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Optical emission spectra of metallic nitrides in the Grimm-type glow discharge

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Goals of this paper:

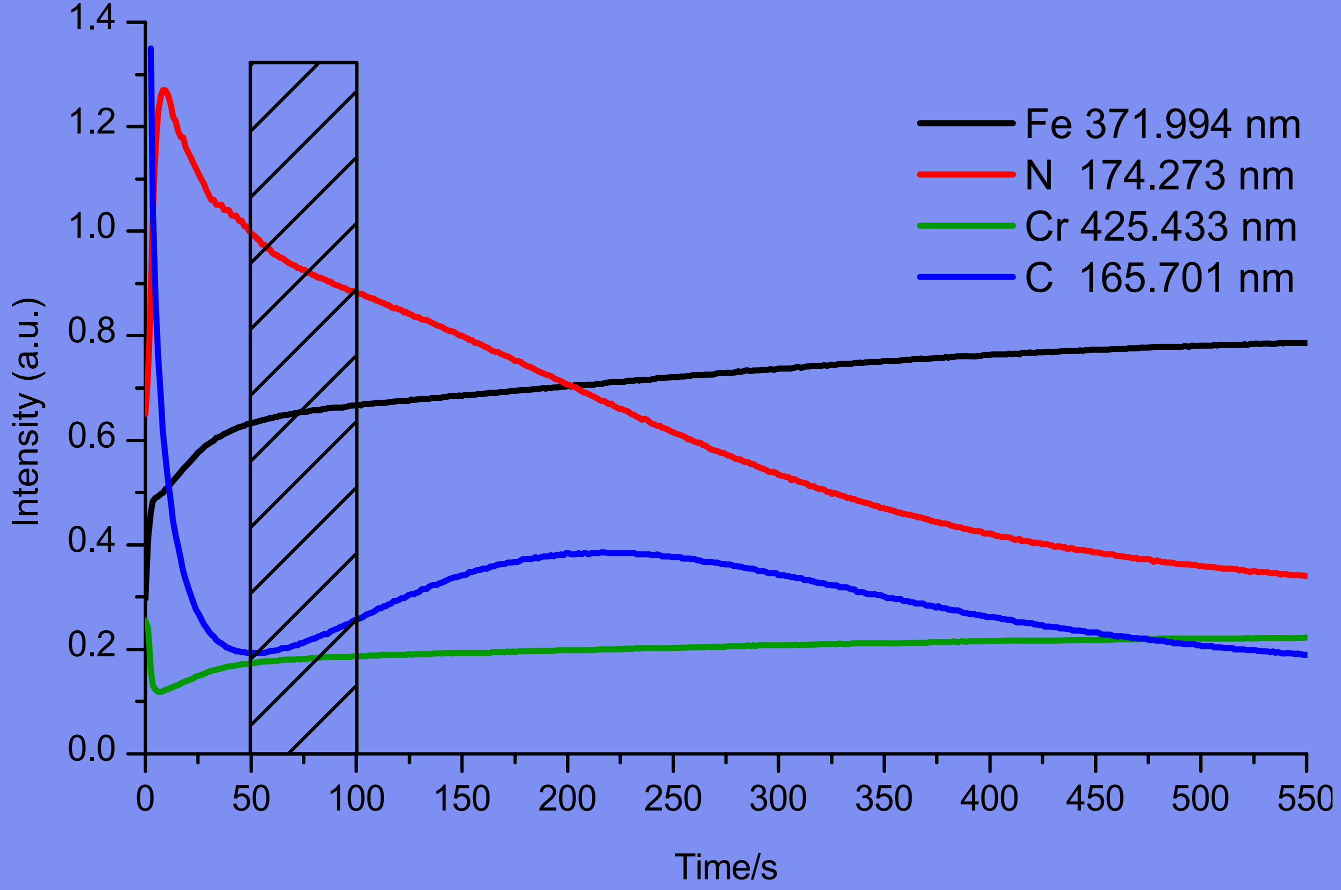
- to compare optical emission spectra of metallic nitrides with corresponding metals and to test validity of matrix independent emission yield concept
- to compare optical emission spectra of the discharge when:
  - nitrogen enters the discharge from a metallic nitride
  - nitrogen is introduced into the discharge as a trace molecular gas

Experimental – metallic nitrides

- commercial instrument LECO GDS500A with a Grimm-type glow discharge sources, 4 mm diameter anode tube
- spectrometer equipped with CCD detector arrays, wavelength range from 165 to 460 nm and spectral resolution of 70 pm (310–460 nm), resp. 85 pm (165–310 nm)
- spectra of metallic nitrides – nitrided steel, CrN, TiN and ZrN (stoichiometry checked with RBS) – compared with spectra of corresponding metals – steel, Cr, Ti and Zr
- constant dc voltage (700 V) and constant current (20 mA)

Experimental – metallic nitrides

Qualitative depth profile of the nitrided steel sample

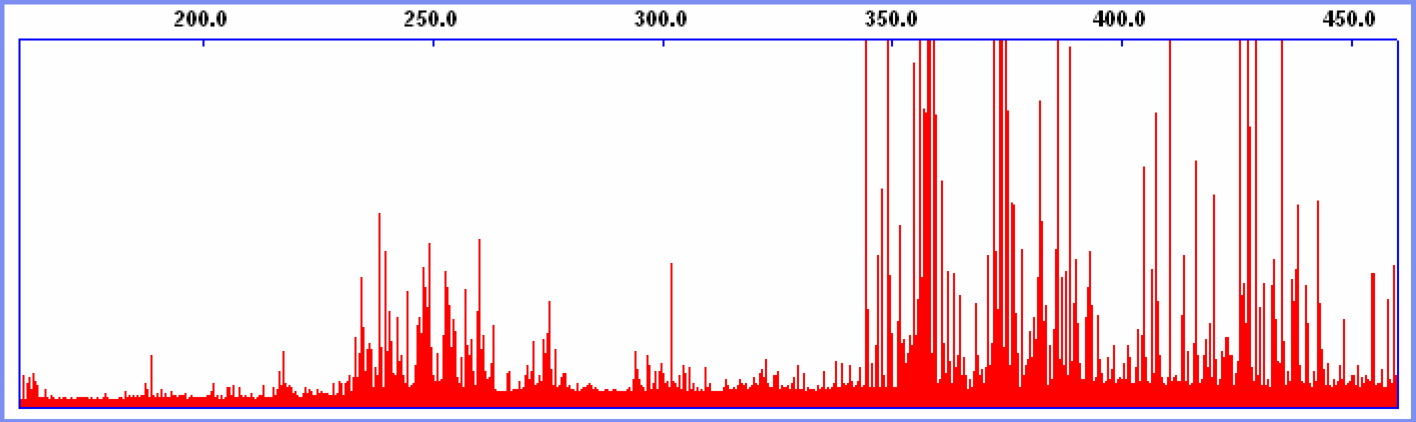


Experimental – Ar/N_2 discharges

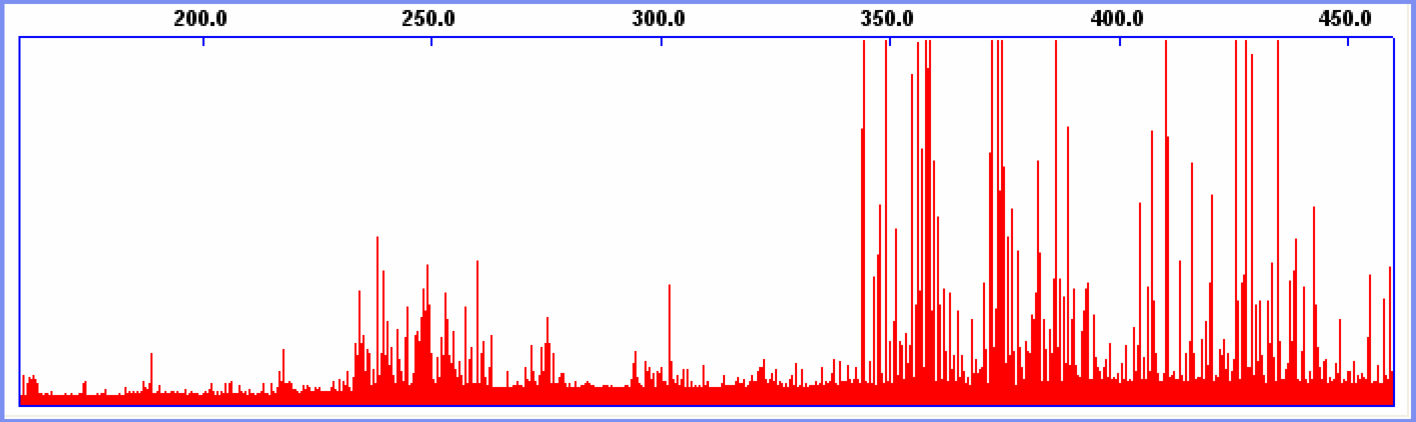
- Grimm-type glow discharge sources, 8 mm diameter anode tube
- Fourier Transform Spectrometer with PMT detection, wide wavelength range (135–900 nm) and high resolution (e.g. 0.85 pm at 300 nm)
- Fe and Ti samples sputtered in the glow discharge running in pure Ar and Ar with small amounts of N_2 (0–2 % vol./vol.)
- constant dc voltage (700 V) and current (40 mA)

Results – metallic nitrides

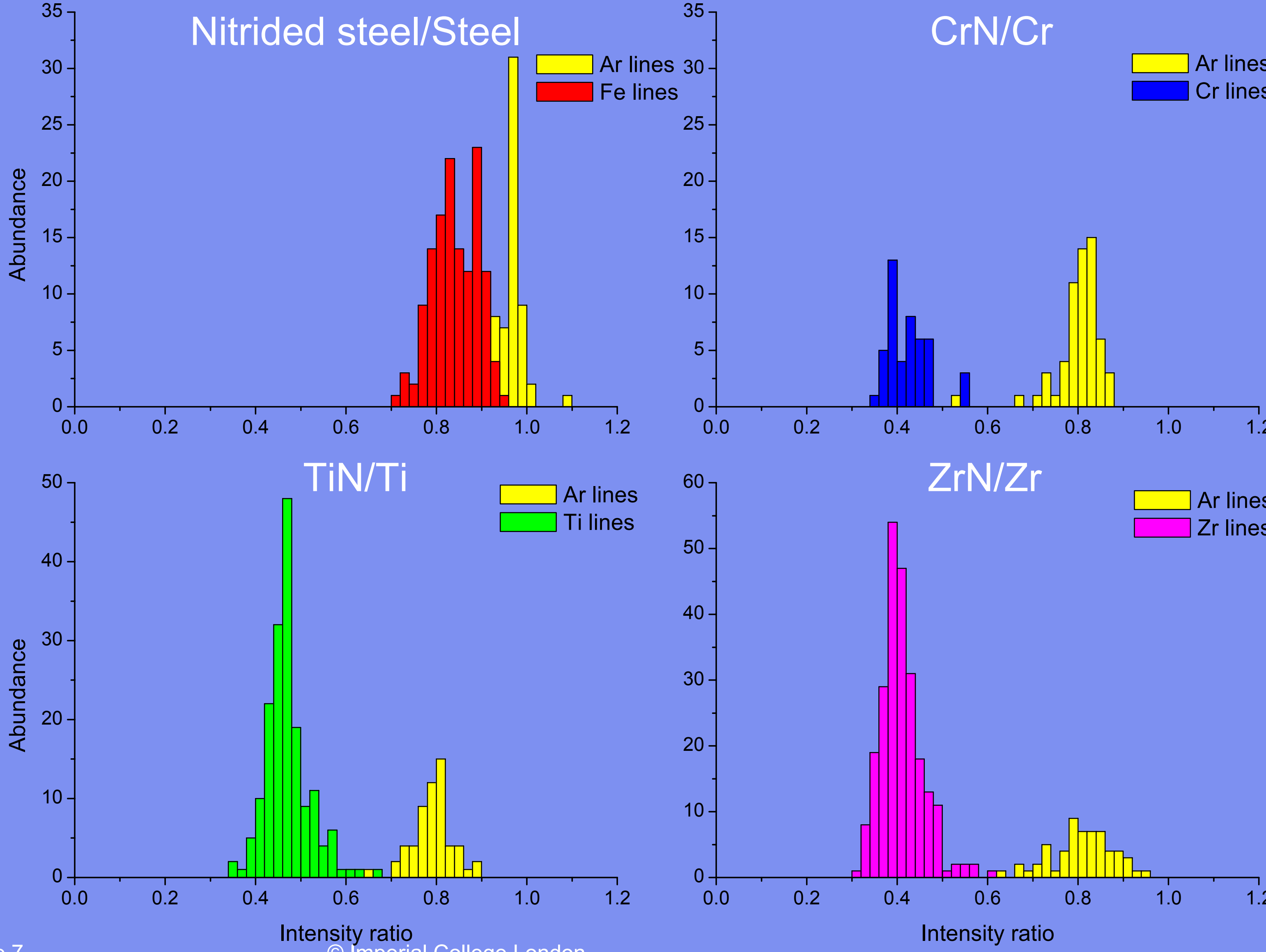
Spectrum of a steel sample (DIN X38-CrMoV51)



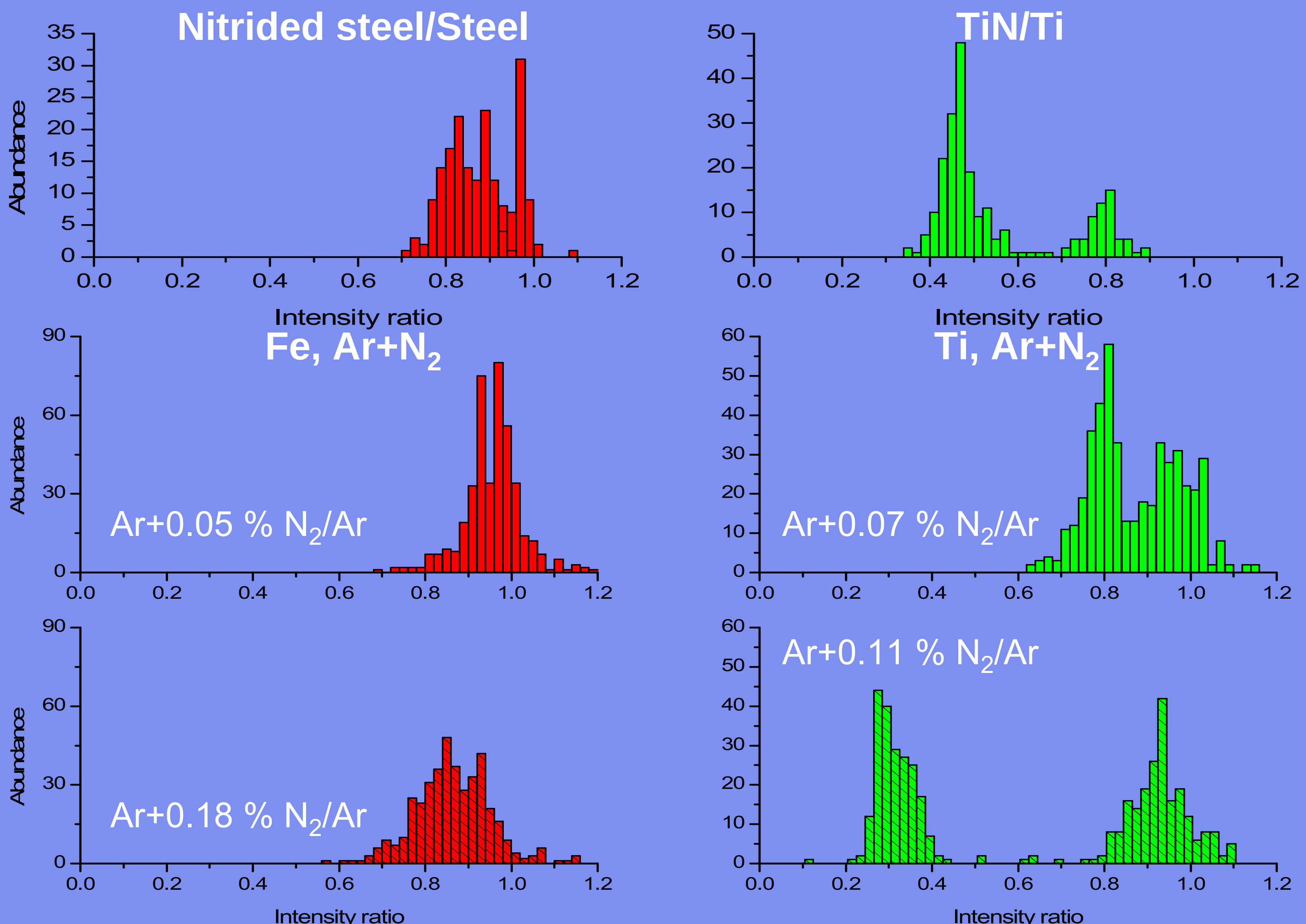
Spectrum of a ***nitrided*** steel sample (DIN X38-CrMoV51)



Results – metallic nitrides



Results – metallic nitrides vs. Ar/N_2 discharges



Results – argon lines

Intensity of an emission line of a wavelength λ:

$$I_{\lambda} \propto n_2 A_{21} \frac{h\lambda}{c}$$

↓

Plasma gas emission line:

$$I_{Ar,\lambda} \propto p \cdot f_{exc}(\lambda, p) \cdot A_{21} \frac{hc}{\lambda}$$

↓

Intensity ratio:

$$\frac{I_{Ar,\lambda}^{MN}}{I_{Ar,\lambda}^{M}} \propto \frac{p_{MN}}{p_M} \cdot \frac{f_{exc}^{MN}(\lambda, p_{MN})}{f_{exc}^{M}(\lambda, p_M)}$$

Results – argon lines

$$\frac{I_{Ar,\lambda}^{MN}}{I_{Ar,\lambda}^{M}} \propto \frac{p_{MN}}{p_M} \cdot \frac{f_{exc}^{MN}(\lambda, p_{MN})}{f_{exc}^{M}(\lambda, p_M)}$$

Comparison of average argon intensity ratios with gas pressure ratios:

Metallic nitrides:

Samples	Intensity ratios of argon emission lines			Gas pressure ratio p_{MN}/p_M
	Mean	STD	Number	
Nitrided steel/steel	**0.96**	0.03	60	**1.04**
CrN/Cr	**0.80**	0.05	60	**1.05**
TiN/Ti	**0.78**	0.05	60	**1.19**
ZrN/Zr	**0.80**	0.07	60	**1.04**

$Ar+N_2$ mixtures:

	% N_2 vol./vol.	Intensity ratios of argon emission lines			Pressure ratio
		Mean	STD	Number	
Fe	0.05	**0.97**	0.05	60	**1.00**
	0.18	**0.92**	0.18	60	**1.02**
Ti	0.07	**0.98**	0.06	60	**1.06**
	0.11	**0.92**	0.12	60	**1.15**

Results – sample metal lines

Intensity of an emission line of a wavelength λ:

$$I_\lambda \propto n_2 A_{21} \frac{h\lambda}{c}$$

↓

Sample emission line:

$$I_{E,\lambda} = R_{E,\lambda} c_{E,M} q_M$$

↓

Intensity ratio:

$$\frac{I^{MN}_{E,\lambda}}{I^{M}_{E,\lambda}} = \frac{R^{MN}_{E,\lambda}}{R^{M}_{E,\lambda}} \cdot \frac{c_{E,MN} q_{MN}}{c_{E,M} q_M}$$

Results – sample metal lines (metallic nitrides)

$$\frac{I_{E,\lambda}^{MN}}{I_{E,\lambda}^{M}} = \frac{R_{E,\lambda}^{MN}}{R_{E,\lambda}^{M}} \cdot \frac{c_{E,MN}\, q_{MN}}{c_{E,M}\, q_{M}}$$

For Matrix Independent Emission Yield:

$$R_{E,\lambda}^{MN} = R_{E,\lambda}^{M} \quad \Rightarrow \quad \frac{I_{E,\lambda}^{MN}}{I_{E,\lambda}^{M}} = \frac{c_{E,MN}\, q_{MN}}{c_{E,M}\, q_{M}}$$

Average intensity ratio vs. flux ratio

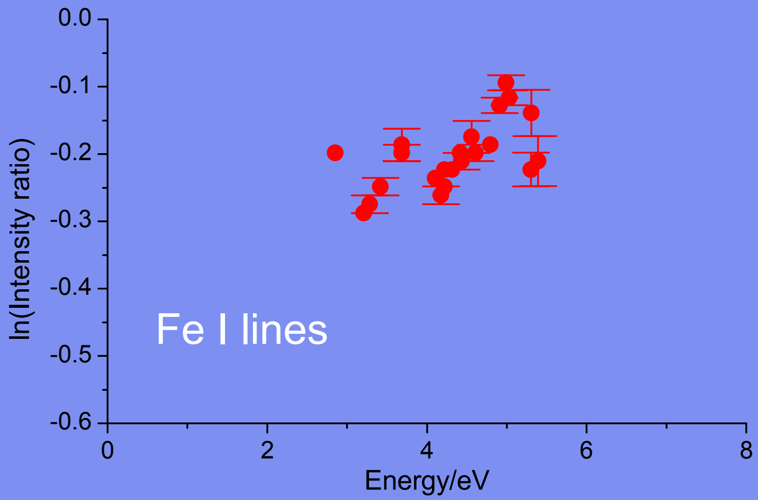
	Intensity ratio	Min	Max	STD	No. lines	Flux ratio	STD
Nitrided steel/steel	**0.84**	0.71	0.95	0.05	134	---	---
CrN/Cr	**0.42**	0.35	0.55	0.05	46	**0.39**	0.05
TiN/Ti	**0.47**	0.34	0.66	0.05	173	**0.49**	0.11
ZrN/Zr	**0.41**	0.31	0.61	0.05	239	**0.43**	0.09

Results – sample metal lines (metallic nitrides)

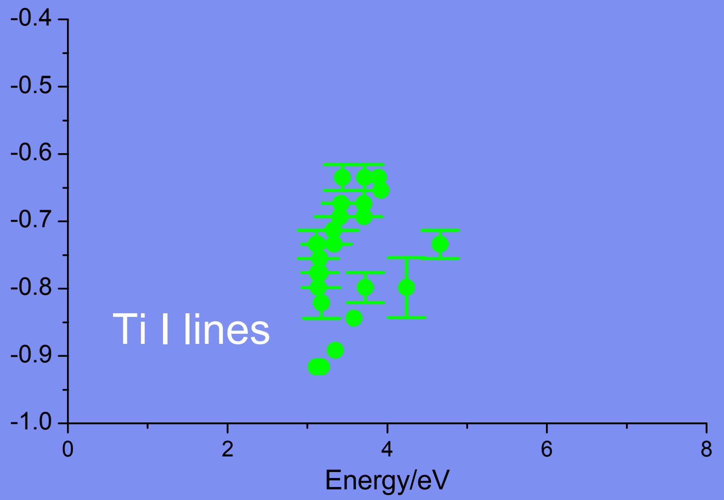
For Matrix Independent Emission Yield:

$$R_{E,\lambda}^{MN} = R_{E,\lambda}^{M} \quad \Rightarrow \quad \frac{I_{E,\lambda}^{MN}}{I_{E,\lambda}^{M}} = \frac{c_{E,MN} q_{MN}}{c_{E,M} q_{M}} \neq \mathrm{f}(\lambda)$$

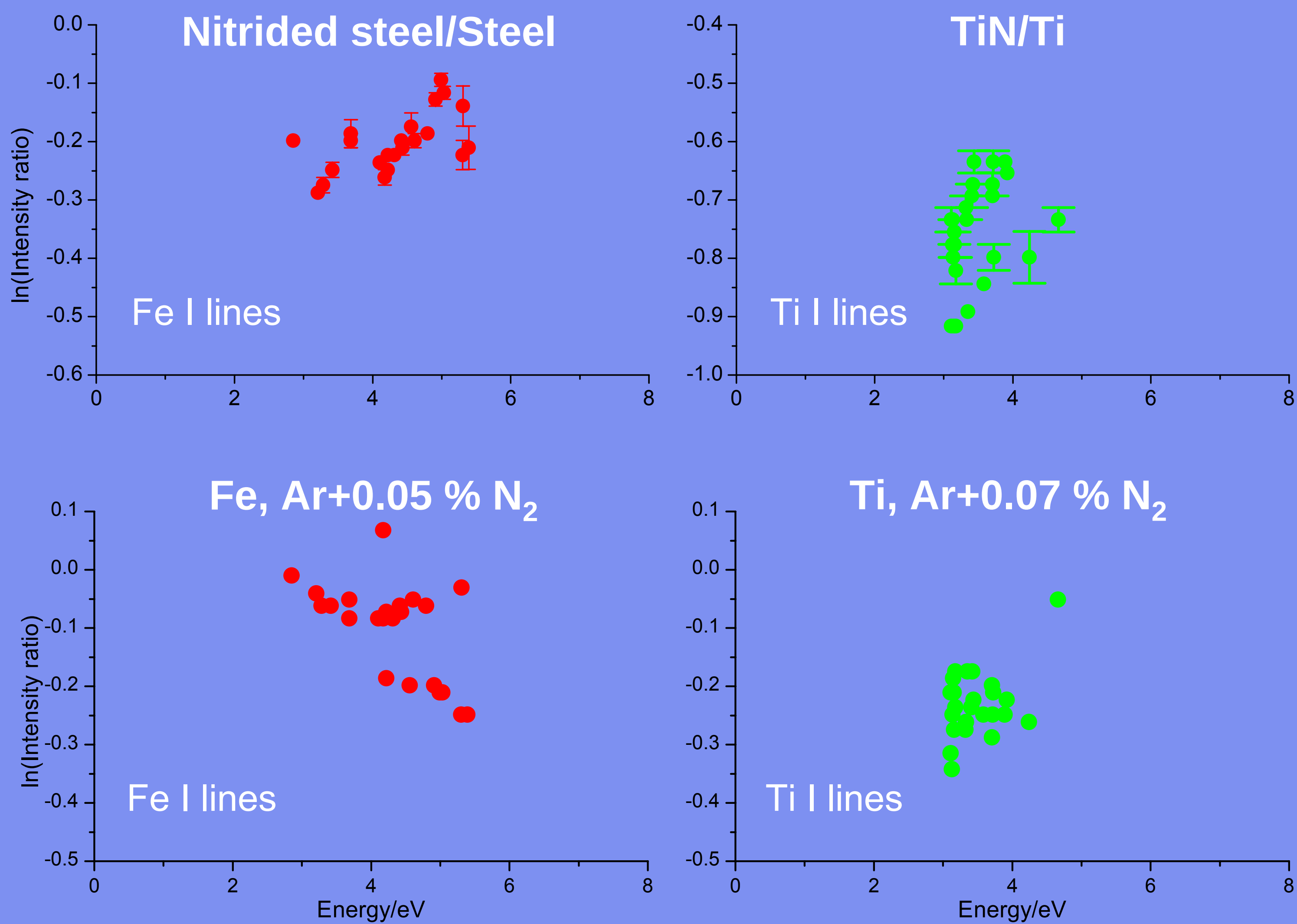
Nitrided steel/Steel



TiN/Ti



Results – sample lines (metallic nitrides vs. Ar/N_2 discharges)

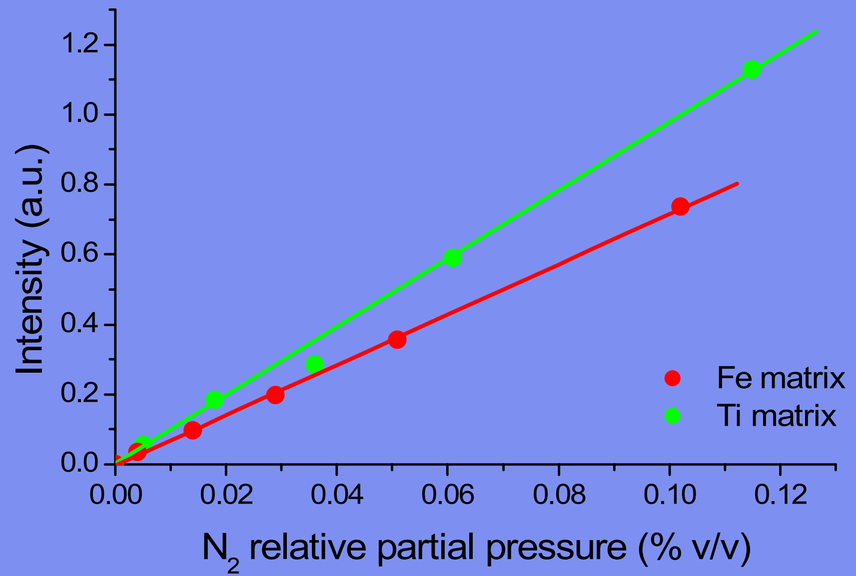


Results – nitrogen lines (metallic nitrides vs. Ar/N_2 discharges)

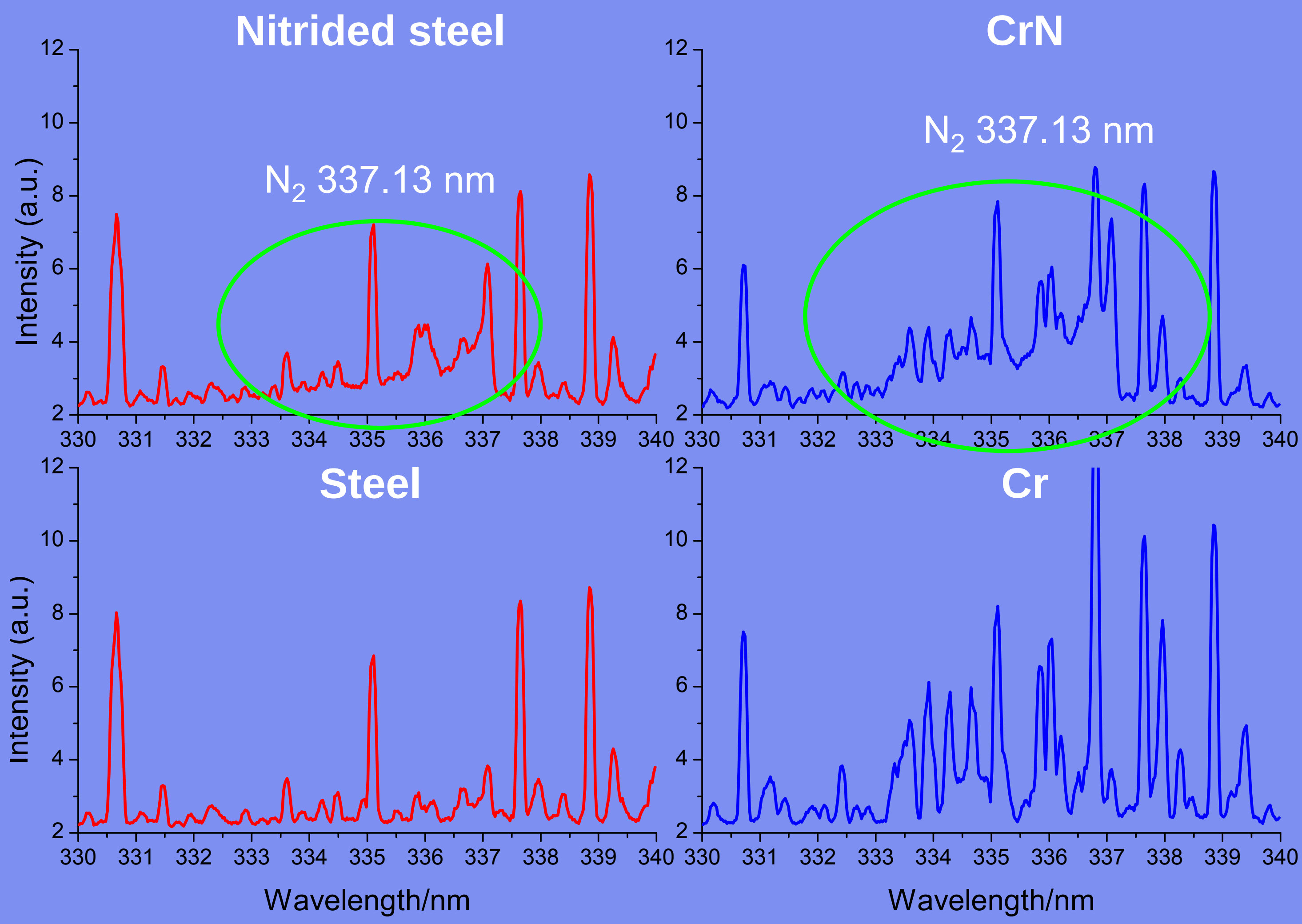
Emission yields for nitrogen atomic lines:

	$R_{N\ I\ 174.273}$	STD	$R_{N\ I\ 174.525}$	STD
Nitrided steel	**---**	---	**---**	---
CrN	**3.9**	0.4	**1.8**	0.2
TiN	**4.1**	0.9	**1.7**	0.4
ZrN	**3.5**	0.5	**1.6**	0.2

Intensity of N I 174.525 nm vs. N_2 concentration in Ar+N_2:



Results – nitrogen molecular bands (metallic nitrides)

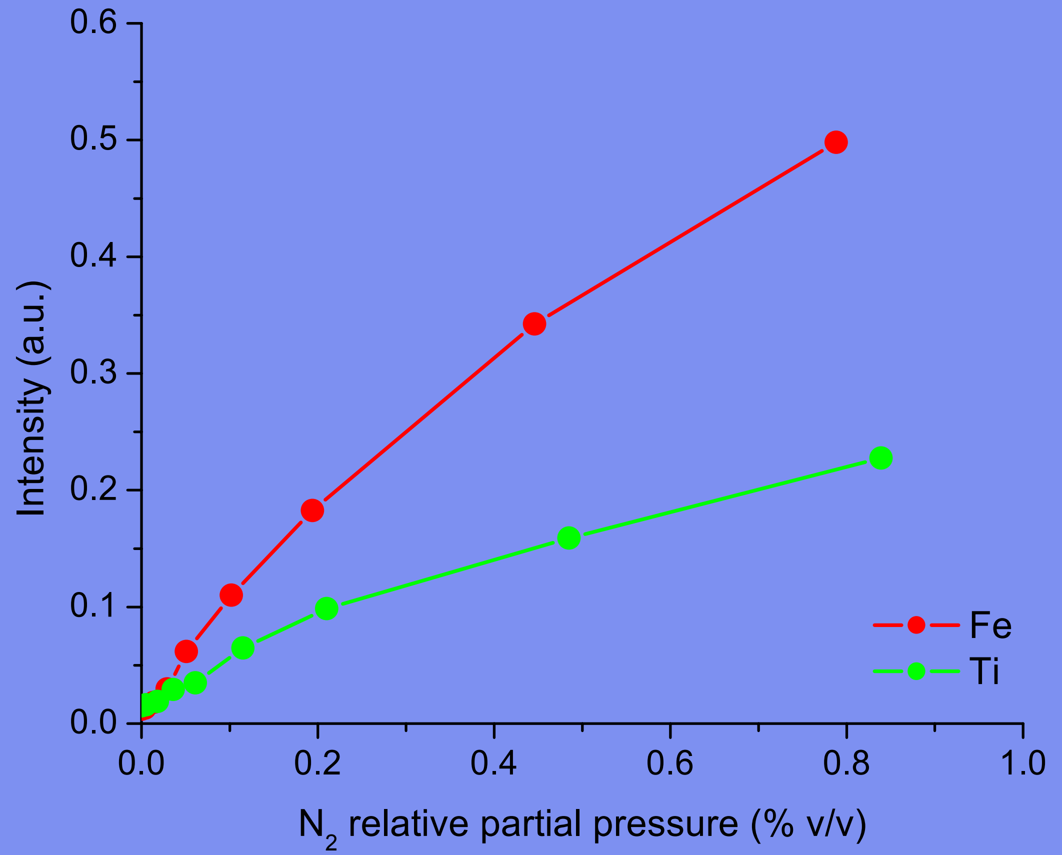


$C^3\Pi_u – B^3\Pi_g$ (0,0)

	ΔG_{300}/kJmol^{-1}
Fe_4N	+4.2
CrN	-96.7
TiN	-308.1
ZrN	-336.2

Results – nitrogen molecular bands (Ar/N_2 discharges)

Intensity of N_2 337.13 nm molecular band vs. N_2 concentration in Ar:



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