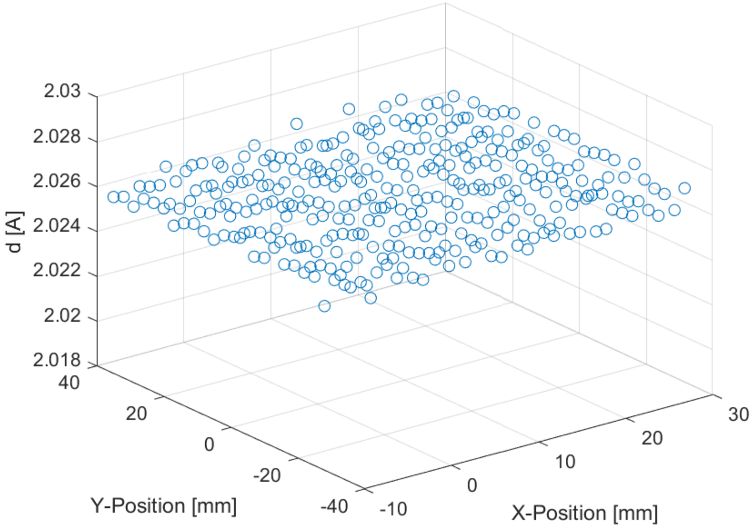
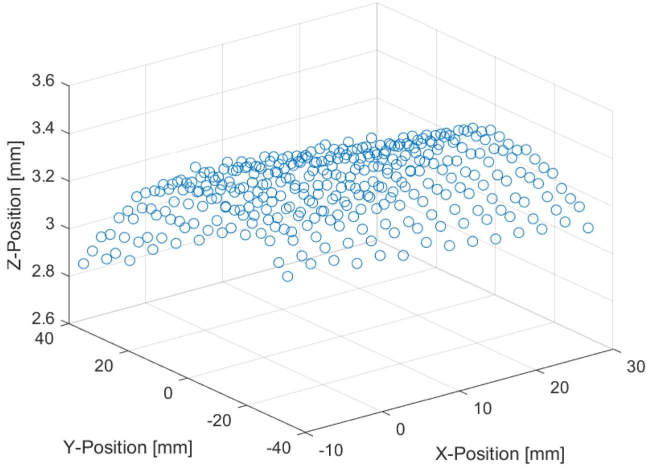
XRD- THICKNESS MAP
Sample height correction



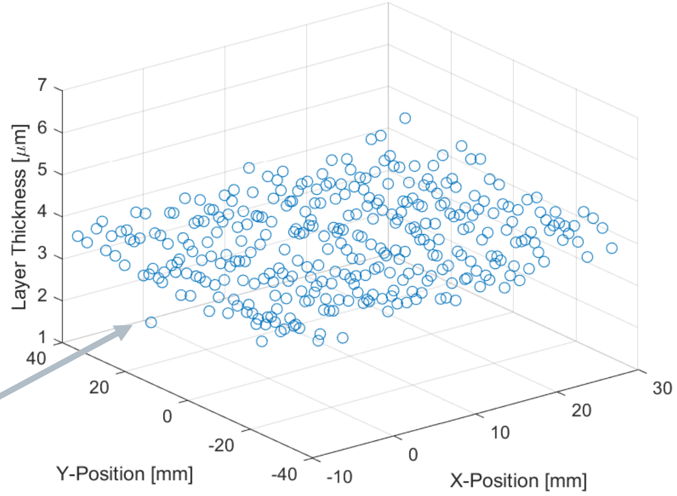
Automated height correction with Video-Alignment



Fe_{111} peak position stable



Corrected sample height

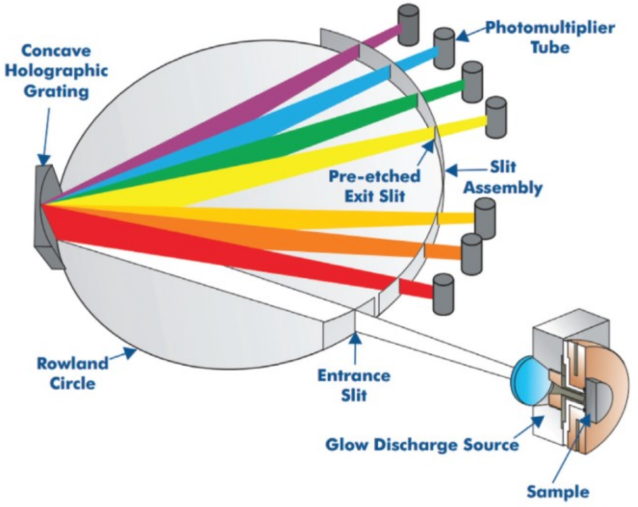


Laser cutting edge

- Reduced scatter
- Consistent results

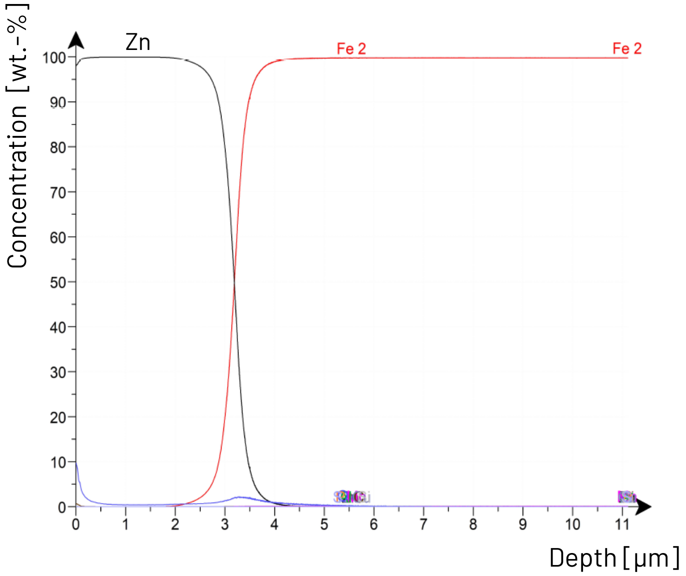
XRD – THICKNESS MEASUREMENT

Comparison with Glow Discharge-Optical Emission Spectroscopy (GD-OES)

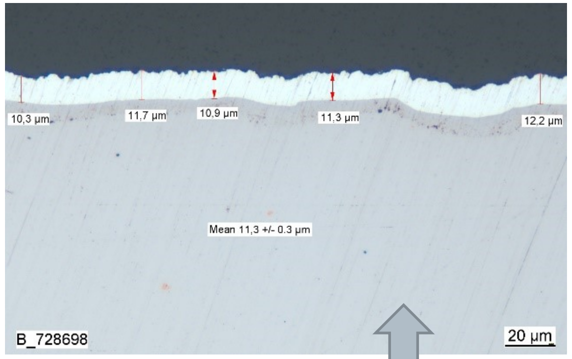


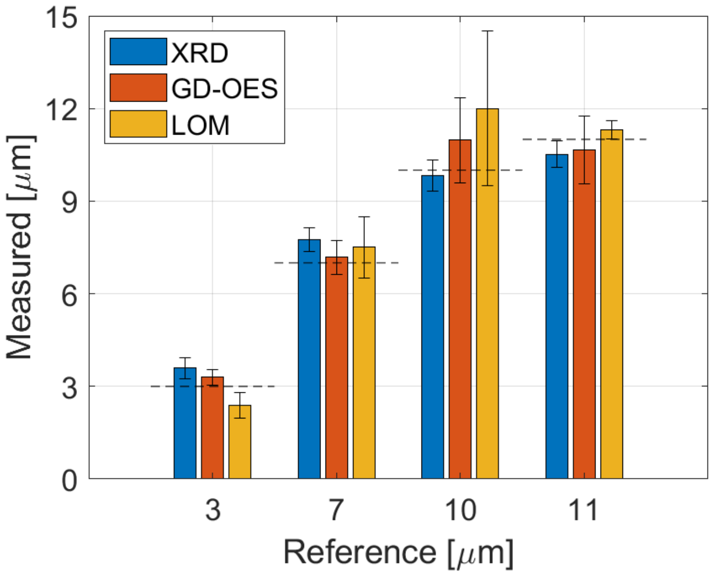
[Lötter, S.J., et al. (2015). *J. Southern African Inst. Mining and Metallurgy*, *115*(10), 966-971.]

GD-OES method



Example GD-OES result





- XRD thickness results fit well to GD-OES and reference values.
- Measurements for 10 & 11 µm with Fe_{200} reflex

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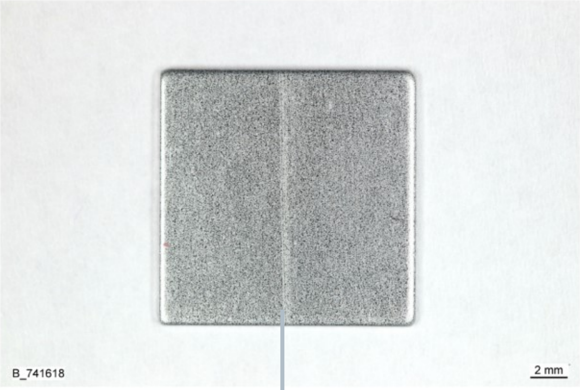
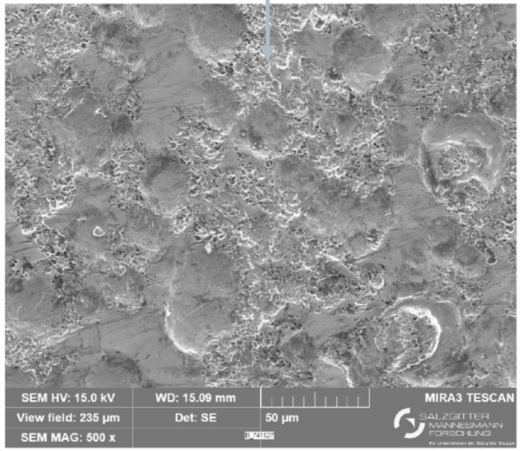
XRD – THICKNESS MEASUREMENT

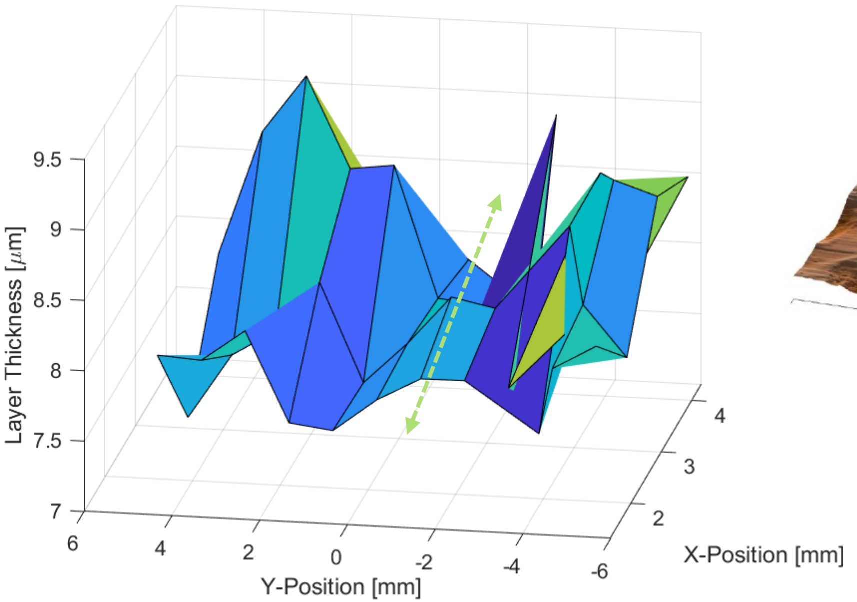
Application – Failure on Zn coating

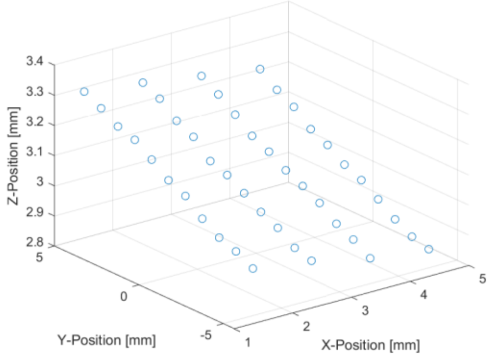




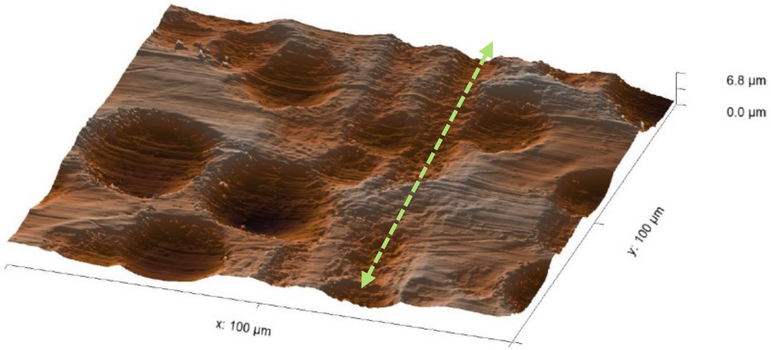
SEM

XRD





Atomic Force Microscope



- Scratch depth of 0.5-1.5 µm is similar for AFM and XRD.
- Scratch is on Zn surface and not on steel substrate.
- Scratch was not detected with micro-XRF thickness measurement!

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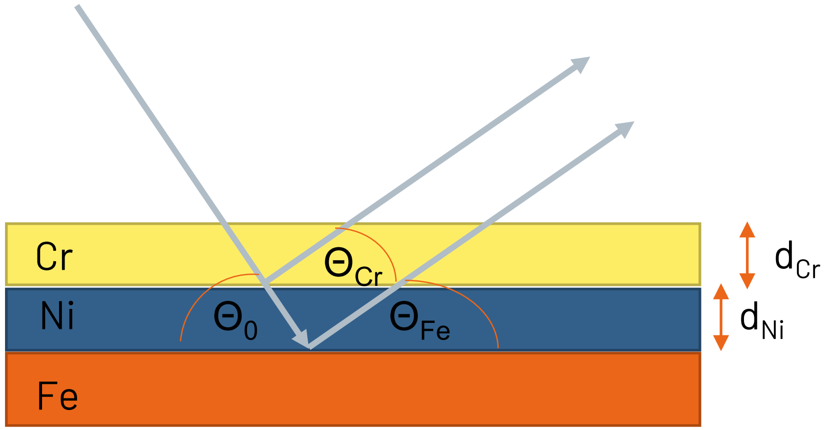
XRD – THICKNESS MEASUREMENT

Multilayer - Standard

- Reference Standard with 0.88 µm Cr / 7.3 µm Ni on Fe-Substrate



- Cr layer thickness from comparison with bulk Cr sample:

$$I_{Cr} = I_{Cr,0} \cdot (1 - \exp(-\mu_{Cr} x_{Cr}))$$

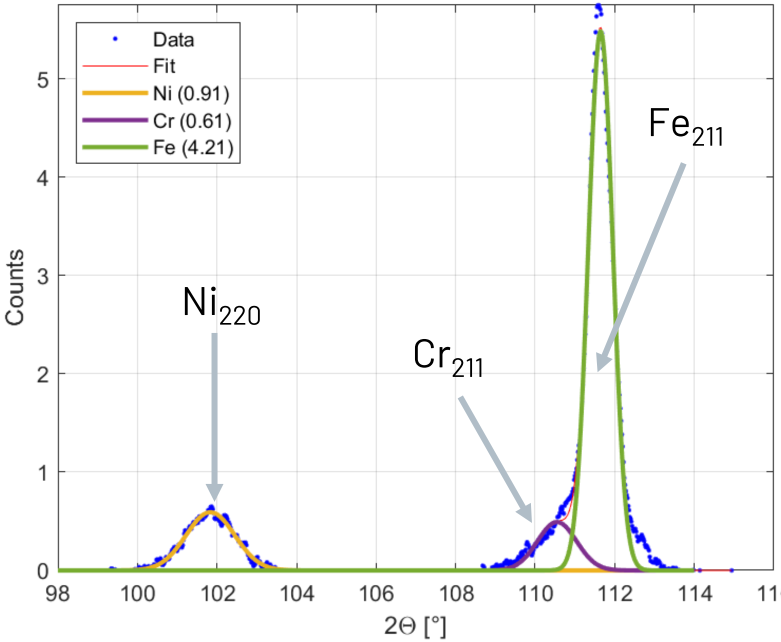
$$\rightarrow d_{Cr} = \frac{\ln\left(1 - \frac{I_{Cr}}{I_{Cr,0}}\right)}{\mu_{Cr}\left(\frac{1}{\sin(\theta_0)} + \frac{1}{\sin(\theta_{Cr} - \theta_0)}\right)}$$

- Removal of absorption from Fe_{211} by Cr layer:

$$I_{Fe,cor} = I_{Fe} \cdot \exp(\mu_{Cr} x_{Cr})$$

- Ni layer thickness:

$$\rightarrow d_{Ni} = \frac{-\ln\left(\frac{I_{Fe,cor}}{I_{Fe,0}}\right)}{\mu_{Ni}\left(\frac{1}{\sin(\theta_0)} + \frac{1}{\sin(\theta_{Fe} - \theta_0)}\right)}$$



Fe-Kα radiation, $\mu_{Ni} = 808\ cm^{-1}$, $\mu_{Cr} = 3157\ cm^{-1}$

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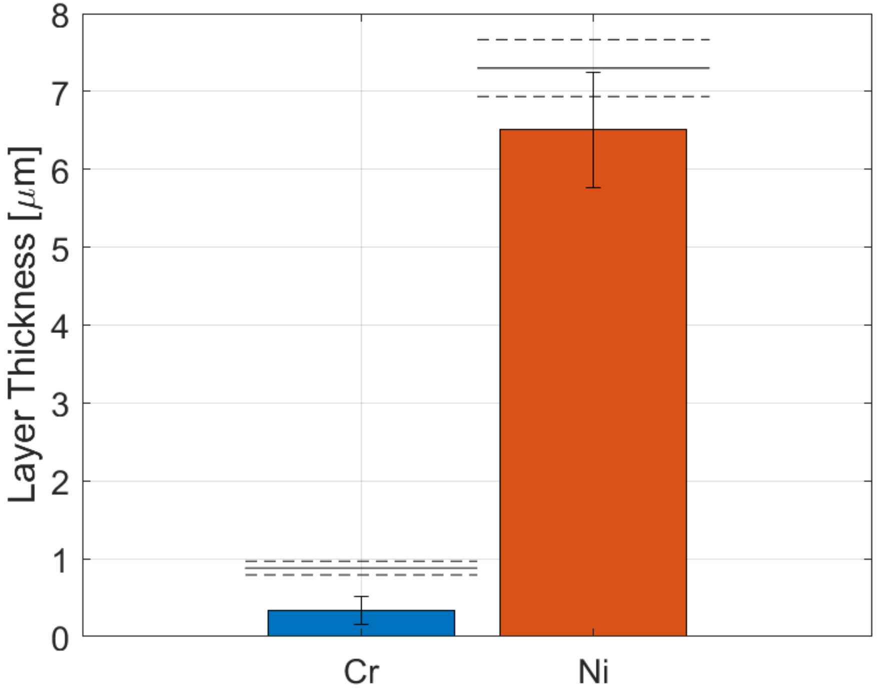
XRD – THICKNESS MEASUREMENT

Multilayer - Standard



- Cr causes strong X-ray fluorescence with Fe-Kα radiation.
  → Low Peak-to-Background ratio
- Overlap of Fe_{211} and Cr_{211} peaks
  → Peak deconvolution
- No measurement of Fe substrate without Cr/Ni layer possible
  → Use of suitable reference sample (low alloyed hot strip)
  → Intensity differences due to texture
- Same problem occurs with bulk Cr reference sample.

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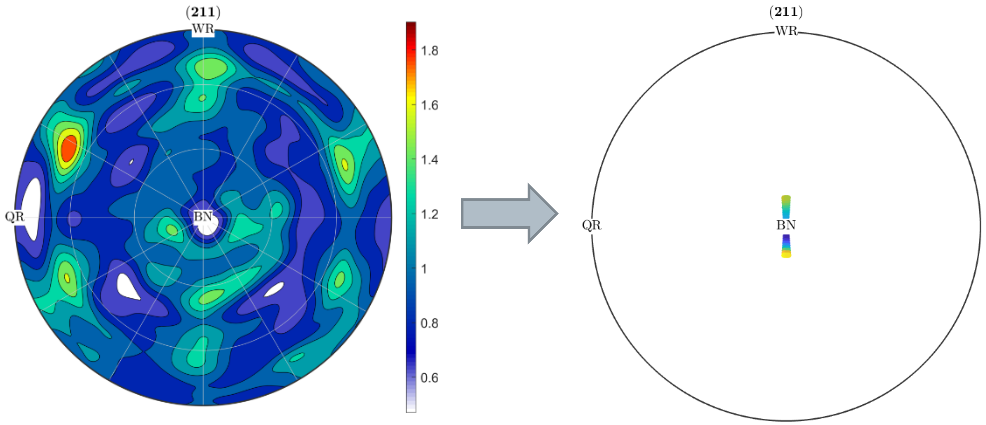
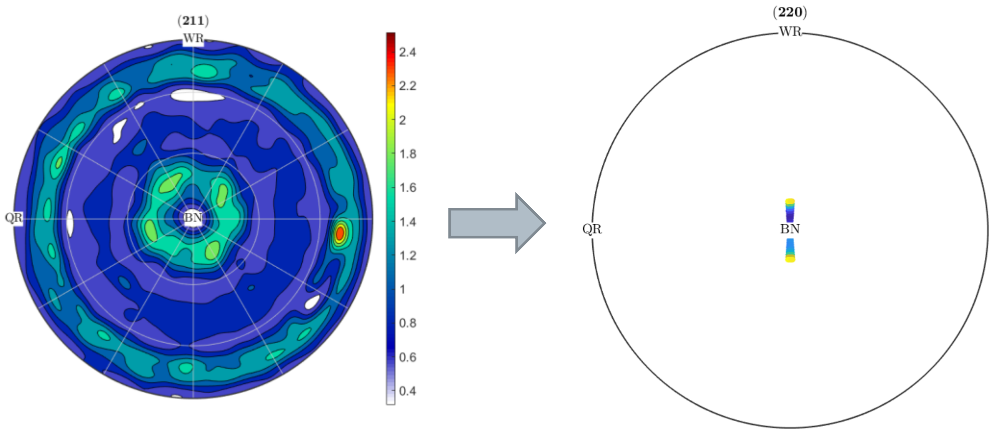
XRD – THICKNESS MEASUREMENT

Multilayer – Standard – Texture corrections



Fe_{211} pole figure of reference sample



Fe_{211} pole figure of standard substrate

- Intensity for thickness measurement is from the pole figure center.
- Intensity can be scaled with pole figure values to the intensity of samples with random texture.
- Since an area dector is used a line section of the pole figures has to be averaged.

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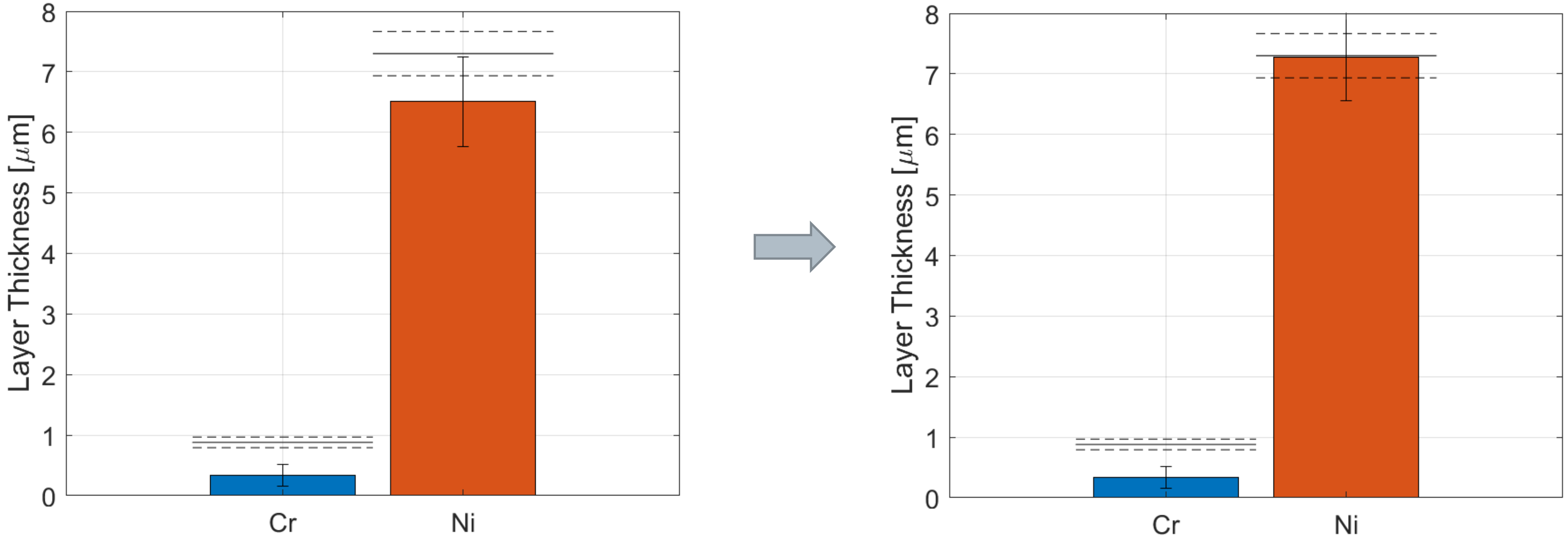
XRD – THICKNESS MEASUREMENT

Multilayer – Standard – Texture corrections

After texture correction



- Excellent agreement for Ni layer thickness
- Poor agreement for Cr layer thickess
  - X-ray fluorescence
  - Texture correction not possible due to low intensity and peak overlap

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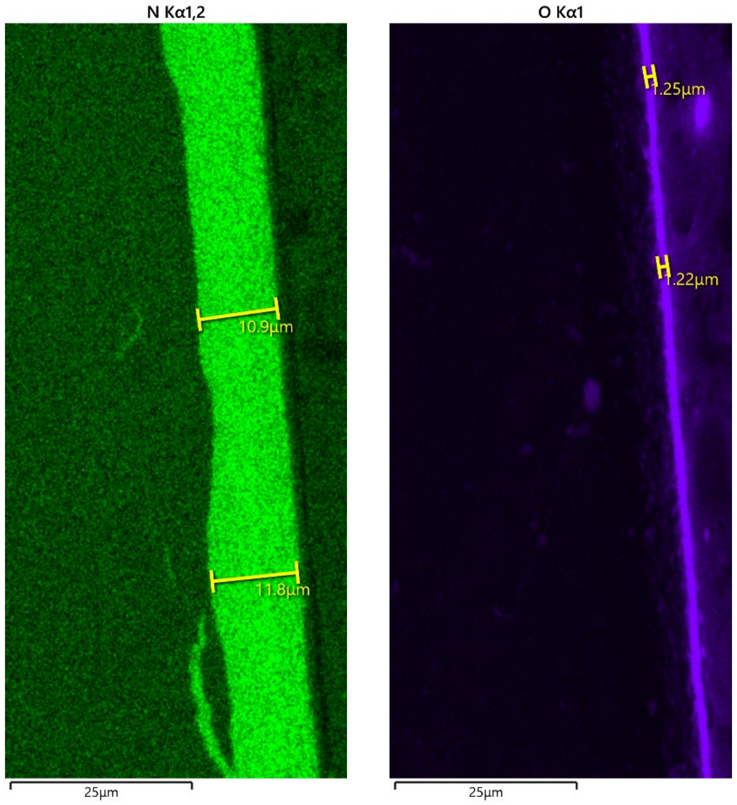
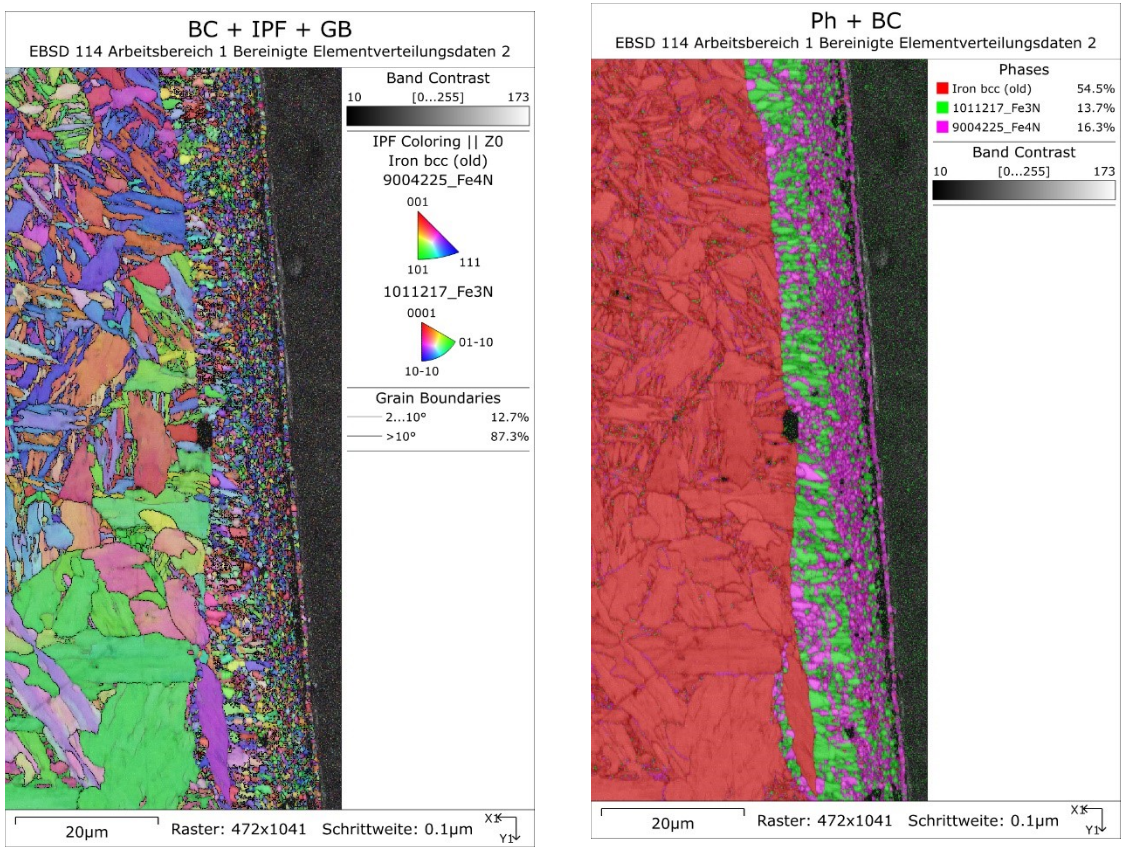
XRD – THICKNESS MEASUREMENT

Nitride/Oxide layer



EDX



EBSD

- Nitriding is used for surface hardening of steel.
- Oxide layer for corrosion resistance
- ~1.2 µm Oxide layer / ~ 11.5 µm Fe-nitride layer / steel substrate
- Only diffraction methods (XRD, EBSD) can discriminate γ-Fe_4N and ε-Fe_3N

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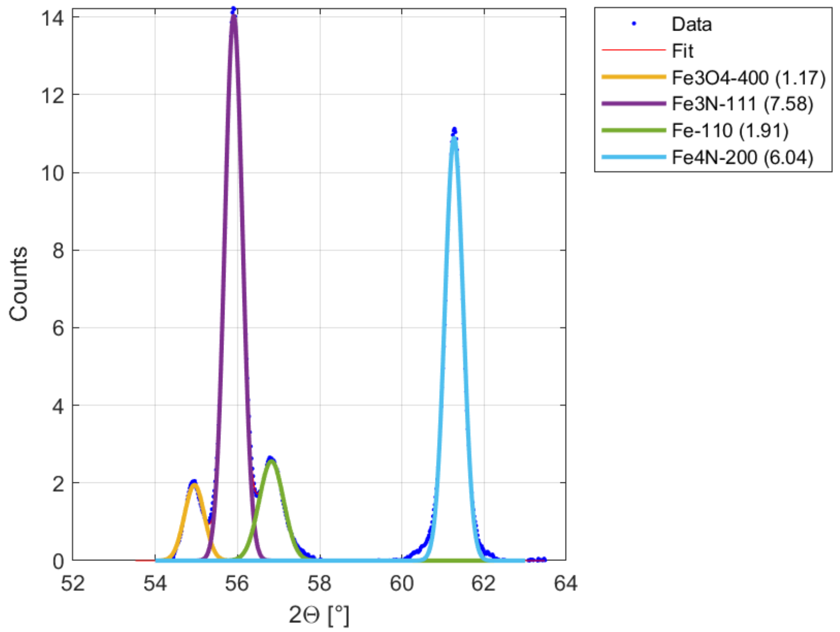
XRD – THICKNESS MEASUREMENT

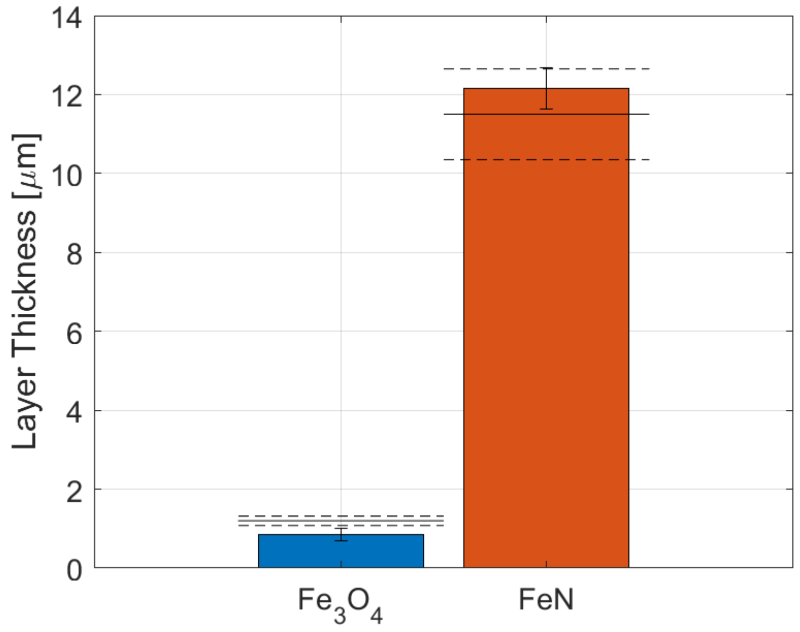
Nitride/Oxide layer

- Fe3N and Fe4N layers are not well separated
  → Treat them as one layer:

  $\mu_{FexN} = 0.5*(\mu_{Fe3N} + \mu_{Fe4N}) = 0.5*(537 + 494)\ cm^{-1} = 516\ cm^{-1}$

- With the same approach as before the layer thickness can be determined.





- With well separated layers and suitable reference materials Fe3N and Fe4N layer thicknesses could be measured with XRD.
  - This would not be possible with XRF.

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XRD – THICKNESS MEASUREMENT
Summary

- XRD is a suitable method to measure layer thicknesses by X-ray absorption!
- N-1 reference materials are necessary for N layers.
  - If possible use substrate after layer removal.
- Corrections
  - Texture differences between layer and reference material
  - Sample height differences for thickness maps of non flat surfaces
- Advantages
  - Differentiation of polymorph layers (e.g. Fe3N/Fe4N or Fe_xO_y) possible
  - Extension of XRD measurement capabilities
  - Non-destructive

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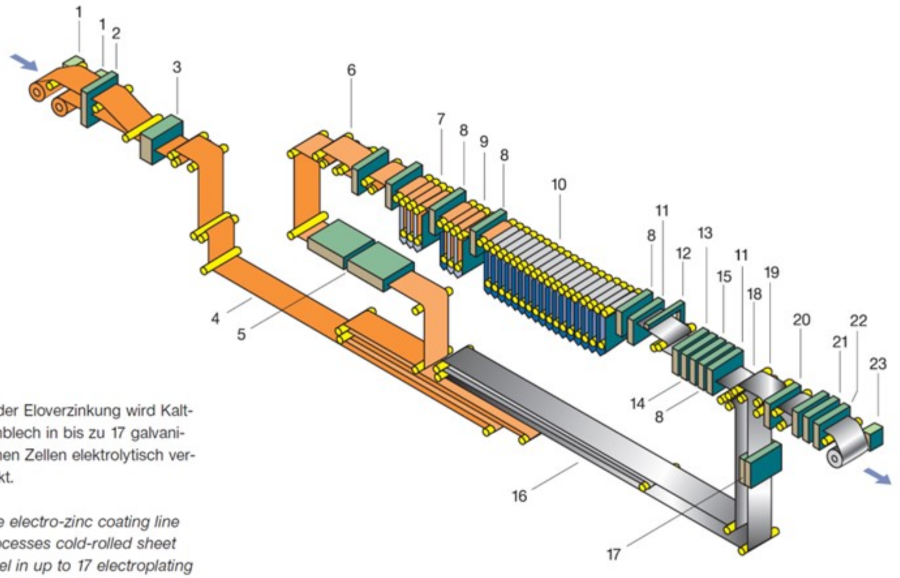
- **Messung von Zink-Texturen**

ELEKTROLYTISCHE VERZINKUNG SZFG

Layout

Eloverzinkung – Anlagenplan
Electro-zinc coating line – Layout



In der Eloverzinkung wird Kaltfeinblech in bis zu 17 galvanischen Zellen elektrolytisch verzinkt.

The electro-zinc coating line processes cold-rolled sheet steel in up to 17 electroplating cells.

Bandbreitenbereich	900 - 1.850 mm	*Strip width range*	*900 - 1.850 mm*
Banddickenbereich	0,5 - 2,5 mm	*Strip thickness range*	*0,5 - 2,5 mm*
Geschwindigkeit	max. 180 m/min	*Speed*	*max. 180 m/min*
Bundgewicht	max. 32 t	*Coil weight*	*max. 32 t*
Stromstärke	50 kA/Zelle	*Current intensity*	*50 kA/Zelle*
Gleichrichterkapazität	850 kA	*Rectifier capacity*	*850 kA*
Anzahl Zellen	17	*Number of cells*	*17*
Zinkschichtdickenbereich	2,5 - 15 µm (ein- und beidseitig)	*Coating range*	*2,5 - 15 µm (one-side and both-side coating)*
Kapazität	38.000 t/Mon.	*Capacity*	*38.000 t/mo*

1. Abhaspel
2. Schopfschere
3. Schweißmaschine
4. Einlaufspeicher
5. Bandvorreinigung
6. Streckrichter
7. Elektrolytische Reinigung
8. Spüle
9. Beize
10. Elektrolytische Verzinkung mit 17 Zellen
11. Trockner
12. Zinkschichtdickenmessung
13. Aktivierung
14. Phosphatierung
15. Passivierung (chromfrei)
16. Auslaufspeicher
17. Inspektionsstand
18. Oberflächeninspektionssystem
19. Rauheitsmessung
20. Besäumschere
21. Elektrostatische Ölmaschine
22. Ölauflagenmessung
23. Aufhaspel

1. *Pay-off reel*
2. *Cropping shear*
3. *Welding machine*
4. *Entry loop accumulator*
5. *Strip pretreatment*
6. *Tension leveller*
7. *Electrolytic cleaning*
8. *Rinsing tank*
9. *Pickling tank*
10. *Electro-zinc coating with 17 cells*
11. *Dryer*
12. *Zinc coating thickness control*
13. *Activation*
14. *Phosphor treatment*
15. *Passivation (chrom-free)*
16. *Exit loop accumulator*
17. *Inspection station*
18. *Surface inspection system*
19. *Roughness measurement*
20. *Edge trimmer*
21. *Electrostatic oiler*
22. *Oiling gauge*
23. *Tension reel*

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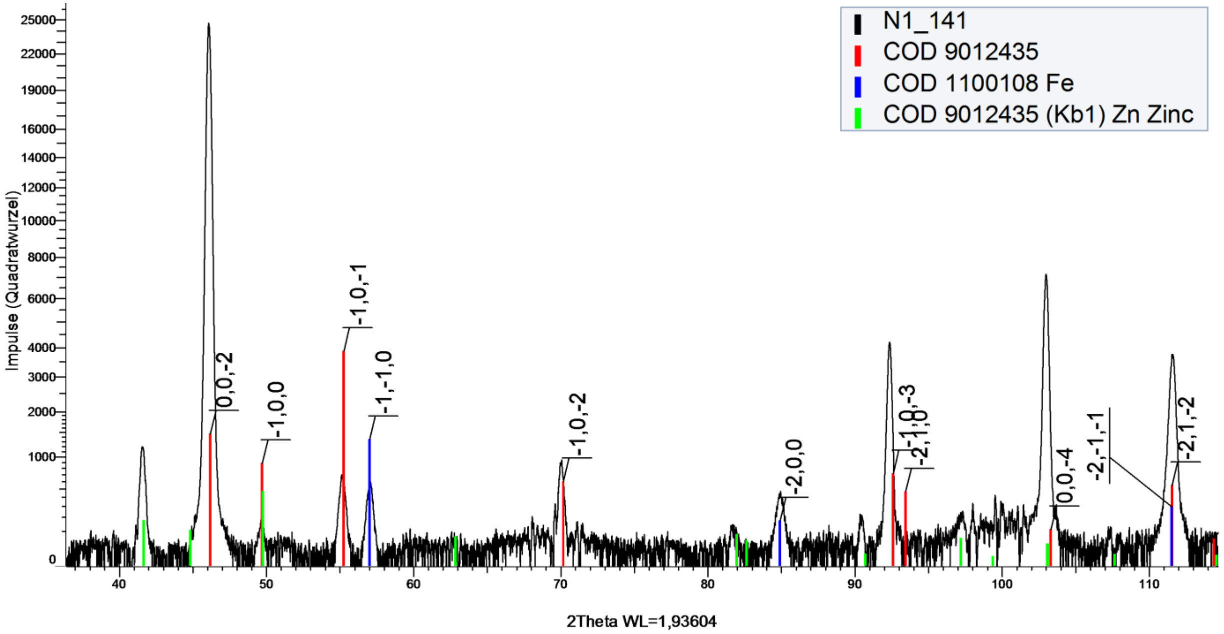
ZINK – TEXTUR

Messschema

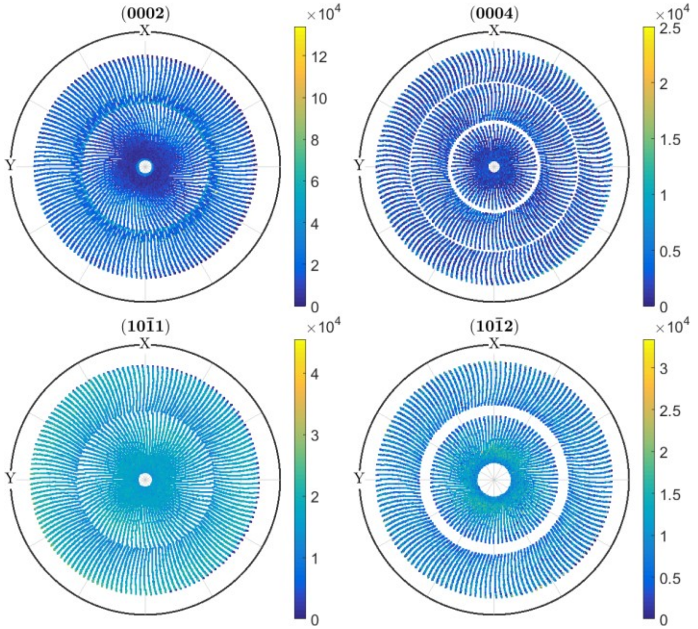
Welche Reflexe eignen sich für Texturmessung?

- {100}-Reflex ungeeignet (Überlappung mit Kβ-{101})
- {103}- und {210} ungeeignet, da zu dicht zusammen (Peakverbreiterung bei höheren Kippwinkeln)
- {212}-Reflex ungeeignet (Überlappung mit {211}-Fe-Reflexe)
- Bleiben: {002}, {101}, {102} und {004} , wobei {002} und {004} äquivalente Information liefern.



Röntgendiffraktometer

- Bruker D8 Discover mit Vantec2000 Flächendetektor
- Fe-Kα Strahlung mit Mn-Kβ-Filter



Messschema

- Equal Area, 2.5° Auflösung
- 2 Detektorpositionen für 4 Polfiguren
- 6 s Messzeit pro Frame
- ~100 min pro Probe

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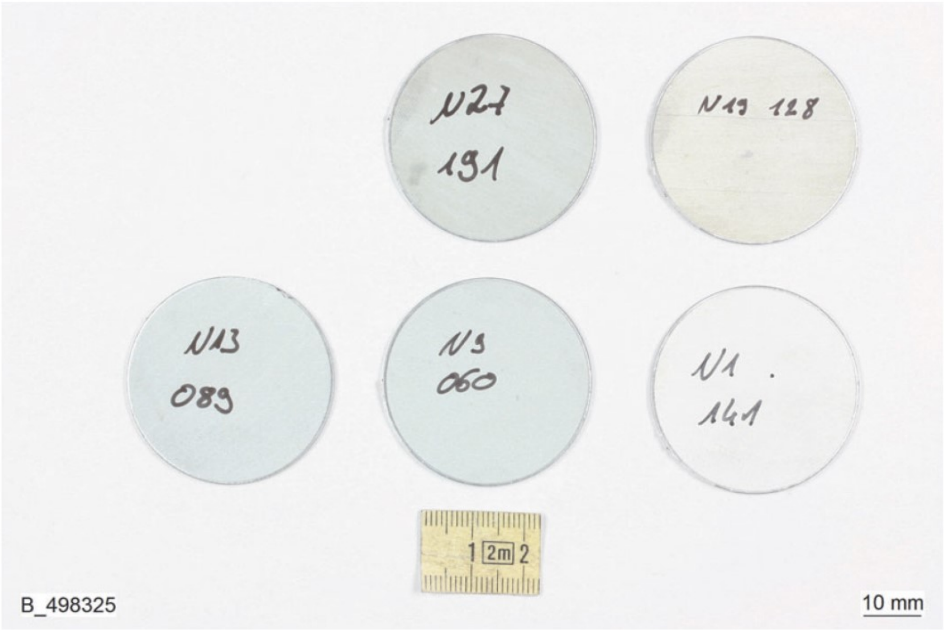
ZINK – TEXTUR
Summary

Proben
- Laborproben (ELViS)
- 5 unterschiedliche Elektrolytzusammensetzungen.
    - Ziel: Reduktion Energieverbrauch durch höhere Elektrolyt-Leitfähigkeit
- Optischer Unterschied Proben N1 & N19 zu restlichen Proben



Texturberechnung
- Mit Matlab Toolbox MTEX
  MTEX Toolbox | MTEX (mtex-toolbox.github.io)
- Berechnung der Orientierungsverteilungsfunktion (ODF) und von Texturfaseranteilen

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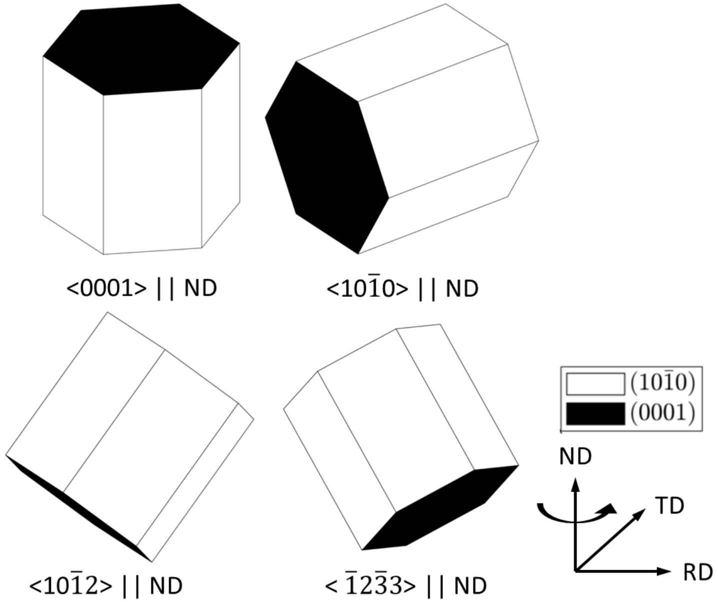
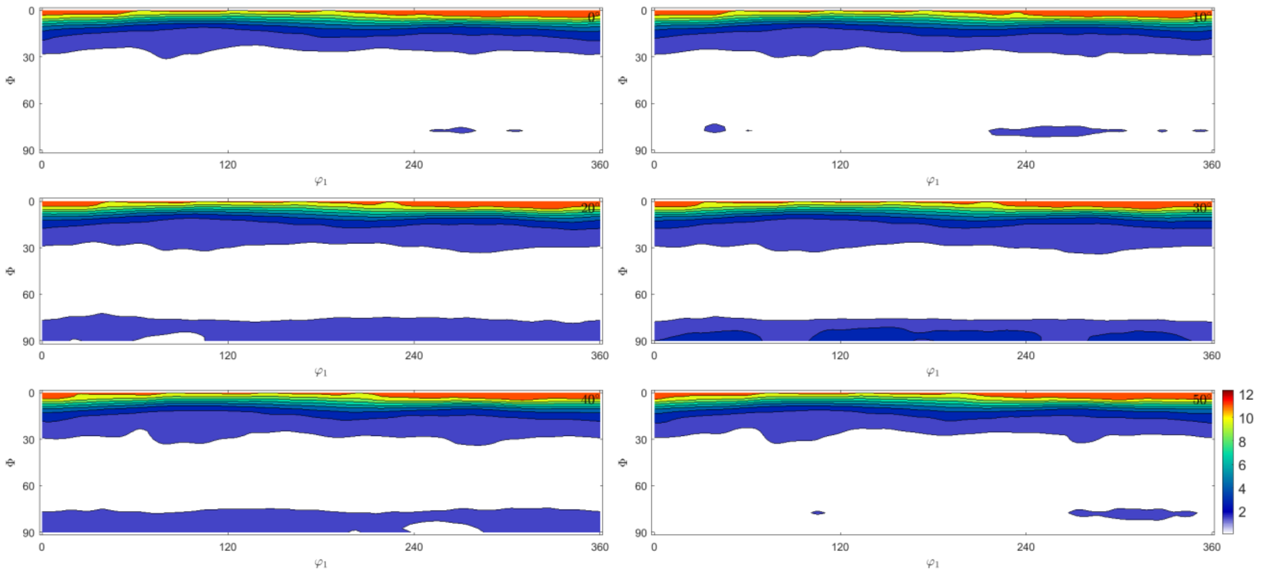
ZINK – TEXTUR
Experimentelle ODFs

- Deutlicher Texturunterschied
- N1: Scharfe Basaltextur
- N13: Schwache Texturfasern

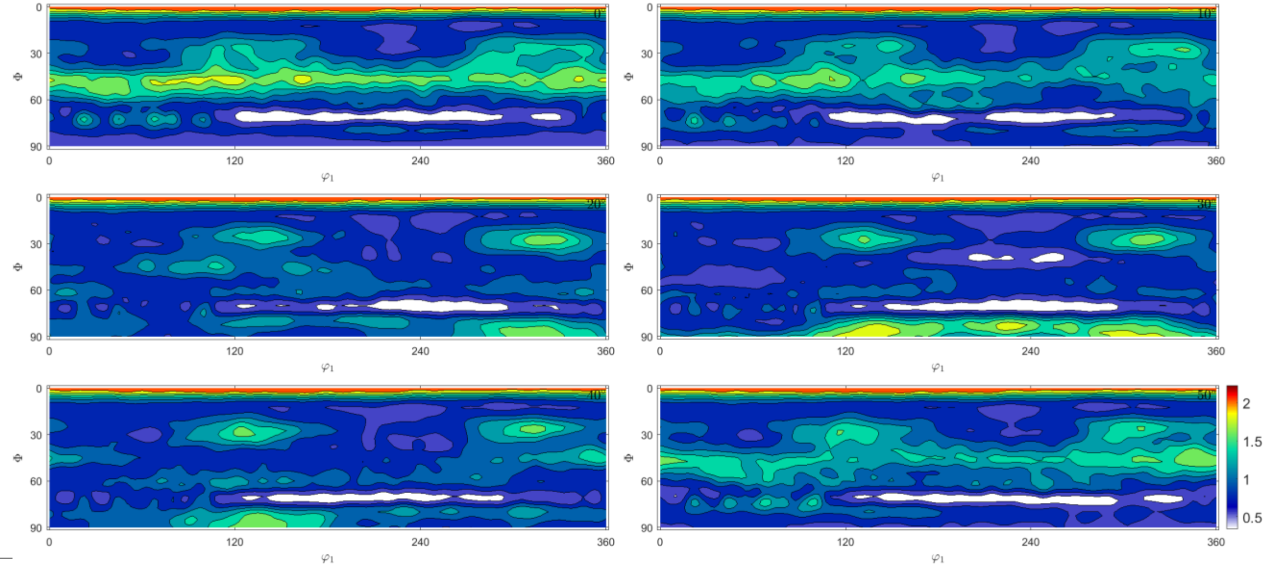
Typische Kristallorientierungen von Zink



N1

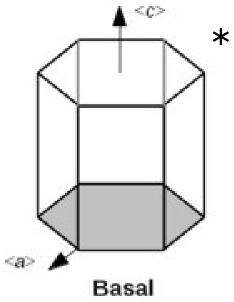


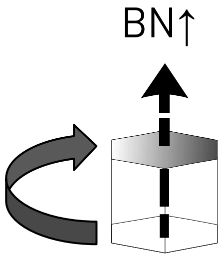
N13

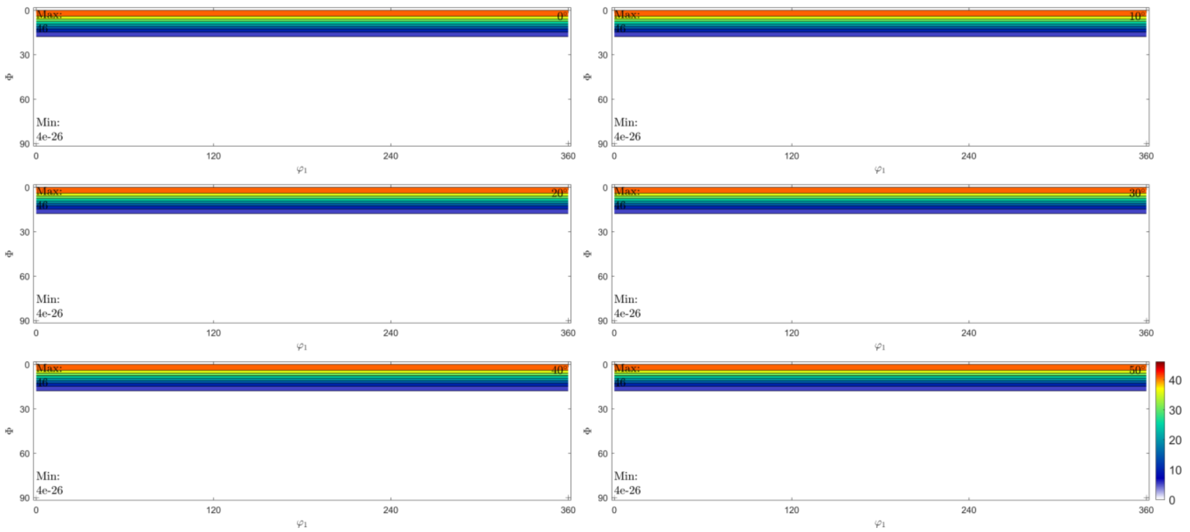


ZINK – TEXTUR
Simulierte ODFs

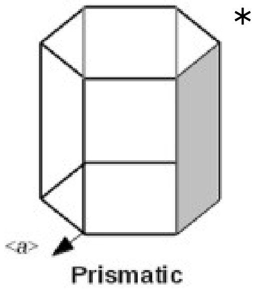
- Basal-Faser
  - <001> ‖ BN
  - ODF_{Max} = 46, homogen

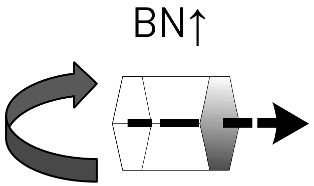


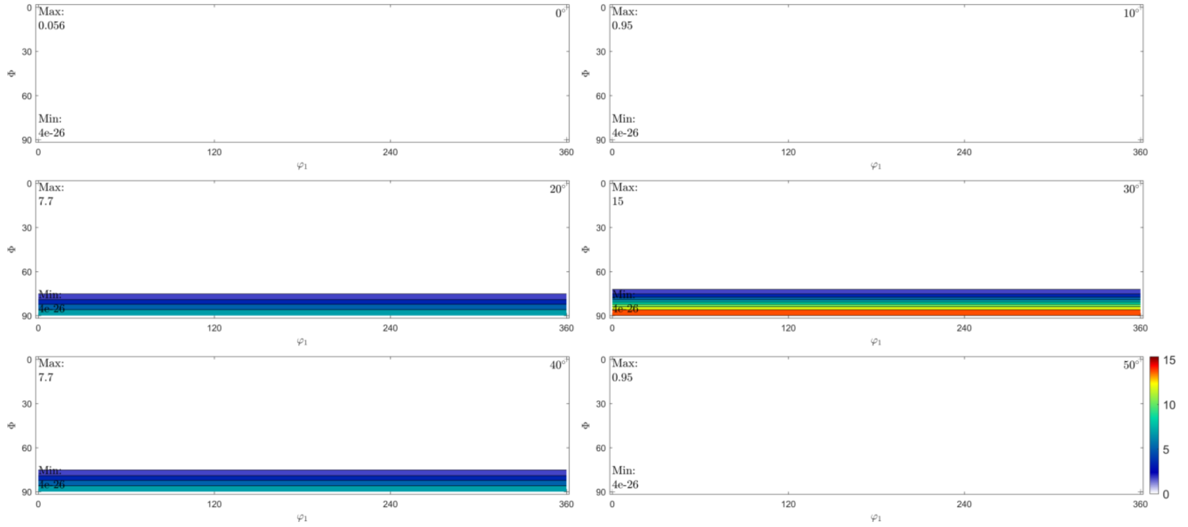




- 90°-Faser (Prismatisch)
  - <100> ‖ BN
  - ODF_{Max} = 15, bei φ_2=30°



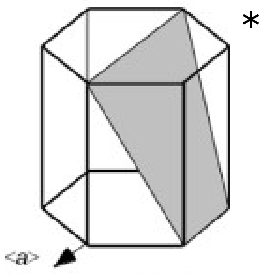




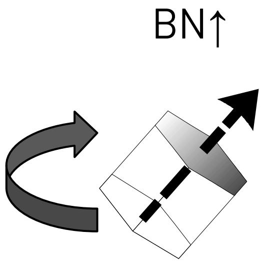
*) Luque, A. et al., W. A., *Mod. Sim. Mat. Sci. Eng.*, **2013**, *21*, 045010.

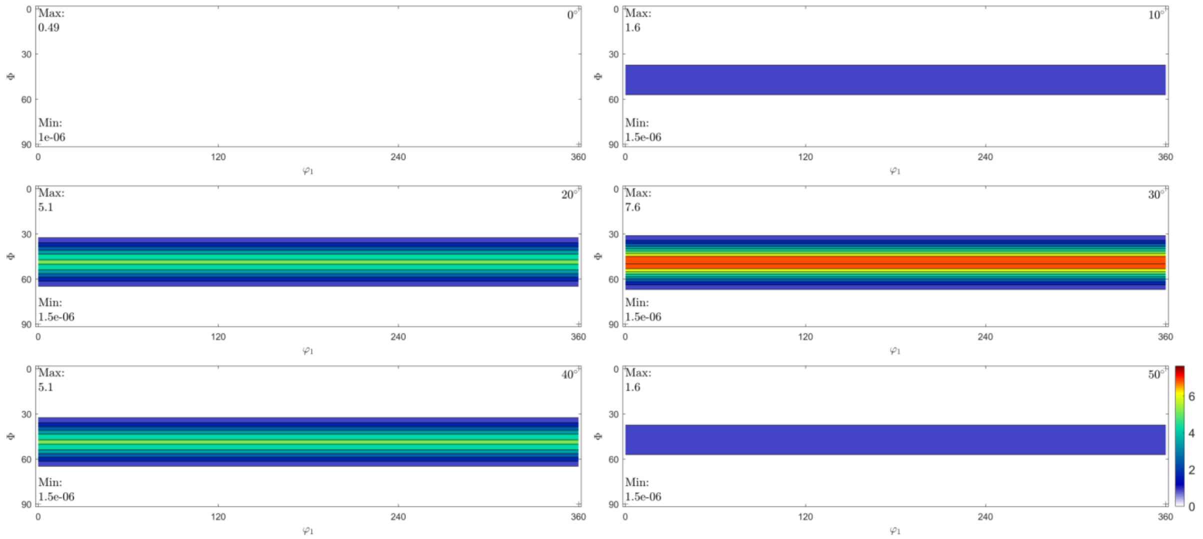
ZINK – TEXTUR
Simulierte ODFs

- 45°-Faser
  - <101> ‖ BN (Pyramidal 1)
  - ODF_{Max} = 7.6, bei φ_2=30°

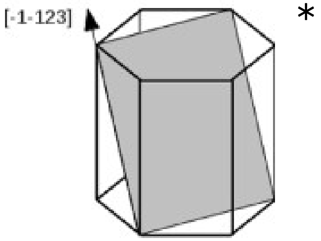


Pyramidal I

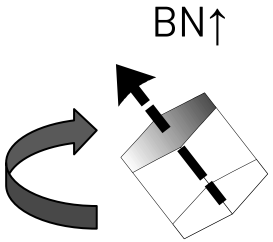


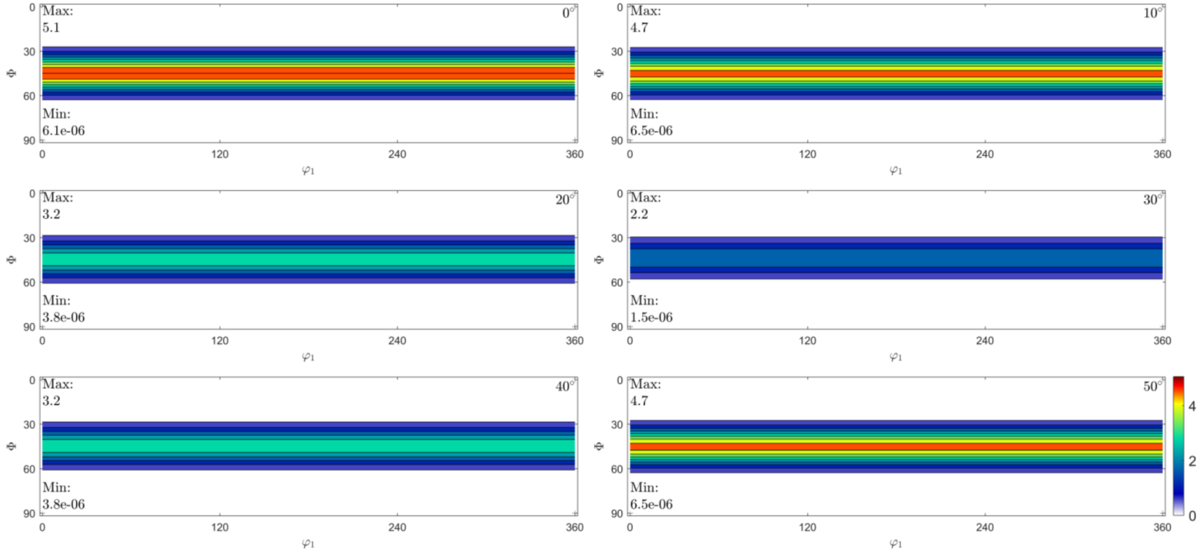


- 45°-Faser
  - <123> ‖ BN (Pyramidal 2)
  - ODF_{Max} = 5.1, bei φ_2=0°



Pyramidal II





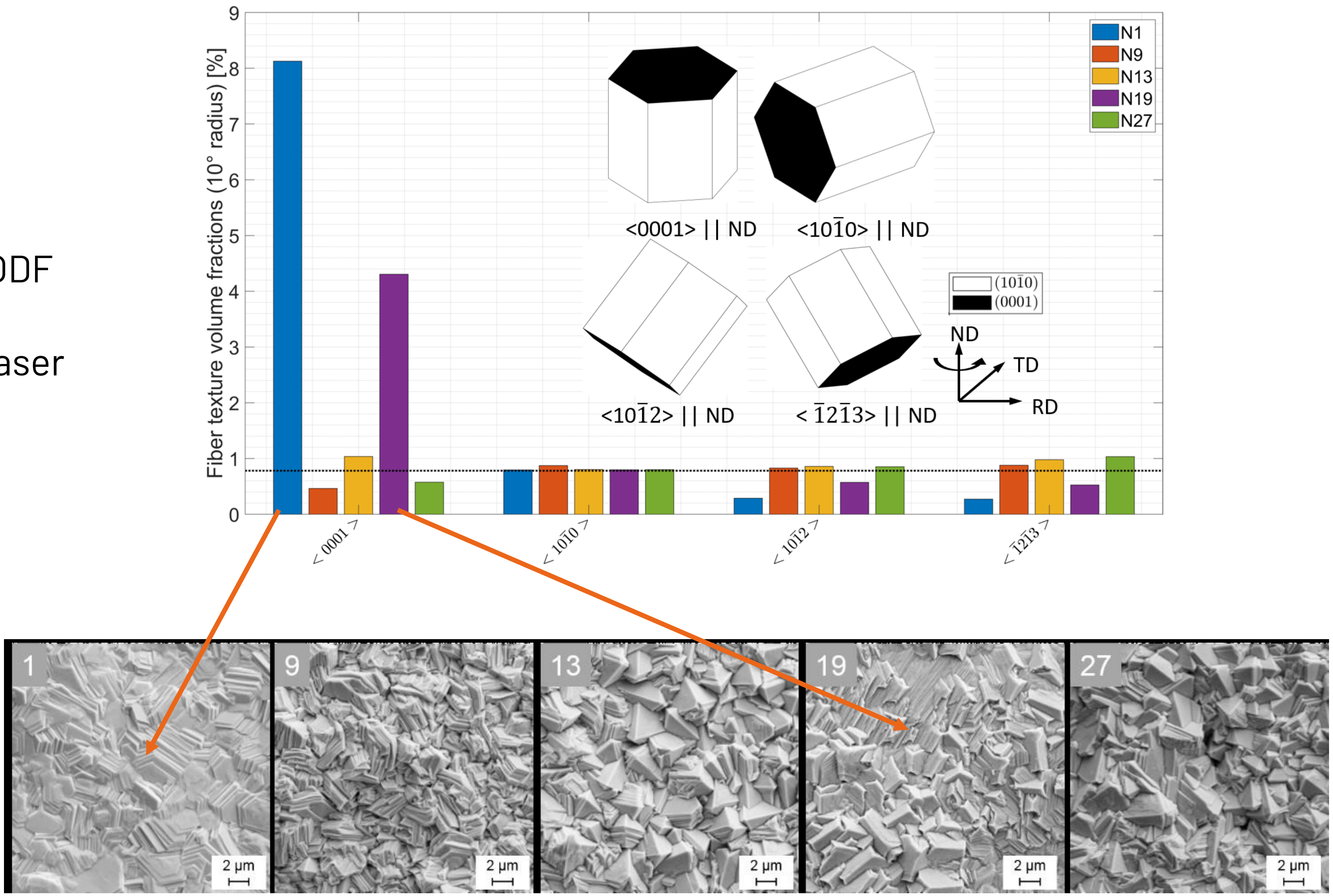
*) Luque, A. et al., W. A., *Mod. Sim. Mat. Sci. Eng.*, **2013**, *21*, 045010.

ZINK – TEXTUR

Texturfasern

- Textur-Faseranteile können aus ODF berechnet werden.
- Dabei muss die Multiplizität der Faser berücksichtigt werden:

Faser ‖ BN	Multiplizität
<0001>	2
<1010>	6
<1012>	12
<1213>	12



→ **Basal-Faser führt zu glatter Oberfläche und höherer Reflektivität**

SALZGITTER MANNESMANN FORSCHUNG
A Member of the Salzgitter Group

XRD – MESSUNG ZN-TEXTUR

Zusammenfassung

- Bei Textur-Messungen an Beschichtungen muss auf Überlagerung mit Röntgenreflexen des Substrats geachtet werden.
- Für eine korrekte Quantifizierung von Texturanteilen muss die Multiplizität von Orientierungen und Texturfasern berücksichtigt werden.
- Die Textur einer Zn-Beschichtung beeinflusst die Oberflächentopographie, sowie
    - Elastische / Plastische Eigenschaften
    - Rissanfälligkeit
    - Korrosionsbeständigkeit
    - …
- Veröffentlichung
    - Schichtdickenmessung: Eingereicht in Advances in X-Ray Analysis
    - Zn-Textur (ohne Simulationsteil): Debeaux, M.; Witte, M.; Koll, T. „Influences of electrolyte composition and temperature on energy demand and zinc structure during electro-galvanizing“, 12th Int. Conf. Zn & Zn Alloy Coated Steel Sheet, 2021, ASMET.

THANKS FOR YOUR ATTENTION!

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