PHASE FORMANTION AFTER NITRIDING OF AUSTENITIC STAINLESS STEEL BY PULSED LEII

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State of Art

Nitriding of austenitic stainless steel

hard and wear resistant surface

no compromised corrosion resistance

large field of applications: food, oil, textile, automotive ...

Phase formation

solid solution of nitrogen up to 38 at. %, expanded phase

anisotropic lattice expansion normal to the surface of up to 8.5% and 12 % for (111) and (200) oriented grains, respectively

broad expanded XRD peaks with FWHM of 2.5 – 3°

PIII vs. LEII

treatment of 3D samples in PIII

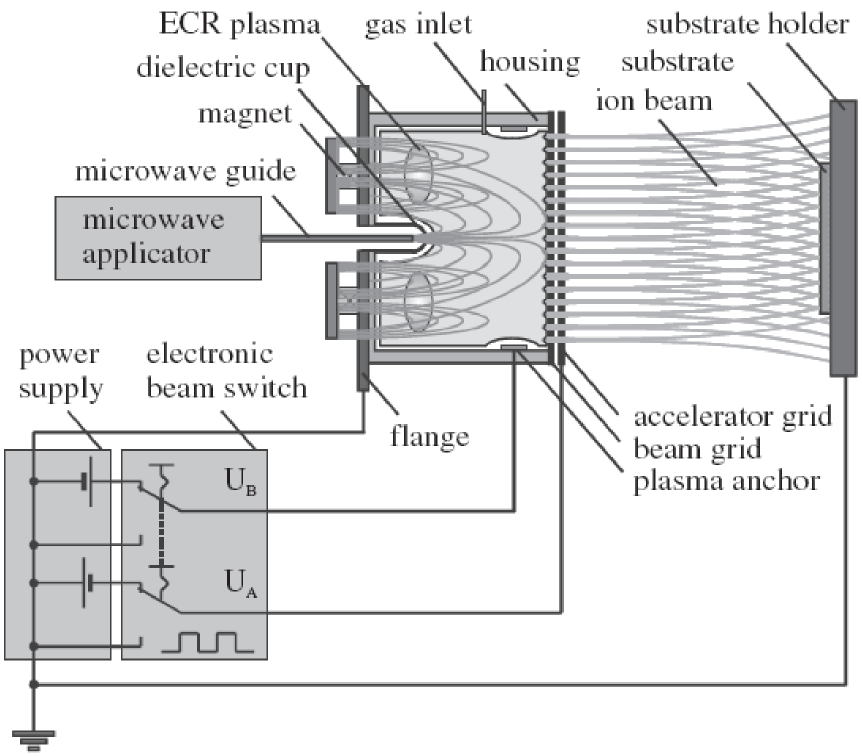
PIII: high voltage up to 20 kV, bias on substrate

LEII: low voltage < 2 kV, high current, high sputtering

experience in PIII and “d.c. LEII” for > 10 years

Idea pulsed LEII ⇒ reduced sputtering, roughness, ...
but additional heating necessary

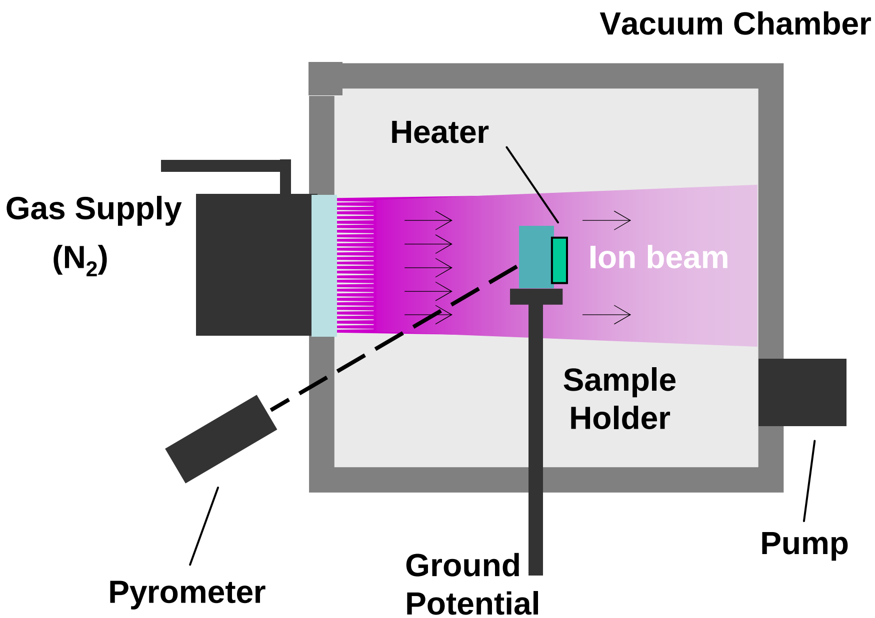
Experiment



- **Concept of electronic beam switch**: decoupling of plasma generation & ion flux at fixed extraction voltage by temporal switching electrostatic potential of ion optics
- **Beam switch parameters**:
  2 A, 2 kV, frequency 0.5 – 20 kHz, PLM 2 – 98%
- Additional **external heating** to decouple ion flux from thermal balance: fast control loop necessary
- **Phase formation depending on process?**

J. Dienelt, K. Zimmer, F. Scholze, B. Dathe, H. Neumann, Plasma Source Sci. Technol. **12** (2003) 489.

Experiment



Analysis methods:

XRD phase formation

GDOS depth elemental distribution

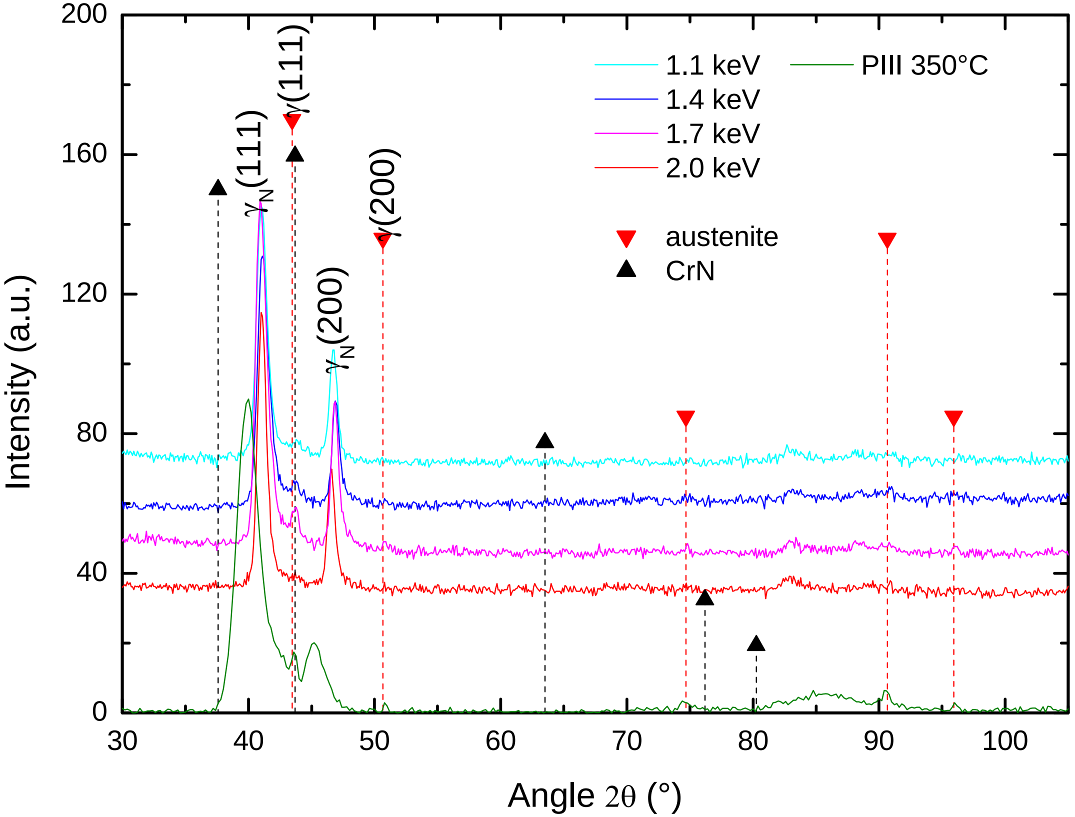
Low Energy Implantation

ECR ion source	Ø 125 mm
Plasma Excitation	2.45 GHz
MW Power	300 W
Base pressure	5×10^{-4} Pa
Working pressure	2 (6) $\times 10^{-2}$ Pa,
Beam switch	1 kHz, 30% PLM, 300 µs
Ion energy	0.8 – 2 keV
Beam switch	1 kHz, 5 – 100% PLM
Ion energy	0.8 keV
Temperature	455 °C (calibrated pyrometer)
Process time	90 min
Substrate	1.4301/304 (X5CrNi18.10)

External heating, rotation of sample holder, variation in incidence angle, ...

Phase Formation

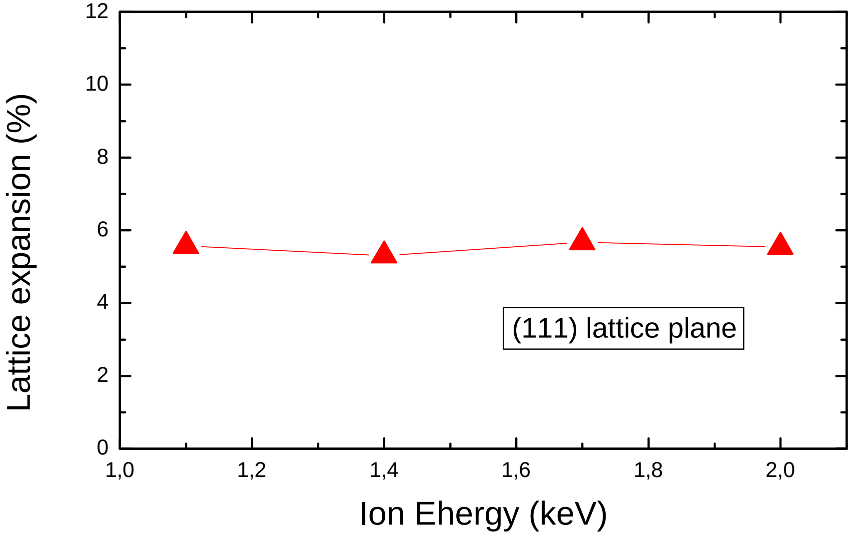
LEI, 1 kHz, 30% PLM, 455 °C, 90 min

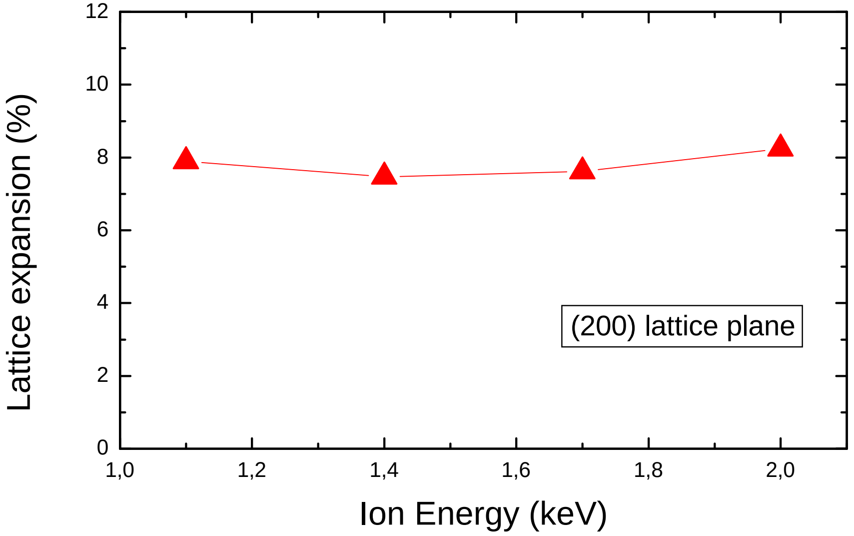


- Expanded austenite formed for all ion energies
- Similar lattice expansion, independent of ion energy
- Very narrow peaks for expanded austenite
- No formation of CrN indicating no compromised corrosion resistance
- Corrosion resistance proved by corrosion test for 24 hours at 40 °C in 3% NaCl
- Hardness ≥ 15 GPa, (excellent value)

Lattice Expansion

LEI, 1 kHz, 30% PLM, 455 °C, 90 min

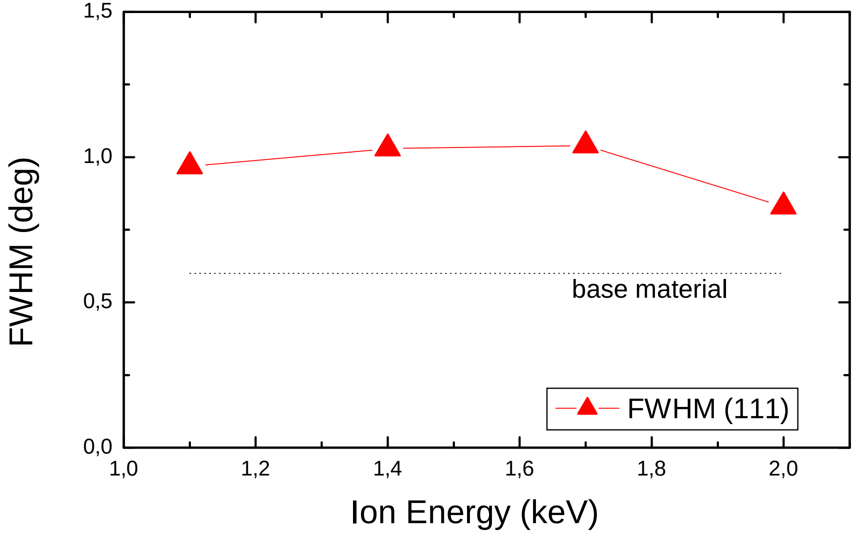


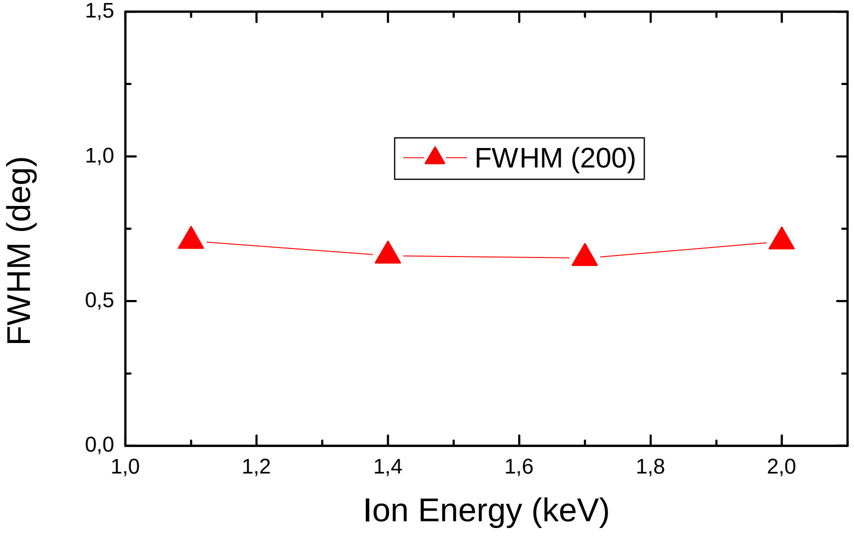


- Lattice expansion calculated from simulation of the measured XRD peaks using commercial software
- Very small variation in expansion for both (111) and (200) lattice planes
- Values of ~ 6% and ~ 8% for (111) and (200) lattice plane
- Lattice expansion independent of ion energy

“Phase Structure”

LEI, 1 kHz, 30% PLM, 455 °C, 90 min

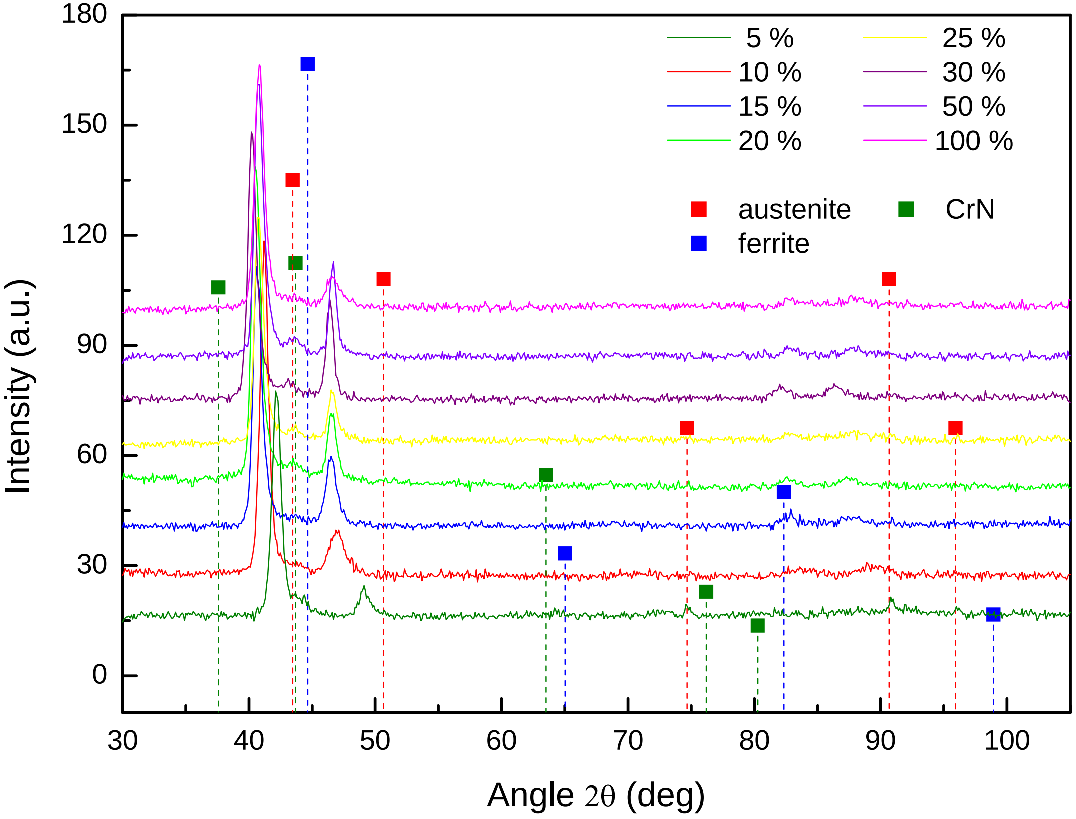




- FWHM of base material ~ 0.6°; FWHM of expanded austenite by PIII ~ 2.5°
- Very narrow peaks for expanded phase, comparable with base material
- Negligible influence of ion energy on FWHM of expanded peaks
- FWHM of expanded peaks ~ 1° and ~ 0.7° for (111) and (200) planes, respectively

Phase Formation

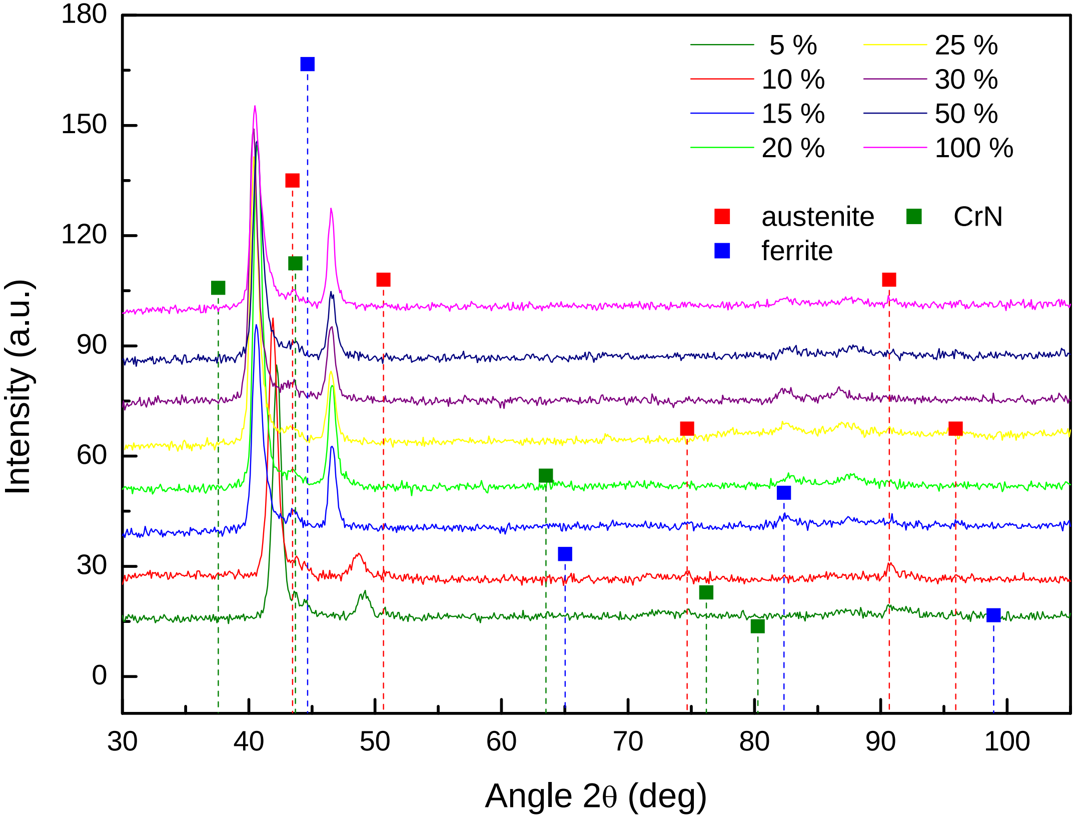
LEI, 1 kHz, 0.8 keV, 455 °C, 90 min



- Working pressure 2 × 10^{-2} Pa
- Expanded austenite formed for all PLM
- Increased lattice expansion with increasing of PLM ≤ 15%
- "Saturation" observed for PLM > 15%
- Very narrow symmetrical peaks for expanded austenite
- No formation of other phases
- Hardness ≥ 15 GPa

Phase Formation

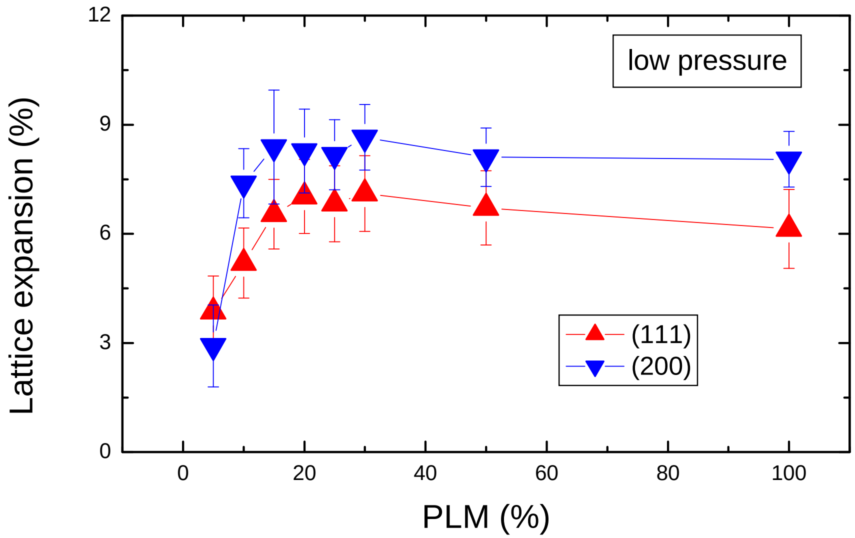
LEI, 1 kHz, 0.8 keV, 455 °C, 90 min

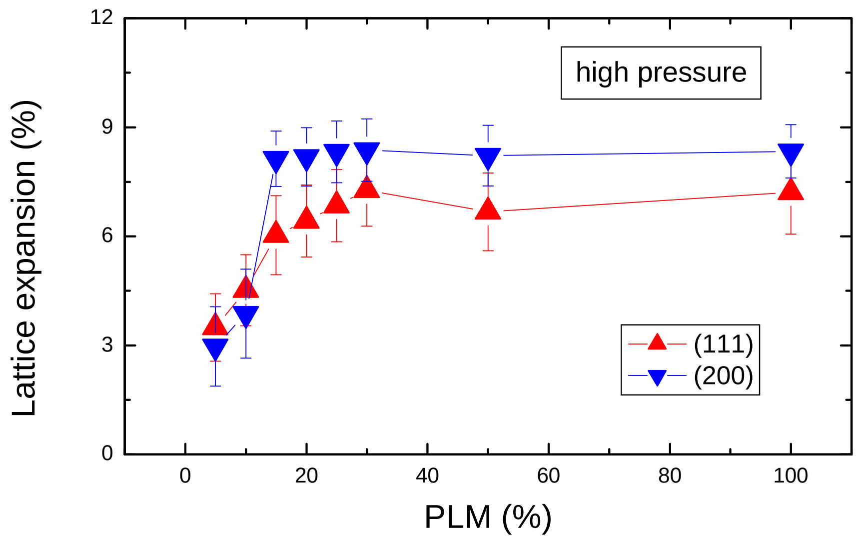


- Working pressure 6×10^{-2} Pa
- Expanded austenite formed for all PLM for higher working pressure
- Increased lattice expansion with increasing of PLM ≤ 15%
- Again, saturation observed for PLM > 15%
- Very narrow symmetrical peaks for expanded austenite
- No other phases observed
- Hardness ≥ 15 GPa

Lattice Expansion

LEI, 1 kHz, 0.8 keV, 455 °C, 90 min

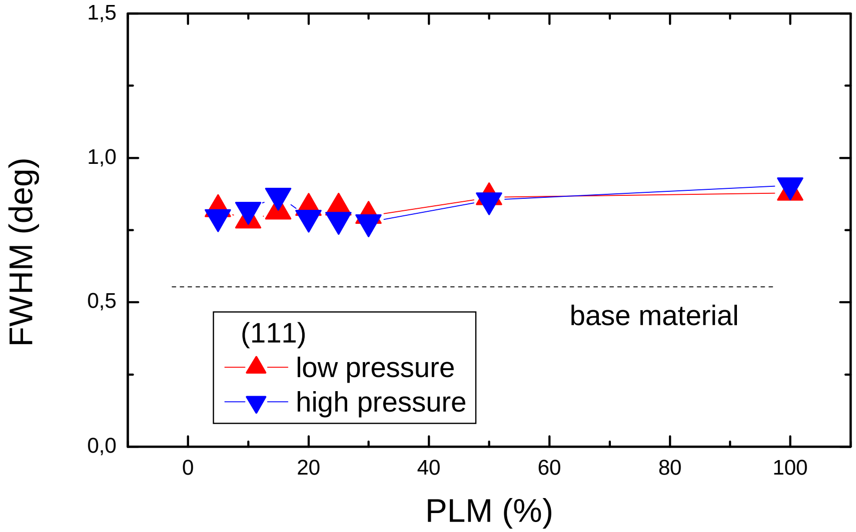


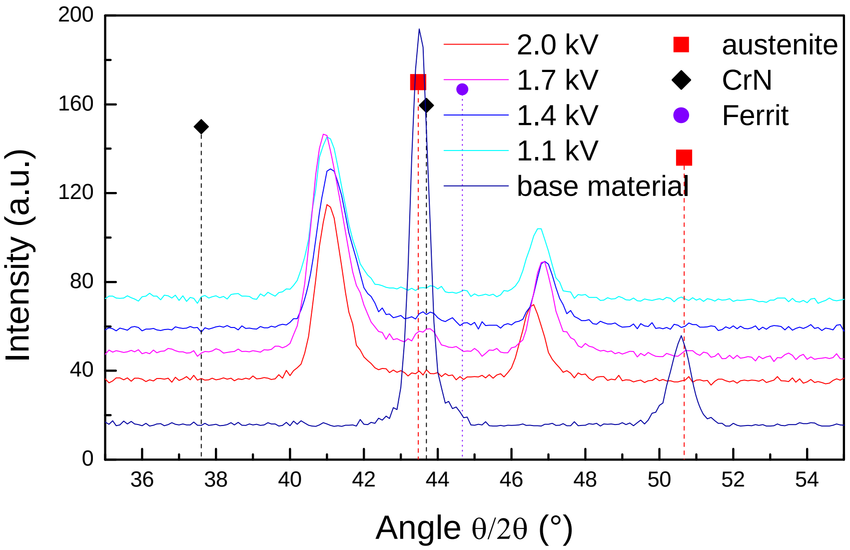


- Increased lattice expansion with PLM up to 15% for both working pressures
- Similar behaviour for (111) and (200) lattice plane
- Saturation observed for PLM > 15% for both working pressure
- No influence of working pressure on the lattice expansion

"Phase Structure"

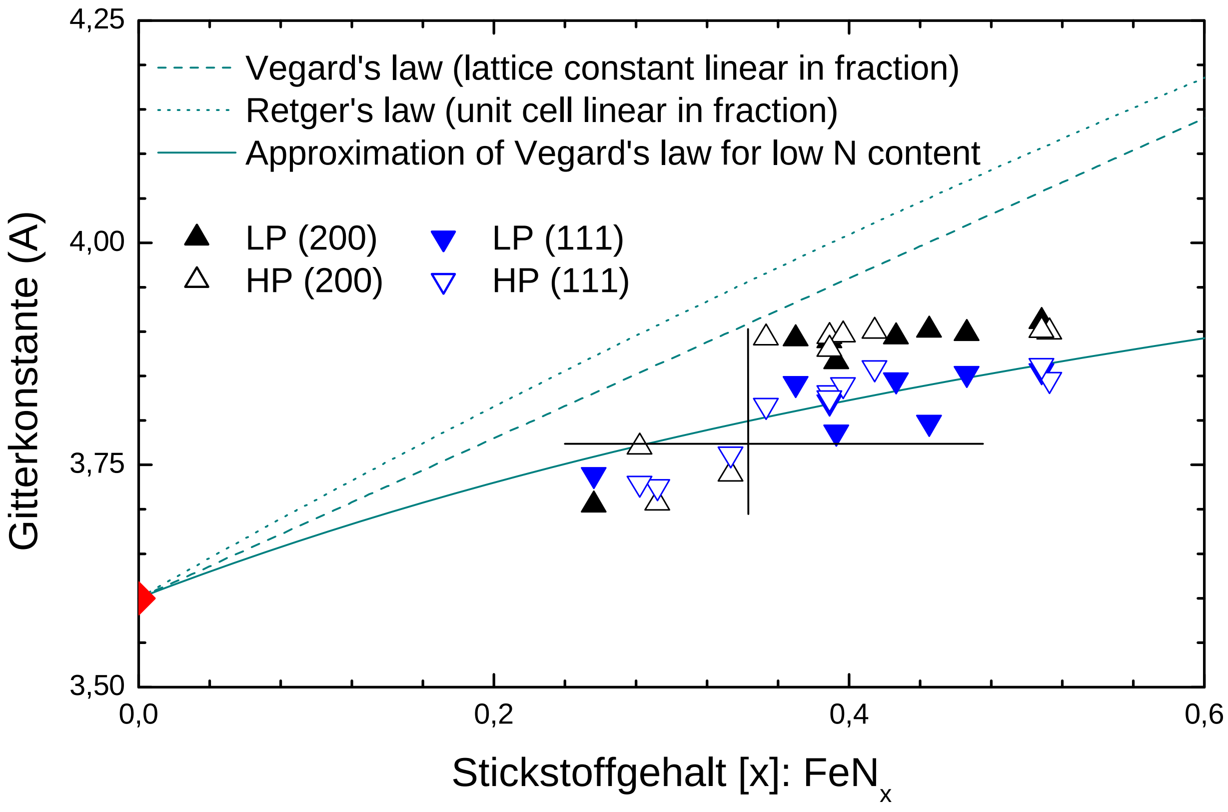
LEI, 1 kHz, 0.8 keV, 455 °C, 90 min





- Very narrow expanded peaks with FWHM of about 0.9° for (111) plane
- Negligible influence of PLM on the FWHM for (111) and (200) lattice plane
- Most probably influence of the additional to the beam heating
- No influence of working pressure on the values of FWHM

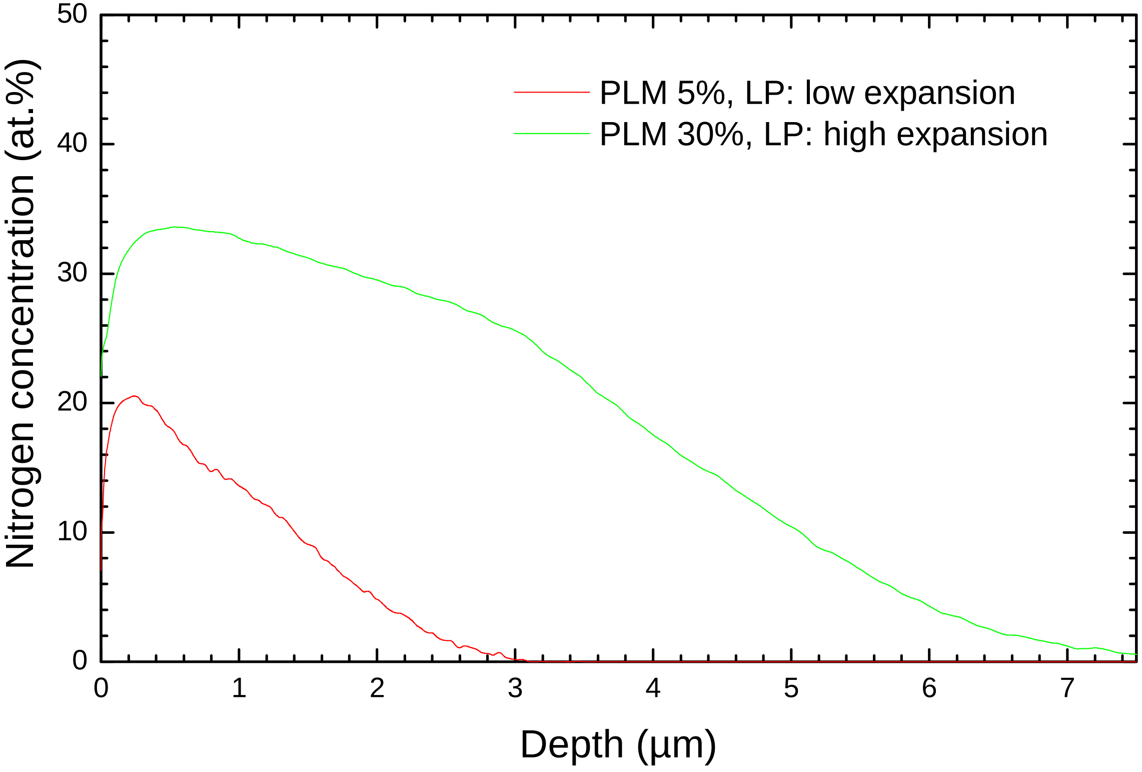
Expansion vs. Concentration



- Nitrogen concentration measured by GDOS
- No direct correlations observed for all nitrided samples
- Nitrogen amount in expanded phase should not be calculated from the lattice expansion
- Independent methods as GDOS or RBS are required for determining the nitrogen content in nitrided austenitic steel

Depth Profiles

LEI, 1 kHz, 0.8 keV, 455 °C, 90 min



- Nitrogen depth profiles obtained from GDOS measurements
- Nearly typical *erfc*-diffusion profile for PLM 5%: single curvature, perhaps hint of kink
- Plateau followed by tail for PLM 30%: turning point in curve near 3.25 µm
- Additionally, good corrosion resistance only observed for PLM 30%.

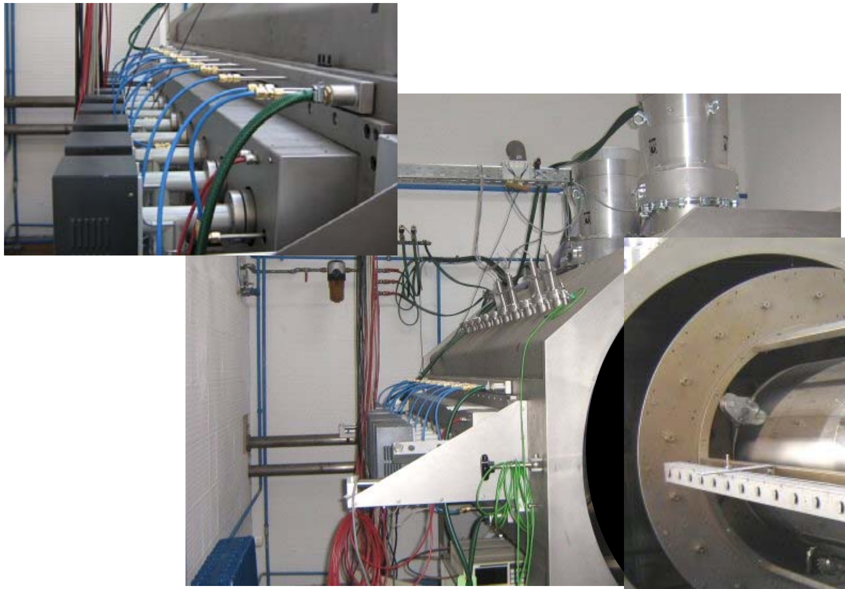
Conclusions

- No influence of ion energy or PLM on the phase formation during nitriding of austenitic stainless steel
- Use of Vegard's low to determine nitrogen content from lattice expansion can lead to wrong results: independent concentration/expansion values not rarely found in literature
- Formation of expanded phase not influenced by pulsed mode: no difference between pulsed low energy implantation, d.c. low energy implantation and PIII $\Rightarrow$ results of pulsed LEI identical to alternatives
  preferable method for industrial applications
- However: reduced ion bombardment + additional heating has other consequences (PLM 100% is also with heating!)
  - o better surface quality, less sputtering, thicker layers, high hardness
  - o threshold in nitrogen flux necessary to obtain "typical depth profiles"
  - o less peak broadening in XRD

  $\Rightarrow$ influence on stress distribution?
  influence on stress corrosion cracking in modified surfaces?
  influence on Cr diffusion?

Transfer to Industry

LEI – Chamber



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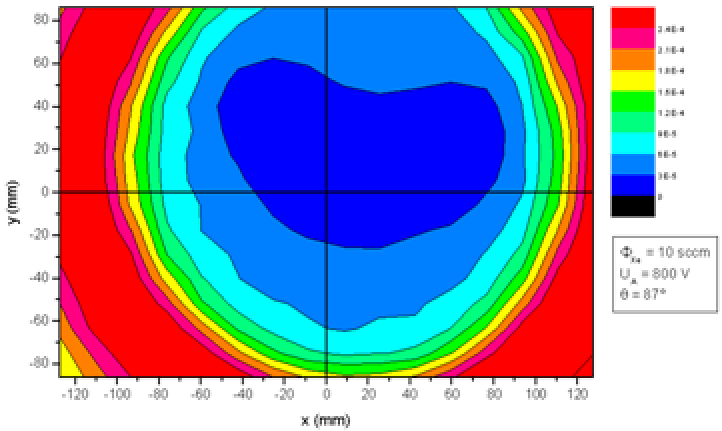
Mechanical and electrical parameter

Faraday Cup Array
probe diameter : 3,2 mm
number of probes : 256 (16x16)
distance between two probes : 11 mm (vertical),
19 mm (horizontal)
measurement area : 200 x 300 mm^2
sampling rate : ~10 measurements per second

graphic program



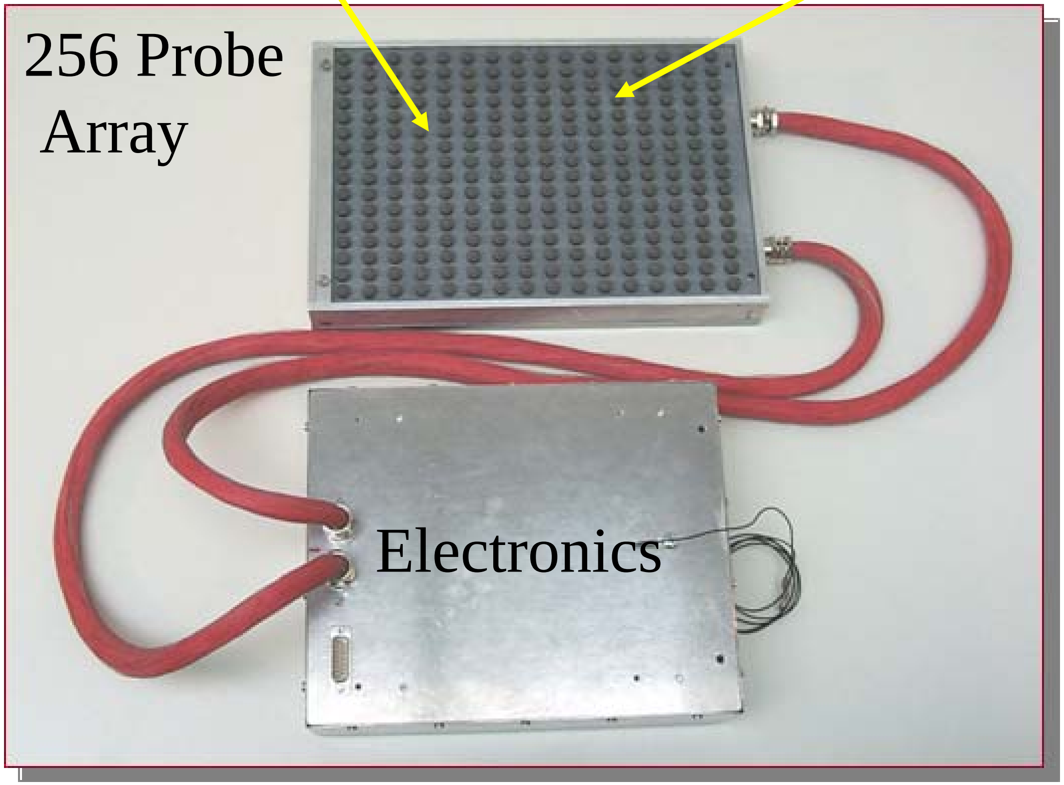
array measurements allow a short beam profile

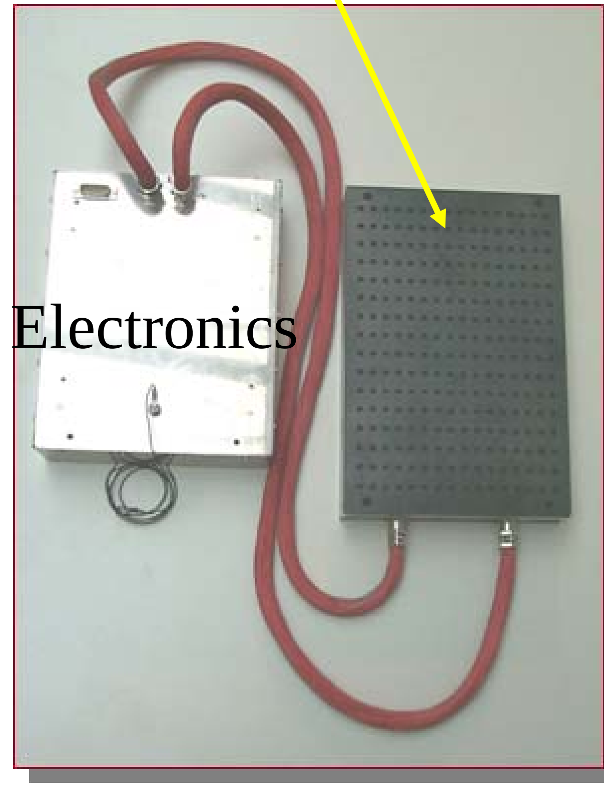
“snap shot” and are useful for determination

of the influence of electric and gas parameter on

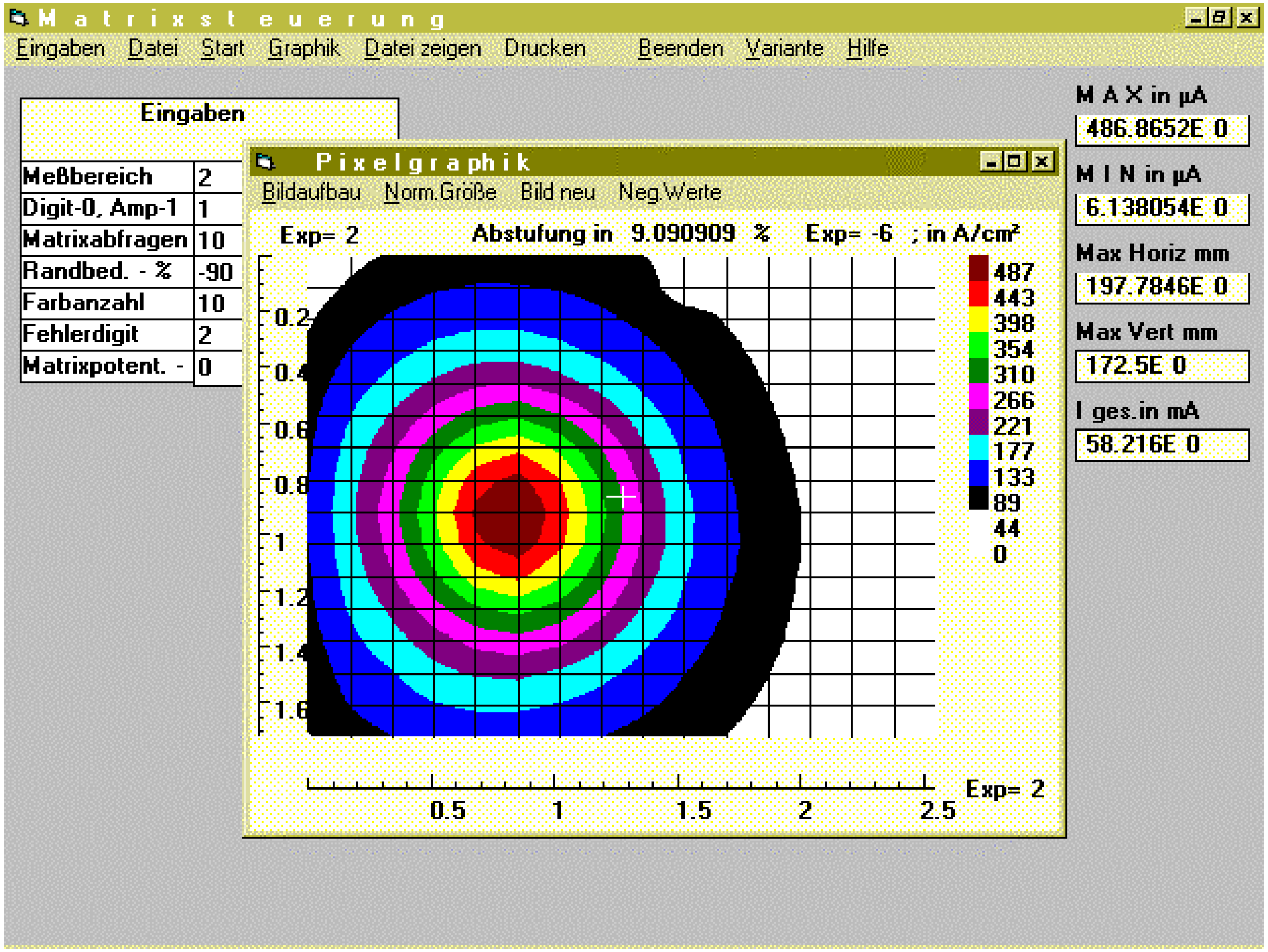
broad beam profile of ion sources

256 Probe Faraday Cup Array





Screenshot of the Special Software



Phase Formation

Different treatments with and without external heating