Crofer® 22 H - a New High Strength Ferritic Steel for Interconnectors in SOFCs

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Outline

- Introduction
- Experimental
- Results and Discussion
- Summary

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Development challenges for SOFC-materials

Material	CTE in 10^{-6} K^{-1} (20 ° C to 800 ° C)
Ni-YSZ-Cermet	12
8YSZ	10

- Coefficient of thermal expansion similar to ceramics (CTE)
- Excellent high-temperature oxidation resistance
- Low area specific contact resistance (ASR)
- Low release rate of volatile chromium species
- Good creep properties
- Good workability

Coefficient of Thermal Expansion

Material	CTE in 10^{-6} K^{-1} (20 ° C to 800 ° C)
Ni-YSZ-Cermet	12
8YSZ	10
Nickel Alloys	14 - 19
Austenitic stainless steel	18 - 20
Ferritic stainless steels	12 - 14
Crofer® 22 APU	12

Crofer® 22 APU

Cr	Mn	Ti	La	Al	Si	Fe
23 %	0.45 %	0.06 %	0.1 %	< 0.05 %	< 0.05 %	balance

- **Joint effort between**

  Forschungszentrum Jülich (laboratory phase), and ThyssenKrupp VDM (commercial production)

- **Commercially available since 2002**

- **Main drawback**

  → **Low creep strength**

High strength Cr ferritic steel

- Fe 22Cr 2W 0.5Nb 0.2Si
- Nb, W, Si: Improved creep strength through laves phase formation
- Si: Suppression of the adverse effect of Nb on oxidation

- Again a joint effort between

  Forschungszentrum Jülich (laboratory phase) and ThyssenKrupp VDM (commercial production)

- Commercially available since 2008 as Crofer® 22 H

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Chemical Analysis

	Cr	C	N	Mn	Si	Al	W	Nb	Ti	La
Crofer® 22 APU*)	23	0.004	0.004	0.45	< 0.05	< 0.05	-	-	0.06	0.1
Crofer® 22 H*)	23	0.007	0.02	0.45	0.25	< 0.05	2	0.5	0.06	0.1
Fe 22Cr 2W 0.5Nb 0.2Si **)	22	0.002	0.007	0.43	0.24	< 0.01	2	0.5	0.06	0.1

in wt.- %, Fe balance, S $\leq$ 0.002

*) typical values of commercial melts

**) analysis of a 10 kg laboratory melt

- **Commercial melts:** **hot rolled to plates of 22 to 5 mm, hot an cold rolled to strip of 3 to 0.2 mm**
- **Laboratory melt:** **hot rolled to plates 16 and 2 mm**

ThyssenKrupp

Experimental

- **CTE:** Misura® 3 OLDT (Expert System Solutions); under Argon
- **Discontinuous oxidation test:** at 800 ° C and 900 ° C,
  - laboratory air, cycle 250 h or 100 h, and
  - simulated anode gas Ar - 4% H_2 - 20% H_2O, cycle 100 h,
- **Cyclic oxidation tests**: 2 h at 900 ° C/ 15 min cooling at RT
- **Examination of oxide scales**: SEM with EDX
- **ASR:** conventional four-point method, monitored in-situ for 300 h at 800 °C in air
  - specimens pre-oxidised for 100 h at 800 °C in air
  - layer of Pt-paste on both surfaces; electrical connection with a Pt-mesh

Experiments

- **Tensile tests:** at room temperature
- **Hot tensile tests:** 100 °C to 800 °C, in air
  - about 1 hour at testing temperature before the test started
- **Creep tests;** in air, continuous and discontinuous measurement of elongation

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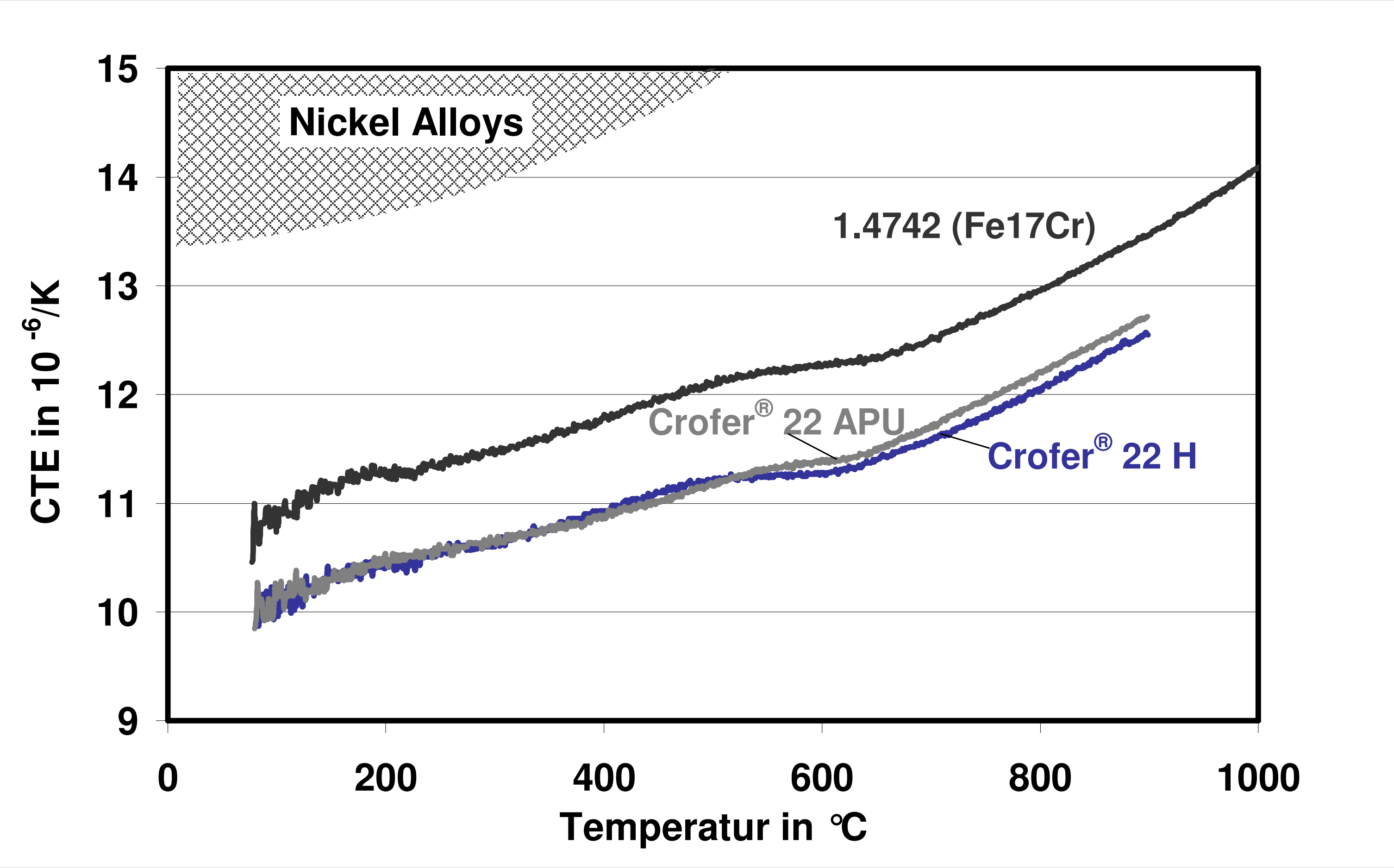
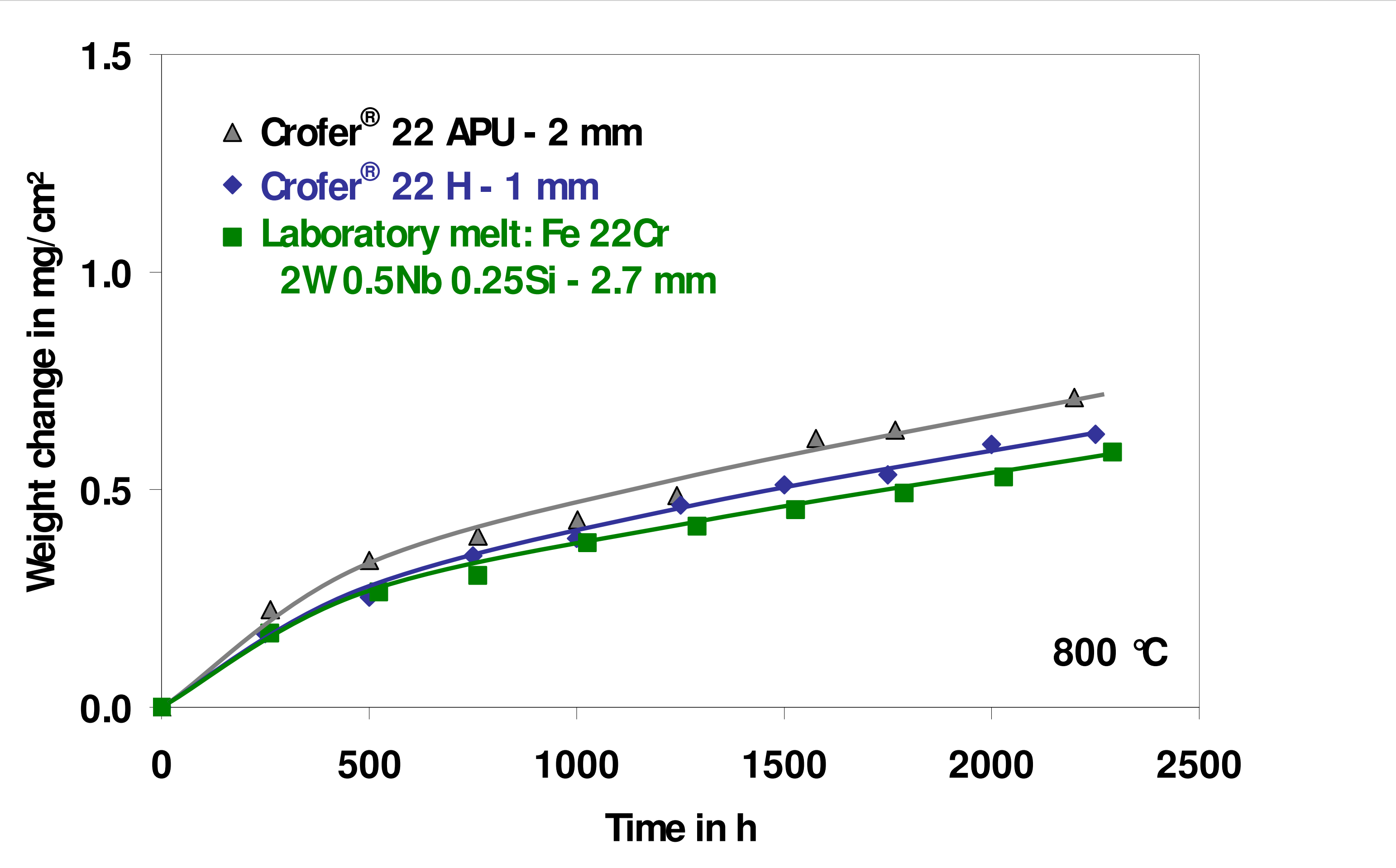
Coefficient of thermal expansion (CTE)

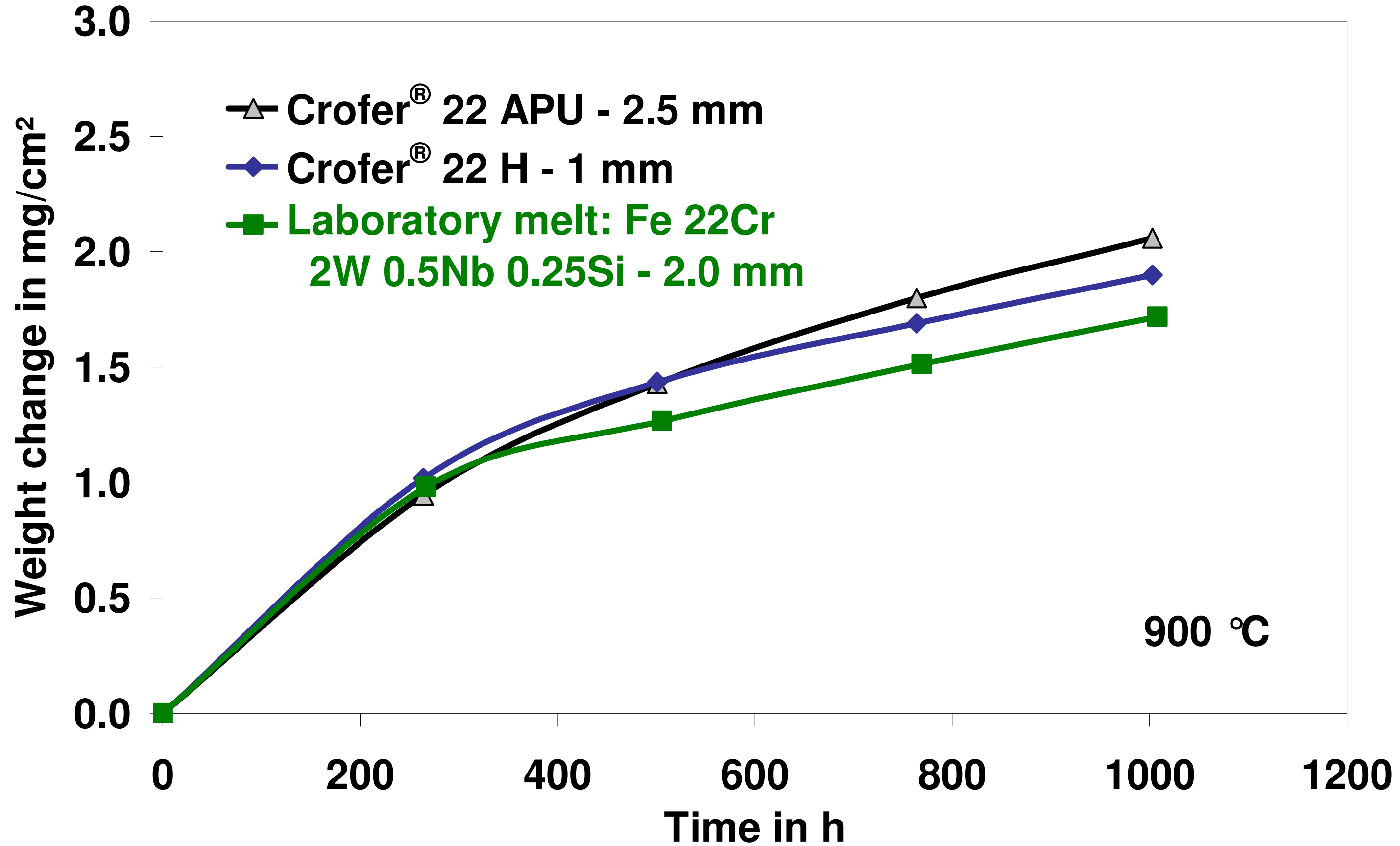


- CTE similar to that of Ni-YSZ-Cermet - Anode

Discontinuous oxidation (250 h cycles) at 800 °C in air; specimen thicknesses ≥ 1 mm



Discontinuous oxidation (250 h cycles) at 900 °C in air; specimen thicknesses ≥ 1 mm



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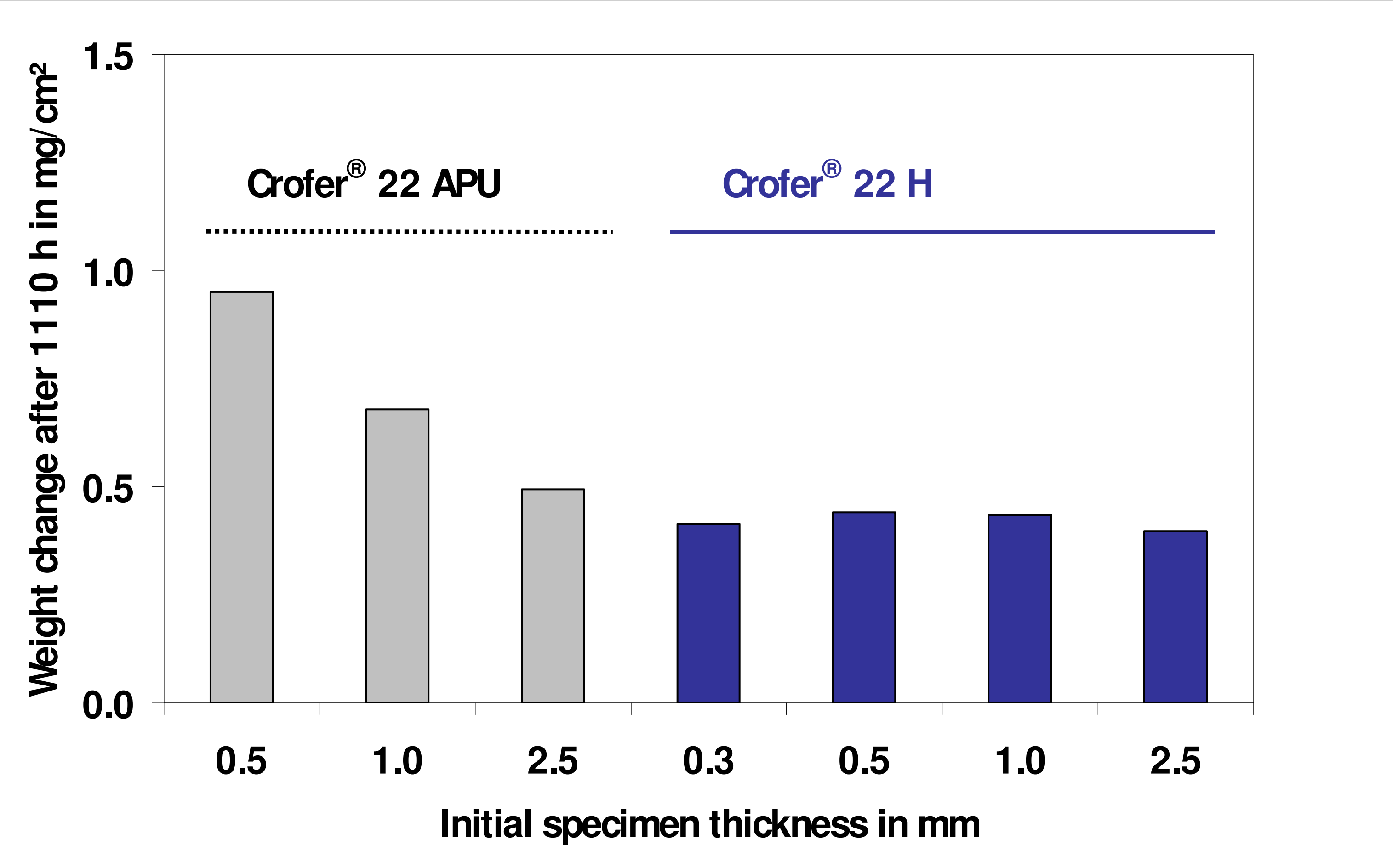
A company of ThyssenKrupp Stainless

ThyssenKrupp VDM

Discontinuous oxidation (100 h cycles) at 800 °C in air
after 1110 h



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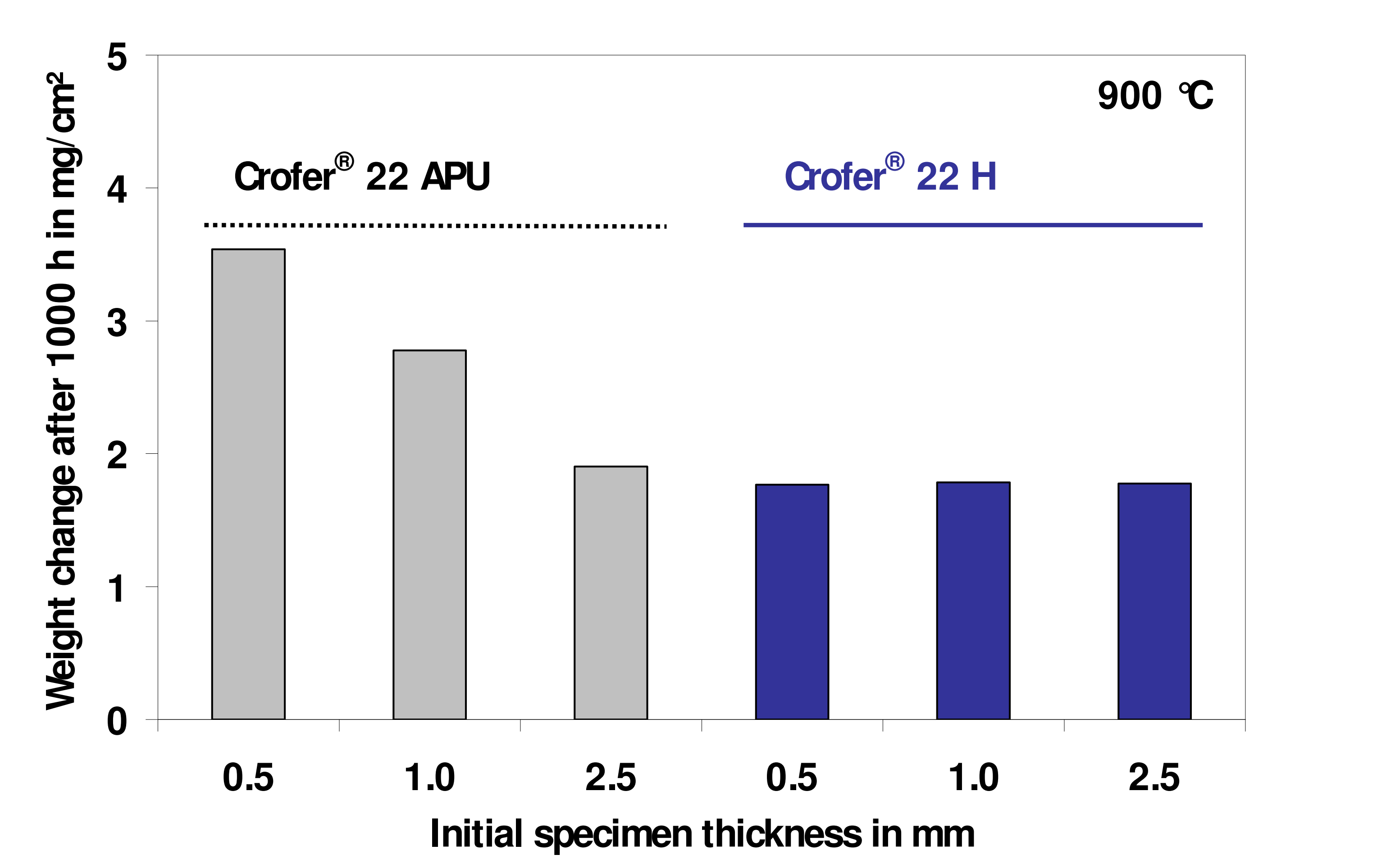
Cyclic oxidation (cycle: 2 h heating/ 15 min cooling) at 900 °C
in air after 1000 h



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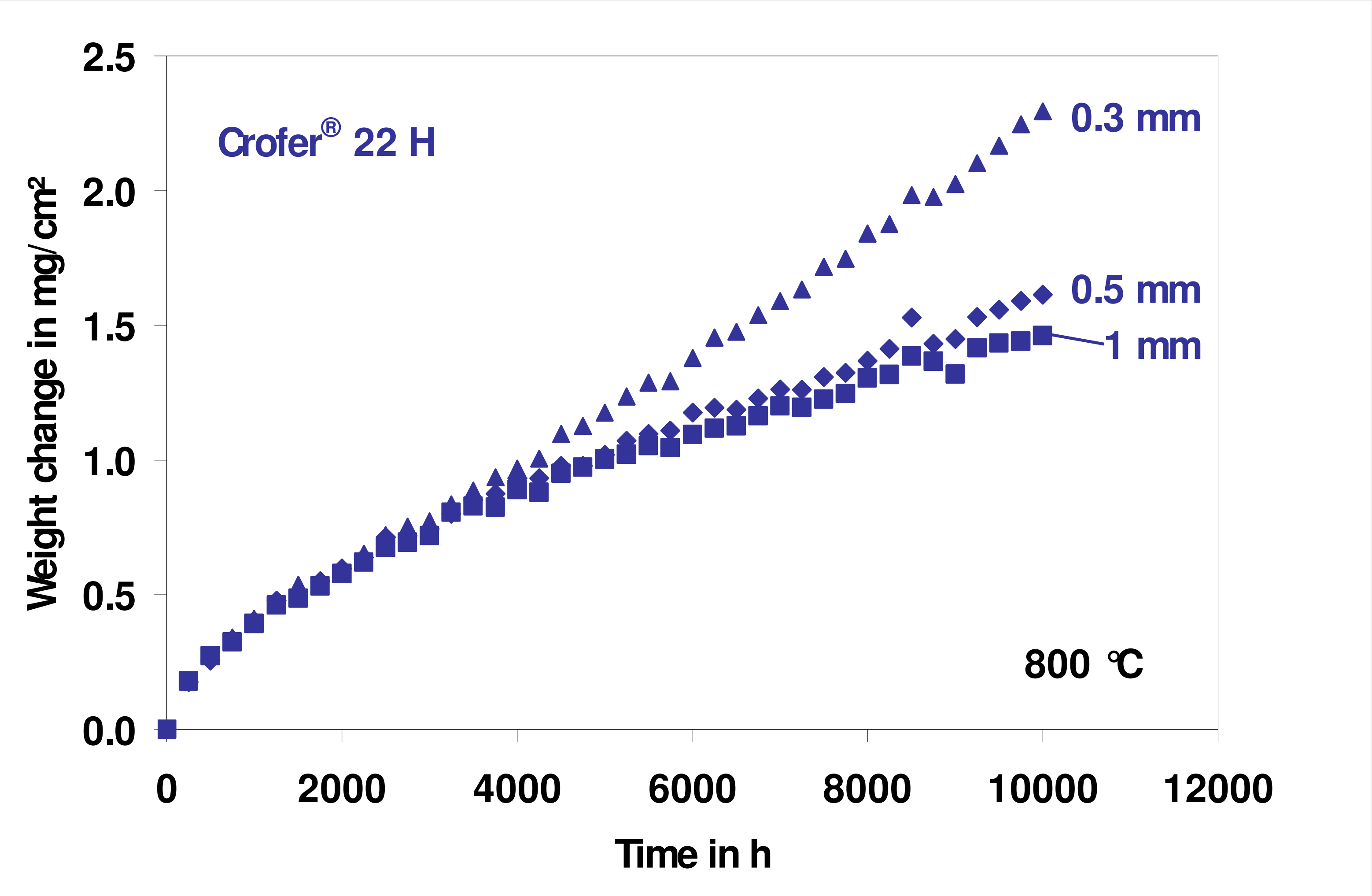
Discontinuous oxidation (250 h cycles) at 800 °C in air.



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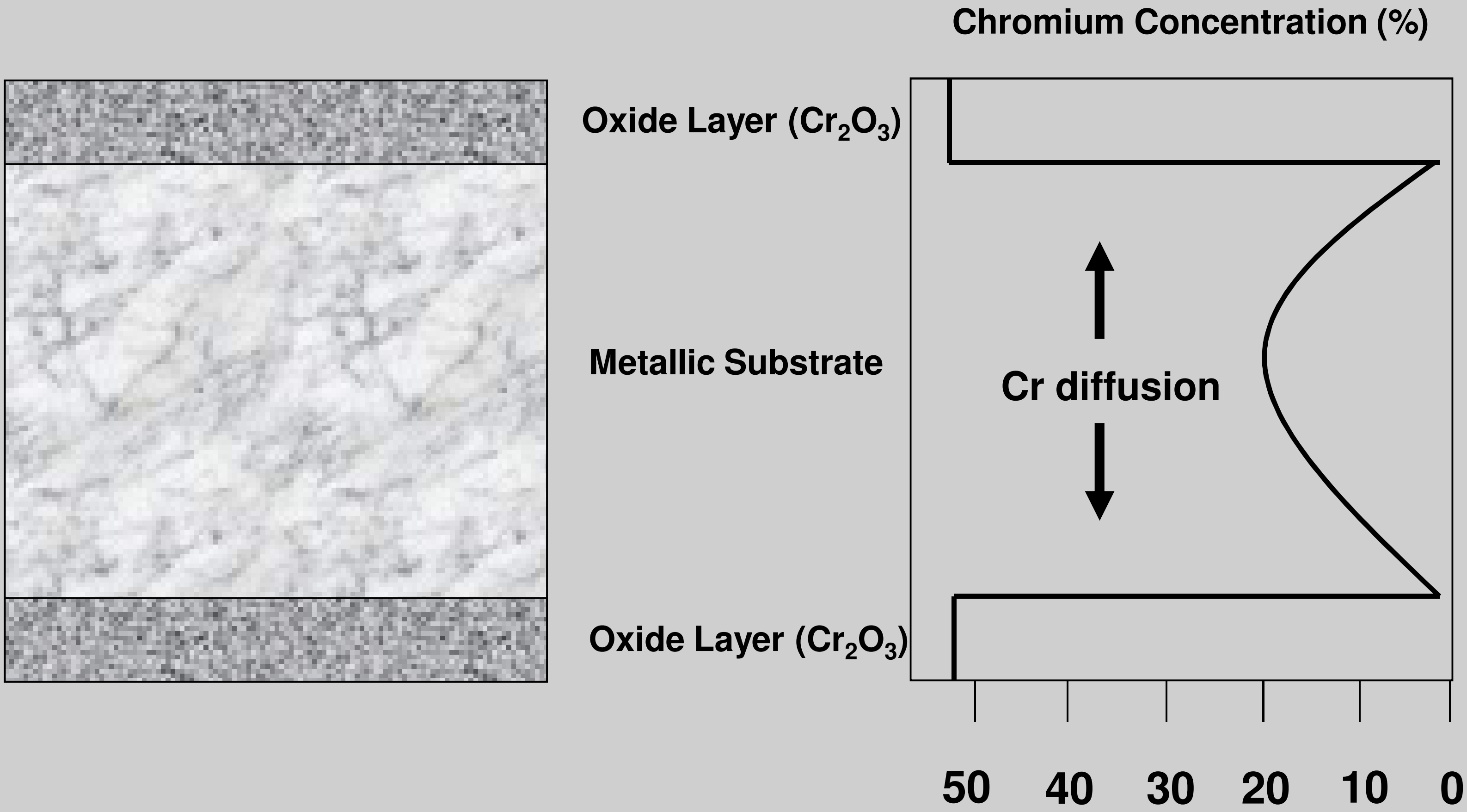
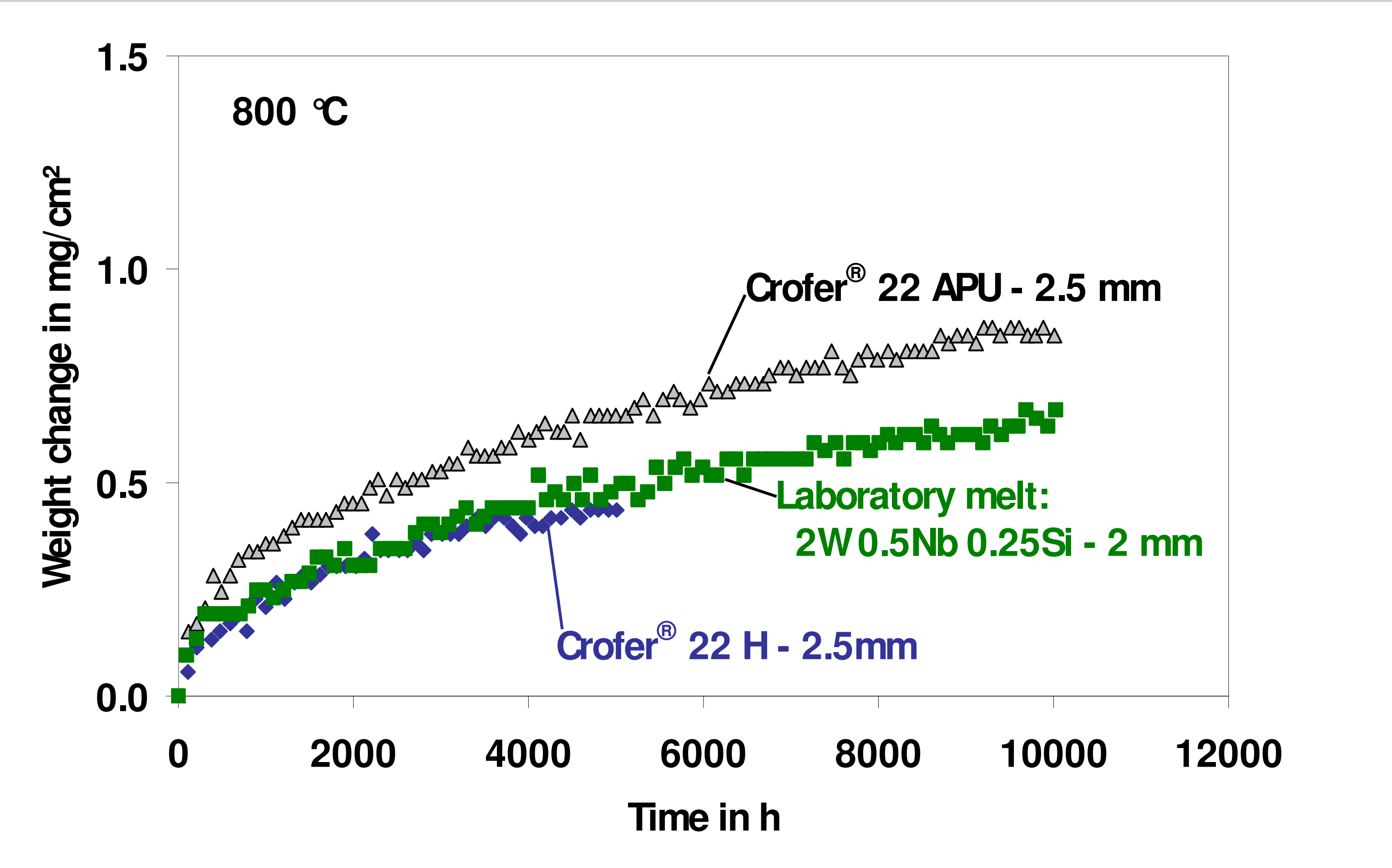
Oxidation and Time to "Breakaway"

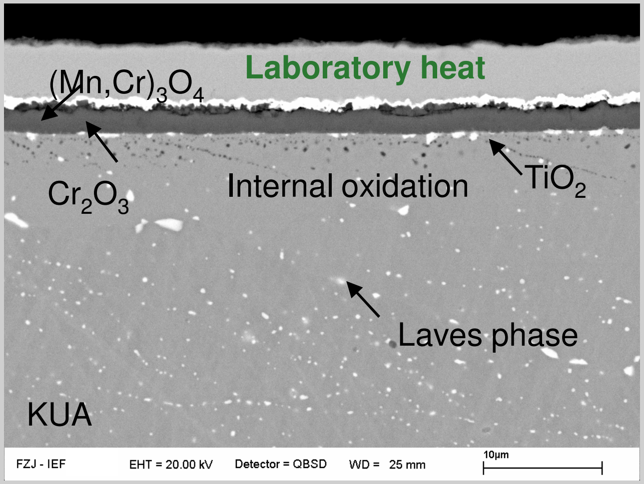


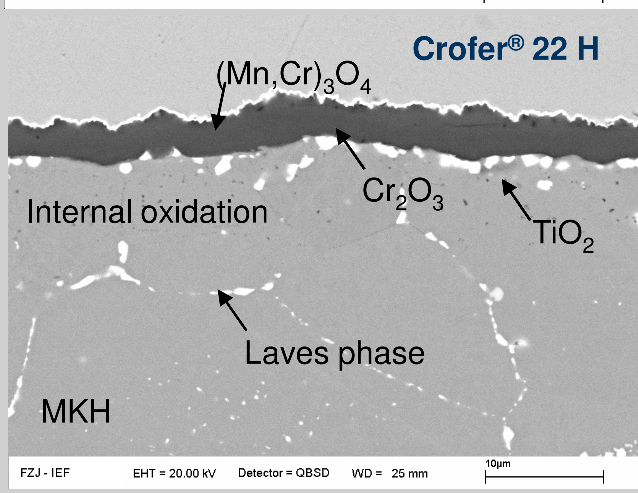
When chromium content of substrate is depleted, then breakaway oxidation occurs

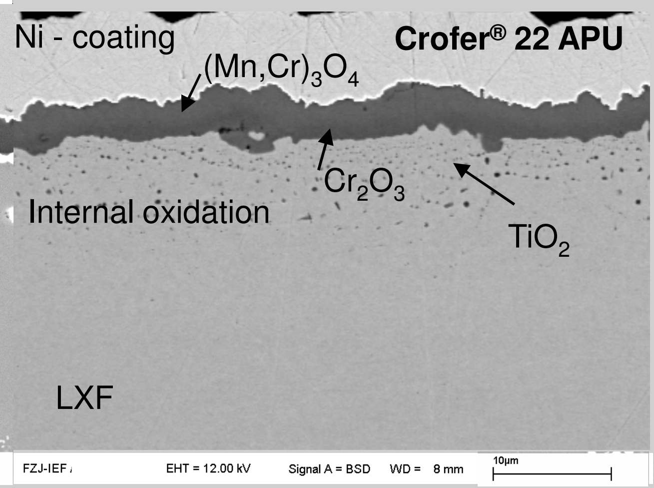
Discontinuous oxidation (100 h cycles) at 800 °C in simulated anode gas Ar 4% H_2 20% H_2O; specimen thicknesses ≥ 2 mm



Oxide scales after 1000 h discontinuous oxidation at 800 ℃ in air



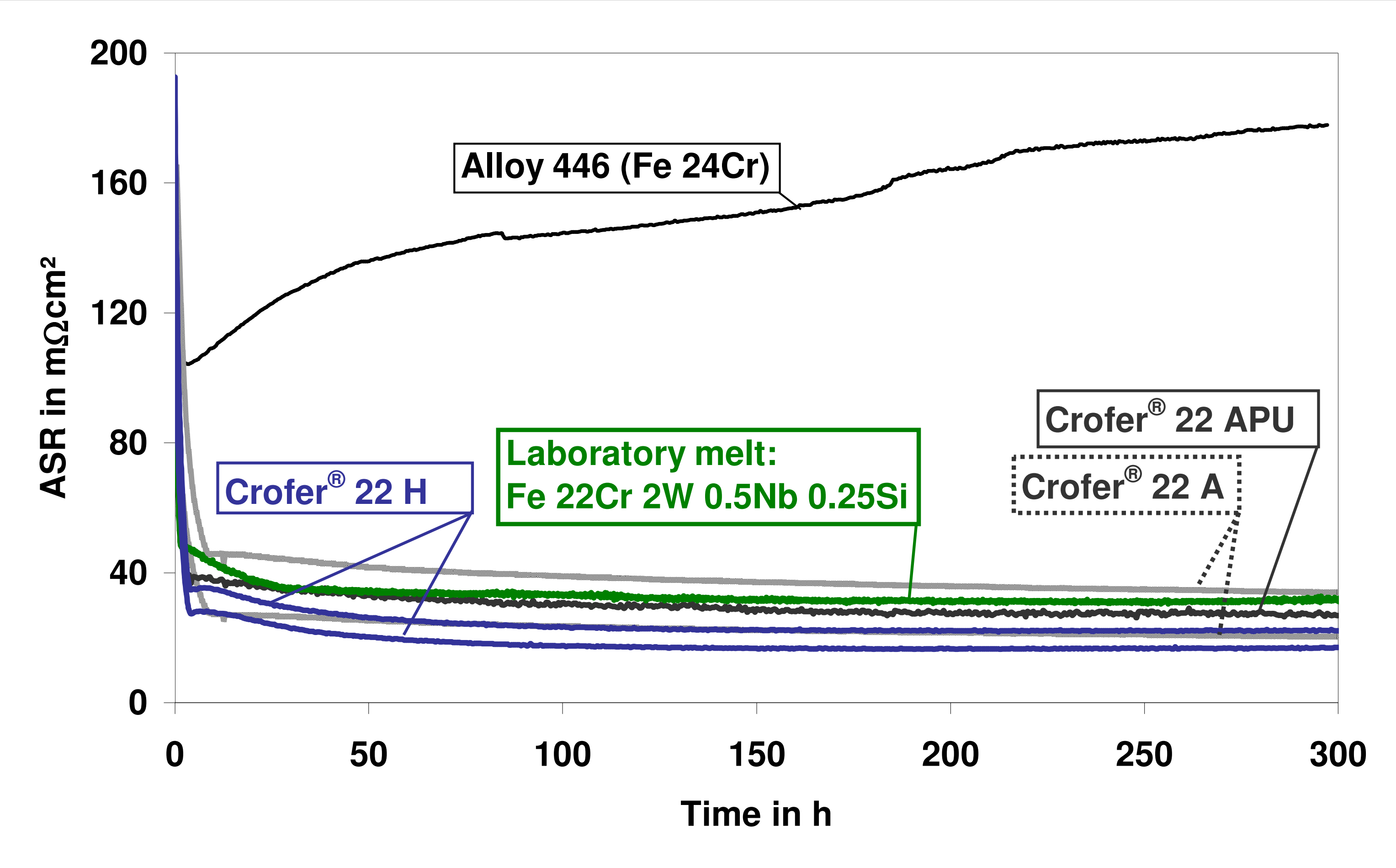




Oxidation properties of Crofer® 22 H

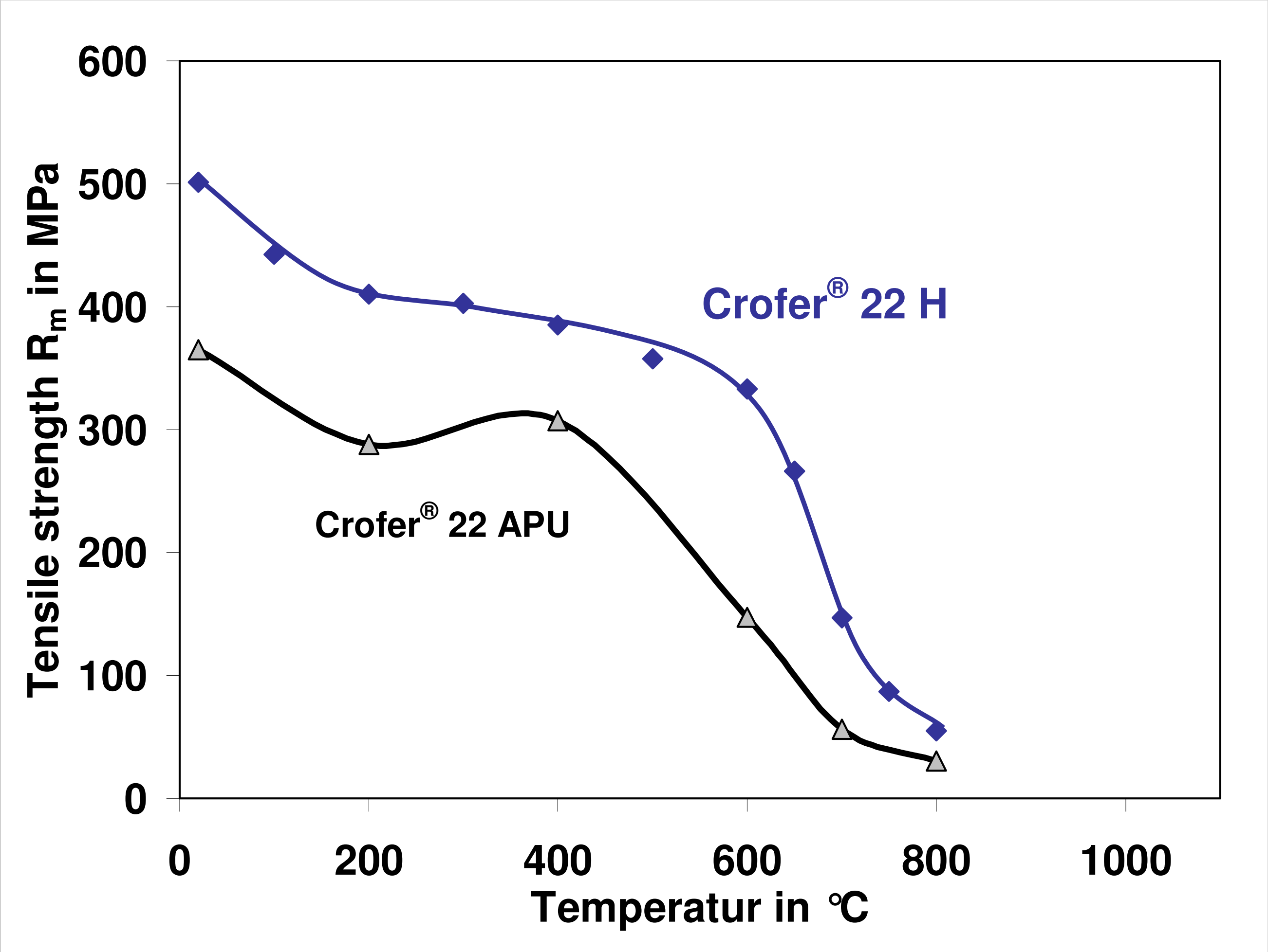
- Weight changes similar to lab melt Fe 22Cr 2W 0.5Nb 0.2Si
- Increasing oxidation rate with decreasing specimen thickness for Crofer® 22 APU
- No thickness dependence of oxidation rate for Crofer® 22 H
  down to 0.3 mm at 800 °C/air till 1110 h in air
  down to 0.5 mm at 900 °C till 1000 h in air
- Start of increase in oxidation rate for Crofer® 22 H, 0.3 mm
  after about 3000 h at 800 °C in air
- No oxide spallation observed.
- No internal oxidation of Al, strongly suppressed subscale formation of Si and formation of Nb oxides
- Finely dispersed internal oxidation of titanium dioxide.
- Scale - outer layer of chromium manganese spinel
  - inner layer of chromia.

Area specific contact resistance (ASR) in air at 800 °C



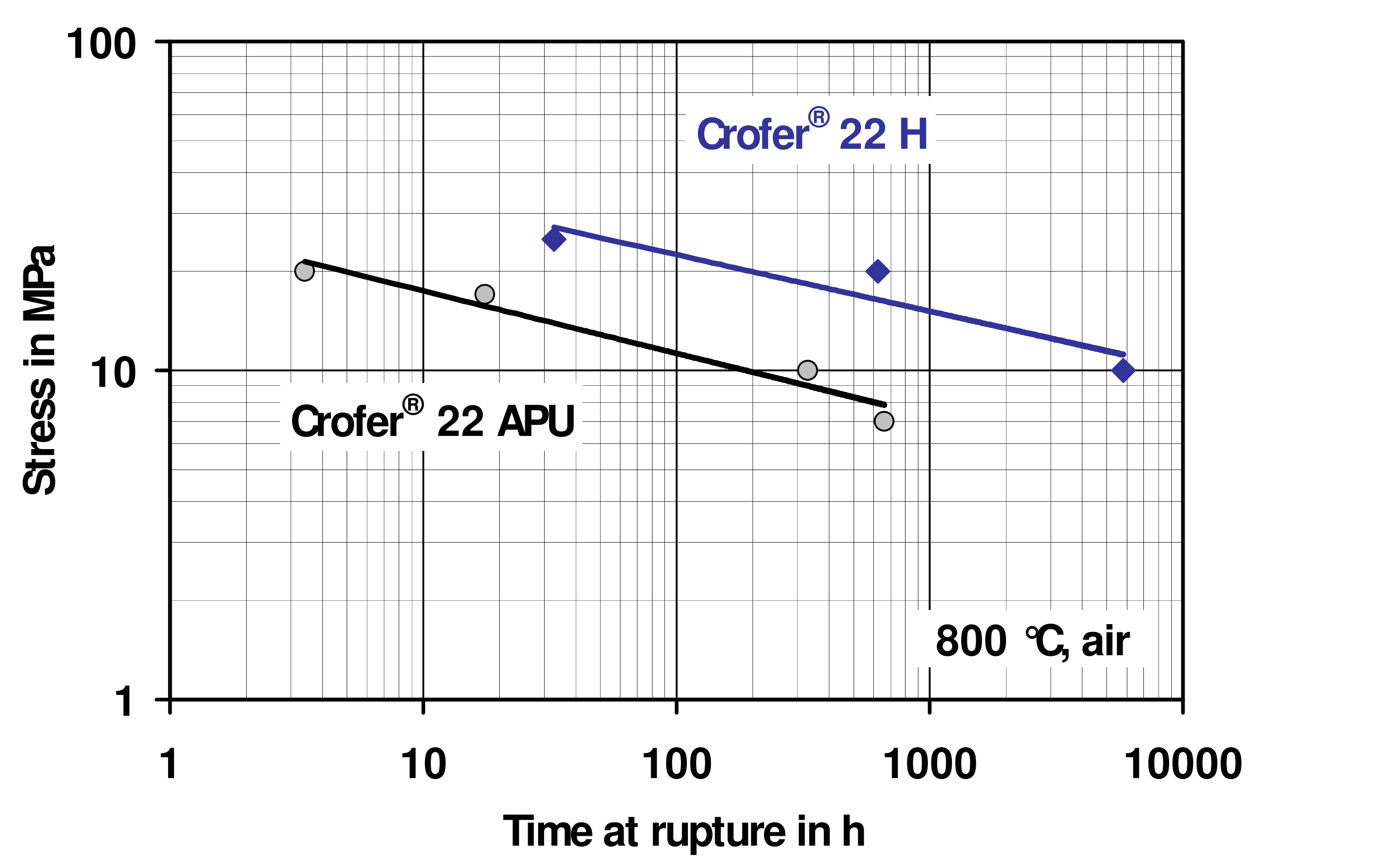
- ASR values for all Crofer types are similar; Range: 20 and 50 mΩcm²

Tensile strength (solution annealed, plate 12 mm)



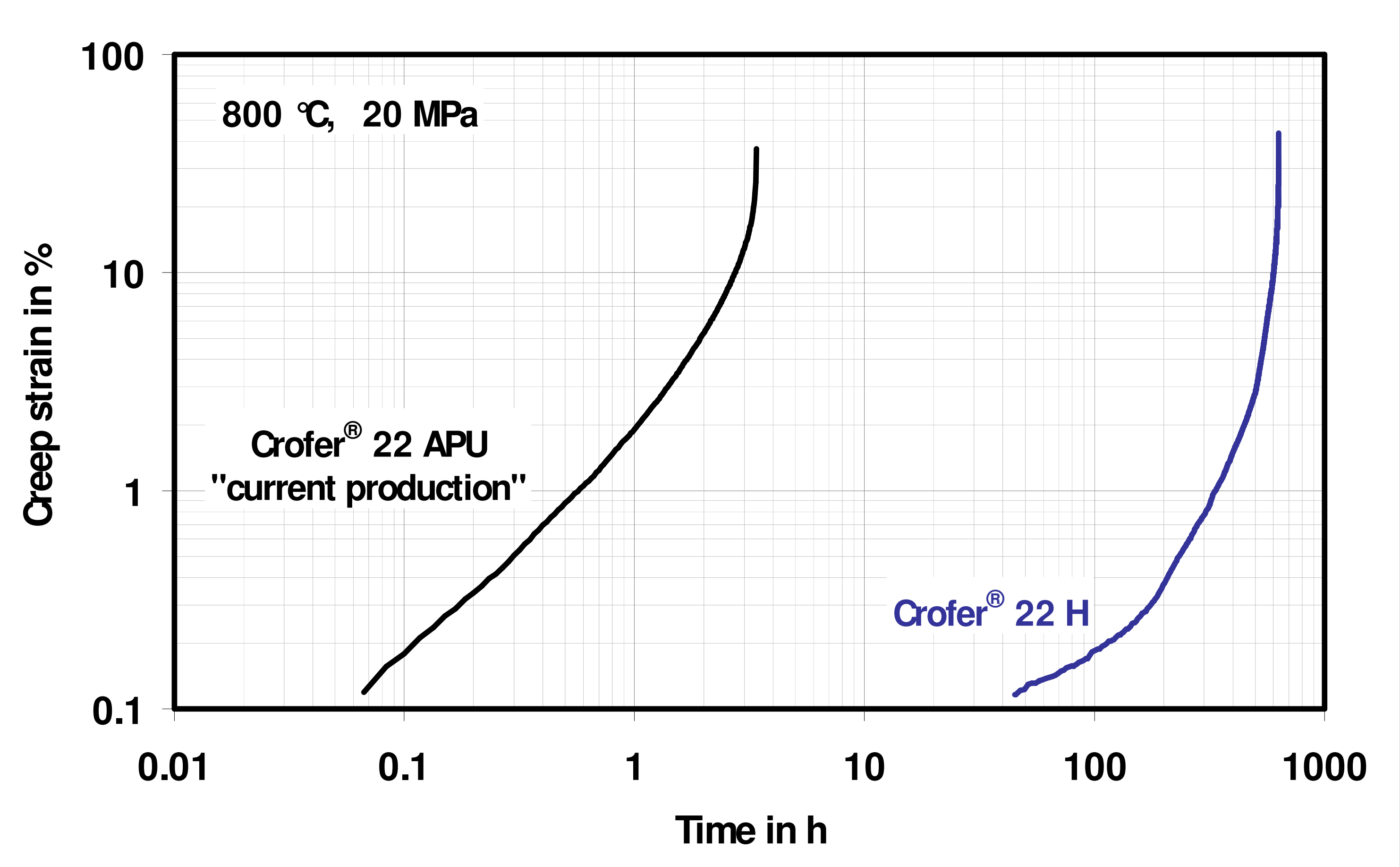
- Tensile strength of Crofer® 22 H higher than that of Crofer® 22 APU

Creep-rupture strength (plate 12 mm; solution annealed)



- Creep strength of Crofer® 22 H higher than that of Crofer® 22 APU

Creep strain (plate 12 mm; solution annealed)



- **Creep strain of Crofer® 22 H more than 300 times smaller than that of Crofer® 22 APU**

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Typical values for tensile test at room temperature

- **Strip material (hot and cold rolled)**

Alloy	$R_{p0,2}$ in MPa	R_m in MPa	A_{50} in %
Crofer® 22 APU (≤ 2.5 mm)	280 - 390	420 - 500	25 - 35
Crofer® 22 H (≤ 2.5 mm)	360 - 440	500 - 650	19 - 27

- **$R_{p0,2}$ and R_m of Crofer® 22 H higher than that of Crofer® 22 APU.**
- **A_{50}, A_5 of Crofer® 22 H lower than that of Crofer® 22 APU.**
- **Overlapping ranges for $R_{p0,2}$ and A_{50}, A_5.**
- **Good workability**

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Summary - specially designed steel Crofer® 22 H

23 % Cr for	- good oxidation resistance - low CTE
0.5 % Mn addition for	- limitation of Cr evaporation - low contact resistance
0.1 % La for improved	- oxide scale adherence - oxidation resistance
≤ 0.05 % Al for	- low oxidation rates
0.5 % Nb for	- high creep strength
2 % W for	- high creep strength - low CTE
0.2 % Si for	- low oxidation rates together with Nb - high creep strength

+ good workability

➡ **Ideally suited construction materials for interconnects in SOFC systems**

Thank you for your attention!

Acknowledgement

Thank you to Mr Cosler and Mrs Kick for carrying out the oxidation tests,
Mr. Lange for the creep experiments,
Mr. Wessel for the SEM analyses and
Mrs. Jänichen for CTE measurements.