Contribution to the analysis of the corrosion process of commercial steels and newly developed laboratory alloys under simulated incineration conditions

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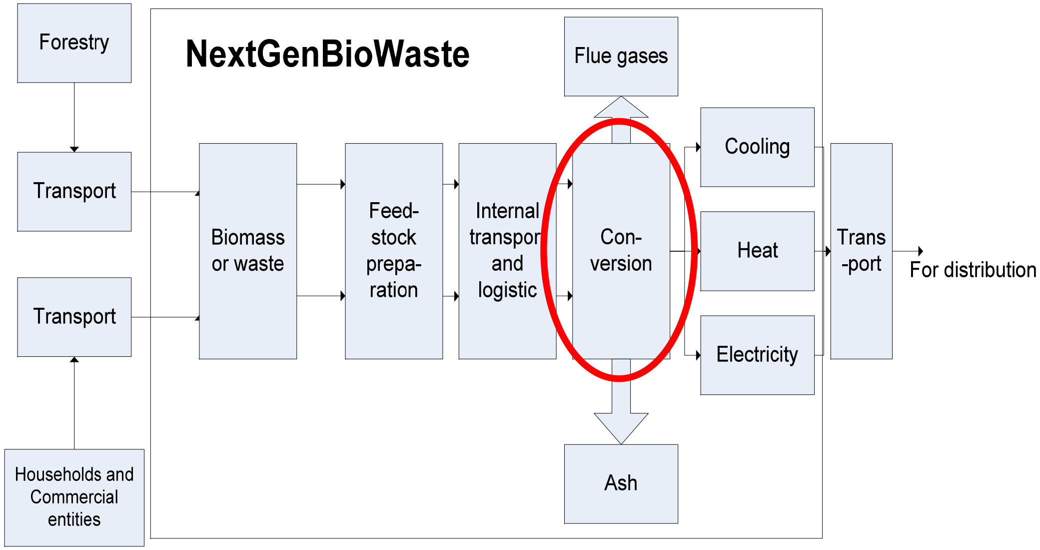
SP2: Conversion technologies

NGBW covers the supply chain:

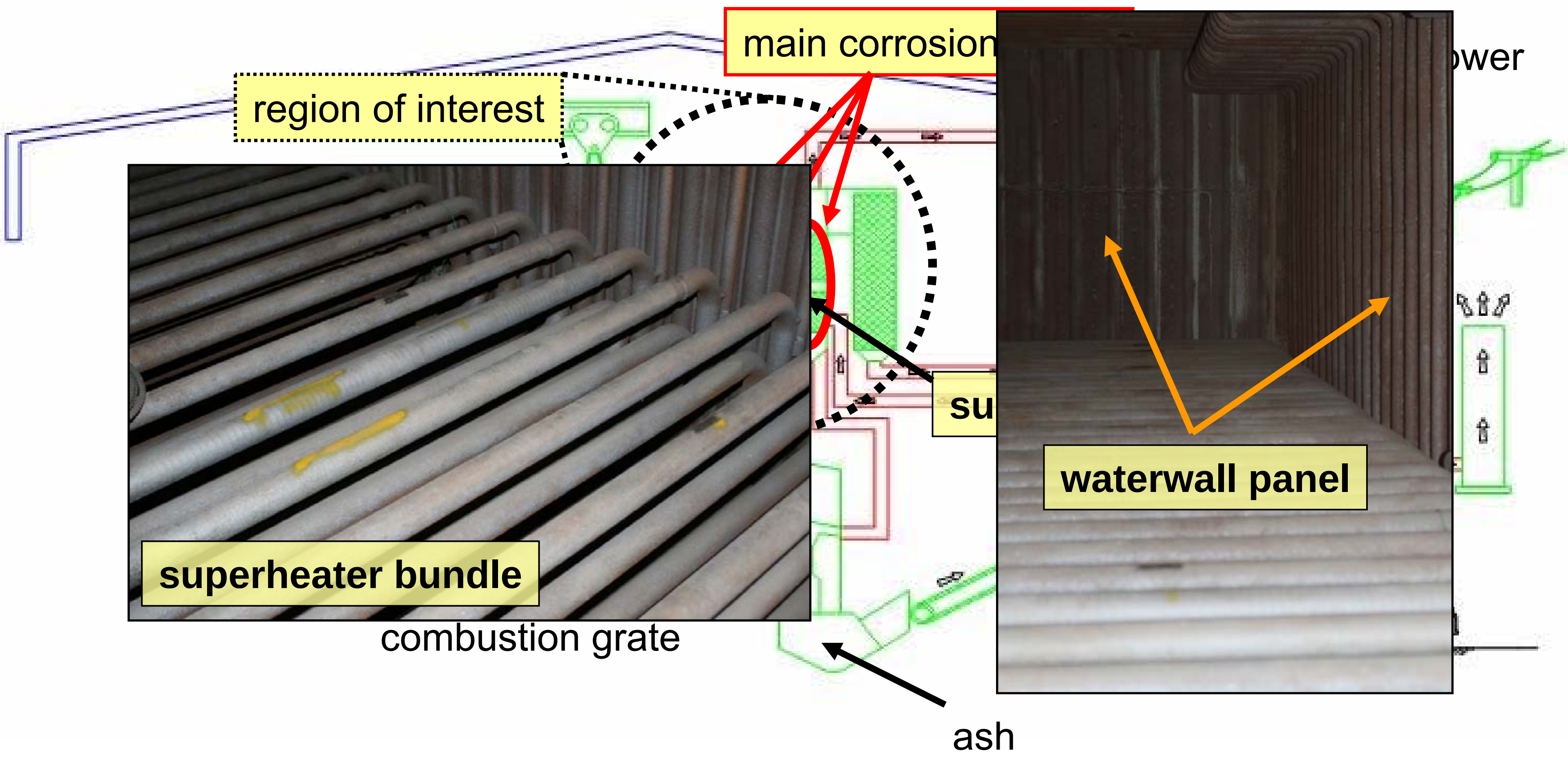
- SP 1: Fuel preparation
- SP 2: Conversion
- SP 3: Residue handling
- SP 4: Wholesale of energy



NGBW objectives SP 2: [excerpt]

- in general: innovative technologies to improve the corrosion resistance with the result of improved energy recovery, reliability and performance of waste and biomass combustion plants
- enhanced process conditions in order to achieve a higher efficiency
  → reduction of corrosion and fouling problems
  ⇒ improving boiler materials in order to withstand HTC
  ⇒ advanced boiler materials and new protecting coatings
- reducing maintenance costs by use of more corrosion resistant, but cost-effective materials and coatings
  → target: double lifetime of heat exchange components at existing steam temperatures

Waste-to-Energy Plant

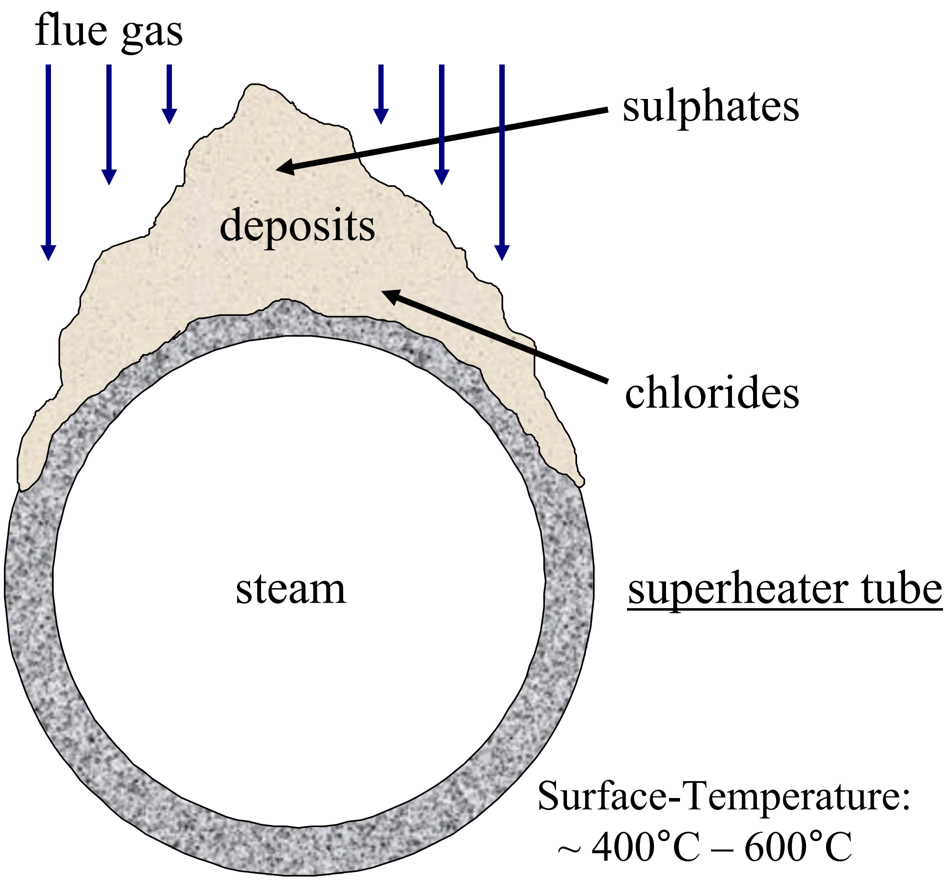


Deposit constituents on WtE superheater in wt.-% [excerpt]

	Na^+	K^+	Ca^{2+}	Pb^{2+}	Zn^{2+}	SO_4^{2-}	Cl^-
№ 1	4.1	7.6	12.5	7.4	2.3	28.0	0.5
№ 2	2.4	3.8	13.0	1.6	9.7	16.6	1.2

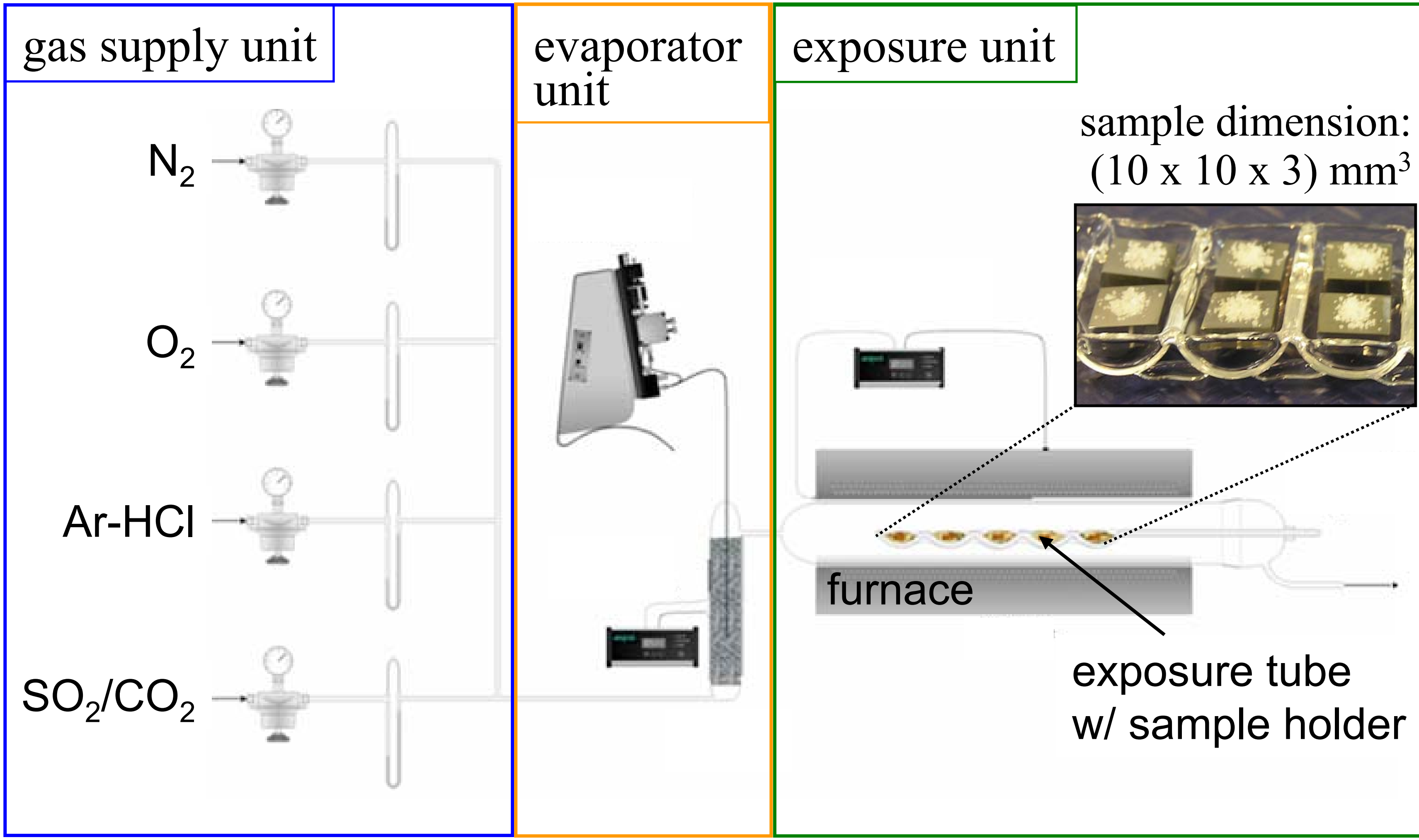
Flue gas concentration [excerpt]

Species	Concentration [vppm]	
HCl	560.0	2240.0
SO_2	35.0	700.0
SO_3	1.4	19.6
NO_2	71.5	214.5
CO	64.0	640.0
Pb	1.1	6.5
Zn	3.5	51.7



HTC Lab-Scale Facility Setup

- Lab-scale testing of materials and validation of testing methods using plant exposures



Testing Conditions

- Gases (based on PREWIN conditions)

	HCl	SO_2	CO_2	H_2O	O_2	N_2
Waste	**2,000 vppm**	**200 vppm**	**-**	**15 vol.-%**	**8 vol.-%**	**Bal.**
Biomass	**200 vppm**	**-**	**13 vol.-%**	**22 vol.-%**	**5 vol.-%**	**Bal.**

- Synthetic deposits

	Na_2SO_4	K_2SO_4	$CaSO_4$	$ZnSO_4$	KCl	$ZnCl_2$
Waste/biomass superheater	**33 wt.-%**	**33 wt.-%**	**33 wt.-%**			
Waste/biomass superheater		**50 wt.-%**			**50 wt.-%**	
Waste superheater	**25 wt.-%**	**25 wt.-%**	**25 wt.-%**	**25 wt.-%**		
Waste water wall					**50 mol.-%**	**50 mol.-%**

Commercial Materials

	Material	Cr	Ni	Mo	Mn	Other
Low Cr-steels	**15Mo3**	–	–	0.30	0.52	C 0.16; Si 0.26
	13CrMo4 4	0.96	0.07	0.48	0.46	C 0.12; Si 0.21
	10CrMo9 10 (T22)	2.10	–	0.92	0.43	C 0.12; Si 0.22
	7CrWMoVNb9 6 (T23)	2.3	–	0.15	0.27	C 0.06; Si 0.15; V 0.2; **W 1.58**; Nb 0.06; B 0.005; N 0.02; Al 0.02
High Cr-steels	**X20CrMoV12 1**	10.45	0.70	0.88	0.60	C 0.18; Si 0.22; V 0.26
	X10CrWMoVNb9 2 (T92)	9.15	0.26	0.50	0.46	**W 1.70**; Si 0.22; Nb 0.6; N 0.05; V 0.2; B 0.003; C 0.11
High Cr-/Ni-steels	**Esshete 1250**	14.90	9.65	0.94	6.25	C 0.084; Si 0.58; Nb 0.86; V 0.22; B 0.004
	TP 347 H	17.60	10.70	–	1.84	Si 0.29; C 0.05; Nb 0.6
	Sanicro 28	27.00	31.00	3.50	≤ 2.00	C 0.02; Si 0.07; Cu 1.0
Ni-base alloy	**Inconel 625**	22.00	Bal.	9.00	–	Fe 3.0; Nb 3.5; C 0.025

Model Alloys

- Modified 9%Cr-Steels (P91/T92)

Material [wt.-%]	Cr	Al	Si	Ni
Fe-9Cr-5Al	9.0	5.0	-	-
Fe-9Cr-2.5Al-2.5Si	9.0	2.5	2.5	-
Fe-9Cr-5Ni-2.5Al-2.5Si	9.0	2.5	2.5	5.0

- Iron Aluminides

Material [at.-%]	Al [wt.-%]	Fe
Fe-15Al	7.9	bulk
Fe-26Al	14.5	bulk
Fe-40Al	24.4	bulk

α-Fe, Al: disordered A2

Fe_3Al: ordered $D0_3$ (600°C B2)

FeAl: ordered B2

Motivation: Modified 9%Cr-Steels

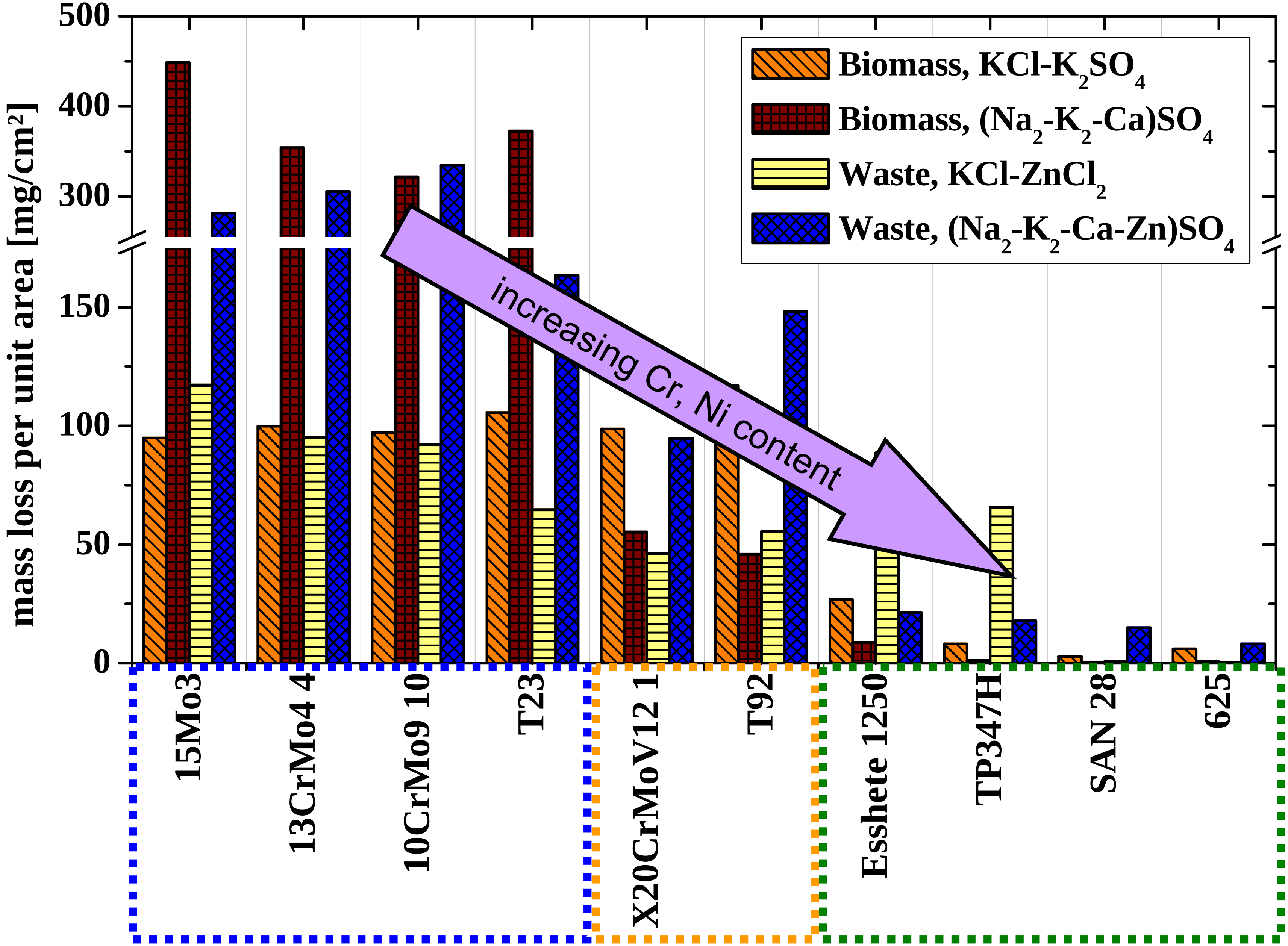
- 9-12%Cr ferritic-martensitic steels:
  - High strength and creep resistant steels suitable for use at temperatures up to 650°C
- Coatings/alloy composition modification in Cr, Si, Al will improve corrosion resistance
- Cr will enable and promote the outwards diffusion of Al
- Cr-reservoir reduces Al/Si-amount needed to maintain external alumina or silica scale
- Alumina scales are not as severely affected by steam as chromia, silica
- > 5wt.% Cr, Si → too high for industrial applications considering detrimental effects on metallurgical and mechanical properties

Motivation: Iron Aluminides

- ☺ Superior corrosion resistance in oxidising/sulphidising atmosphere
- ☺ Much improved corrosion resistance under molten salt compared to Fe-Cr alloys
- ☺ Light-weight structural materials
- ☺ Recent efforts led to Fe-Al alloys have the potential to be used for structural applications at least between 650-800°C
- ☺ Development and improvement of Fe_3Al and FeAl concerning high strength, high ductility and high creep resistance between 500-1,000°C
- ☺ Fe-Al-X alloys show better creep rates than P92

Corrosion Test: Commercial Steels

Corrosion Tests at 600°C for 336 h



Waste, $(Na_2\text{-}K_2\text{-}Ca\text{-}Zn)SO_4$, 600°C, 336 h

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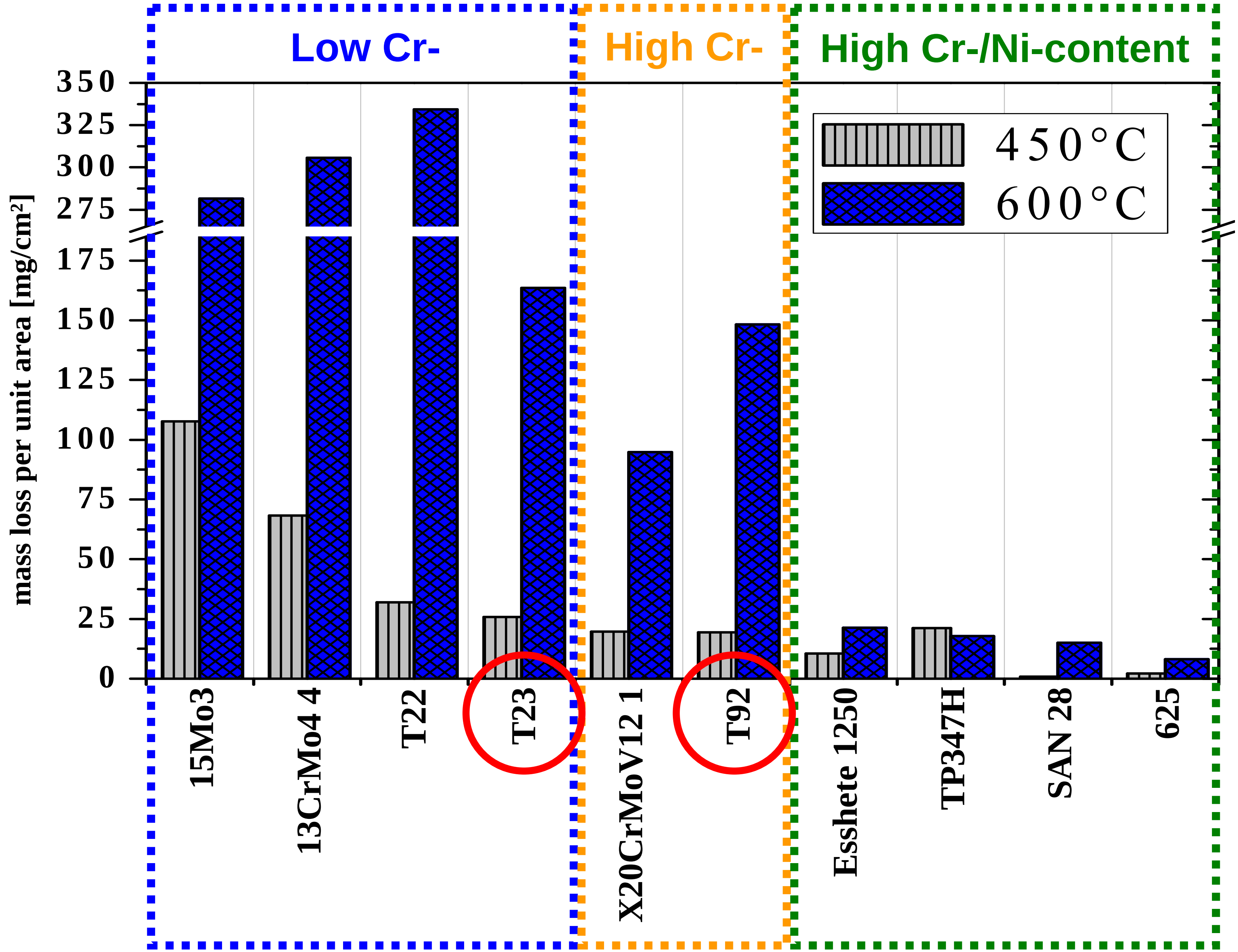
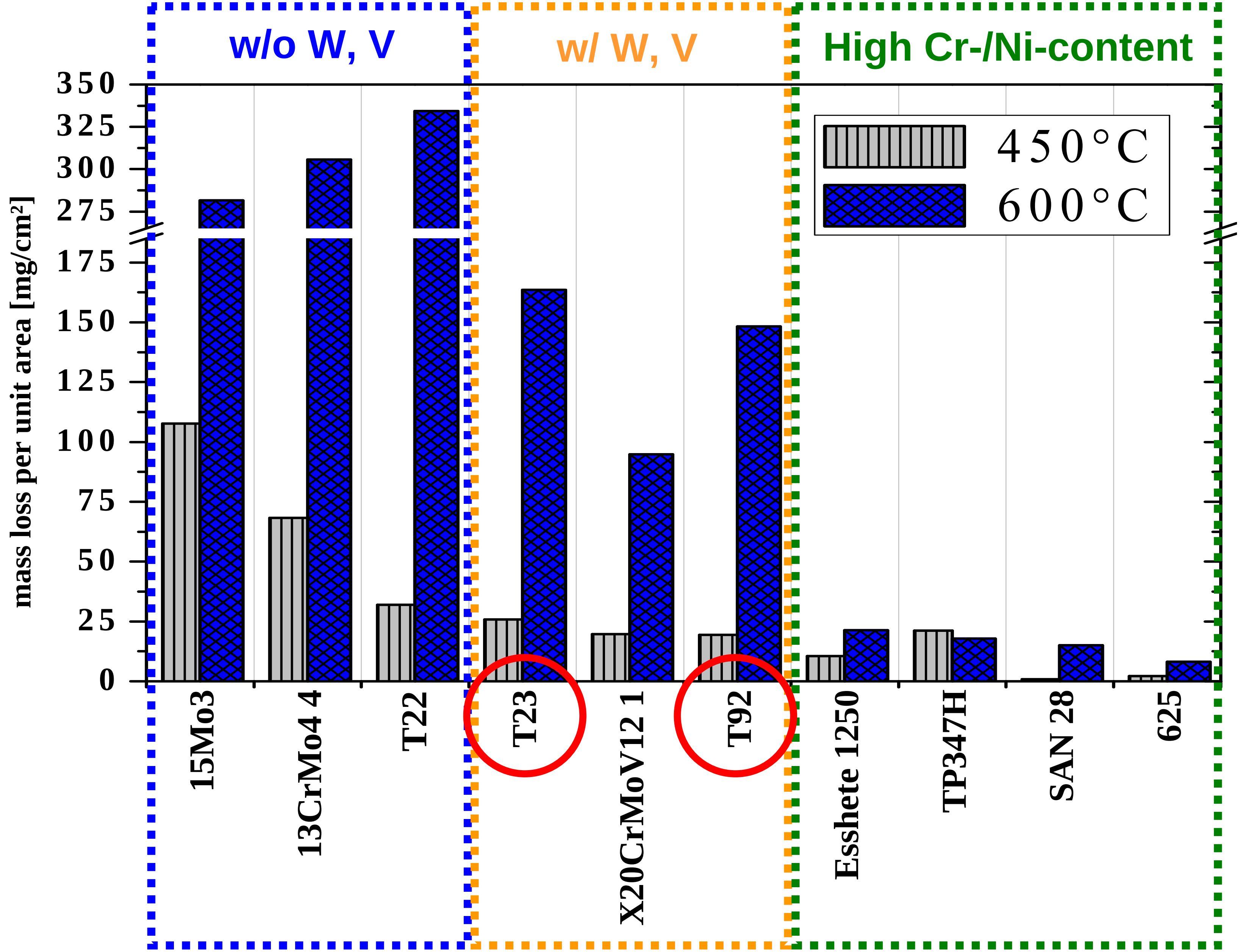
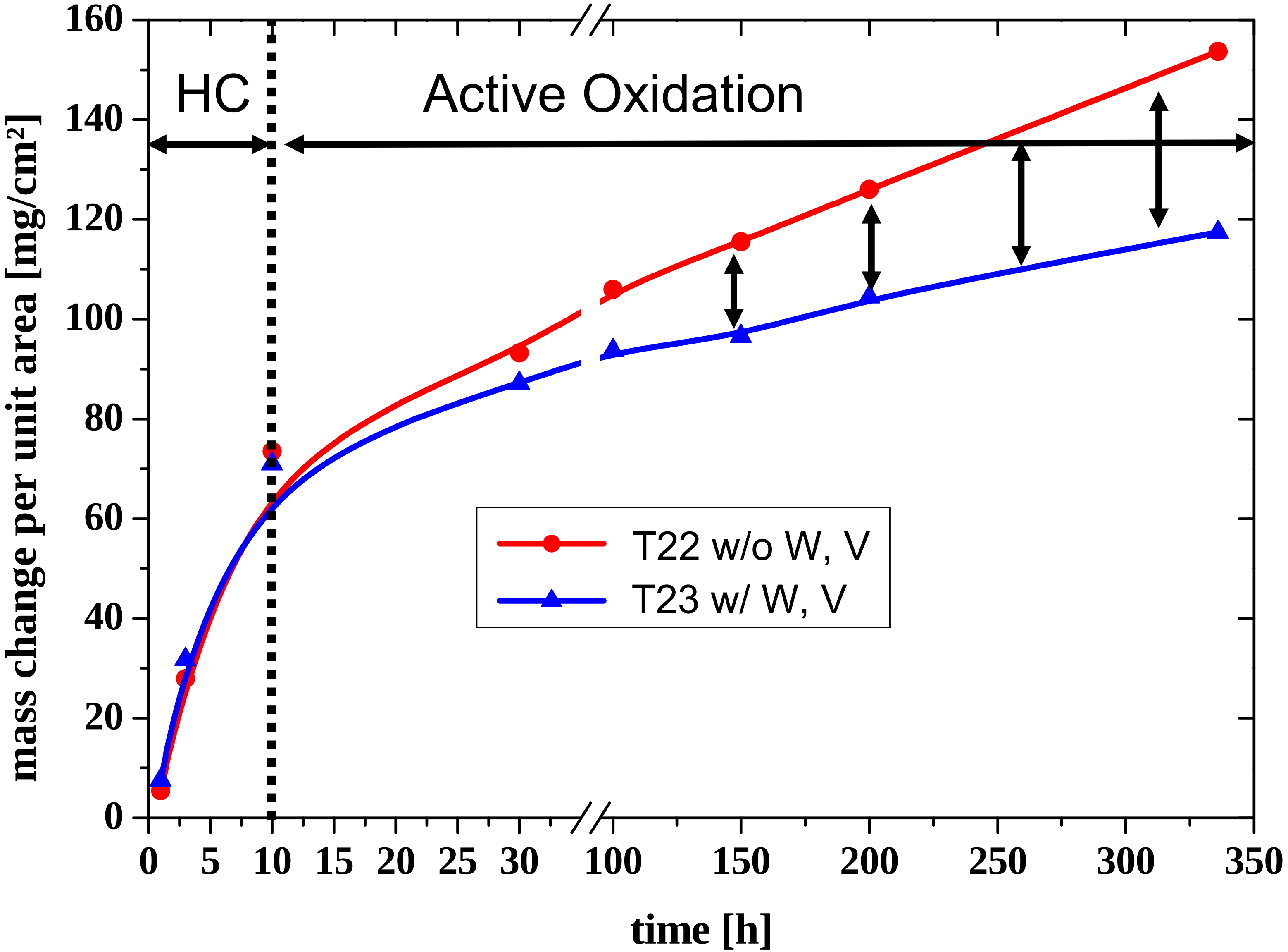


Waste, $(Na_2\text{-}K_2\text{-}Ca\text{-}Zn)SO_4$, 600°C, 336 h



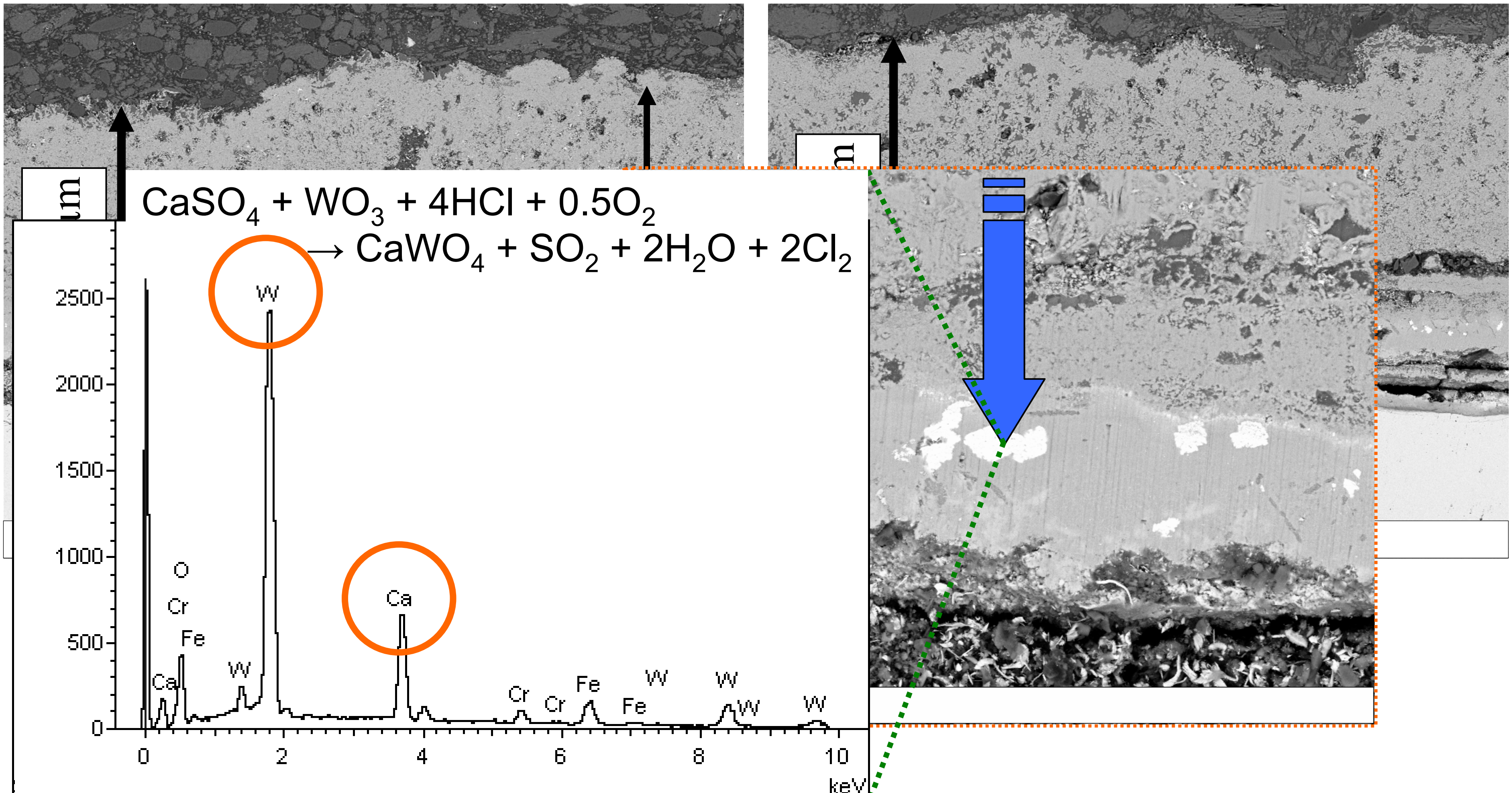
Waste, $(Na_2\text{-}K_2\text{-}Ca\text{-}Zn)SO_4$, 600°C, 336 h



Waste, $(Na_2\text{-}K_2\text{-}Ca\text{-}Zn)SO_4$, 600°C, 336 h

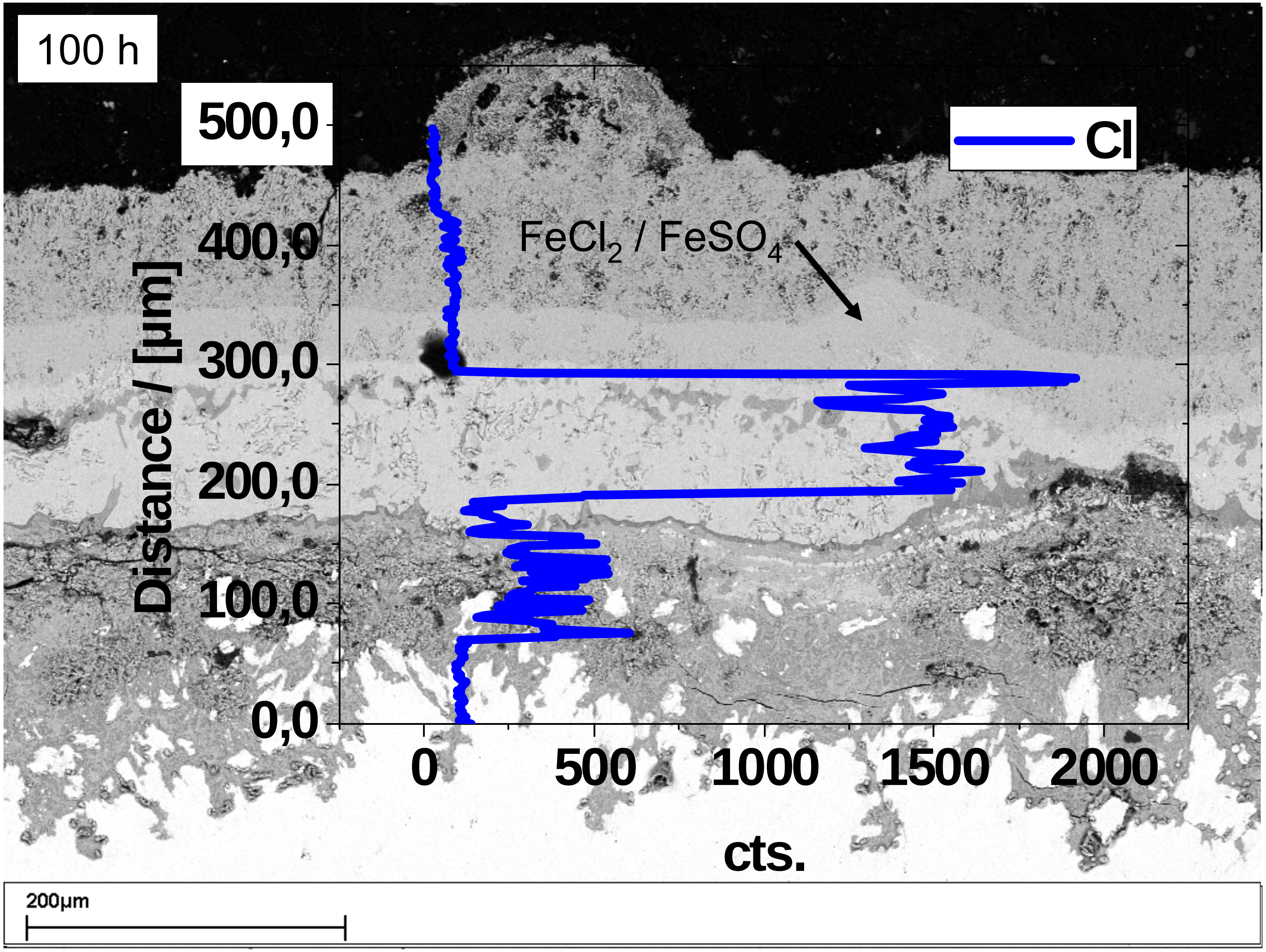
Low alloyed steel: **T23**

High alloyed steel: **T92**

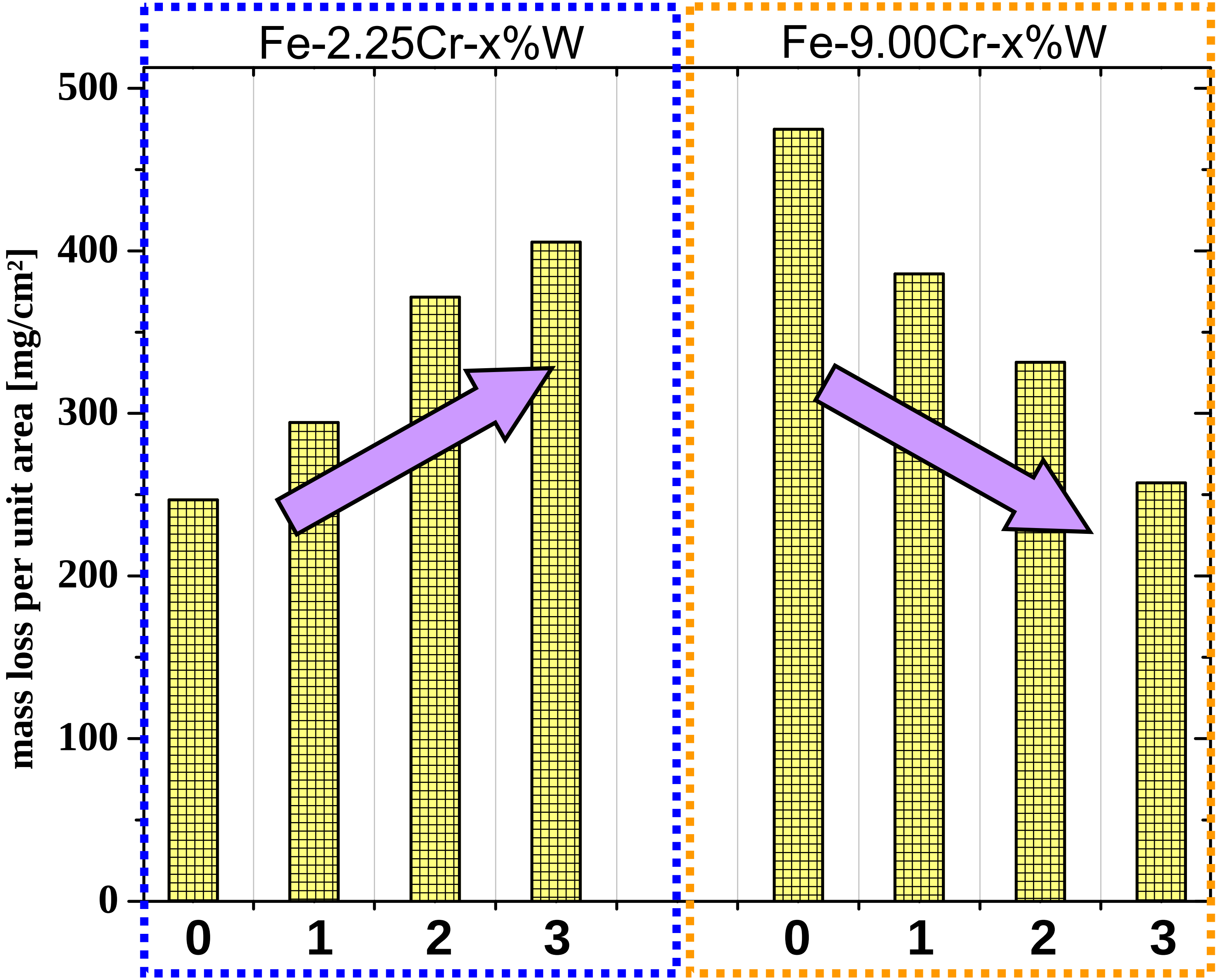


$$CaSO_4 + WO_3 + 4HCl + 0.5O_2 \rightarrow CaWO_4 + SO_2 + 2H_2O + 2Cl_2$$

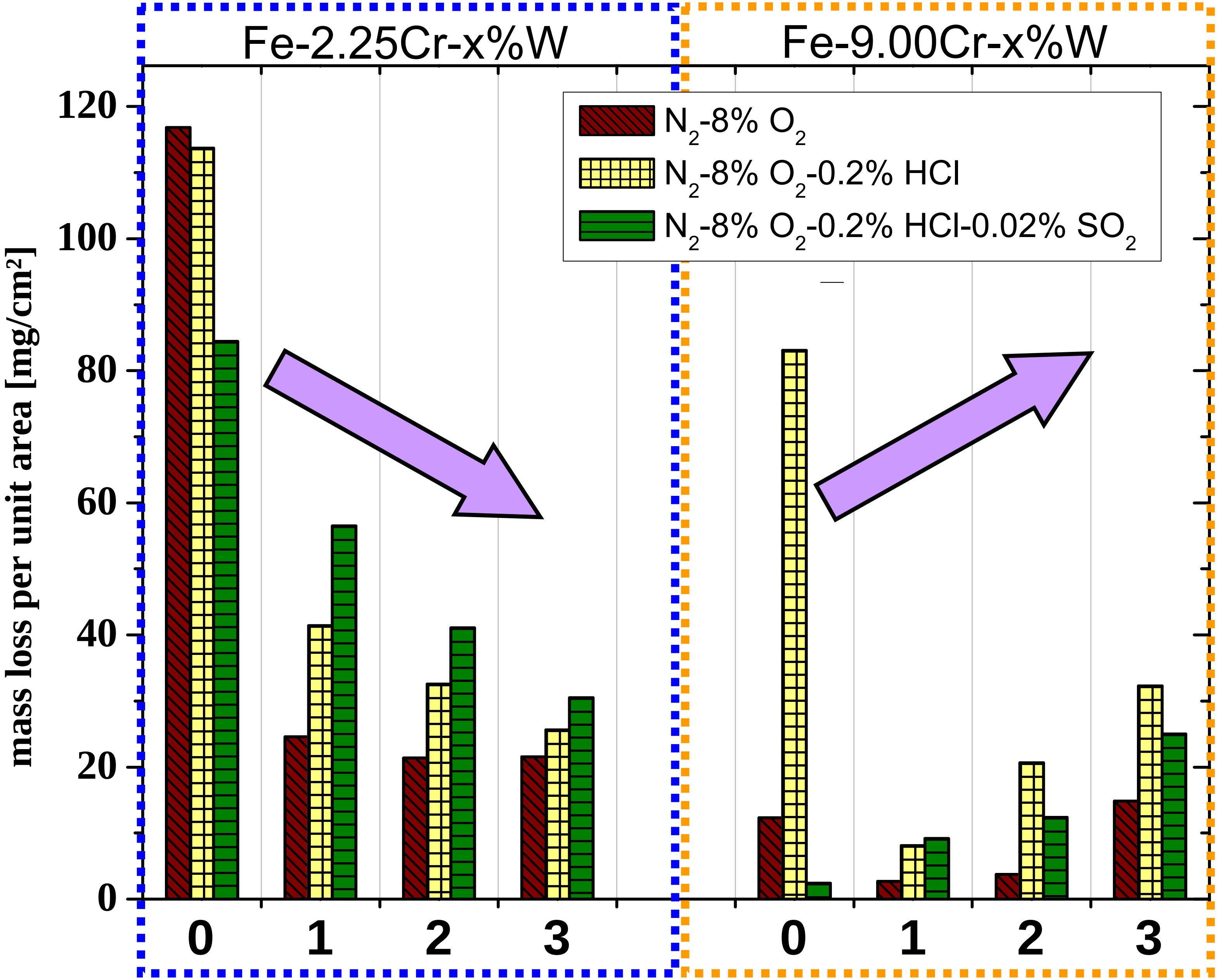
T23: Waste, $(Na_2-K_2-Ca-Zn)SO_4$, 600°C



Fe-Cr-W: Waste, (Na-K-Ca-Zn)SO_4, 600°C, 168 h

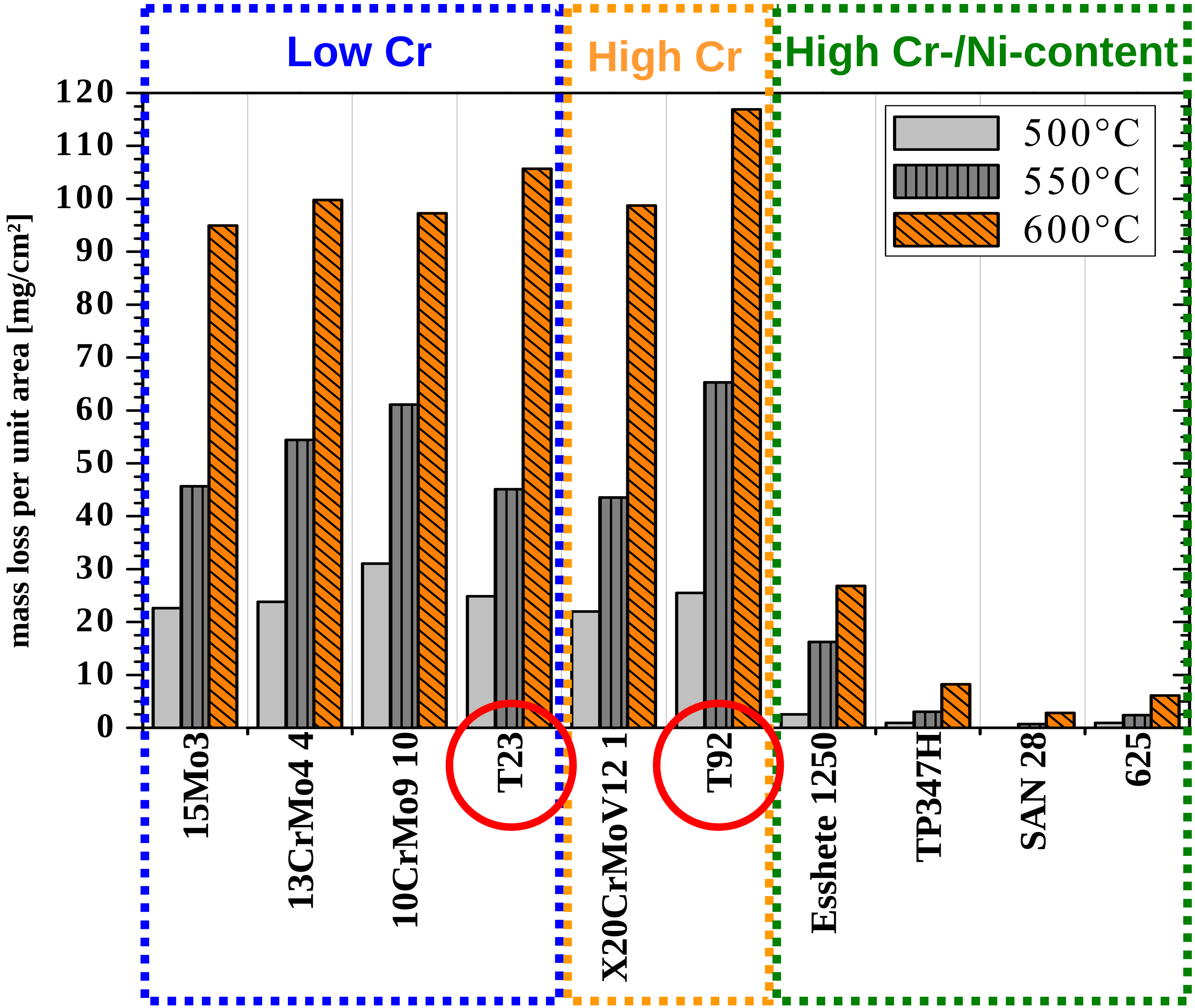


Fe-Cr-W: 600°C, 168 h w/o deposit

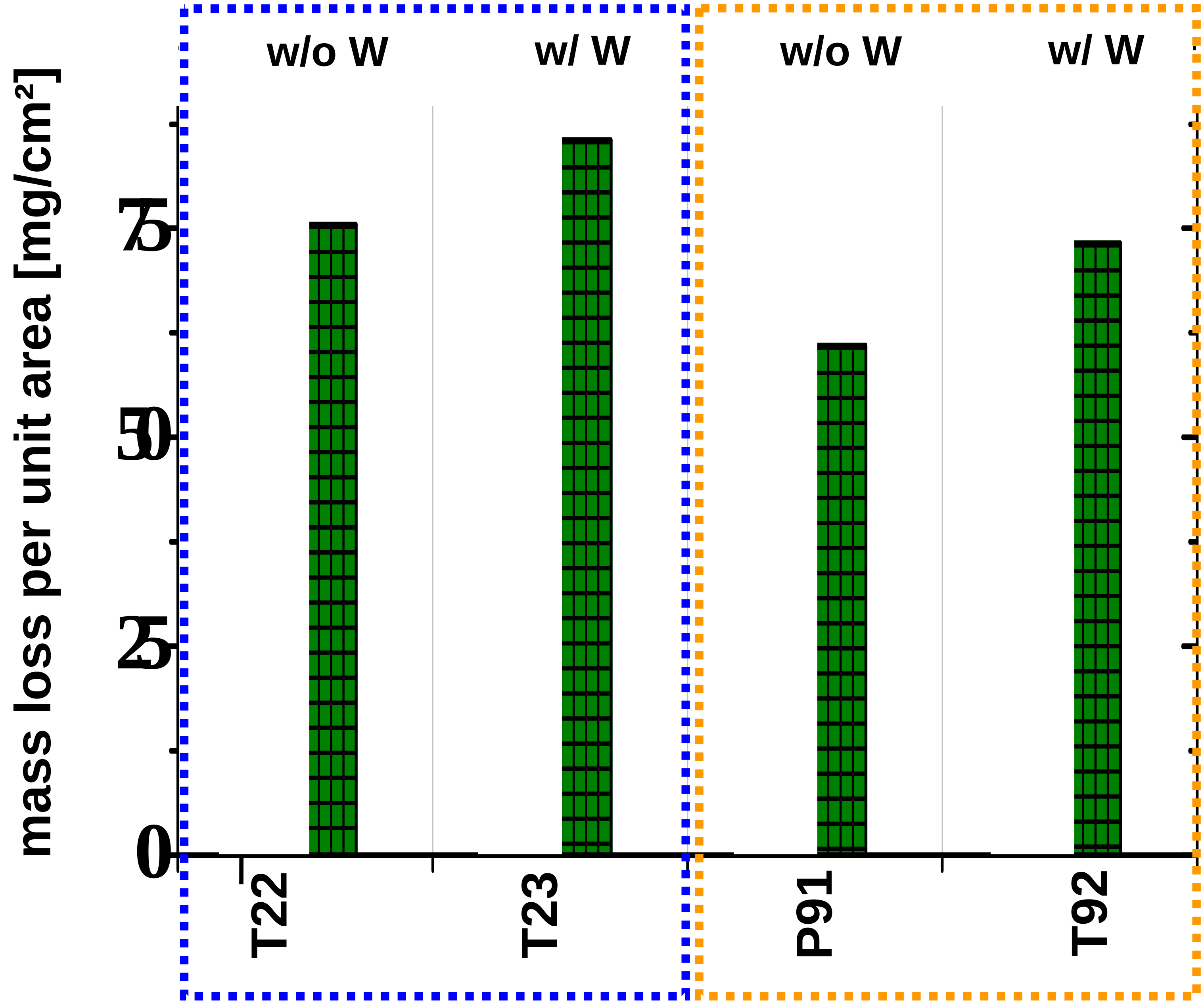


Biomass, $KCl-K_2SO_4$, 600°C, 336 h

Biomass, KCl-K_2SO_4, 336 h

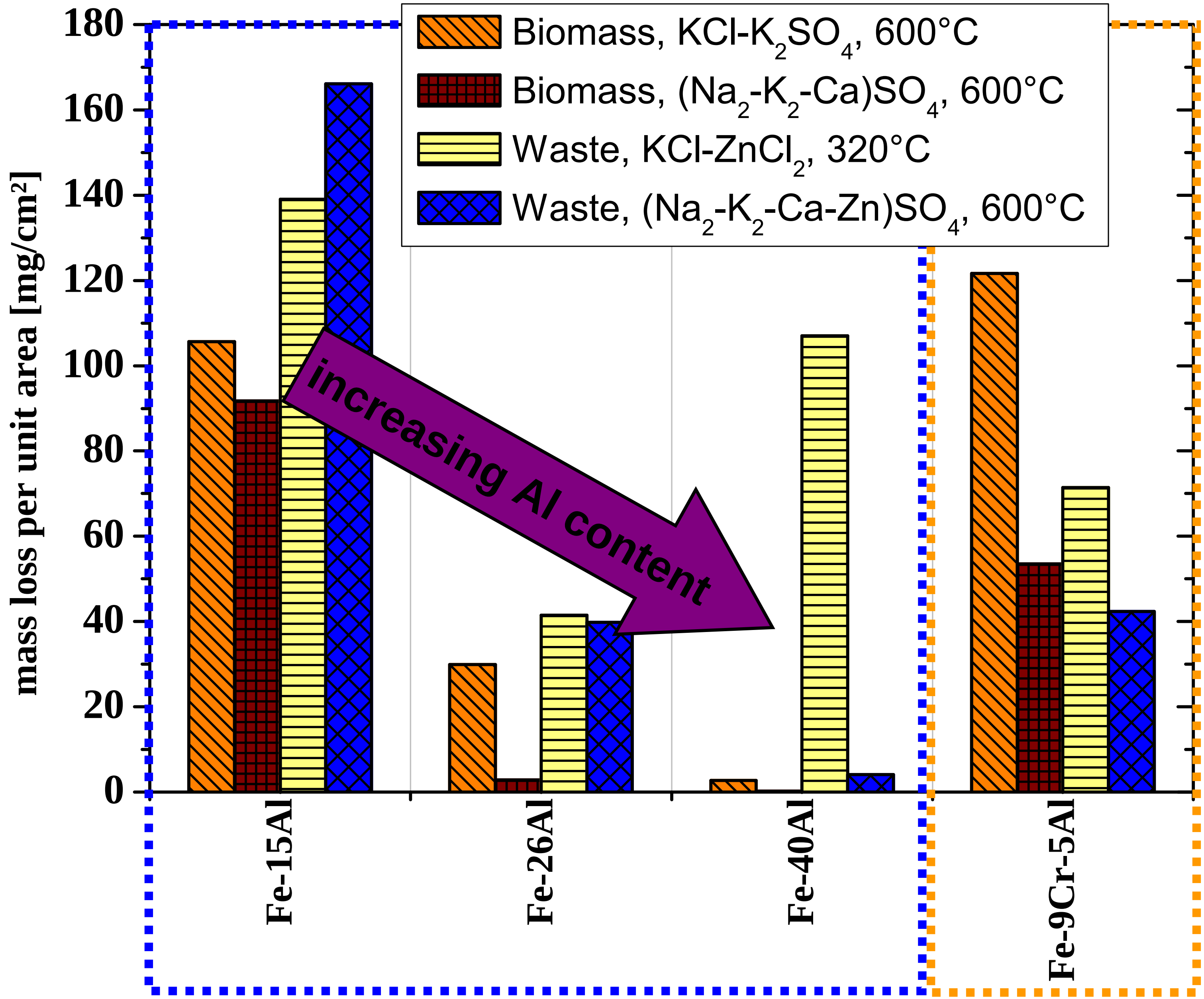


Biomass, KCl-K_2SO_4, 600°C, 168 h



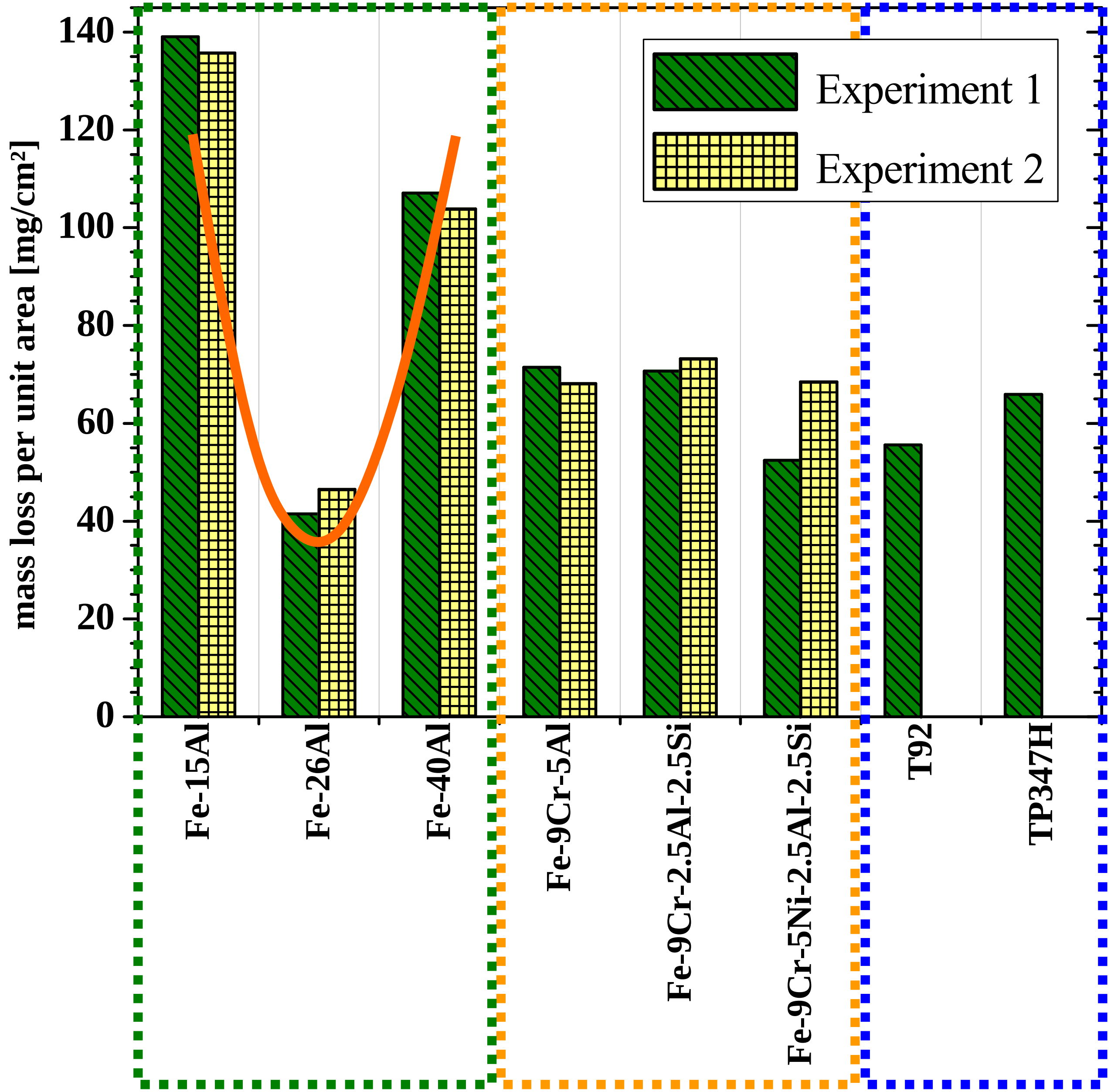
Corrosion Test: Modified 9%Cr-Steels / FeAl

Summary: Corrosion Tests Fe-Al for 336 h

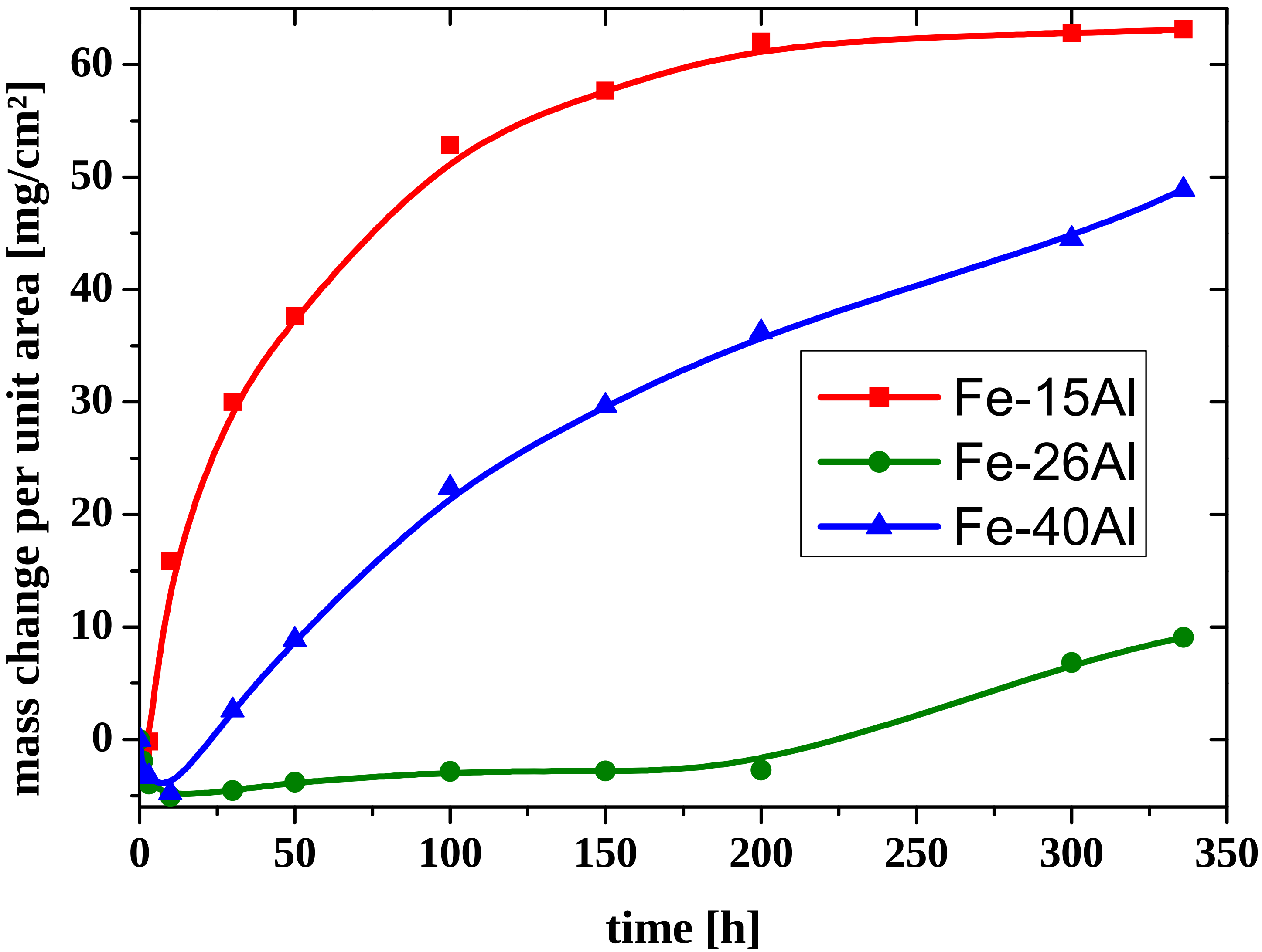


Waste, $KCl-ZnCl_2$, 320°C, 336 h

Mass Loss: 320°C, 336 h

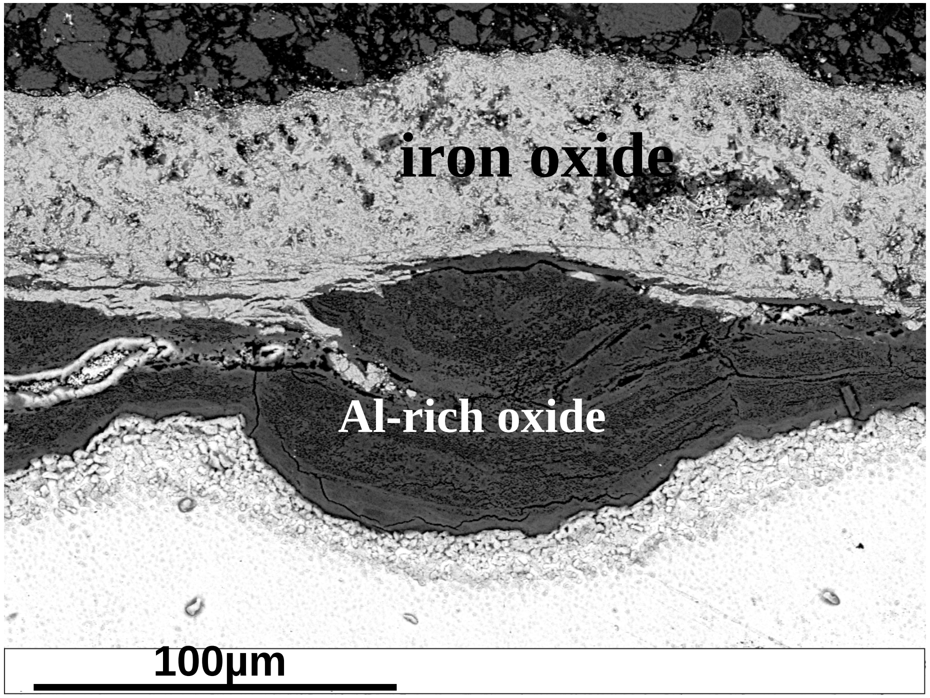


Kinetic: Iron Aluminides, 320°C, 336 h

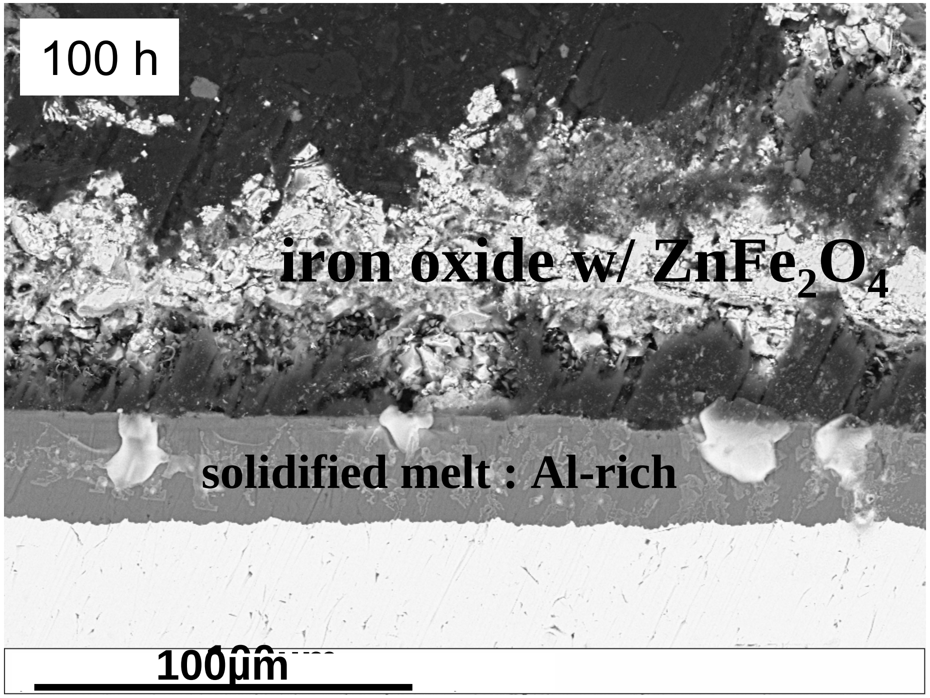


Iron Aluminides: 320°C, 336 h

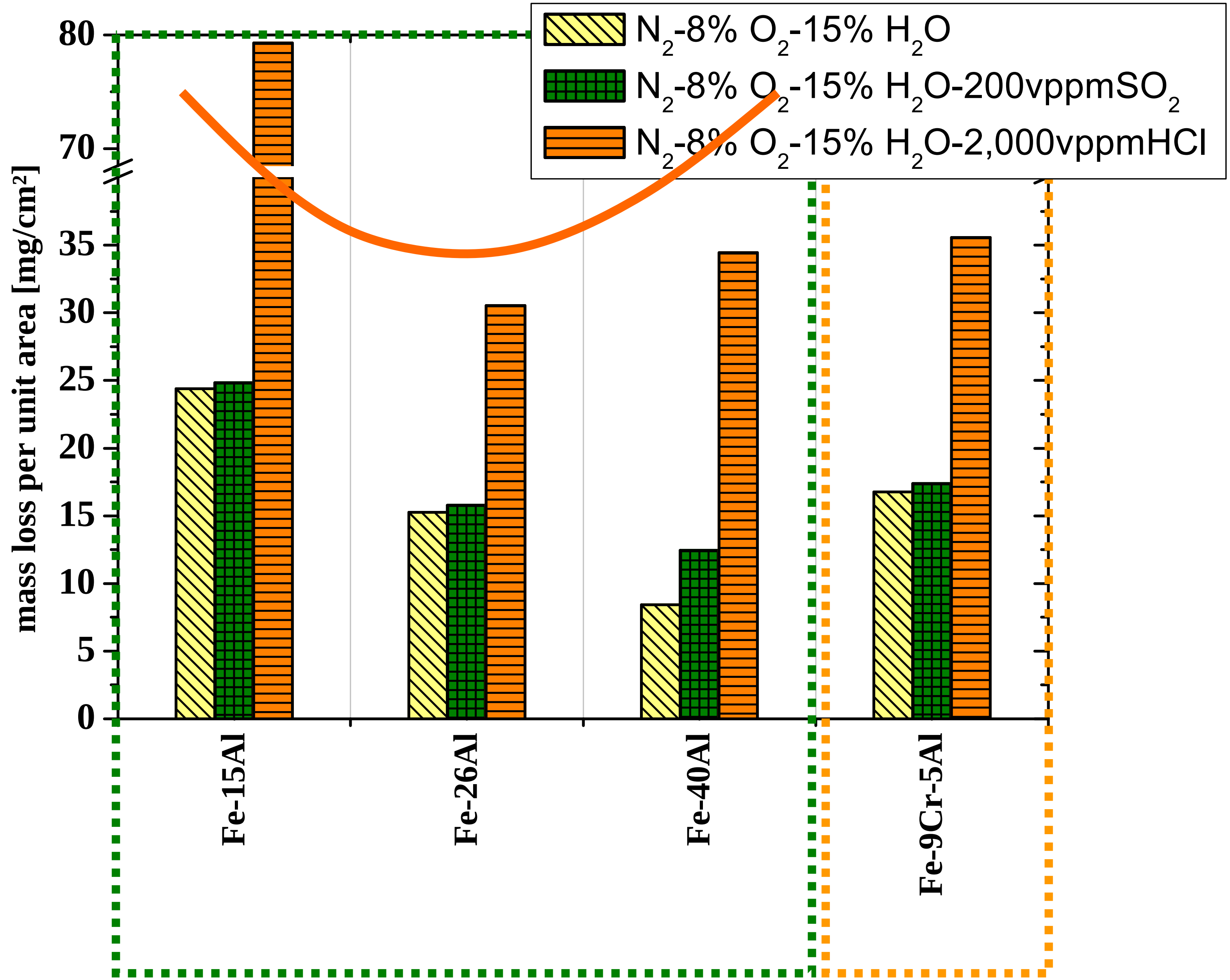
Fe-26Al



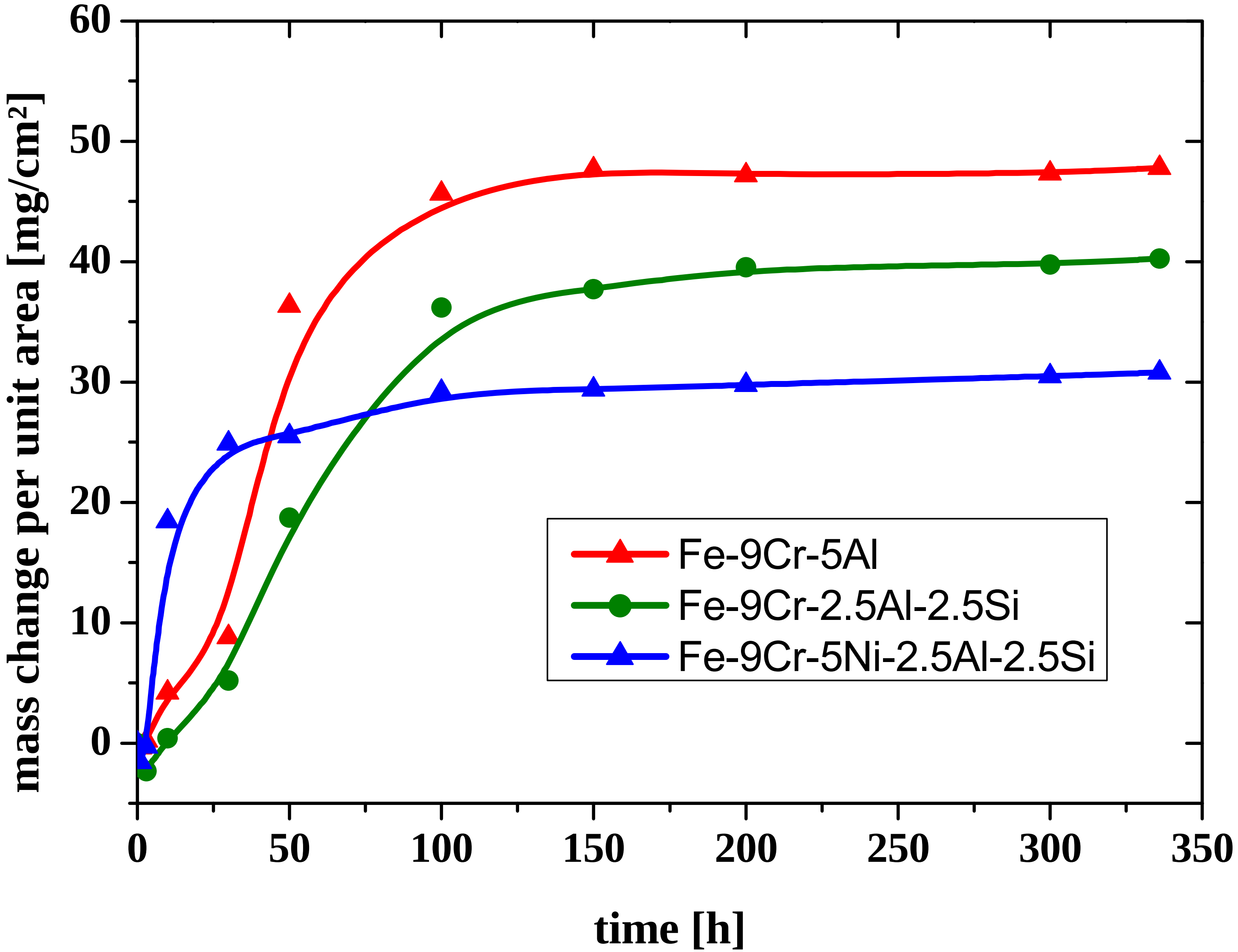
Fe-40Al



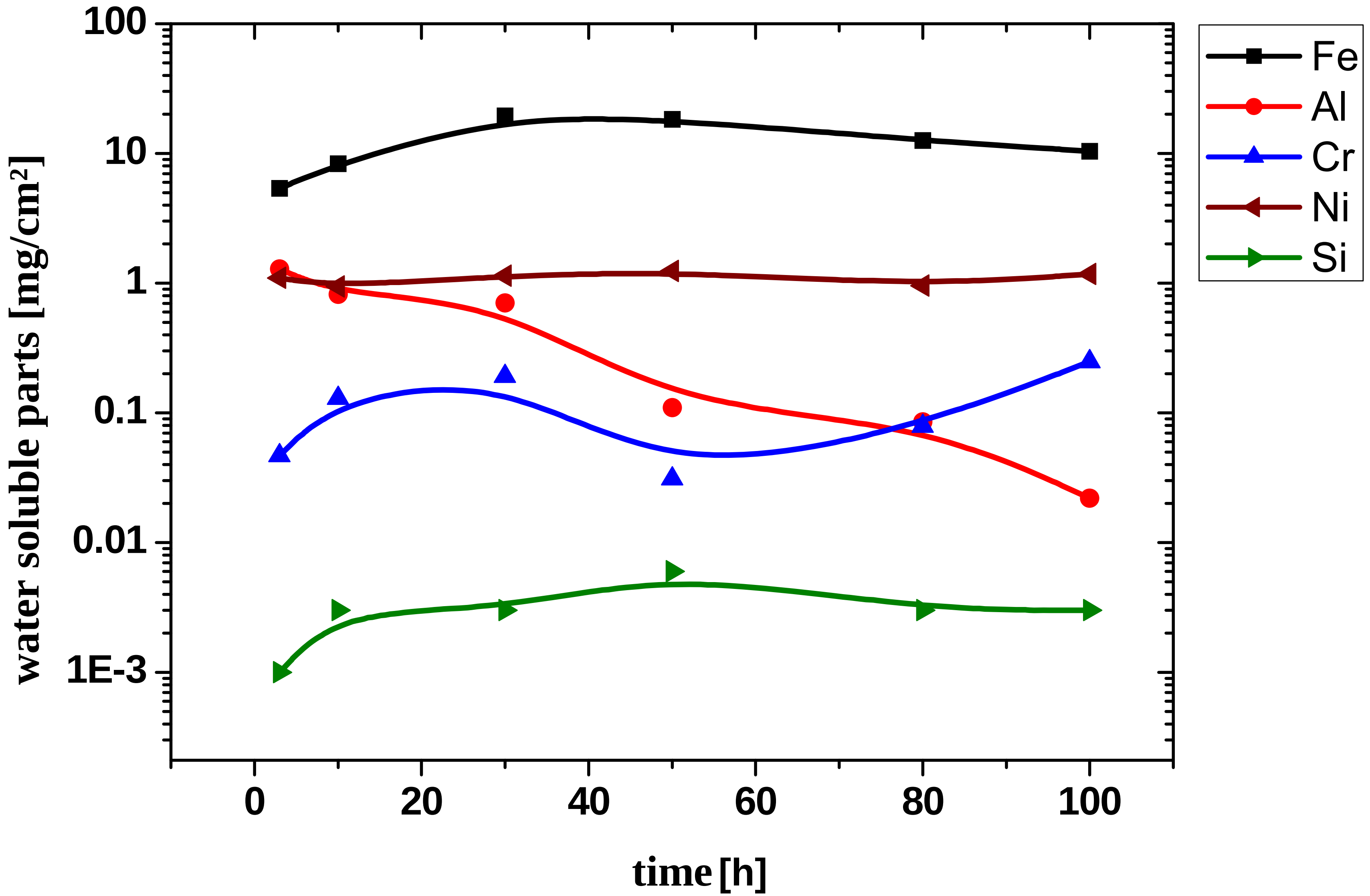
Mass Loss: 320°C, 96 h, w/ $KCl-ZnCl_2$



Kinetic: Modified 9%Cr-Steels, 320°C, 336 h

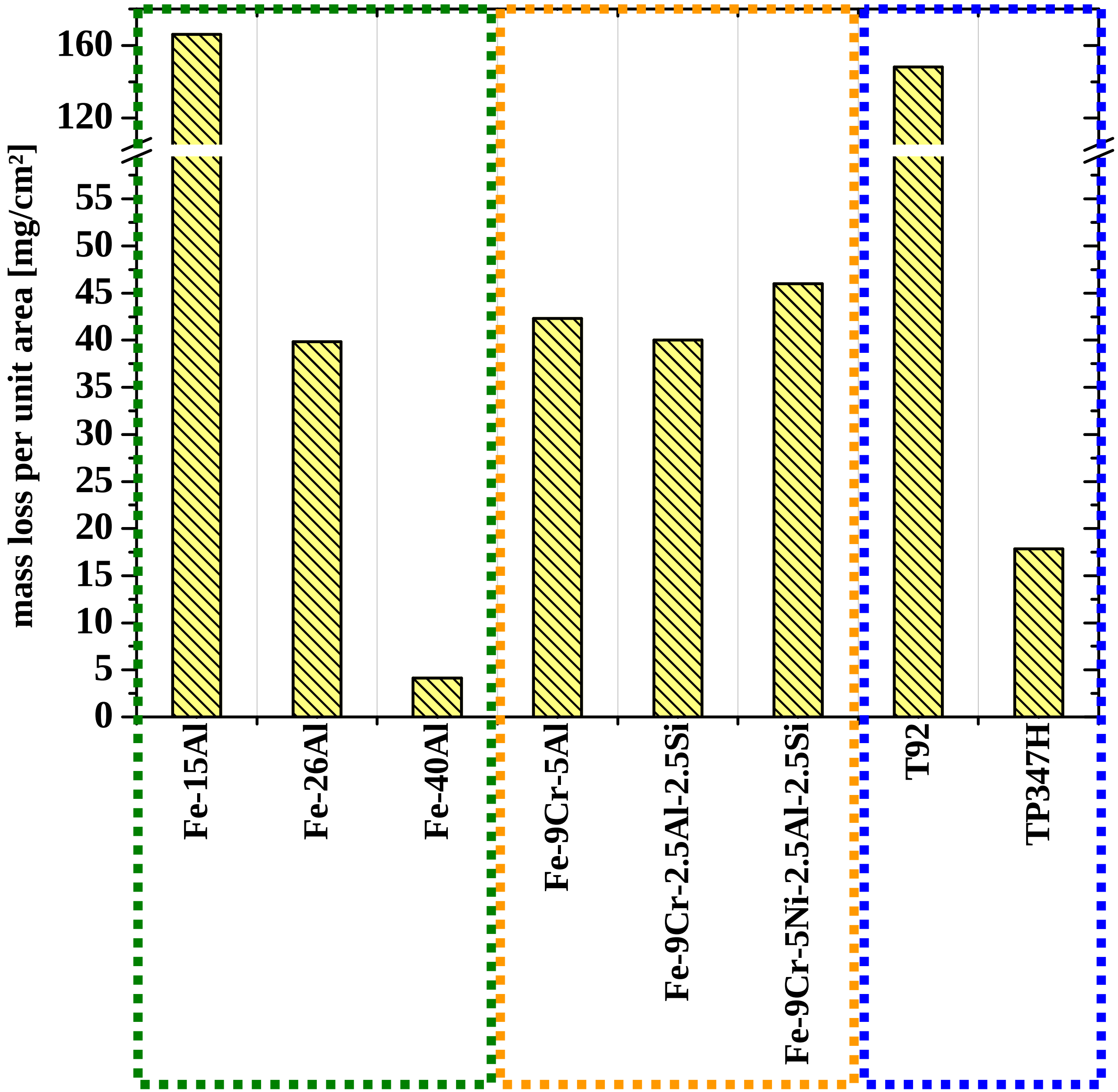


Solubility of Pure Metals: 320°C, 100 h



Waste, $(Na_2$-K_2-Ca-Zn$)SO_4$, 600°C, 336 h

Mass Loss: 600°C, 336 h



Summary

- Commercial steels
  - decrease in mass loss by increasing Cr-/Ni-content
  - strong interaction of Cr and W concerning the degradation mechanism

- Iron aluminides:
  - improved corrosion resistance by increasing the Al-concentration
  - except: KCl-$ZnCl_2$ -> Fe/Al ratio important for low corrosion

- Modified 9%Cr-steels:
  - beneficial behaviour of Al, Si, Ni concerning 'Active Oxidation'
  - Modifications show no increased corrosion performance at combined degradation mechanisms, i.e. 'Hot Corrosion' and 'Active Oxidation'

Thank you for your attention!