Effects of Cr and Ni Contents on High Temperature Oxidation of Stainless steels in mixed Air and Water Vapor

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Introduction

- **Stainless steels :**
  - Combination of corrosion resistance and high strength attractive for some power generation applications.
- **Under dry air :**
  - Protective Cr_2O_3 scale growth.
- **Under wet air, steam or exhaust gas :**
  - Rapid acceleration in attack is observed for some composition: fast growth of an iron oxide scale results in a shorter lifetime.
  - More problems can occur with higher water vapor content.
- **Standard alternatives:**
  - Selection of steels with higher Cr contents (20-25%).
  - Ferritic rather austenitic.
  - smaller grain size and higher surface deformation.

Is it possible to improve corrosion performance while keeping alloy cost low ?

Model Alloys Studied

		Ni (wt%)					
		0	10	15	20	25	30
Cr	10	F					
	12	F					
	14	F					
	16	F	F+A	A	A	A	A
	18	F	F+A	A	A	A	A
	20	F	F+A	A	A	A	A

→ Ni content

Cr 16–20 → Ferritic Austenitic

↓ Cr content

Cast and Rolled Specimens → Grain size effect

Doped Materials (Ti, Al, La, Mn, Mo,Si) → Alloying element effect

Composition of the Model Alloys Studied

Nominal compositions	Fe	Cr	Ni	B	P	Si	C	S	N	O
Fe-10Cr	Bal.	9.44	<0.01	<0.001	0.002	0.02	44	44	10	608
Fe-12Cr	Bal.	11.85	<0.01	0.002	0.006	<0.01	45	45	8	548
Fe-14Cr	Bal.	13.84	<0.01	0.003	0.003	<0.01	16	52	9	609
Fe-16Cr	Bal.	15.71	<0.01	0.009	0.005	<0.01	9	46	10	657
Fe-18Cr	Bal.	17.78	<0.01	0.012	0.005	<0.01	13	43	15	554
Fe-20Cr	Bal.	19.64	<0.01	0.016	<0.002	<0.01	17	48	8	635
Fe-20Cr-30Ni	Bal.	19.59	30.07	<0.001	0.004	0.01	20	47	44	409
Fe-20Cr-25Ni	Bal.	19.52	24.82	0.007	0.004	<0.01	18	45	24	434
Fe-20Cr-20Ni	Bal.	19.68	20.12	<0.001	0.005	0.01	10	41	9	421
Fe-20Cr-15Ni	Bal.	19.38	15.27	0.002	<0.002	0.01	20	47	8	428
Fe-20Cr-10Ni	Bal.	19.85	9.89	0.002	<0.002	<0.01	20	50	223	944
Fe-18Cr-30Ni	Bal.	17.76	30.04	<0.001	0.004	<0.01	10	42	6	385
Fe-18Cr-25Ni	Bal.	17.53	24.60	0.006	0.008	<0.01	17	40	6	378
Fe-18Cr-20Ni	Bal.	17.75	20.05	0.003	0.004	0.01	30	36	7	464
Fe-18Cr-15Ni	Bal.	17.85	15.04	<0.001	0.004	0.01	10	42	7	564
Fe-18Cr-10Ni	Bal.	17.86	9.92	0.001	0.002	<0.01	16	46	8	441
Fe-16Cr-30Ni	Bal.	15.68	29.60	0.012	0.011	<0.01	39	31	6	356
Fe-16Cr-25Ni	Bal.	15.97	24.84	0.001	0.006	<0.01	19	40	8	373
Fe-16Cr-20Ni	Bal.	15.61	19.54	0.010	0.005	<0.01	20	38	45	351
Fe-16Cr-15Ni	Bal.	15.80	14.82	<0.001	0.004	<0.01	19	43	9	389
Fe-16Cr-10Ni	Bal.	15.79	9.88	<0.001	0.005	<0.01	20	45	8	494
		Wt. %					Wt. ppm			

Inductively Coupled Plasma (ICP) quantitative analyses

Specimen Preparation

- **Vacuum induction melted castings.**
- **Vacuum annealing 4h at 1100°C.**
- **Disc shape specimen (1mm thick – 15mm diameter).**
- **Mechanically polished to 600-grit SiC paper.**

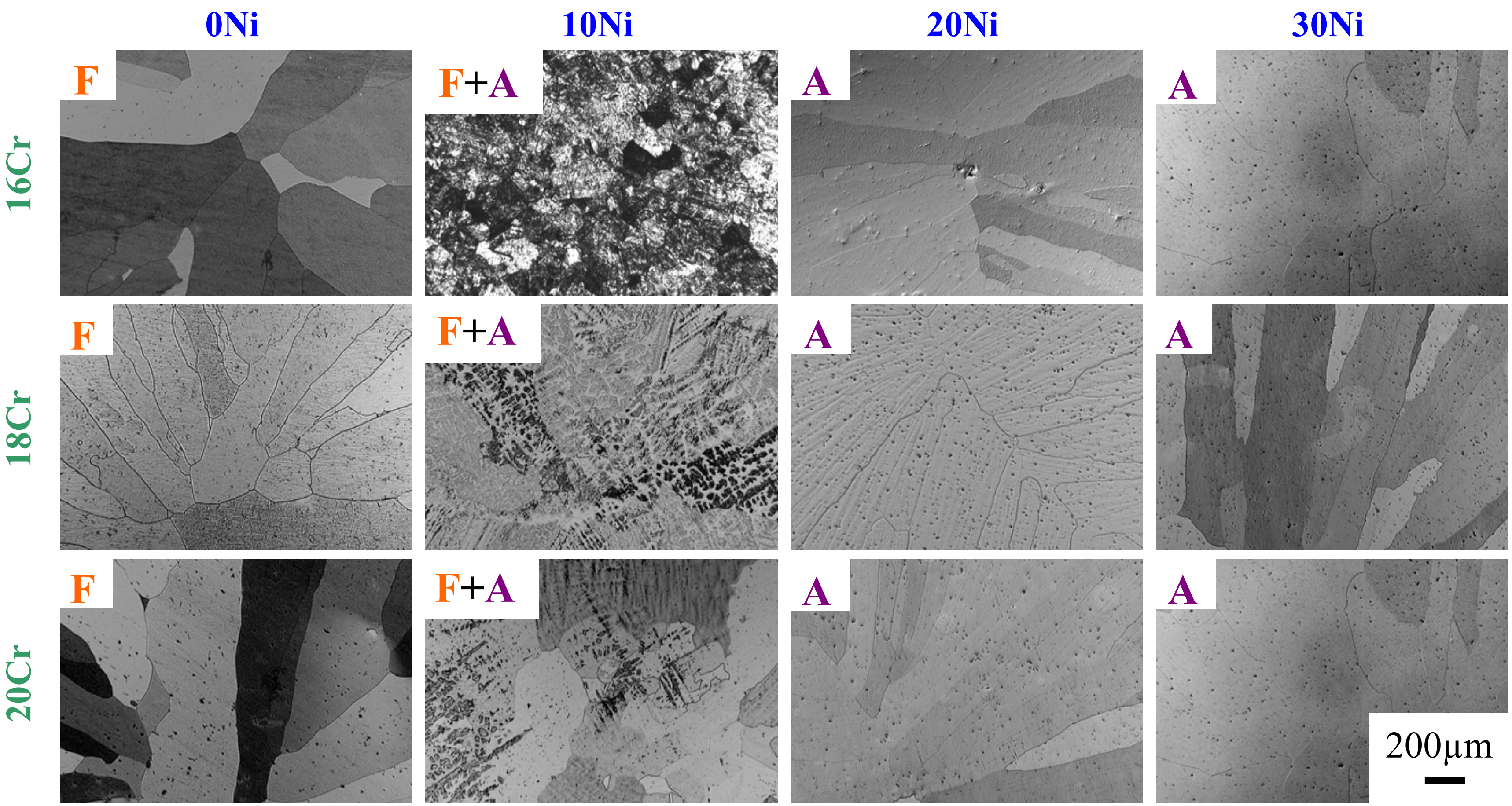
Experimental Conditions

- **Temperature: 650 - 700 - 750 - 800°C.**
- **Cyclic oxidation: 1h cycle - 100h cycle.**
- **Atmosphere: Air+10% Water Vapor – Air.**

Characterization

- **Behavior / kinetics: Specimen Mass Change.**
- **Morphology of the oxide scale: LM + SEM.**
- **Microstructure of the oxide scale: LM + SEM + EDX + EPMA + XRD.**

Microstructure of the alloys before oxidation

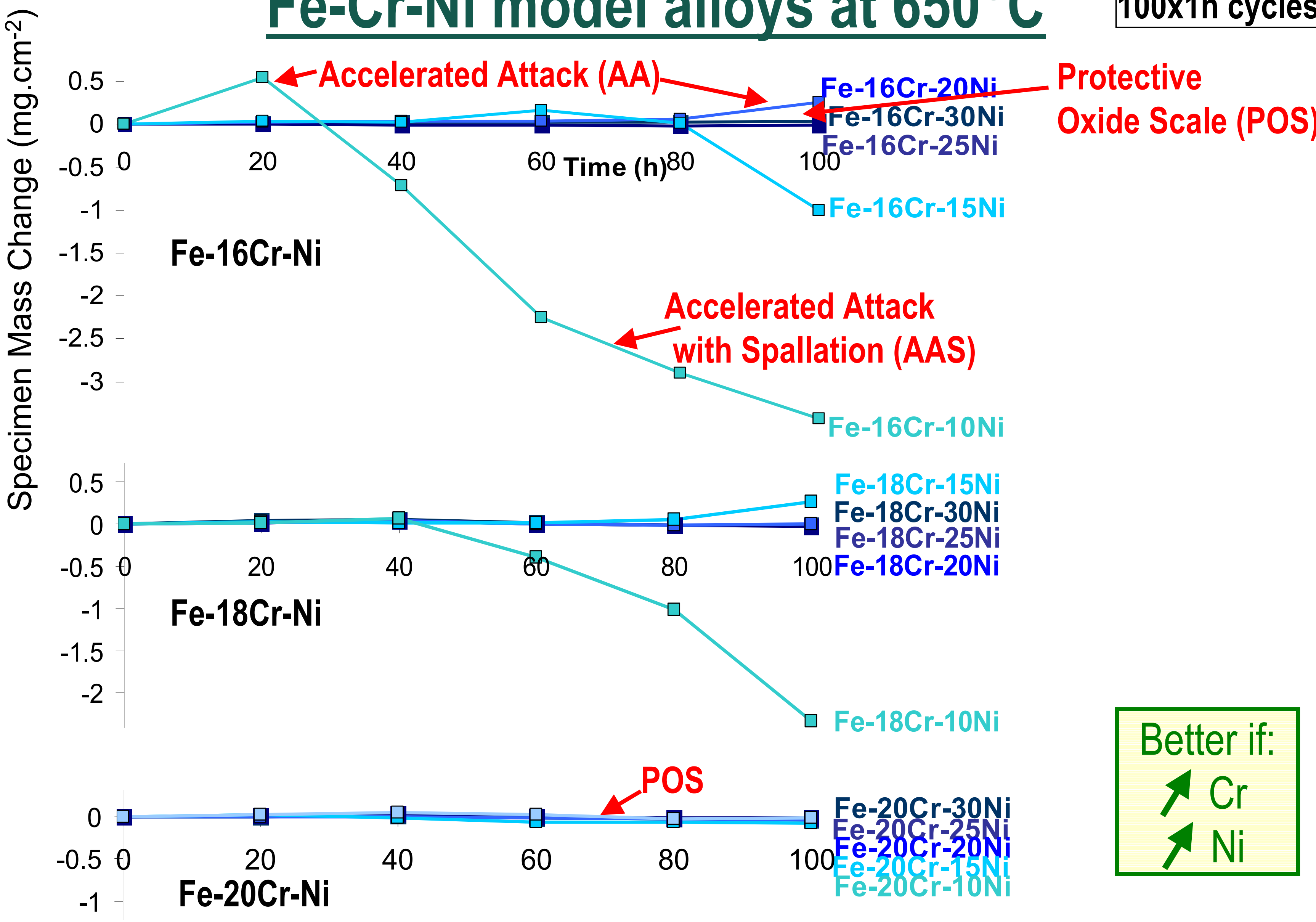


Light microscopy of etched specimens after annealing and before oxidation.

F: ferritic
A: austenitic
} from XRD

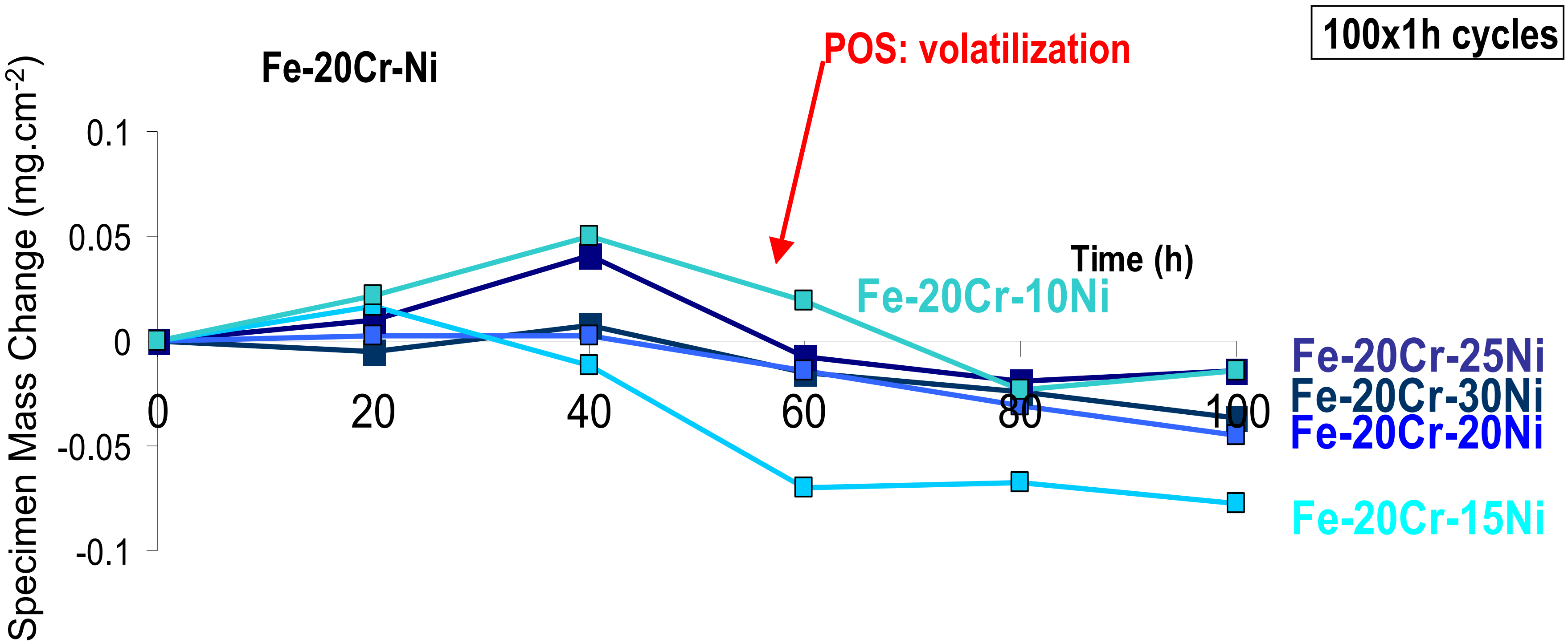
Fe-Cr-Ni model alloys at 650°C

100x1h cycles



Better if:
↗ Cr
↗ Ni

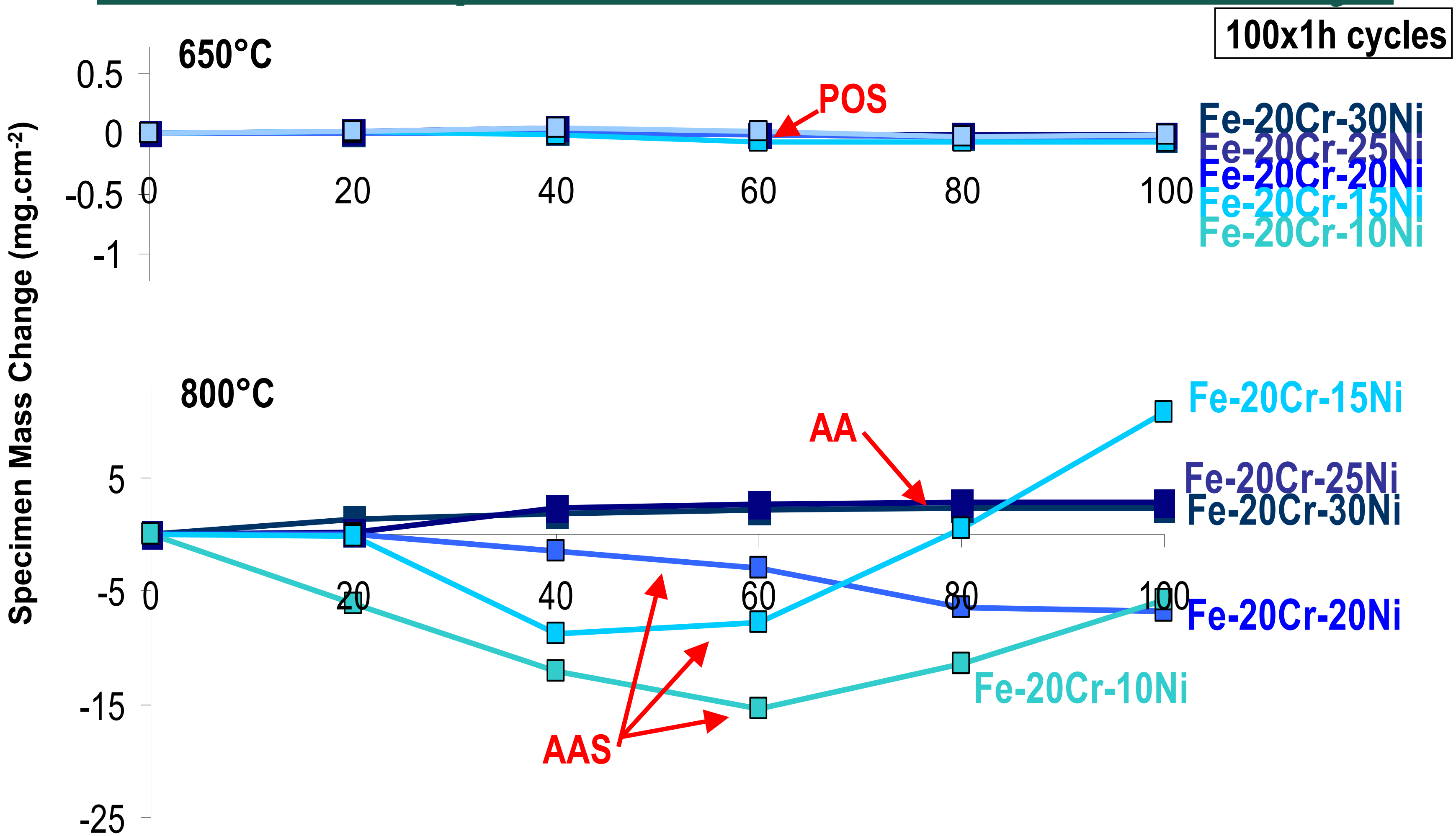
Fe-Cr-Ni model alloys at 650°C



During the growth of the POS:

- ➢ Slight loss of mass: volatilization of Cr-species.

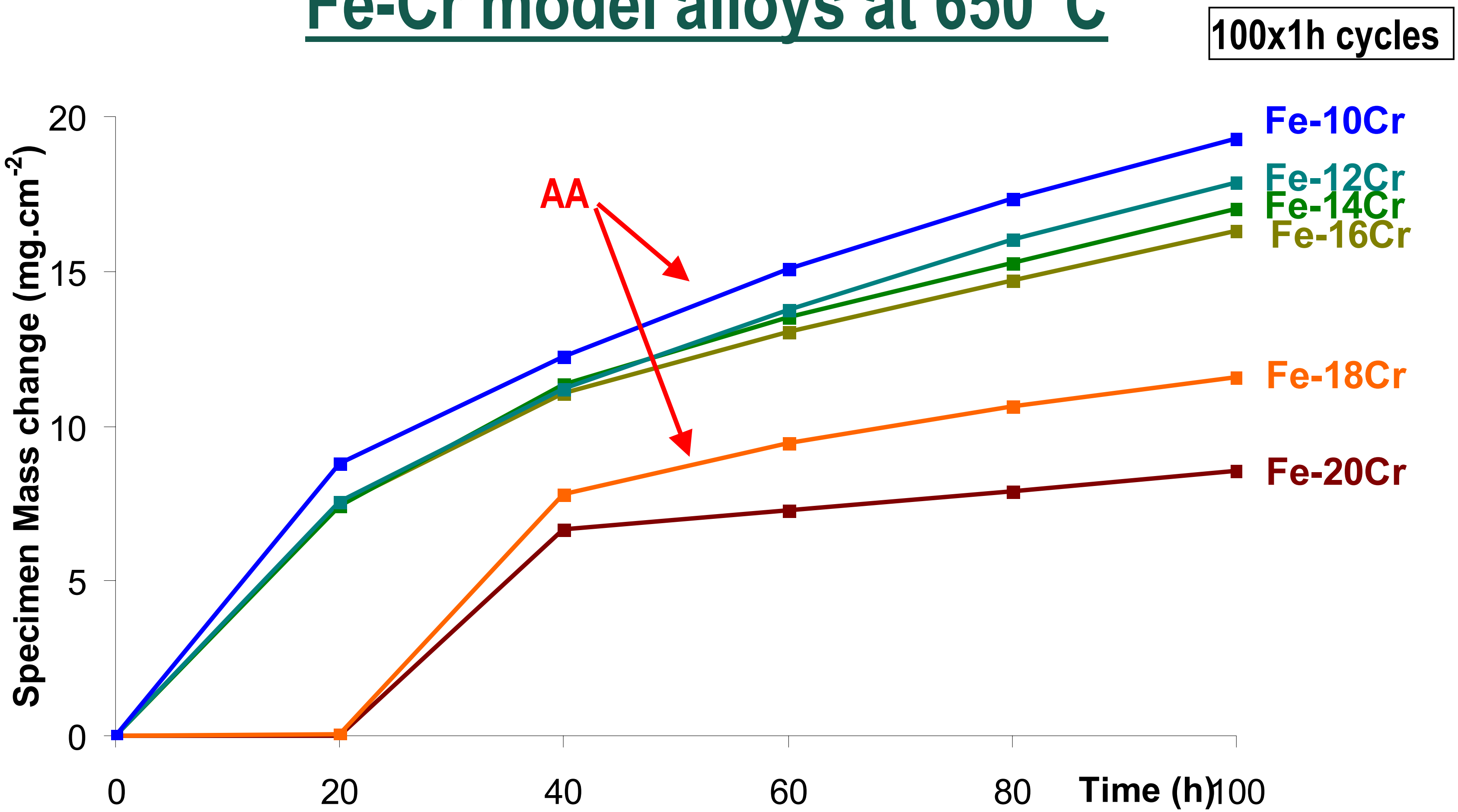
Effect of temperature on Fe-Cr-Ni model alloys



For Fe-Cr-Ni model alloys:

- Increasing temperature: not beneficial.
- But beneficial effect of higher Cr and Ni contents still important.

Fe-Cr model alloys at 650°C

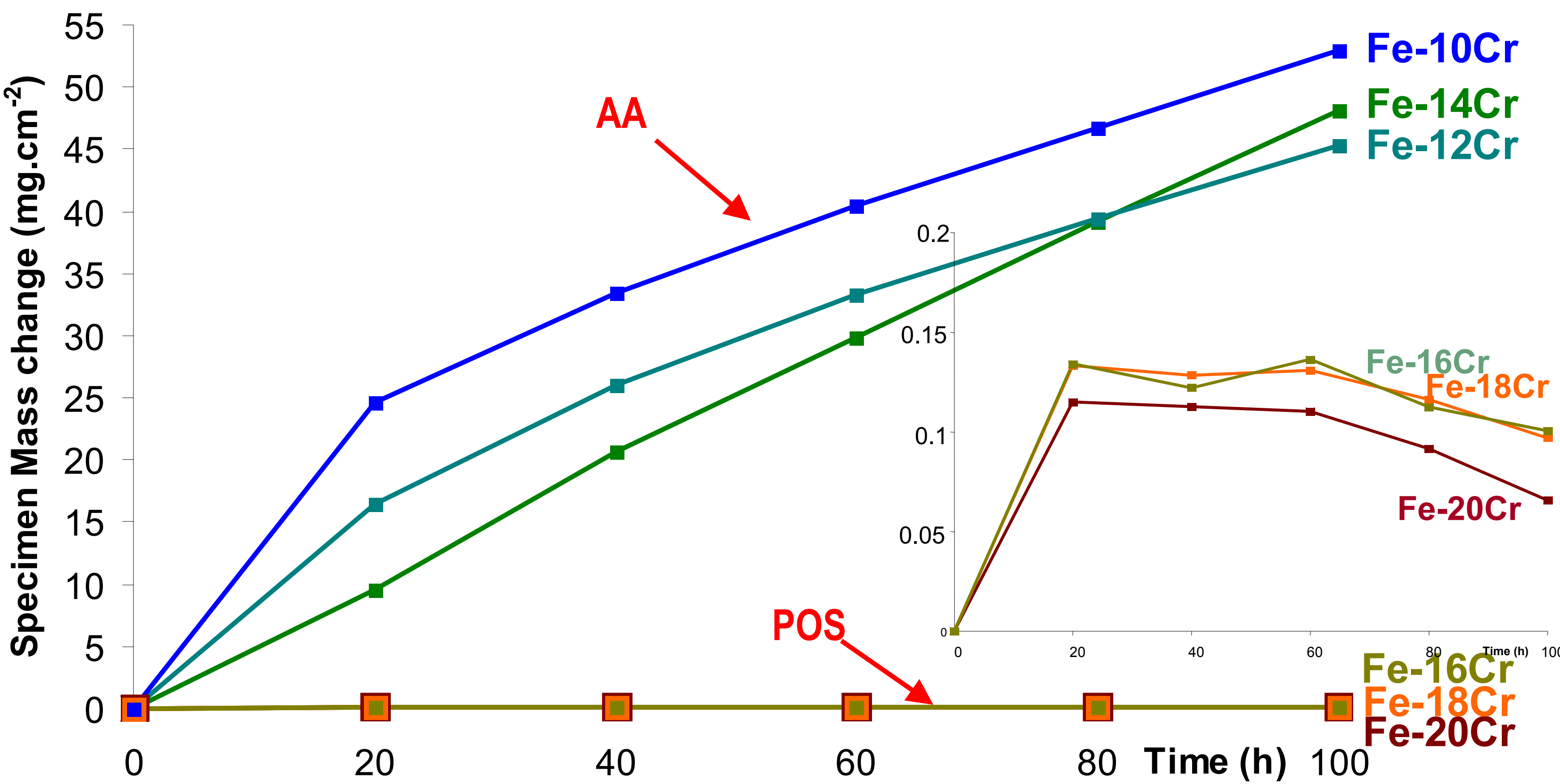


For Fe-Cr model alloys:

- No spallation
- Increasing the Cr content delayed the AA.

Fe-Cr model alloys at 800°C

100x1h cycles



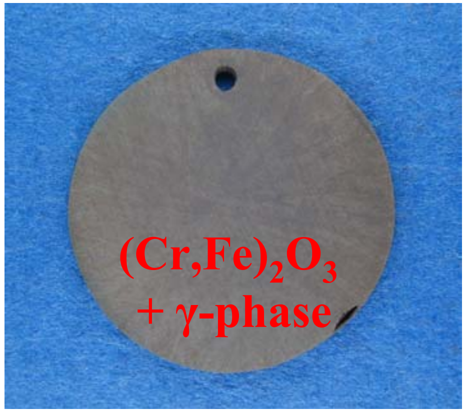
For Fe-Cr model alloys:

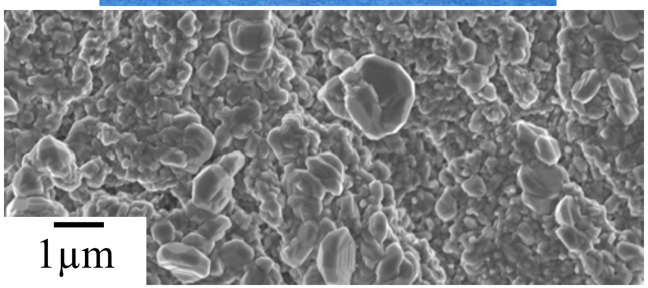
- Increasing both Cr content and temperature delayed AA

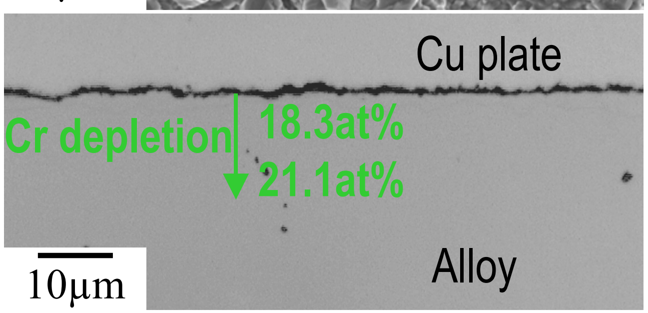
Protective Oxide Scales: POS

100x1h cycles

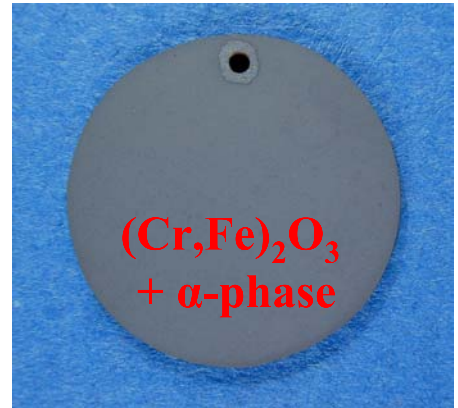
Fe-20Cr-30Ni at 650°C

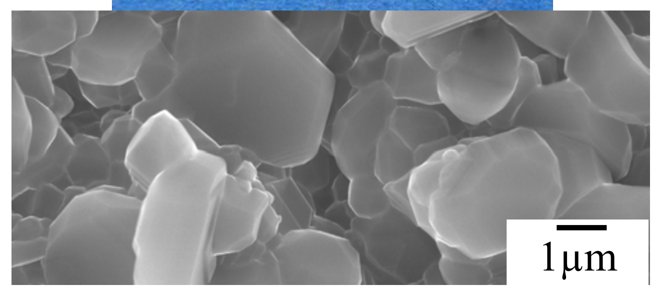


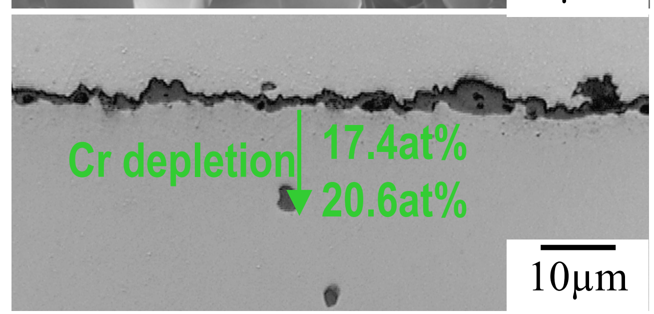




Fe-16Cr at 800°C

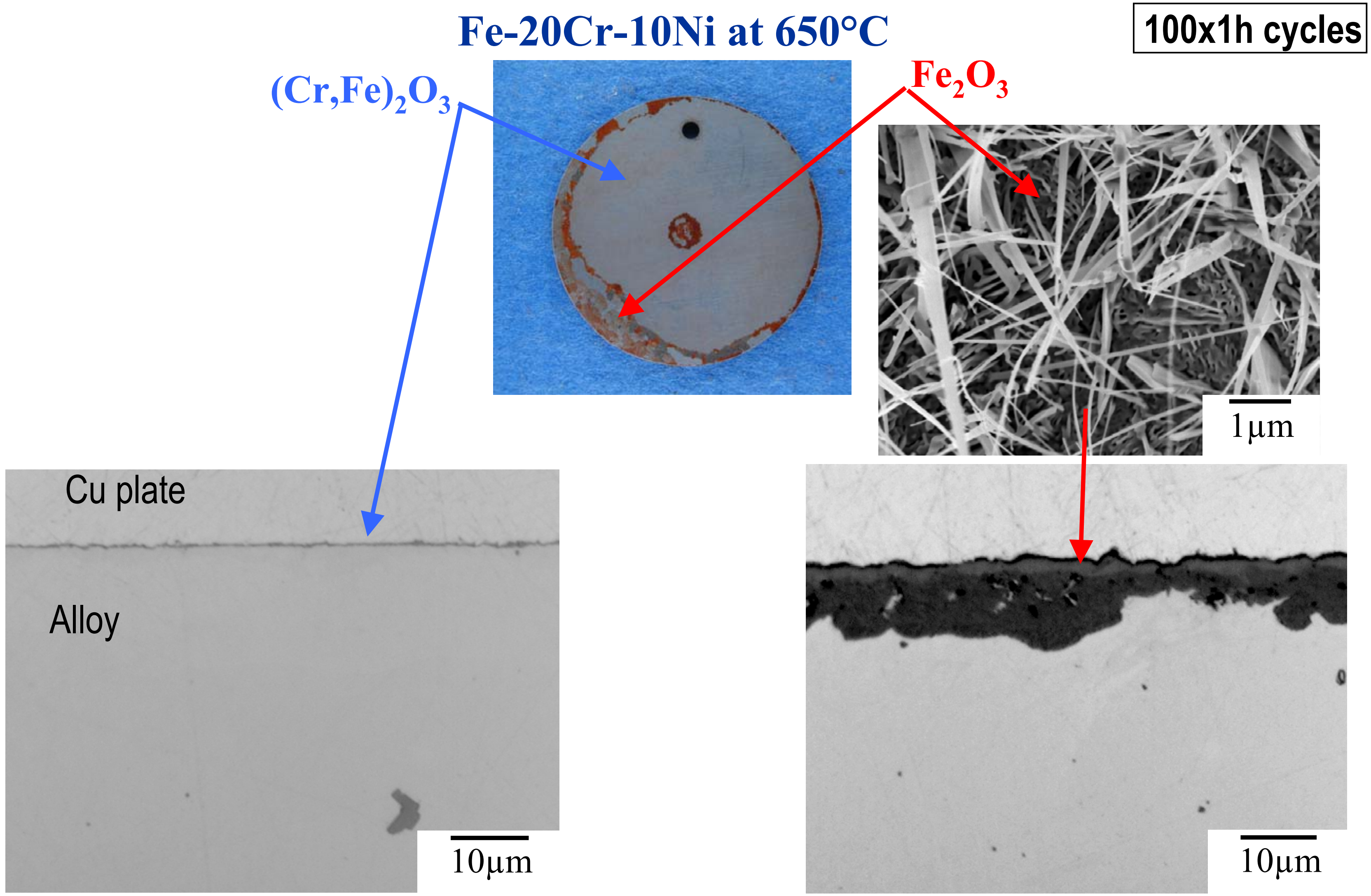






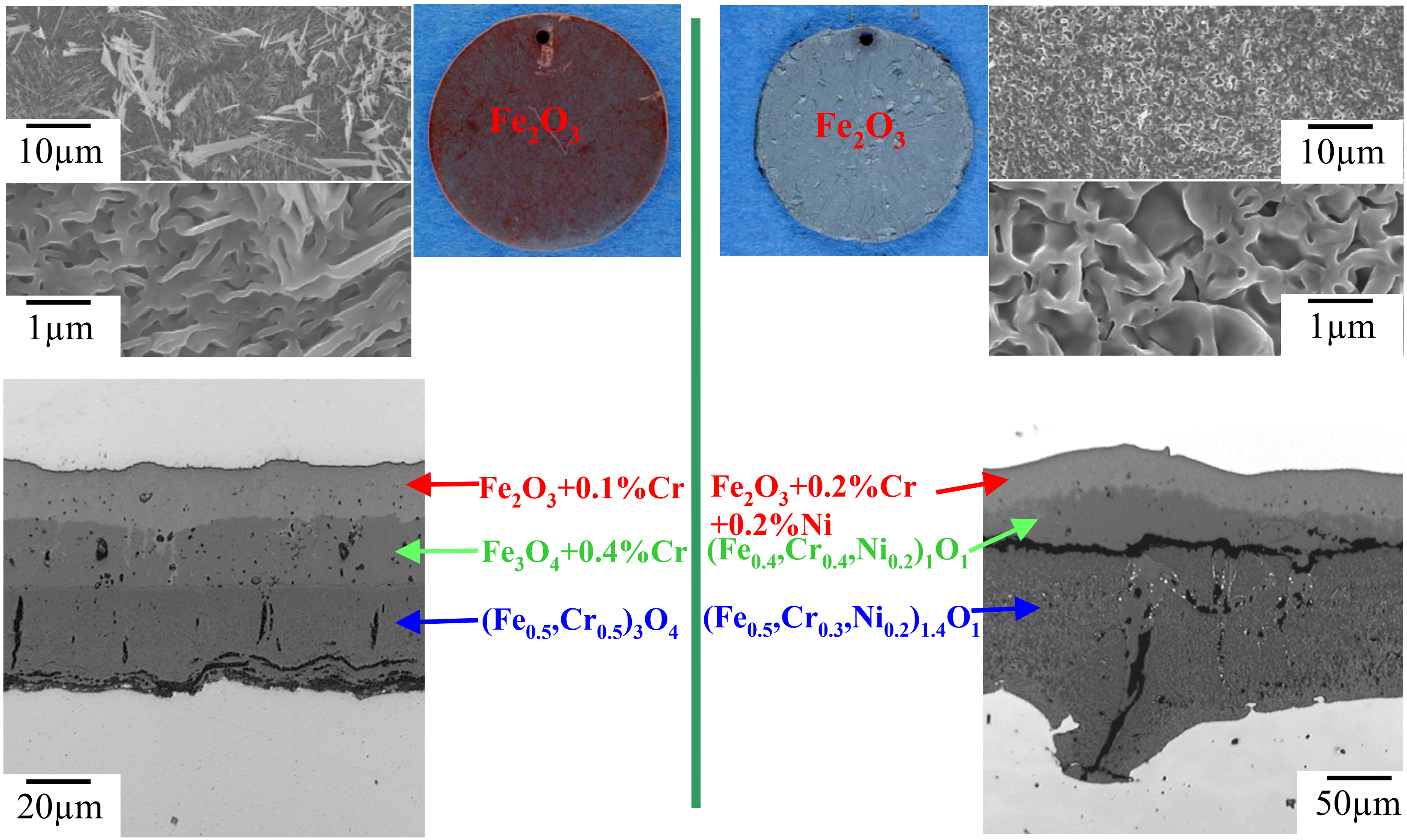
POS: Cr-rich $(Cr,Fe)_2O_3$ - Cr depletion in the alloy

First signs of the accelerated attack (AA)



Accelerated Attack Scales with or without Spallation

Fe-20Cr at 650°C | **100x1h cycles** | **Fe-20Cr-10Ni at 800°C**



AA or AAS: Fer: Fe_2O_3 - Fe_3O_4 - $(Fe,Cr)_3O_4$

Aus: Fe_2O_3 - (Fe,Cr,Ni)O - (Fe,Cr,Ni)O+alloy

Maps of the different behaviors under air+10% water vapor after 100x1h cycles

POS
AA
AAS

650°C

		Ni					
		0	10	15	20	25	30
Cr	10	F					
	12	F					
	14	F					
	16	F	F+A	A	A	A	A
	18	F	F+A	A	A	A	A
	20	F	F+A	A	A	A	A

750°C

		Ni					
		0	10	15	20	25	30
Cr	10	F					
	12	F					
	14	F					
	16	F	F+A	A	A	A	A
	18	F	F+A	A	A	A	A
	20	F	F+A	A	A	A	A

700°C

		Ni					
		0	10	15	20	25	30
Cr	10	F					
	12	F					
	14	F					
	16	F	F+A	A	A	A	A
	18	F	F+A	A	A	A	A
	20	F	F+A	A	A	A	A

800°C

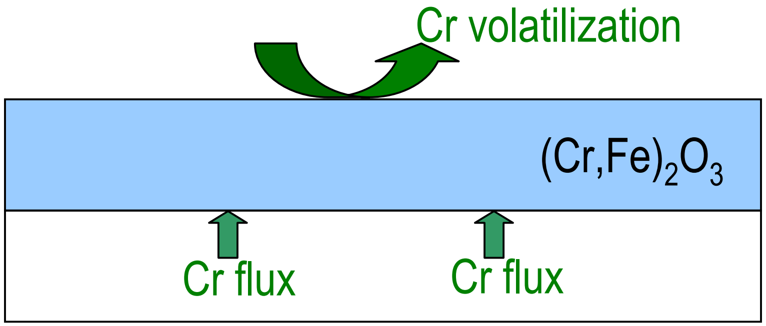
		Ni					
		0	10	15	20	25	30
Cr	10	F					
	12	F					
	14	F					
	16	F	F+A	A	A	A	A
	18	F	F+A	A	A	A	A
	20	F	F+A	A	A	A	A

Effect of Cr content

- Increasing Cr content delayed AA or AAS for both Fe-Cr and Fe-Cr-Ni alloys.
- Cr depletion found below the POS in the alloy
- Slight loss of mass observed during the growth of the POS could correspond to volatilization.

Explanation:

- Failure of the scale: described by Evans et al. [H.E. Evans et al., Ox. of Met., 1999]:
    - Intrinsic Chemical Failure: loss of Cr
    - Mechanically Induced Chemical Failure: contribution of 1h cycles
- Enhanced by volatilization of Cr species $Cr_2O_2(OH)_2$. [H. Asteman et al., Mat. Sci. Forum, 2001]

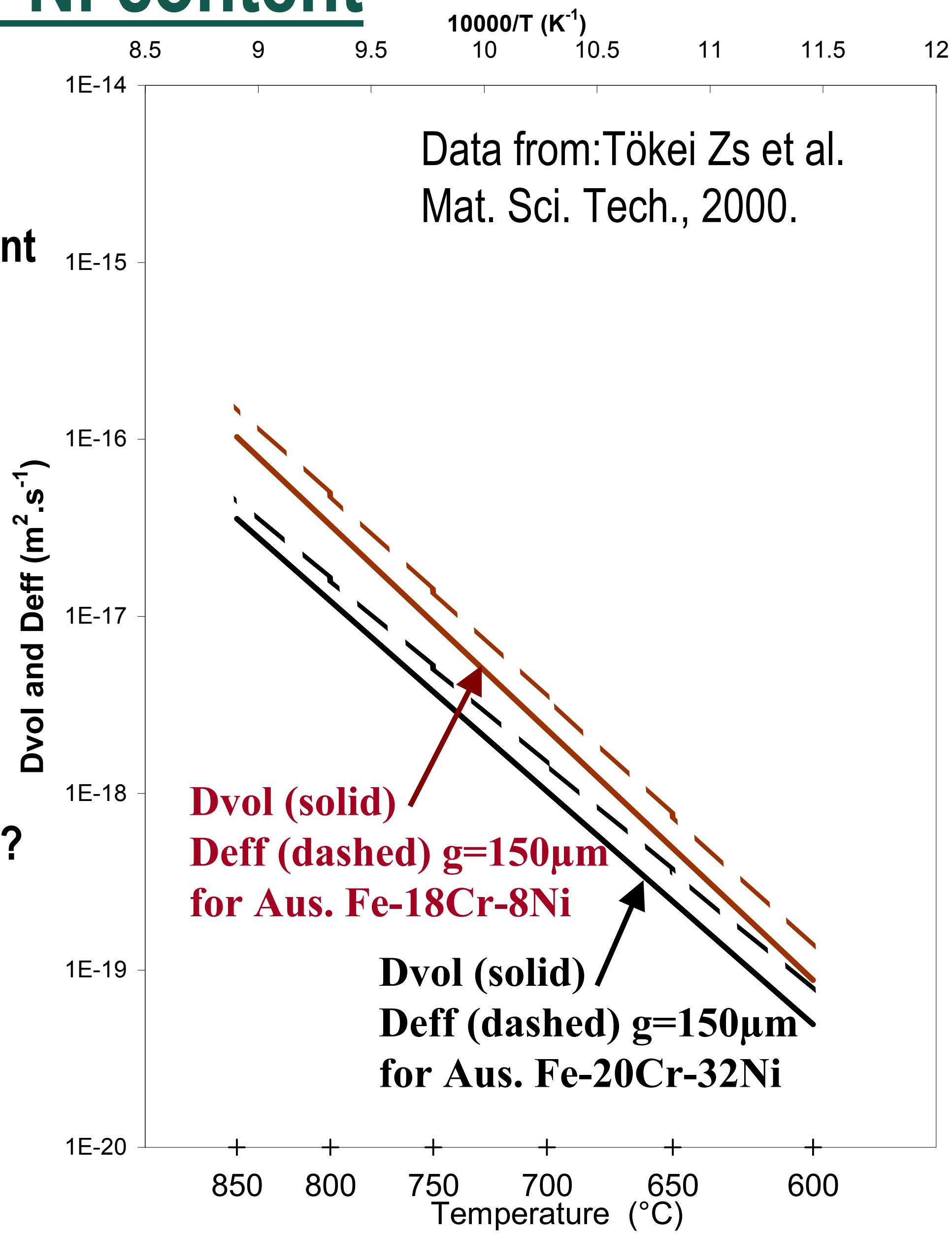


Effect of Ni content

- Increasing Ni content delayed AA or AAS for Fe-Cr-Ni alloys.
- Increasing Ni content decreased the amount of spallation

Explanation:

- Ni could increase the diffusivity of Cr ?
  Not from Tökei et al. data →
- Ni could reduce the volatilization of Cr ?
  Unlikely
- Ni could change the charge defect in POS ?
  Unlikely
- Ni could increase the a_{Cr} and/or decrease the a_{Fe} at the alloy/oxide interface ?
  Need further investigation

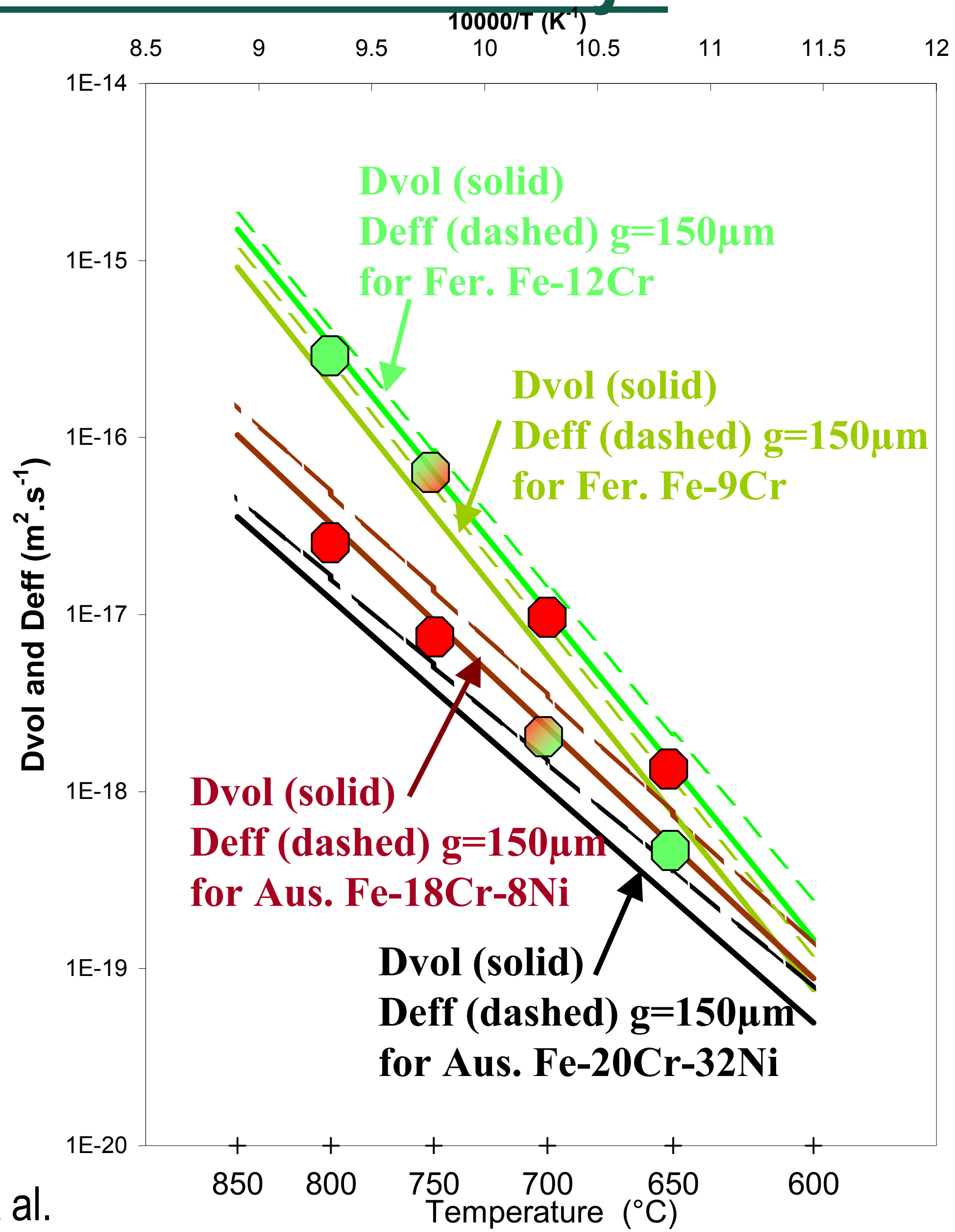


Comparison Ferritic/Austenitic alloys

- ➢ No spallation with Fe-Cr alloys.
- ➢ Fe-Cr alloys performed better at higher temperature (800°C).
- ➢ Fe-Cr-Ni alloys performed better at lower temperature (650°C).

Explanation:

- ➢ Spallation: Difference in CTE between Ferritic and Austenitic.
- ➢ At 800°C: faster Cr diffusivity in ferritic than in austenitic phase.
- ➢ At 650°C: Cr diffusivity similar – Beneficial effect of Ni.



Data from:
Tökei Zs et al.
Mat. Sci. Tech., 2000.

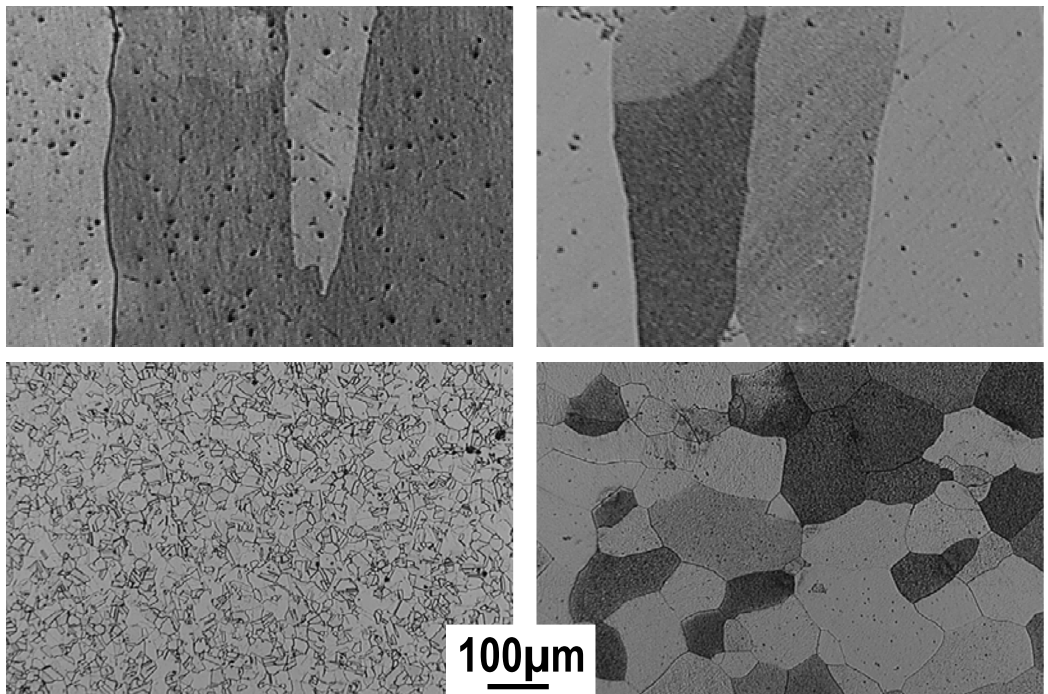
Fe-Cr-Ni and Fe-Cr alloys: Effect of the grain size

- Rolled alloys prepared from cast material:
  - Hot forged and hot rolled at 1100°C to 2.5mm thickness
  - Cold rolling to 1.25mm.

Fe-16Cr-30Ni | **Fe-16Cr**

Cast alloy after vacuum annealing at 1100°C for 4h (Fe-16Cr-30Ni)

Rolled alloy after Ar+4%H_2 annealing at 1000°C for 2min (Fe-16Cr-30Ni)



Cast alloy after vacuum annealing at 1100°C for 4h (Fe-16Cr)

Rolled alloy after Ar+4%H_2 annealing at 900°C for 2min (Fe-16Cr)

More realistic than cast microstructure
Similar to foil materials

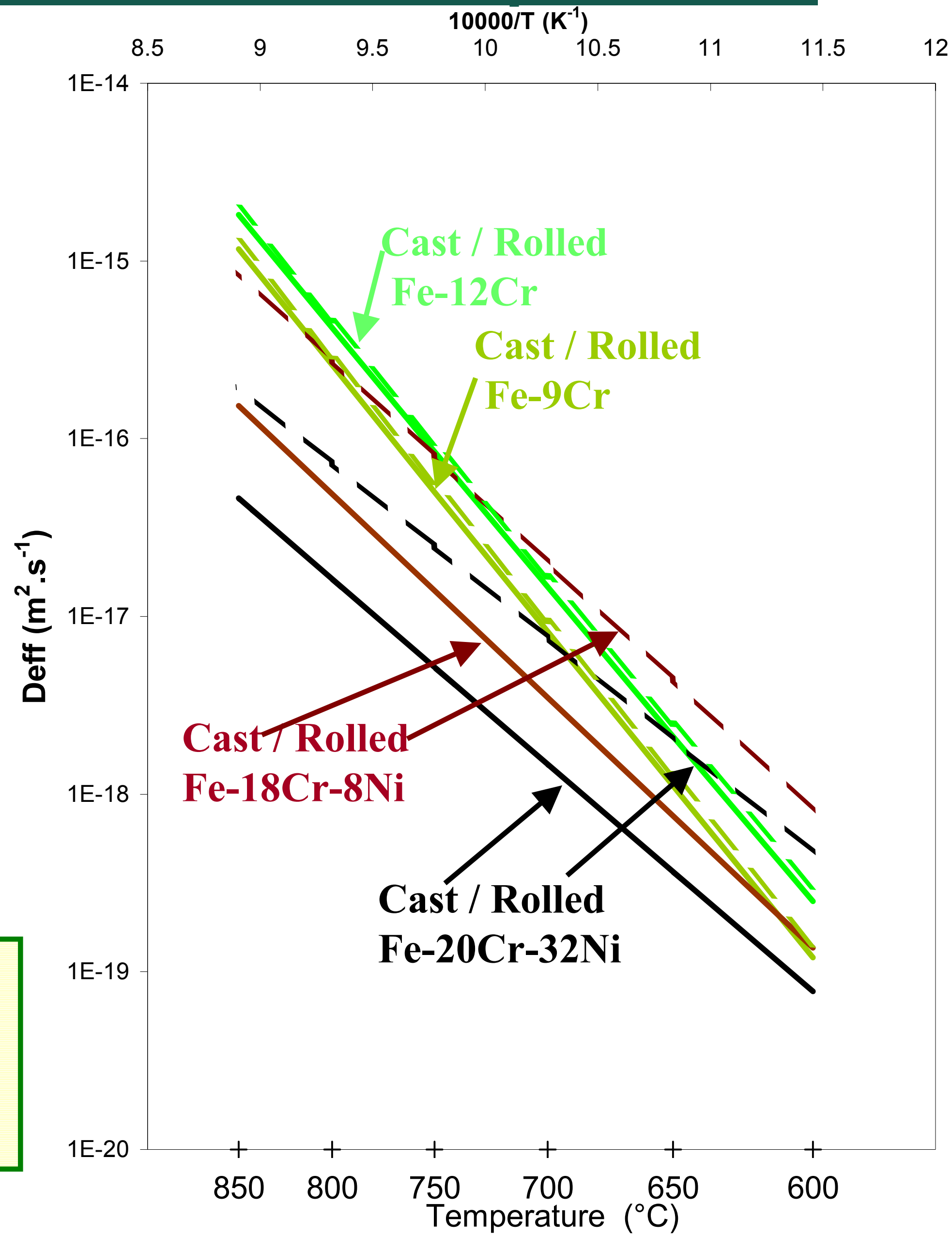
Expected behavior for rolled specimens

Calculated Cr effective coefficient from tokei et al. data with:

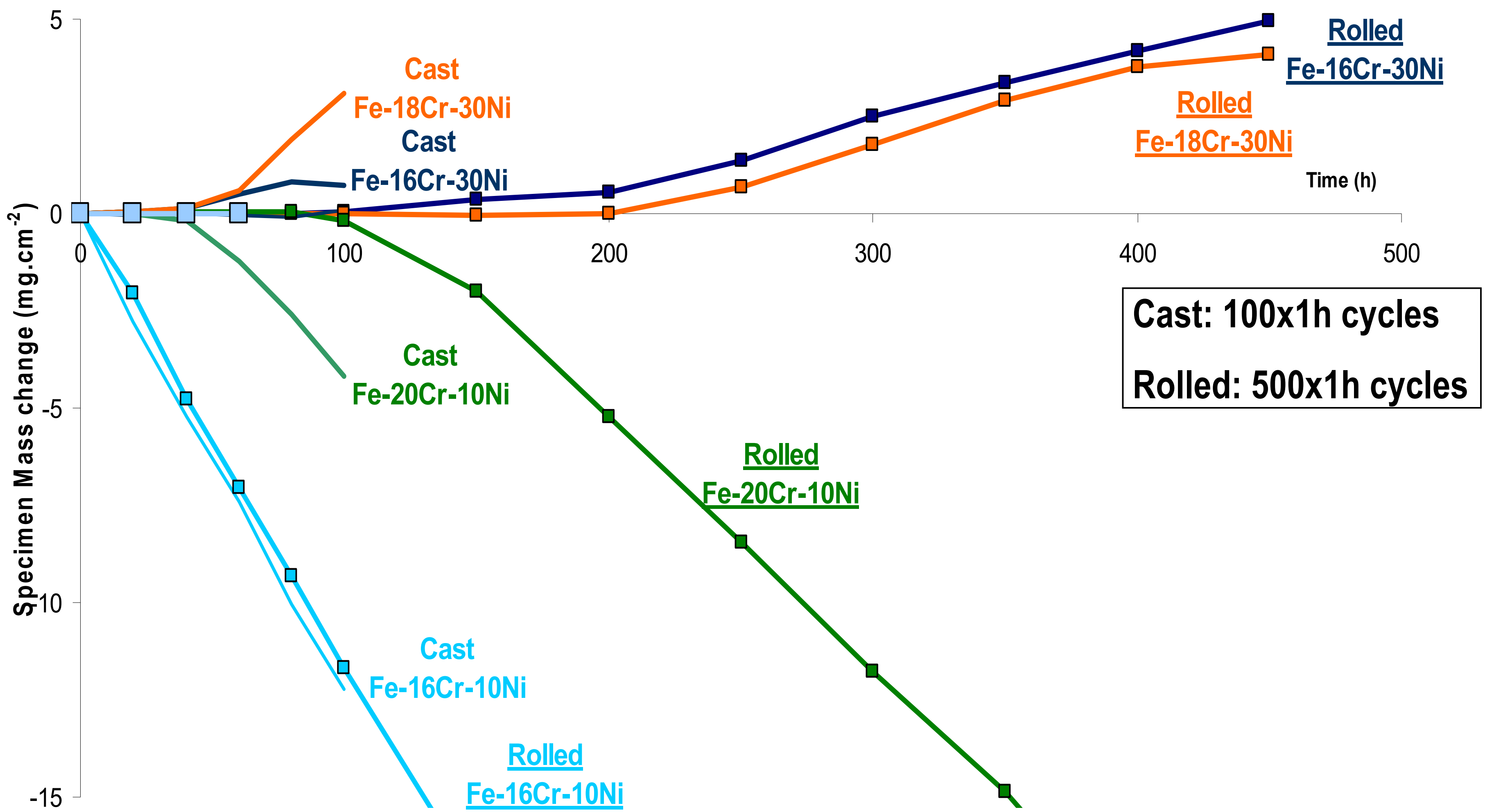
- Cast Fe-Cr-Ni : g=150µm
- Rolled Fe-Cr : g=100µm

- Cast Fe-Cr : g=150µm
- Rolled Fe-Cr-Ni : g=10µm

Expected grain size effect:
-Strong for Fe-Cr-Ni
-Slight for Fe-Cr



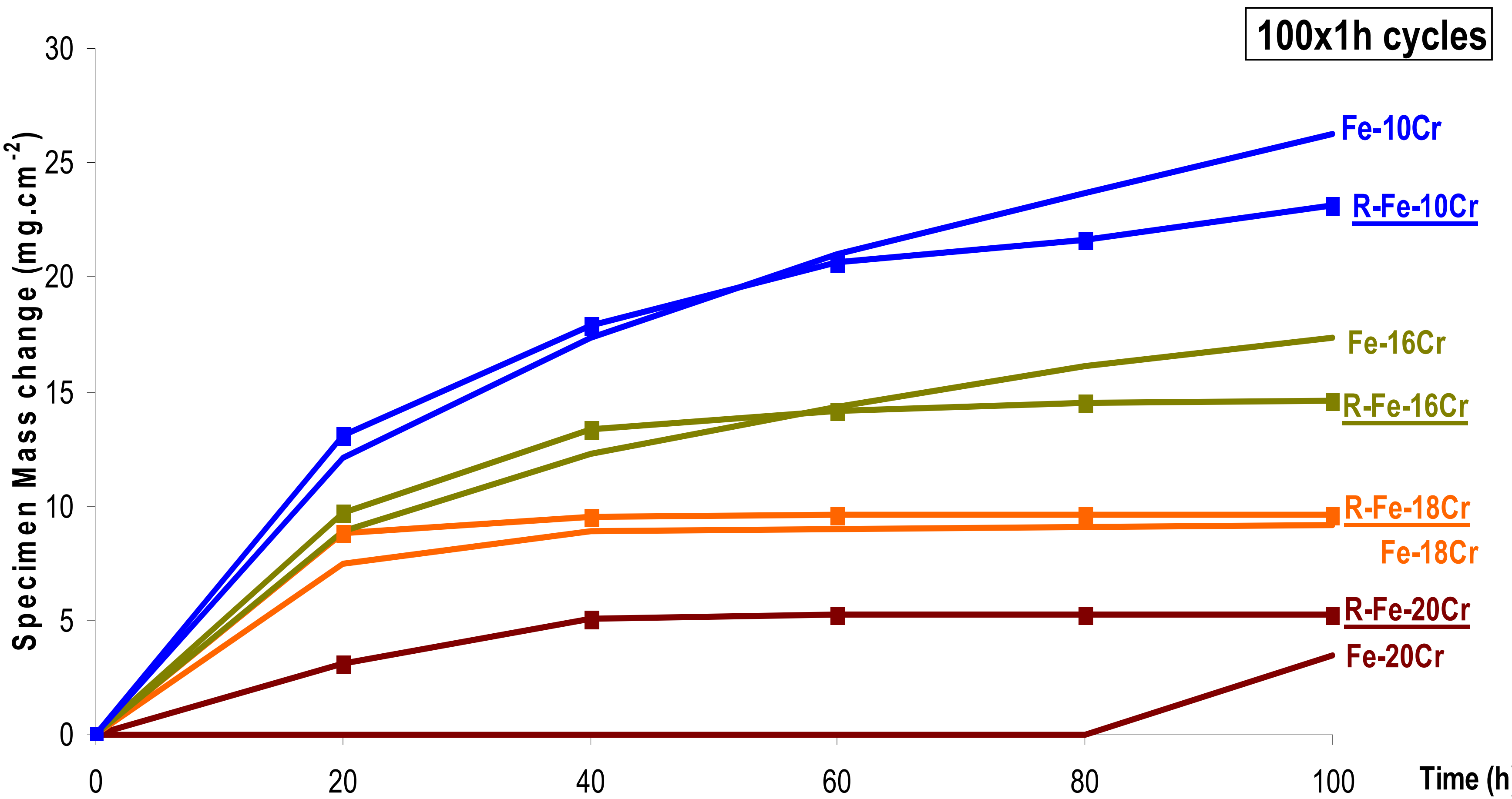
Rolled Fe-Cr-Ni model alloys at 700°C



For Fe-Cr-Ni model alloys at 700°C:

- Reducing the grain size delayed the AA for higher Cr and Ni contents

Rolled Fe-Cr model alloys at 700°C



For Fe-Cr model alloys at 700°C:

- No beneficial effect reducing the grain size.

Cast – Rolled alloys

- For Fe-Cr-Ni alloys:
  - Rolling: strong effect reducing the grain size.
  - Better performance at 700°C for rolled alloys.
- For Fe-Cr alloys:
  - Rolling: slight effect reducing the grain size
  - Similar behavior between cast and rolled alloys at 700°C

700°C

		Ni					
		0	10	15	20	25	30
Cr	10	F					
	12	F					
	14	F					
	16	F	F+A	A	A	A	A
	18	F	F+A	A	A	A	A
	20	F	F+A	A	A	A	A

AA / POS — Rolled

AA / POS — Cast

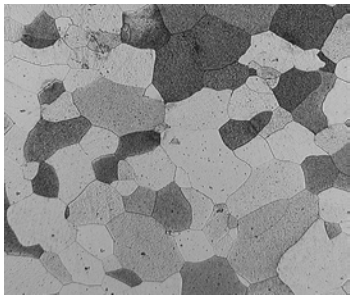
Explanation:

- Faster Cr diffusivity due to smaller grain size

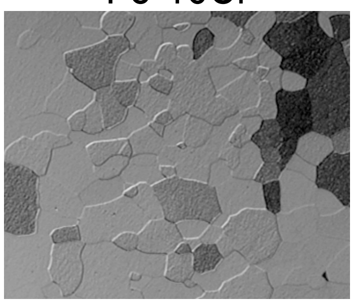
> - Lower Cr and Ni contents needed
> - Lower alloy cost.

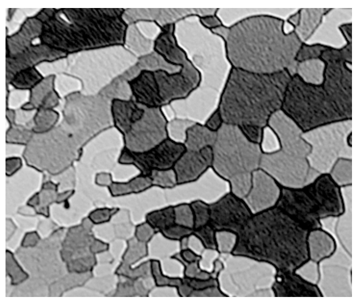
Rolled alloys with minor alloy additions

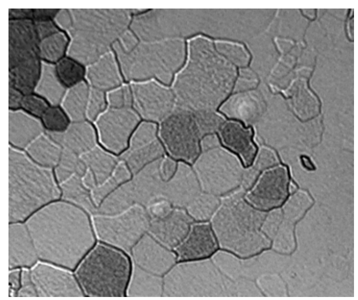
Nominal compositions	Fe	Cr	Ni	La	Al	Si	Ti	Mo	Mn	C	S	N	O
Fe-16Cr	Bal.	15.71	<0.01			<0.01				0.0009	0.0046	0.0010	0.0657
Fe-16Cr+La	Bal.	15.94	<0.01	0.31	<0.01	<0.01	<0.01	<0.01	<0.01	0.003	0.0010	0.0017	0.0048
Fe-16Cr+Al	Bal.	16.03	0.01	<0.01	0.07	<0.01	<0.01	<0.01	<0.01	0.004	0.004	0.0004	0.0038
Fe-16Cr+Si	Bal.	16.06	<0.01	<0.01	<0.01	0.17	<0.01	<0.01	<0.01	0.003	0.003	0.0023	0.0241
Fe-16Cr+Ti	Bal.	16.02	0.01	<0.01	<0.01	<0.01	0.14	0.01	<0.01	0.003	0.004	0.0004	0.0065
Fe-16Cr+Mo	Bal.	16.06	<0.01	<0.01	<0.01	<0.01	<0.01	2.04	<0.01	0.004	0.003	0.0006	0.0303
Fe-16Cr+0.1Mn	Bal.	16.03	0.02	<0.01	<0.01	<0.01	<0.01	0.01	0.12	0.003	0.003	0.0005	0.0281
Fe-16Cr+0.6Mn	Bal.	16.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.57	0.003	0.004	0.0015	0.0281
Fe-16Cr+1.1Mn	Bal.	16.04	0.01	<0.01	<0.01	0.01	<0.01	<0.01	1.13	0.002	0.004	0.0022	0.0300
Fe-16Cr+2.2Mn	Bal.	16.08	0.01	<0.01	<0.01	0.01	<0.01	<0.01	2.19	0.003	0.003	0.0005	0.0249
Fe-16Cr+3.5Mn	Bal.	15.93	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	3.46	0.002	0.004	0.0008	0.0204


Fe-16Cr

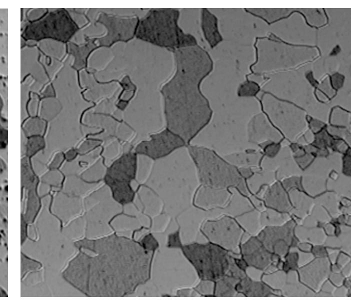
100µm

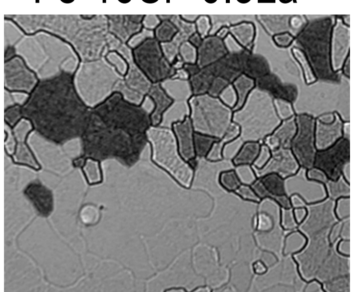

Fe-16Cr+0.3La

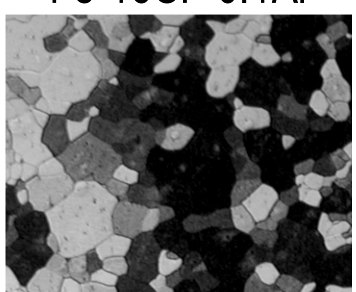

Fe-16Cr+0.1Al

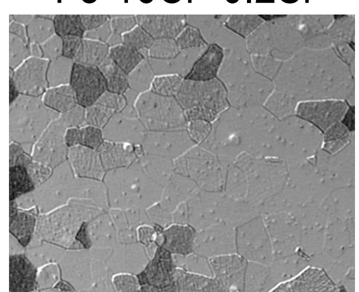

Fe-16Cr+0.2Si

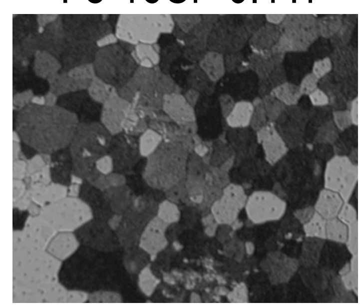

Fe-16Cr+0.1Ti

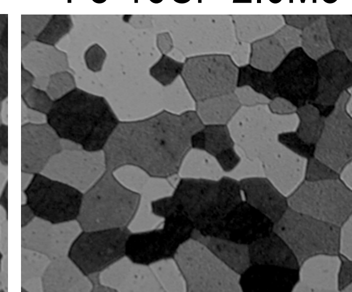

Fe-16Cr+2.0Mo


Fe-16Cr+0.1Mn

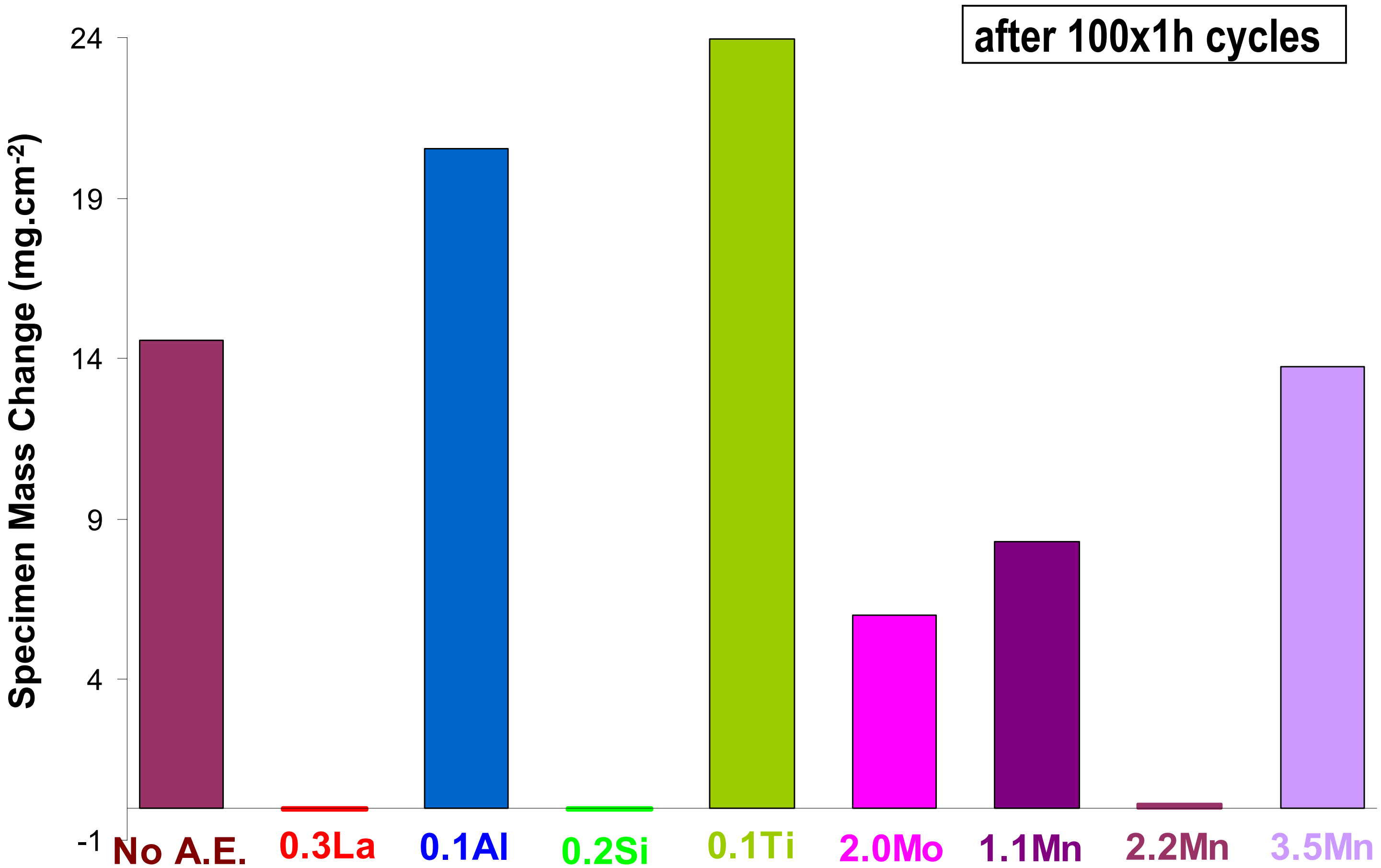

Fe-16Cr+0.6Mn


Fe-16Cr+1.1Mn


Fe-16Cr+2.2Mn


Fe-16Cr+3.5Mn

Initial results on Fe-16Cr alloys at 700°C with minor alloy addition



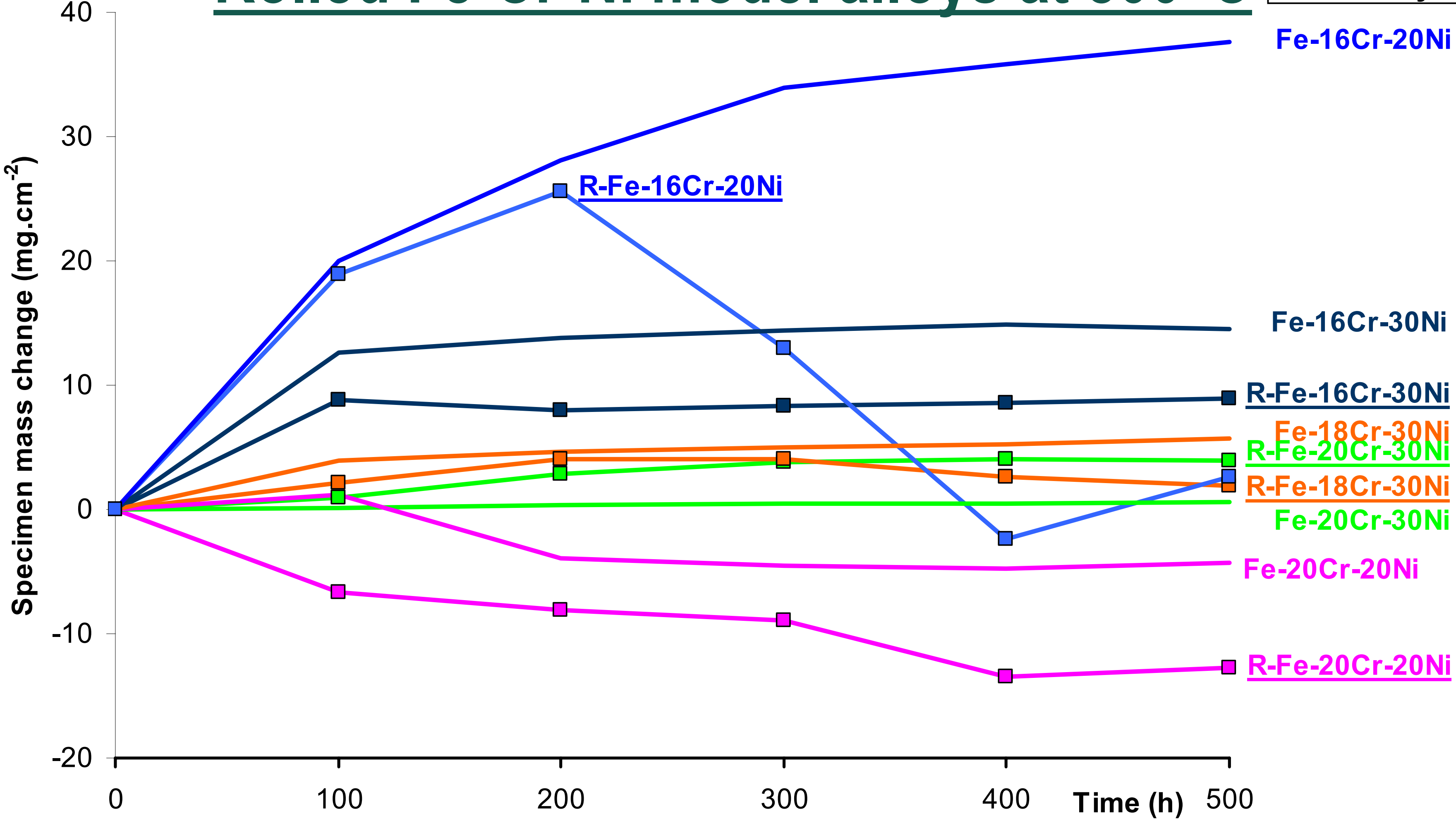
- Direction of future work: La, Si, Mn

Summary

- **Role of Cr:**
  - **Increasing Cr content delayed AA for both Fe-Cr and Fe-Cr-Ni alloys.**
- **Role of Ni:**
  - **Increasing Ni content delayed AA for Fe-Cr-Ni alloys and lowered spallation.**
- **Role of the alloy phase:**
  - **Ferritic never showed spallation of the oxide scale.**
  - **Ferritic better than austenitic at high temperature (800°C).**
  - **Austenitic better than ferritic a low temperature (650°C).**
- **Role of grain size:**
  - **For Fe-Cr-Ni alloys: better behavior of rolled specimens at 700°C with lower Ni and Cr contents.**
- **Role of minor alloying additions:**
  - **Future work will focus on fined grained materials with alloy additions such as: Si, Mn, and La.**

Rolled Fe-Cr-Ni model alloys at 800°C

5x100h cycles

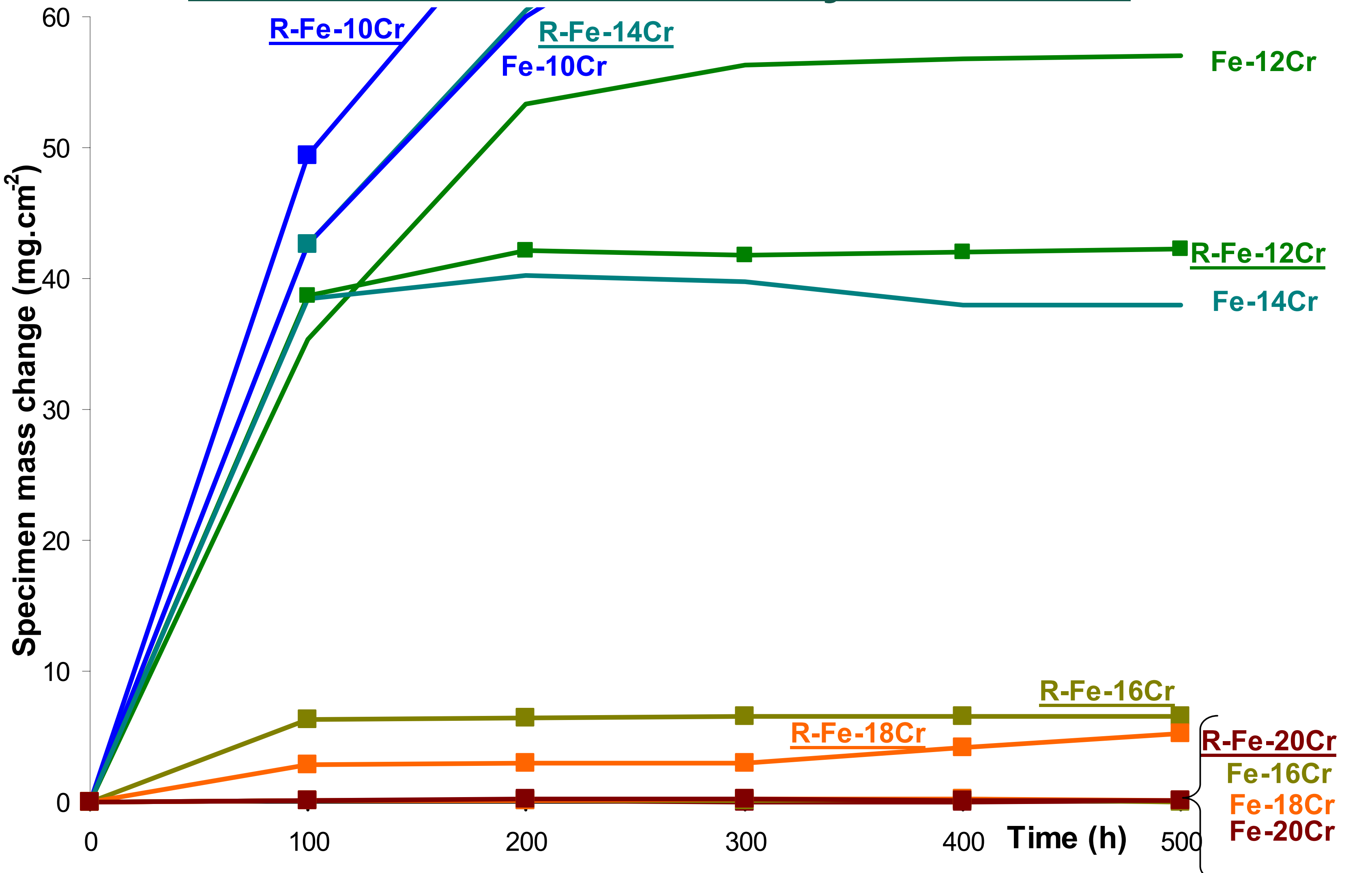


For Fe-Cr-Ni model alloys at 800°C:

➢ Reducing the grain size : no beneficial effect.

Rolled Fe-Cr model alloys at 800°C

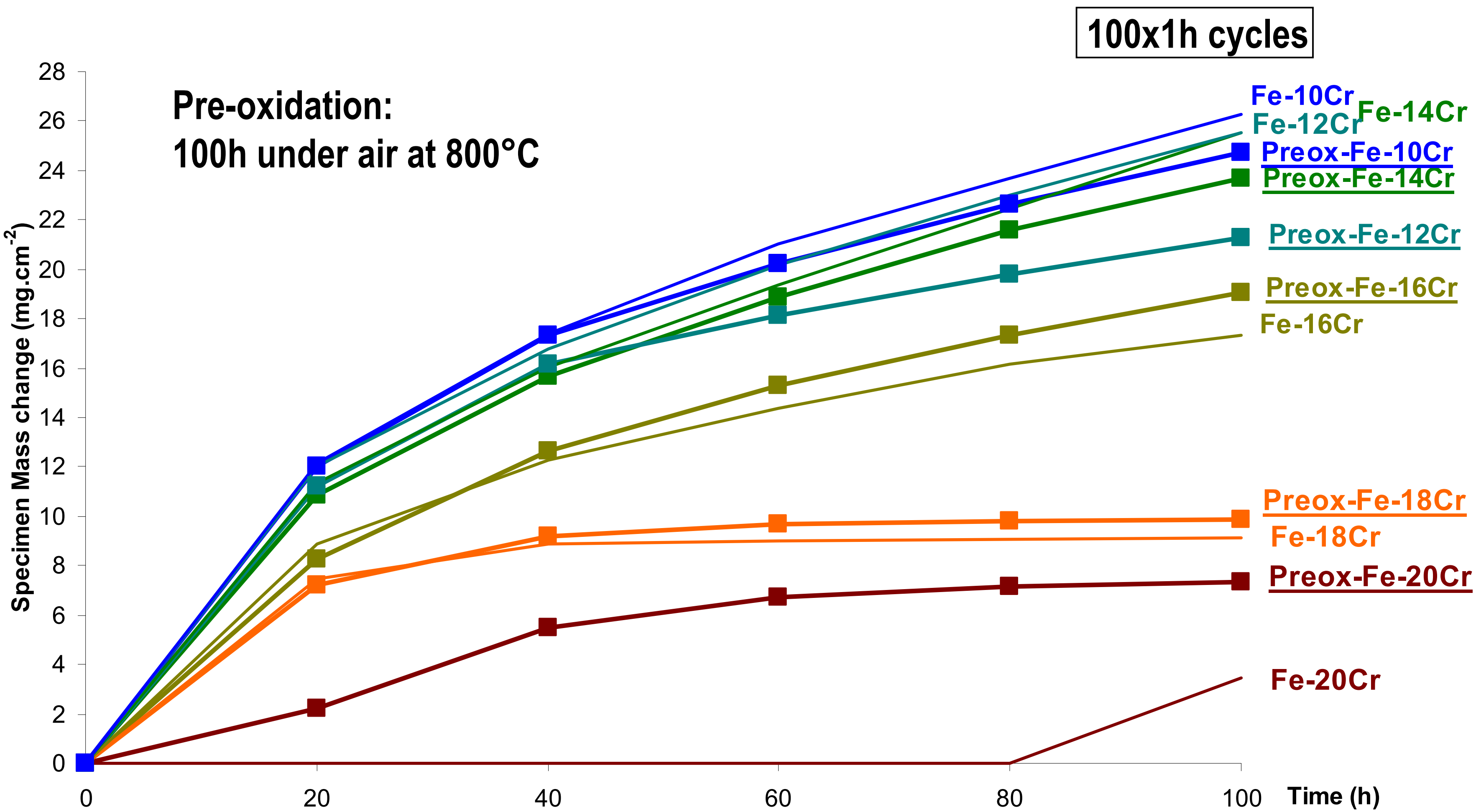
5x100h cycles



For Fe-Cr model alloys at 800°C:

➢ No beneficial effect reducing the grain size.

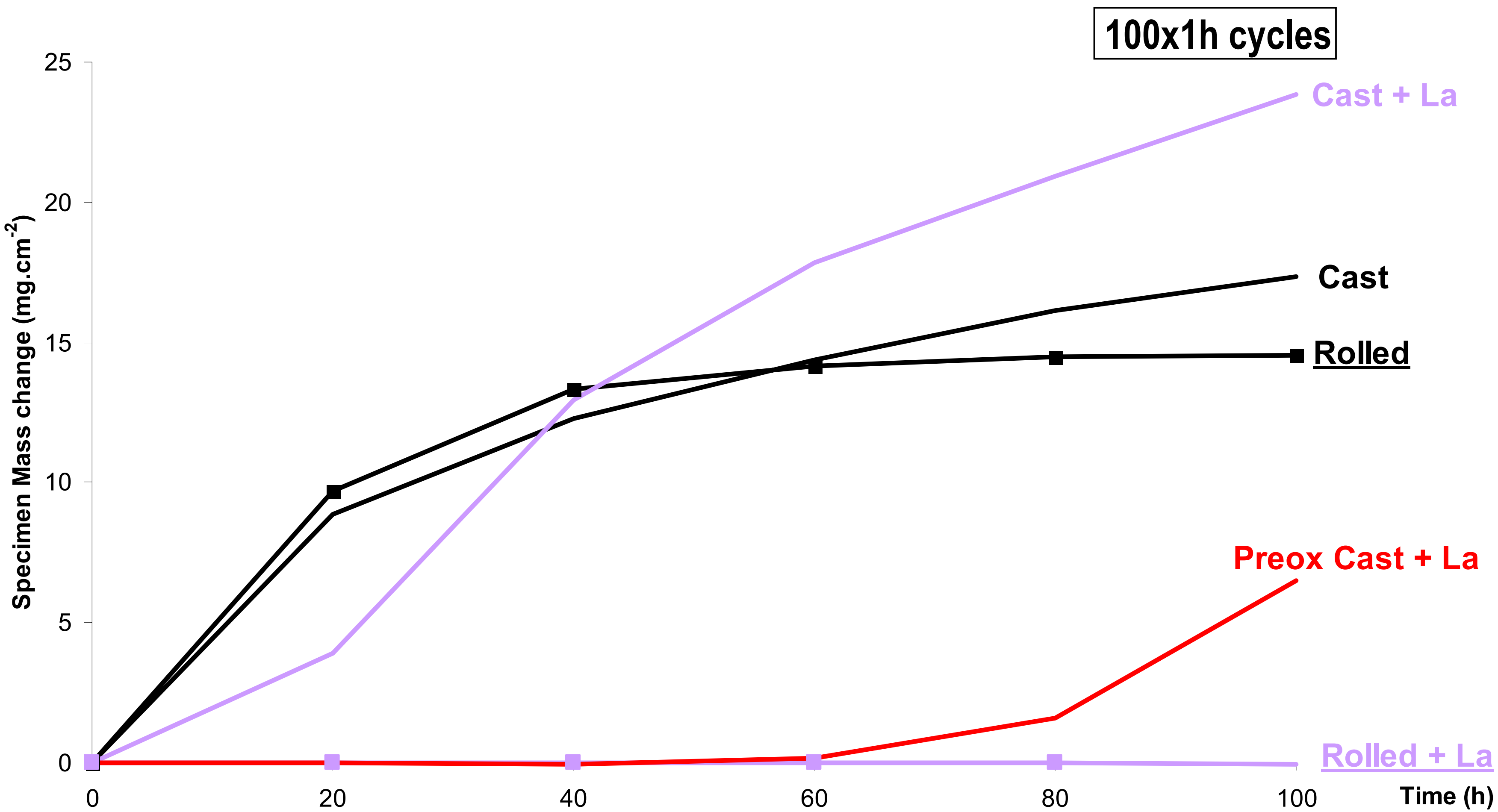
Fe-Cr cast alloys at 700°C: Pre-oxidation treatment



For Fe-Cr cast alloys:

➢ No protection possible with a Cr_2O_3 scale

Fe-16Cr+La at 700°C: Cast and Rolled / Pre-oxidation



- No beneficial effect of La on Cast material
- Beneficial effect of La on Pre-oxidized Cast material and Rolled alloy

Behavior of model alloys after 100x1h cycles in mixed air+10 water vapor