Development of New Commercial ODS Alloys

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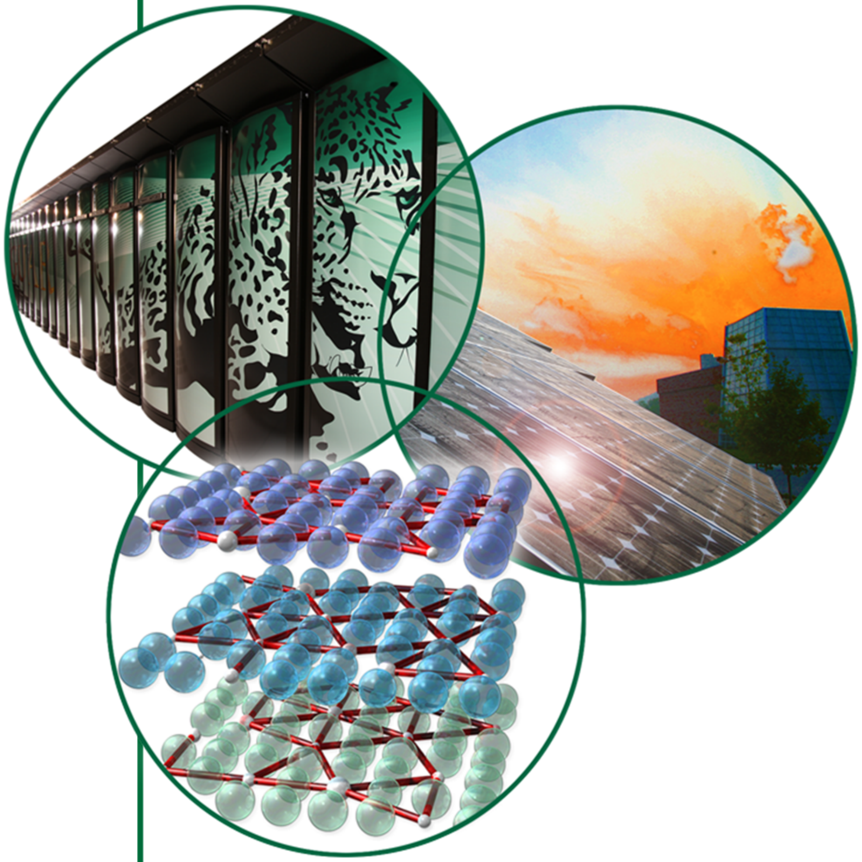
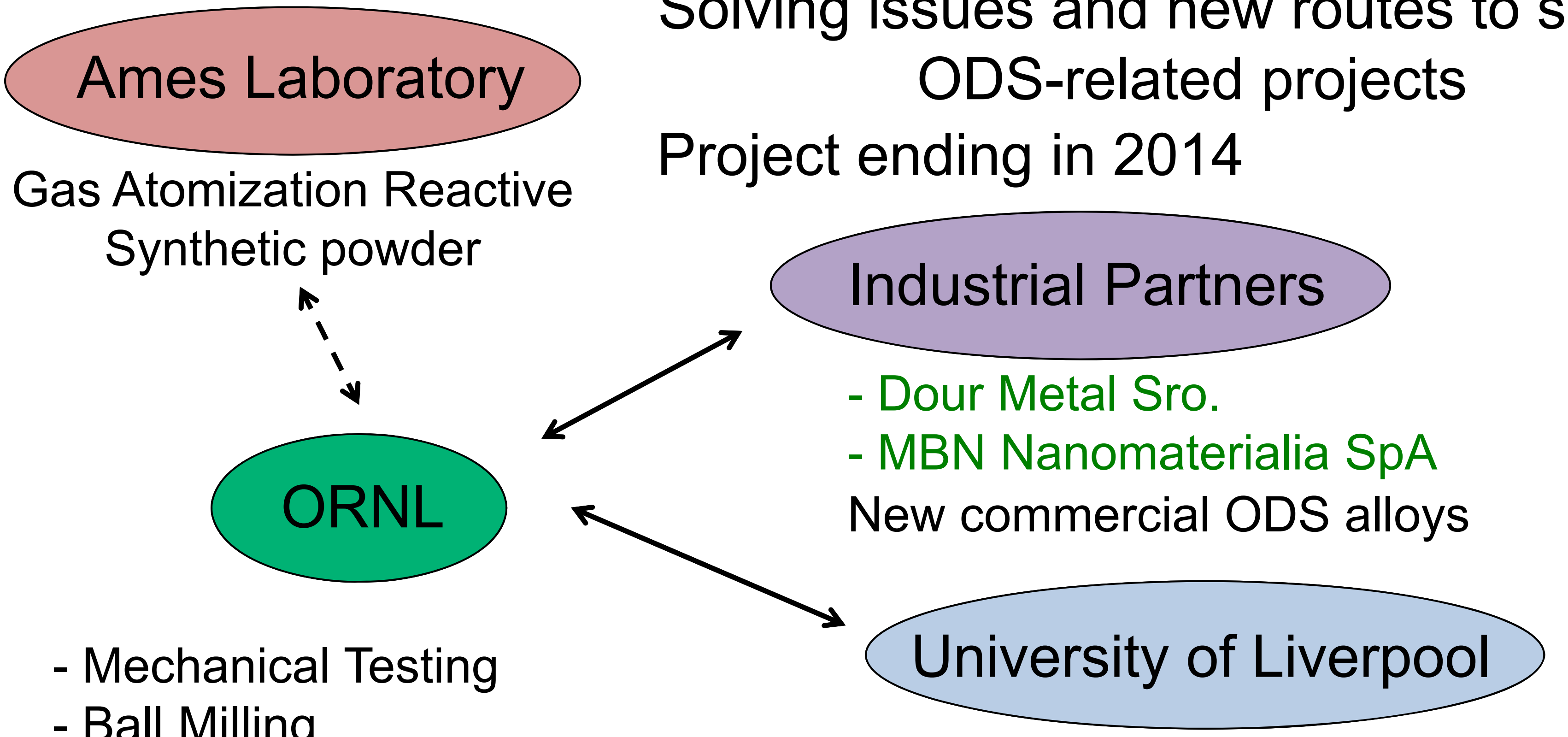


OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Collaboration to develop new commercial FeCrAl ODS alloys

Solving issues and new routes to spin off ODS-related projects

Project ending in 2014



Ames Laboratory

Gas Atomization Reactive Synthetic powder

ORNL

- Mechanical Testing
- Ball Milling
- Oxidation testing in complex environments (H_2O, CO_2)
- Lifetime Modeling

Industrial Partners

- Dour Metal Sro.
- MBN Nanomaterialia SpA

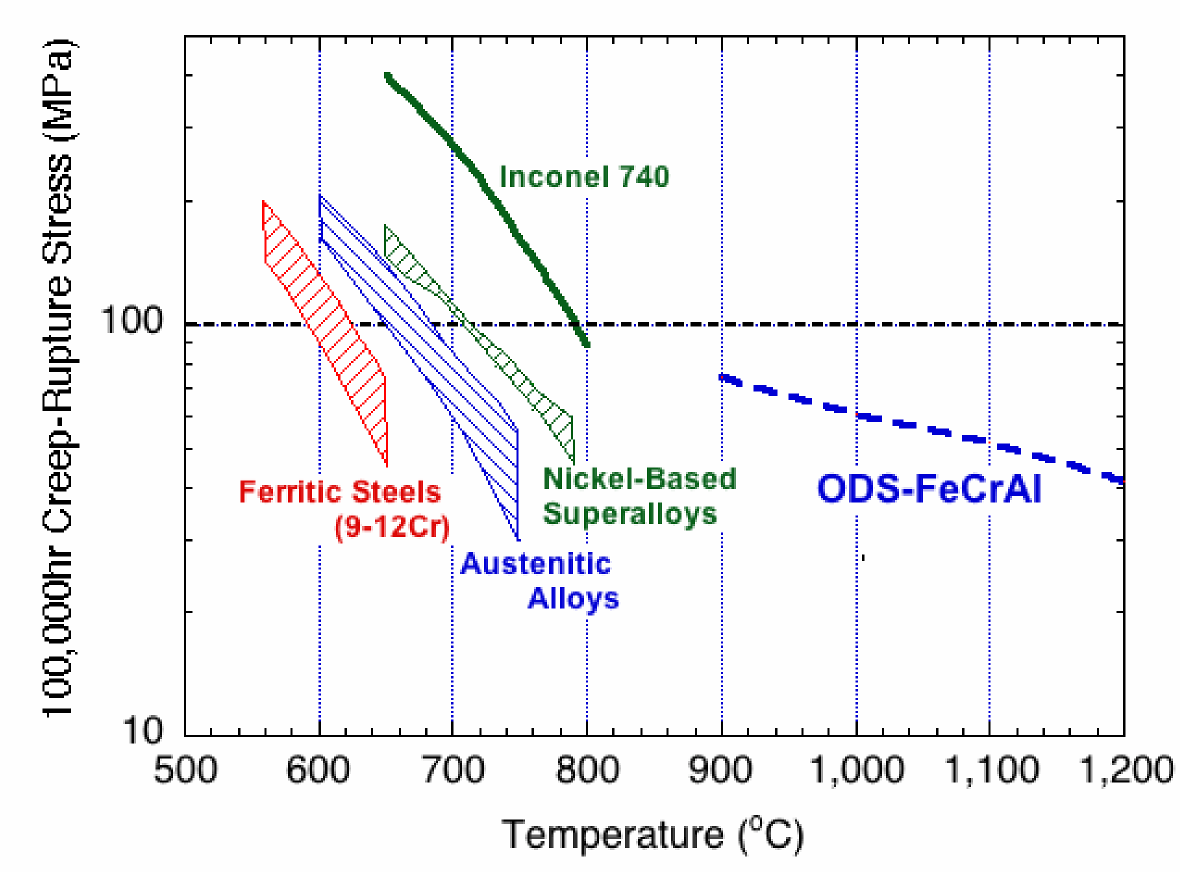
New commercial ODS alloys

University of Liverpool

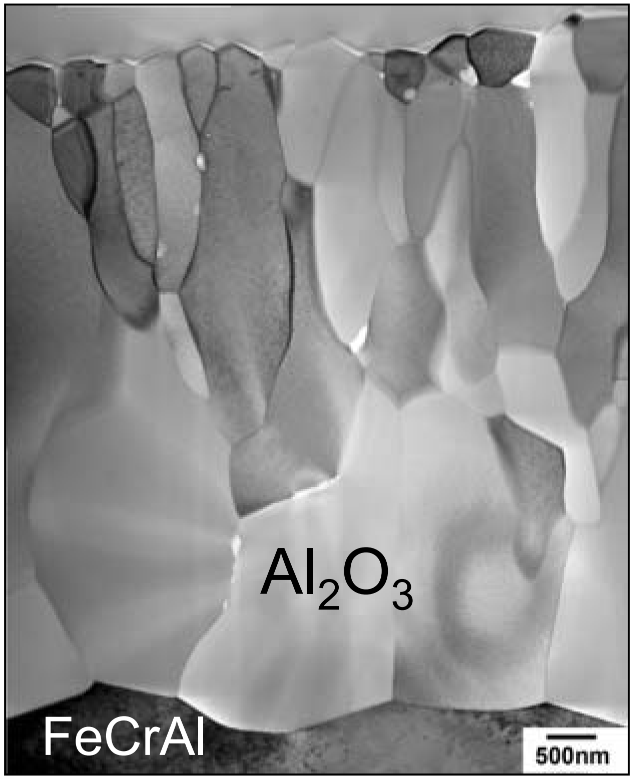
- Selective Laser Melting of ODS alloys
- Friction Stir Welding of ODS alloys (TWI)
- US/UK partner

Great potential for high efficiency systems using FeCrAl-ODS alloys

- Oxide Dispersion Strengthened FeCrAl alloys exhibit excellent creep and oxidation properties at T>1200ºC.

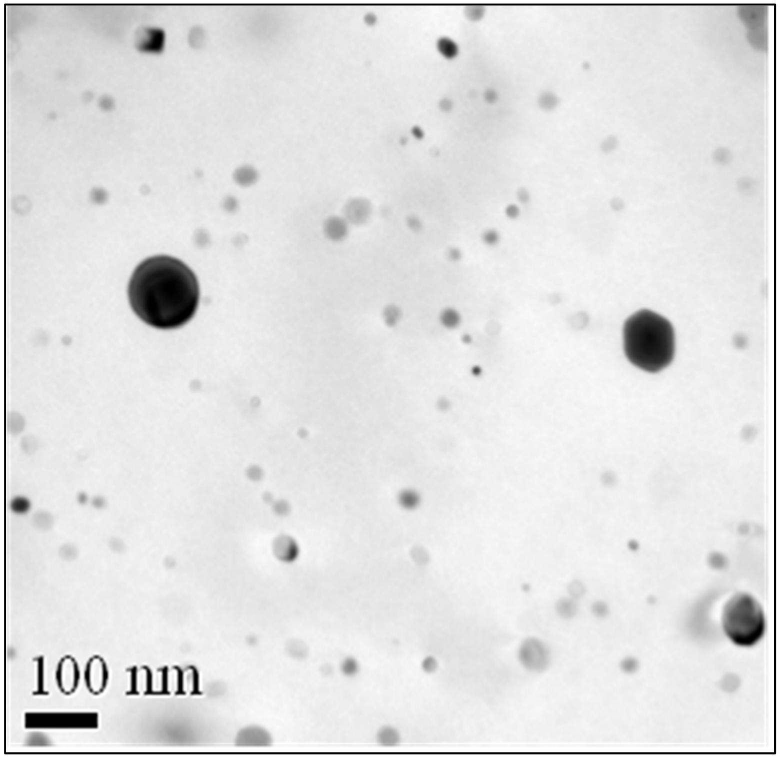


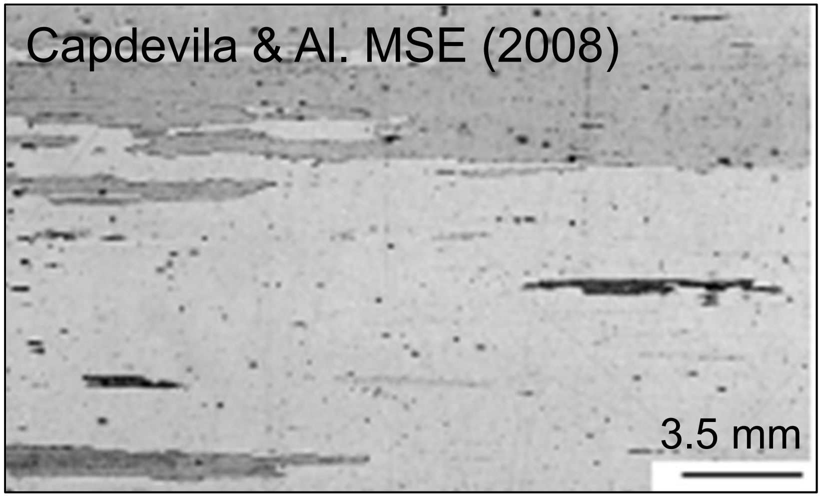
500h, 1100ºC, O_2



courtesy Kinga A. Unocic

FeCrAl ODS alloy microstructure




Capdevila & Al. MSE (2008)

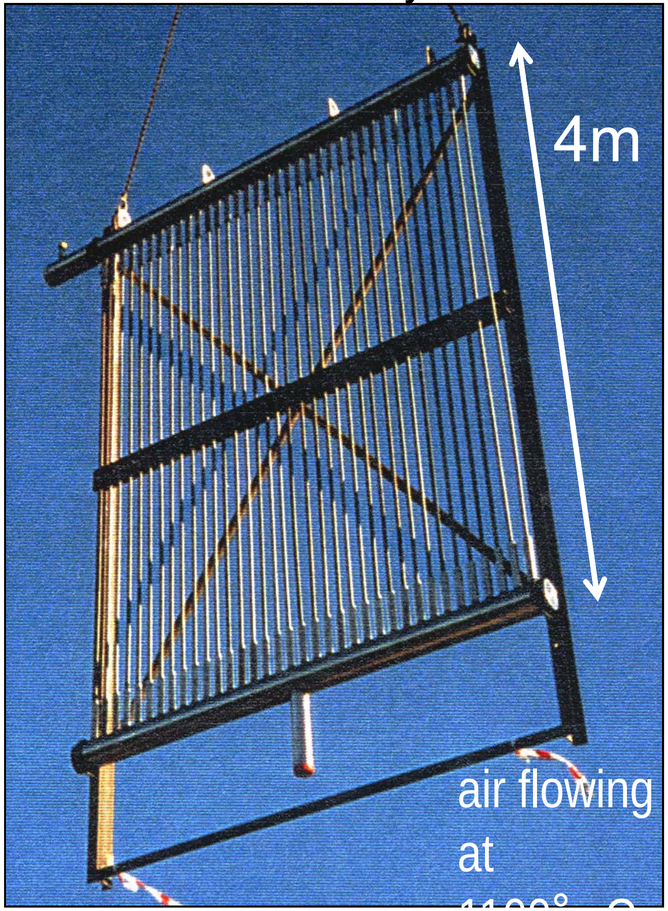
- Nano precipitates ~30nm obtained by mechanical alloying
- Recrystallisation at HT for large grains (>10mm)

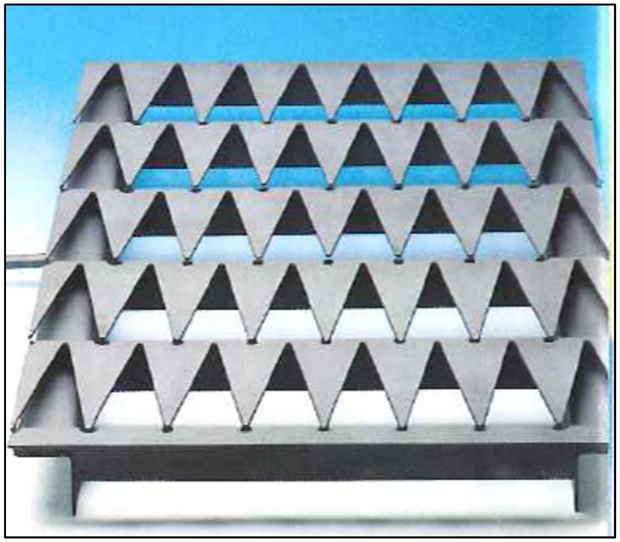
Alloy	**Composition (wt.%)**					
	Cr	**Al**	**Mo**	**Ti**	**Y_2O_3**	**Fe**
PM 2000	**20**	**5.5**	**<0.02**	**0.5**	**0.5**	**bal**
MA 956	**20**	**4.5**	**-**	**0.5**	**0.5**	**bal**
ODM 751	**16**	**4.5**	**1.5**	**0.6**	**0.5**	**bal**

High Temperature Heat Exchanger Furnace components

British Gas demonstrator HTHE

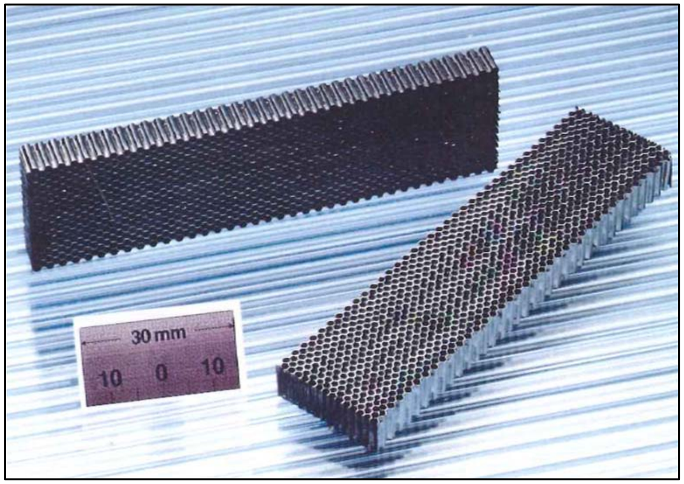
25 mm dia. x 4 m long ODM751 tube
fabricated by Dour Metal





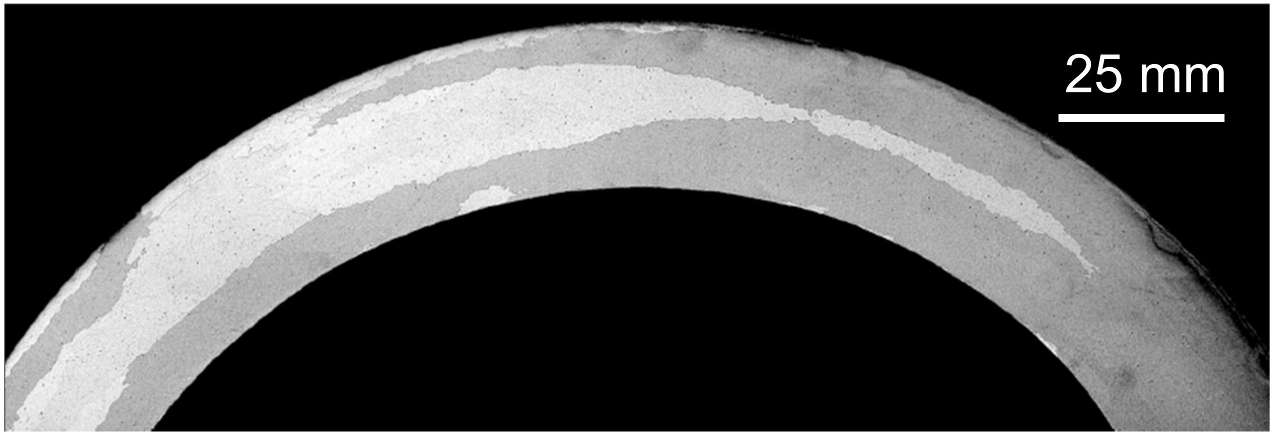
PM2000 Furnace ware for high vacuum furnace

Brazed PM2000 honeycomb sealing segment for gas turbine



Dour Metal: Regular production of ODS FeCrAl powder + tools acquisition

- ~300kg of ODS powder produced
- Hot press is operational for powder compaction
- Working on hot press hydraulic system to increase extrusion speed
- Acquisition of new pieces of equipment to fabricate tubes with “onion shape” structure
- Partnership with Academy of Sciences, Czech Republic



MBN: Production of two batches of ball-milled Fe-20Cr-5.5Al +Y_2O_3 powder

- MBN has done trials with its own PM2000-like powder to optimize ball mill parameters regarding microstructure and cost

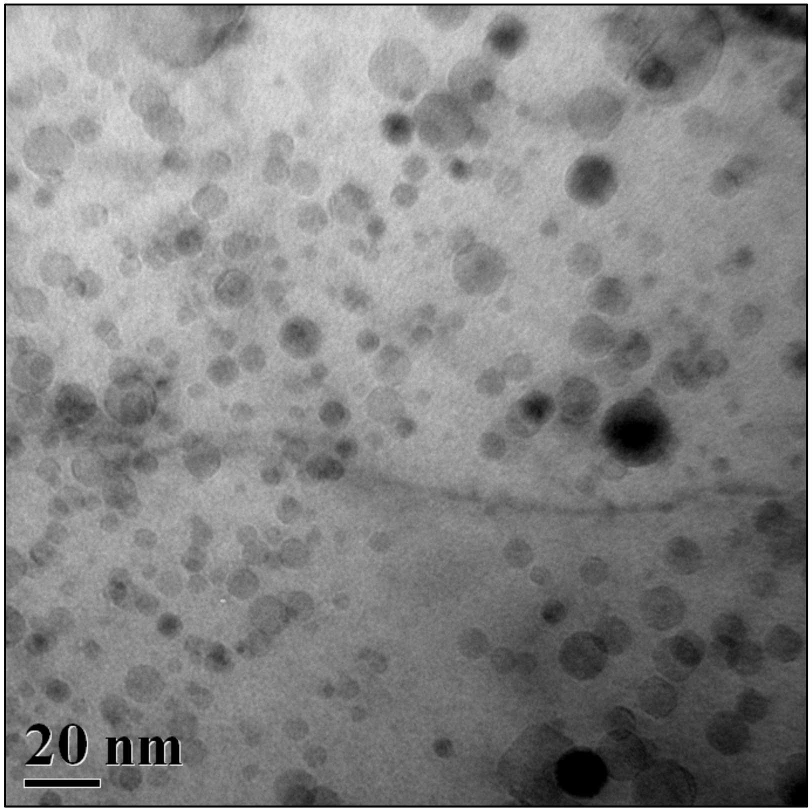
- ORNL (NE) purchased Fe-20Cr-5.5Al gas atomized powder and shipped it to MBN

- MBN ball-milled ORNL powder & produced 2 batches of powder (short and long ball milling time)

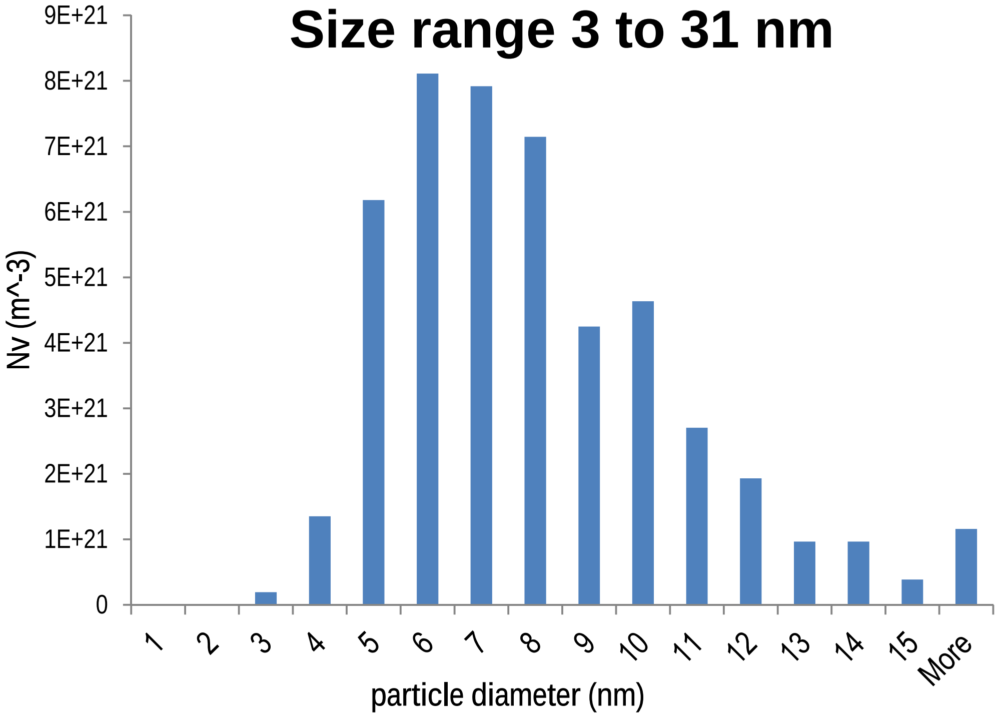
- Small W contamination led MBN to machine a new chamber and ~50kg of precursor powder was purchased

- Working on parameter optimization to produce ODS powder for additive manufacturing

Initial results from MBN powder show very promising microstructures



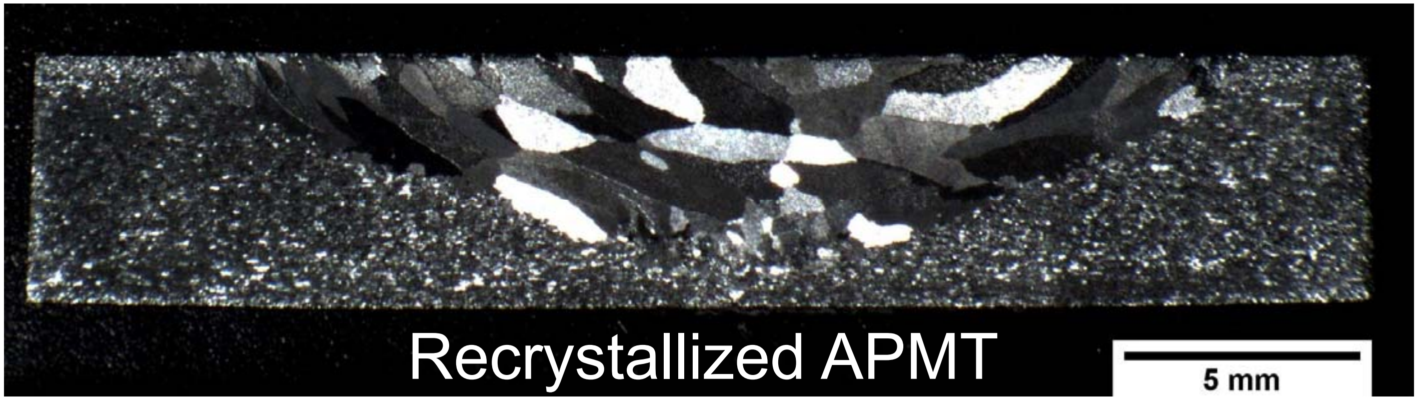
Mean diameter 7.6 nm
(~30nm for PM2000)
Size range 3 to 31 nm



-Heat treated MBN powder (long mill duration) contains a high number density of sub 30nm diameter dispersoids.
-Oxides are distributed homogeneously throughout the matrix.

Friction Stir Welding (FSW) of PM2000 and commercial APMT (closest to ODS)

Recrystallized PM2000 (1h 1380ºC)

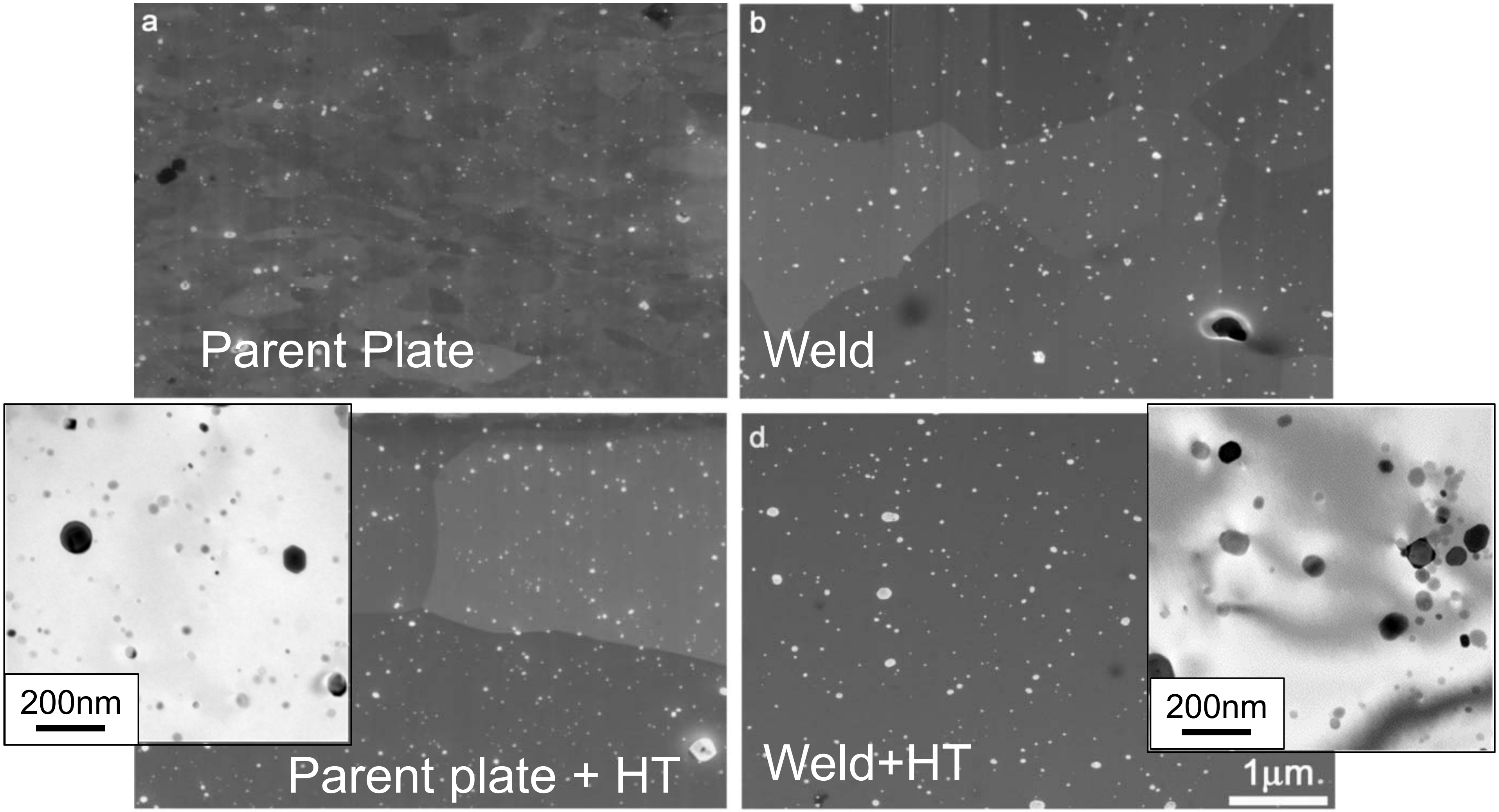


Recrystallized APMT

Limited PM2000 supply so optimization of welding parameters with APMT (Fe-21Cr-5Al-2.8Mo +Y,Hf,Zr,Ti dopants)

Collaboration with TWI, UK

Nano-particles in PM2000 FSW zone



After recrystallisation, oxides particles in the FSW zone were only slightly coarser than in parent material

Friction Stir Welding Summary

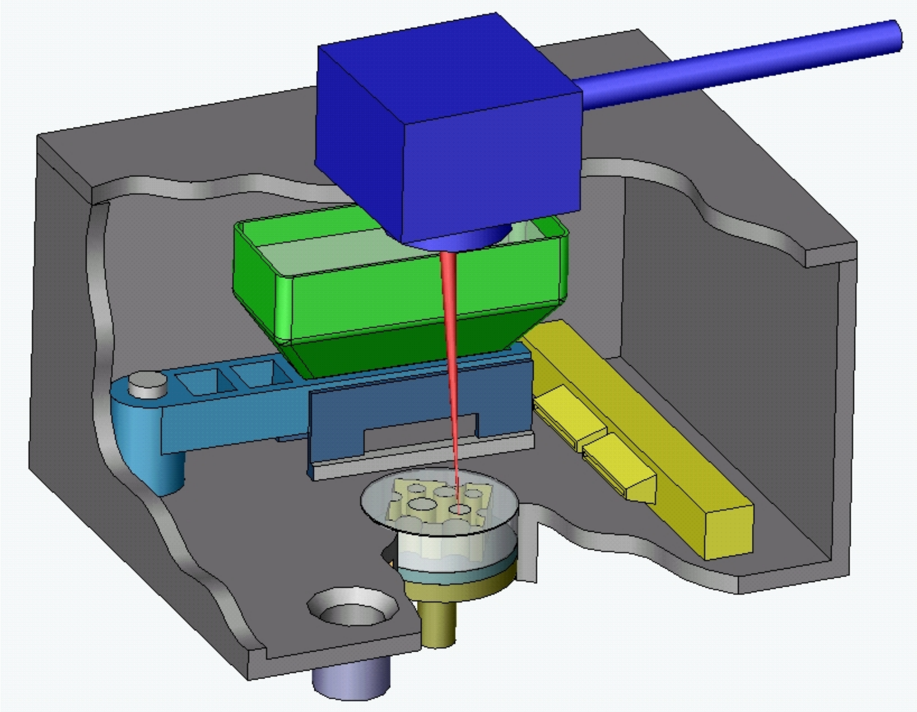
As-welded stir and thermo-mechanically affected zones displayed a dynamically recrystallised microstructure.

Standard recrystallisation heat treatment (1380° C for 1 hour) resulted in a coarse (mm scale) recrystallised grain structure throughout the weld zone.

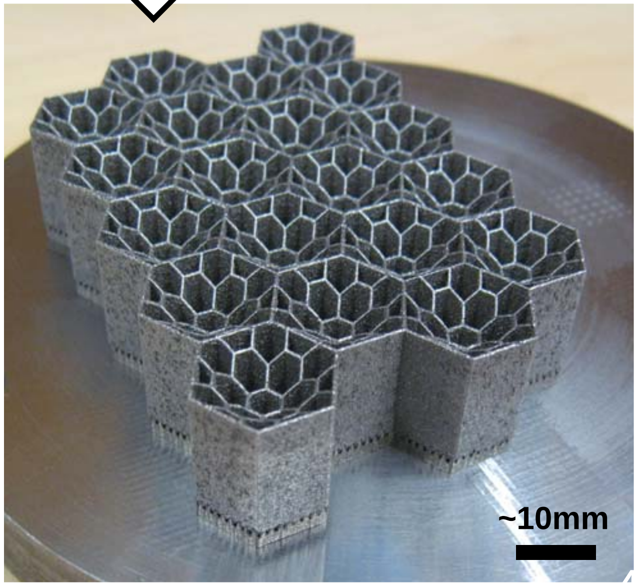
After recrystallisation, oxides particles in the FSW zone were slightly coarser & volume fraction lower than in parent material

Microstructure characterization and mechanical testing of APMT weld is on going: Similar room properties for parent material and weld

Selective laser melting (SLM) at Liverpool



(real time)

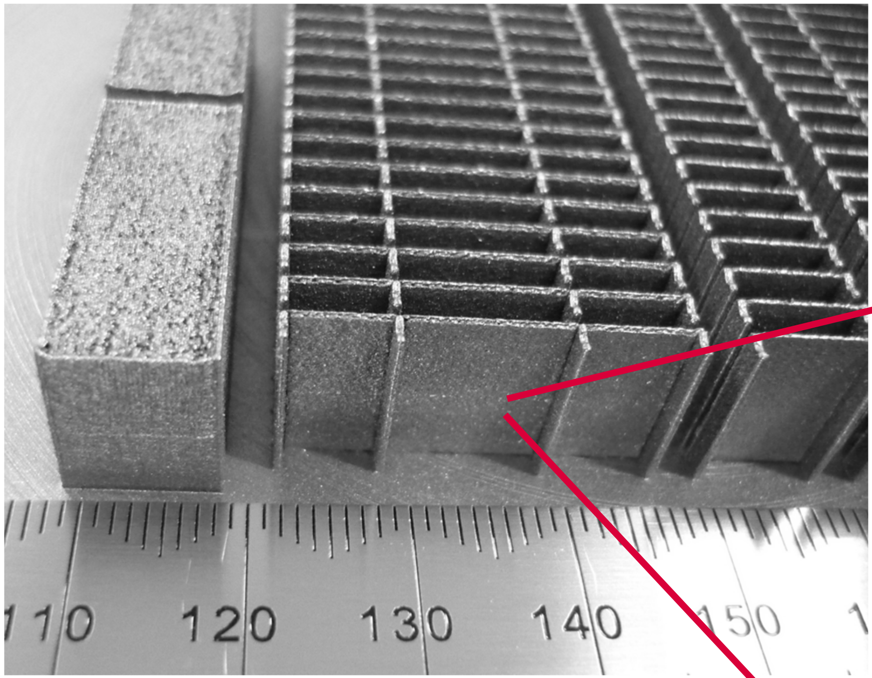


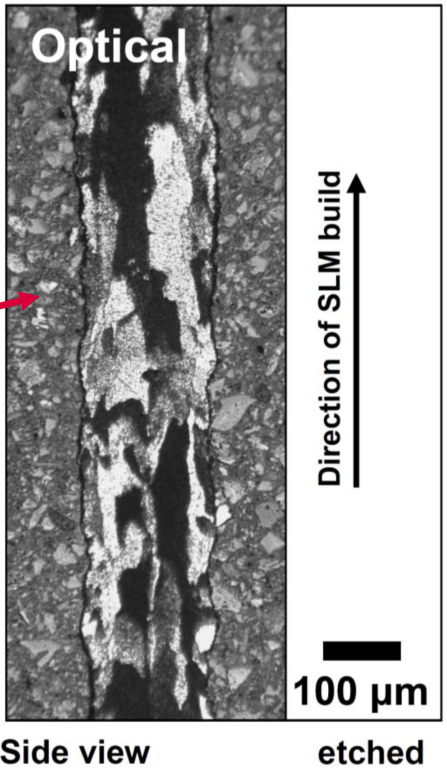
Additive layer by layer rapid prototyping technique

Repeated deposition of thin layers (50 μm) by successively laser melting

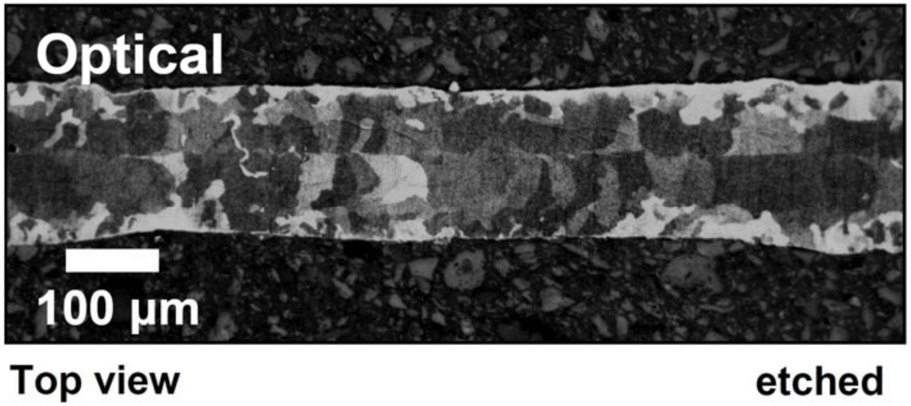
Fully dense solid freeform components

Fabrication of Blocks and thin walls by SLM

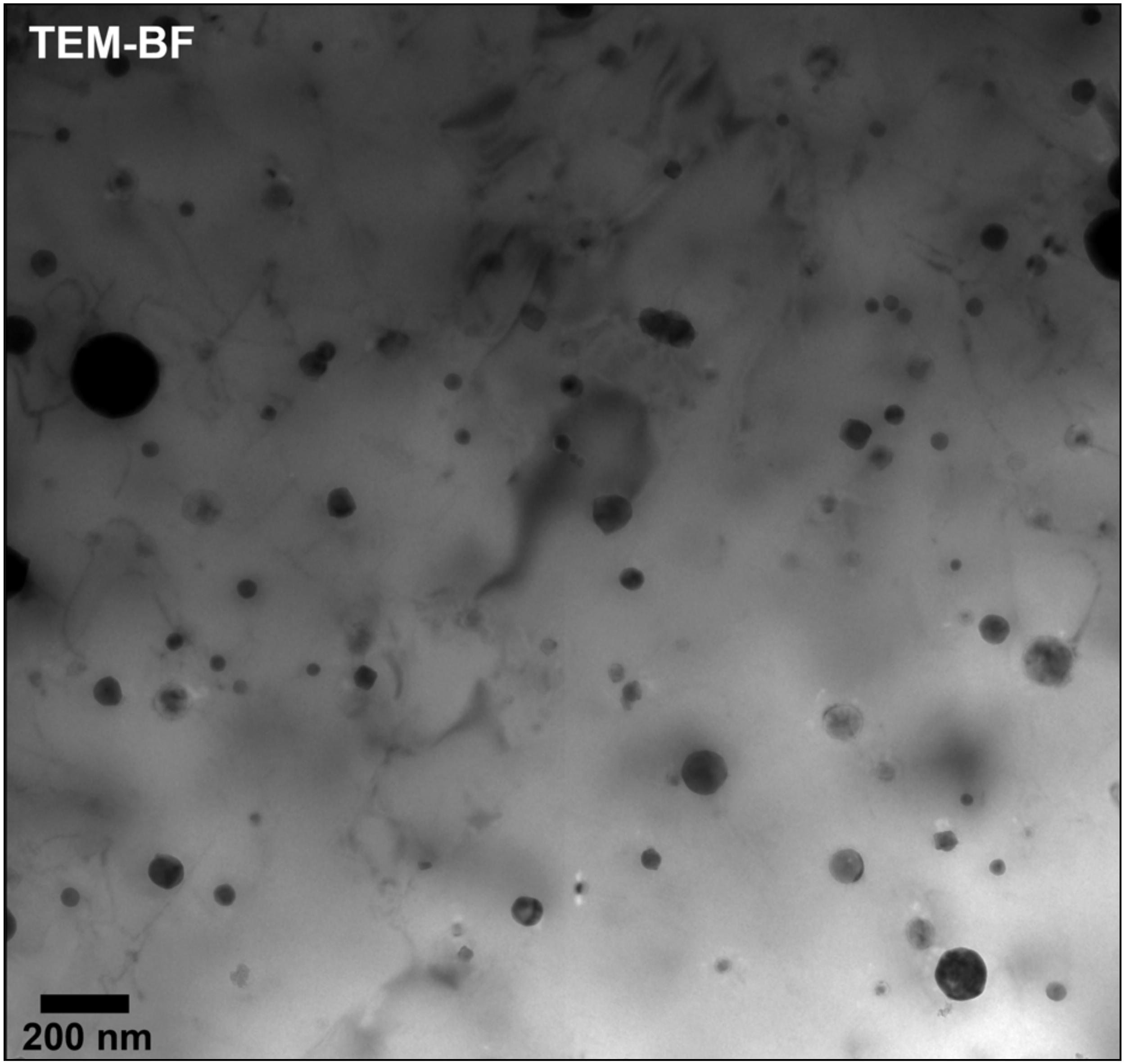




Elongated grains along the extrusion direction

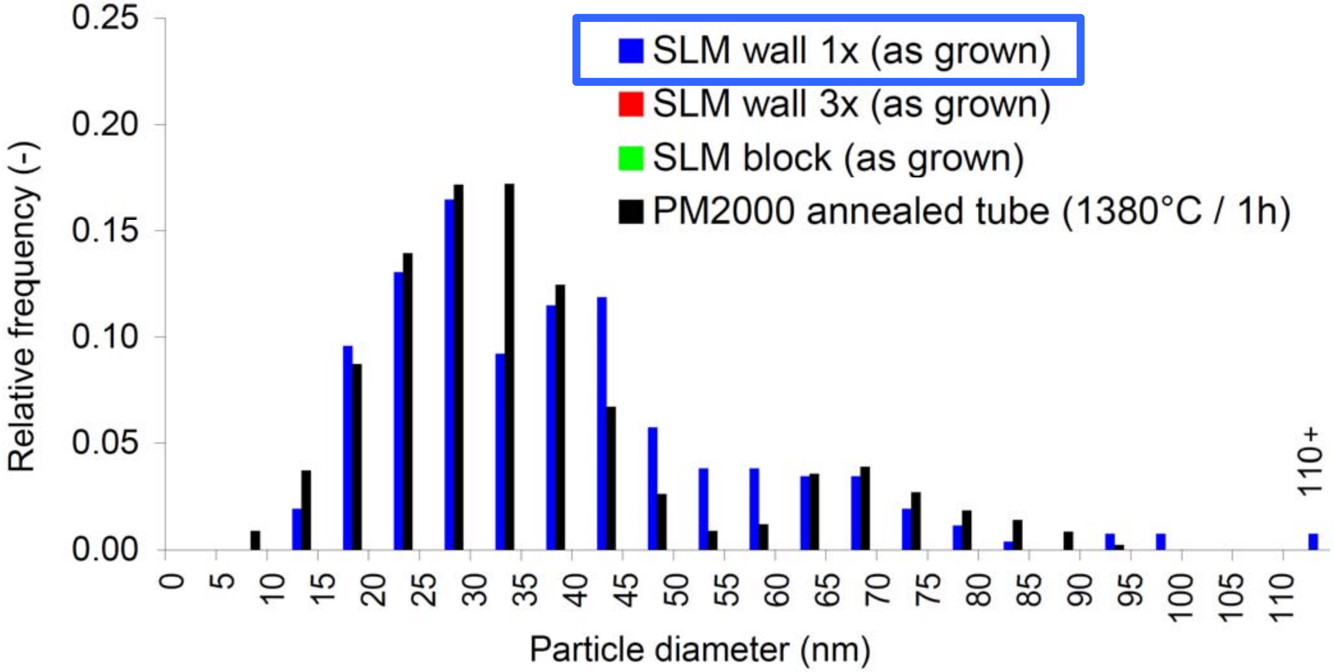


Fine homogeneous distribution of ODS particles retained for all builds



Agglomeration of particulates was not observed

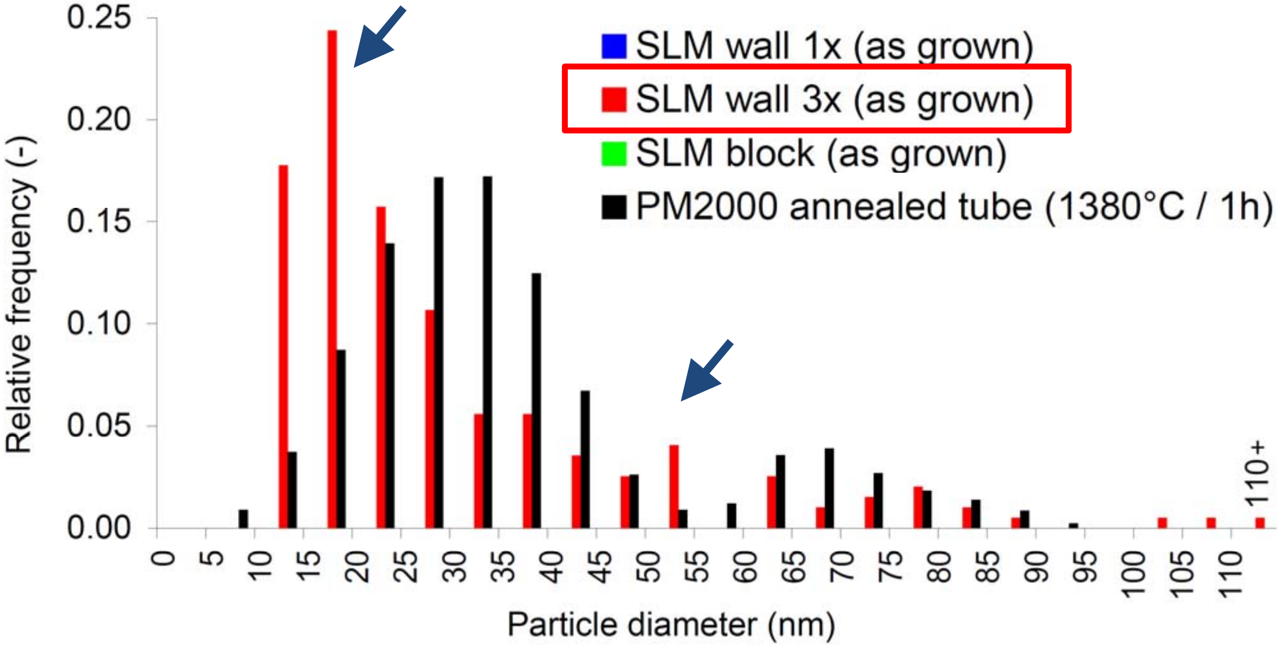
Size distribution similar between SLM thin walls and conventional PM2000



A certain amount of Y is probably still in solution in the matrix

After 1200ºC heat treatment, increase in yield strength due to nucleation and growth of new particles

Thicker walls (3x) show significantly finer dispersoids



Nucleation and particle growth due to an increased number of repeated heating cycles compared to the thin wall

SLM Conclusion

SLM builds display a stirred microstructure when viewed from the top and elongated in growth direction

Some Y is still in solution for SLM walls (more for thinner walls)

This Y is utilized for particulate nucleation and growth during heat treatment or the growth of thicker structures leading to an increase in YS

Despite some porosity, YS of solid builds with similar values as recrystallized reference material can be achieved

Need to develop new strategies to eliminate build defects and adjust ODS particle size

Experimental work for predictive model development

Materials

Alloys	Fe	Cr	Al	Si	Ti	Y	C (ppm)	N (ppm)	O (ppm)	S (ppm)
MA956	69.45	20.07	8.78	0.13	0.4	0.24	640	608	6490	41
PM2000	69.4	18.91	9.82	0.07	0.49	0.22	430	104	8050	34
PM2K	68.7	19.13	10.48	0.04	0.52	0.23	60	318	8028	13
MA956 HT	65.7	21.7	10.67	0.11	0.43	0.23	1696	1006	6771	70

2 different batches of PM2000, one with very low impurities level

Experiments *1h cycle, 1200ºC*

specimen mass change + time to breakaway

- O_2, air+10%H_2O, ~50%CO_2/50%H_2O + 0.075 O_2

100h cycle, 1100ºC & 1200ºC

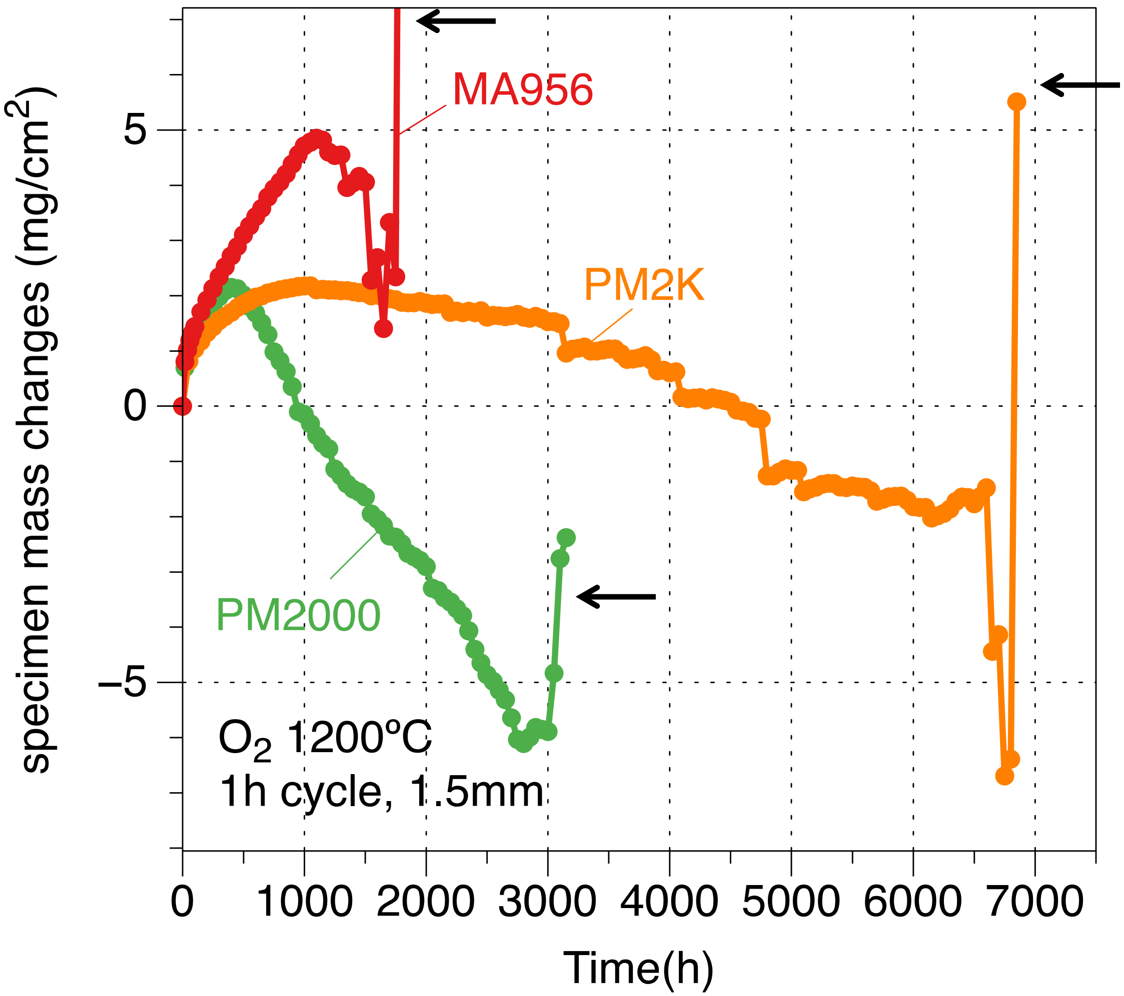
specimen mass change + total mass gain

-air, air+10%H_2O

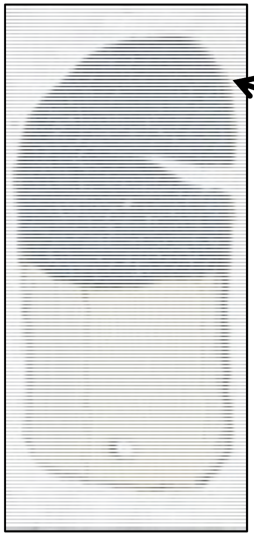
Objective

Predictive lifetime model based on Al consumption to form Al_2O_3 in representative environments

1h cycle at 1200ºC: end of life = Fe oxide formation (breakaway oxidation)

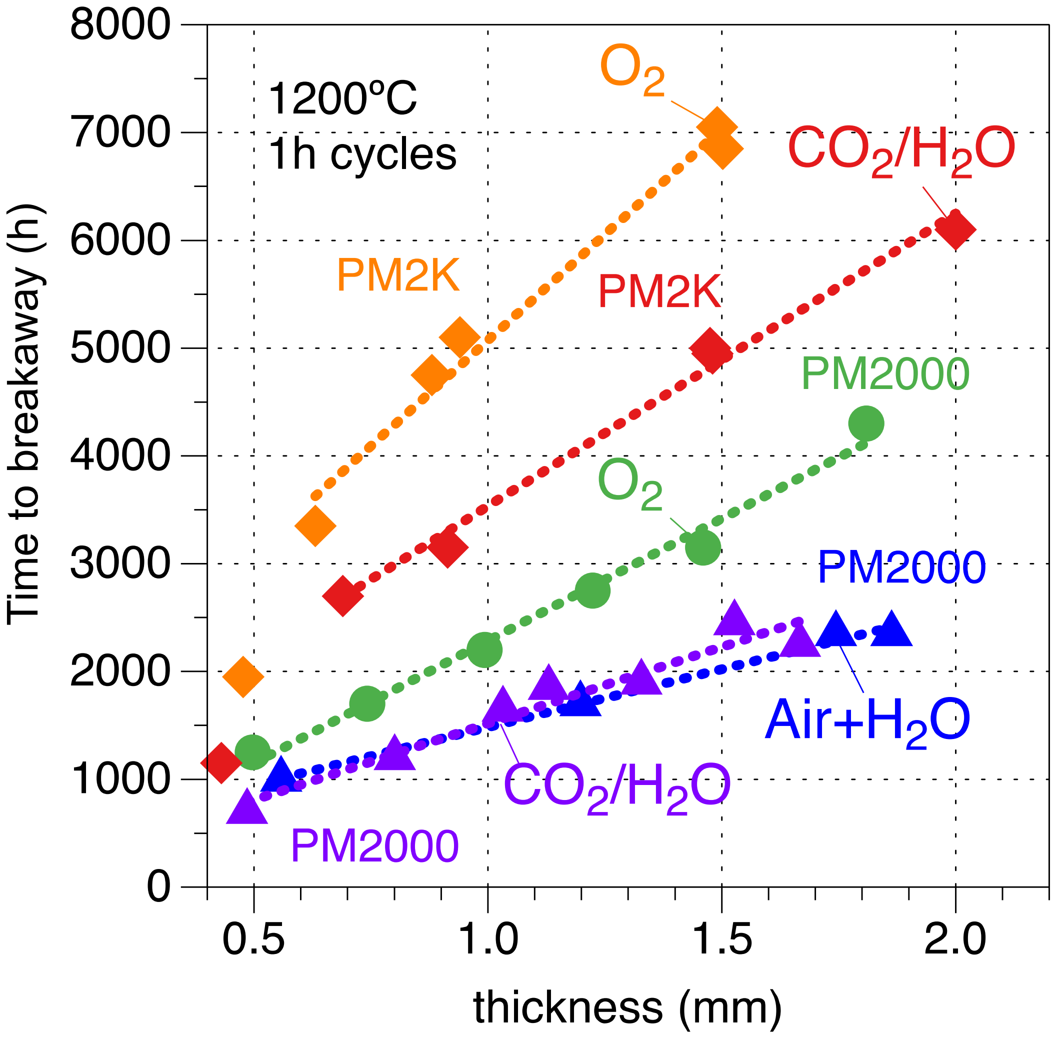


breakaway oxidation



Fe oxide

Most of the specimens tested reached breakaway oxidation

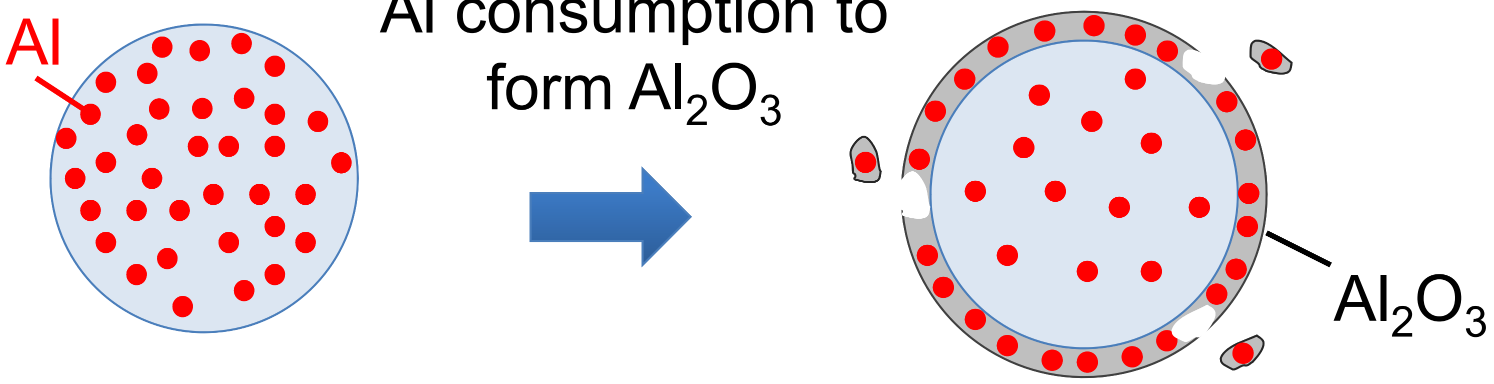


- Decrease of lifetime with H_2O and H_2O+CO_2

- Low S level results in low spallation rate and high lifetime

- Linear relationship between lifetime and specimen thickness

Lifetime Model based on Al consumption down to critical Al content



S: Surface area
V: Volume

$$\boxed{S \cdot F_{Al}(t_b) = \rho \cdot V \cdot C_{Al0} - \iiint_V \rho \cdot C_{Alb} \, dV}$$

Al consumption $F_{Al}(t)$
due to cyclic oxidation

Critical Al content

Determination of Al consumption $F_{Al}(t)$ using existing cyclic oxidation models

pkp model

k_p = oxidation kinetics
p = oxide scalling probability

DICOSM Good-Smialek Approximation (GSA)

k_p = oxidation kinetics
Fa = spall area fraction constant

2-stage parabolic linear model

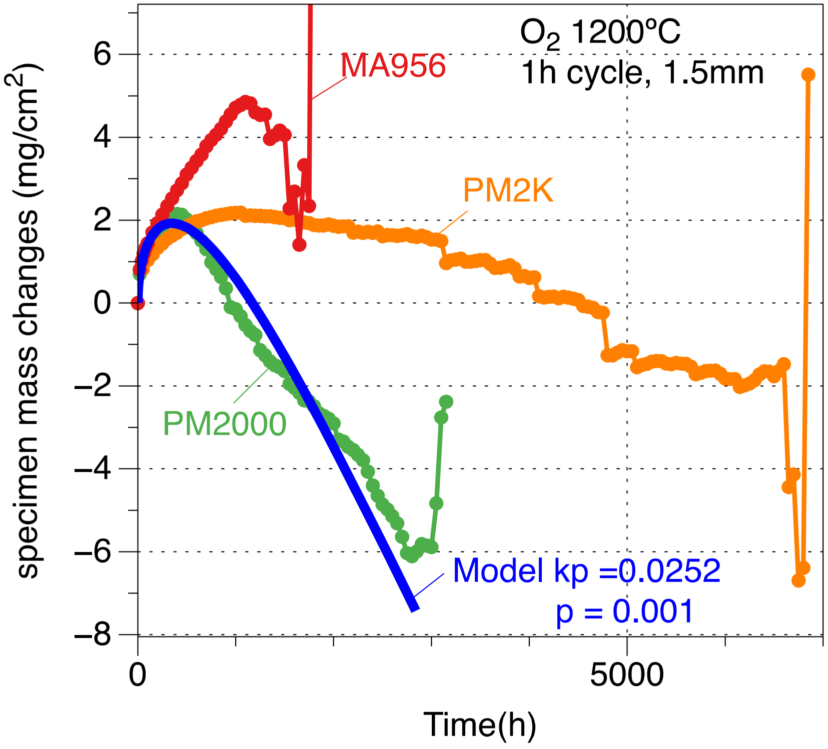
k_p = oxidation kinetics
t_p = transition time
k_l = linear rate

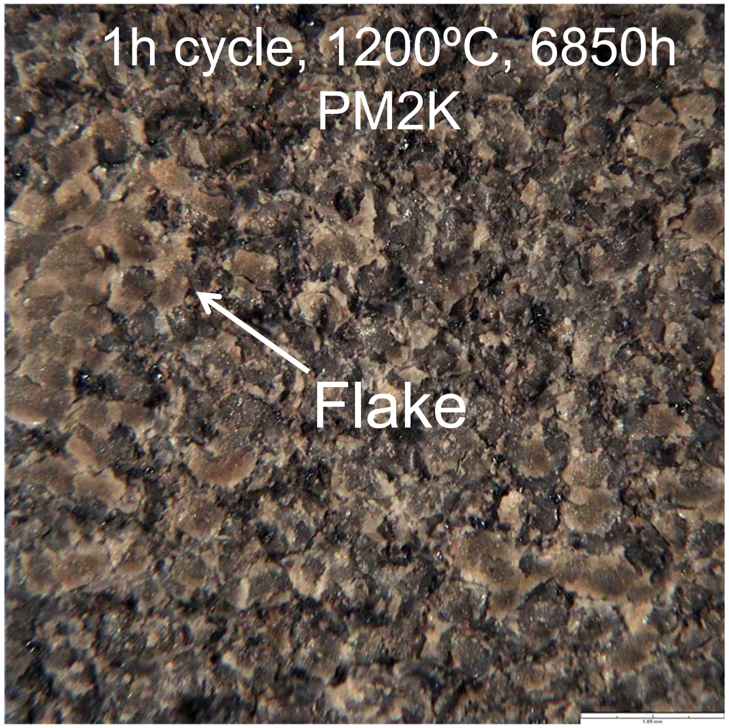
Parabolic oxide scale growth

$$\left(\frac{\Delta W}{S}\right)^2 = k_p \mathrm{t}$$

ΔW Weight change
S: Surface area

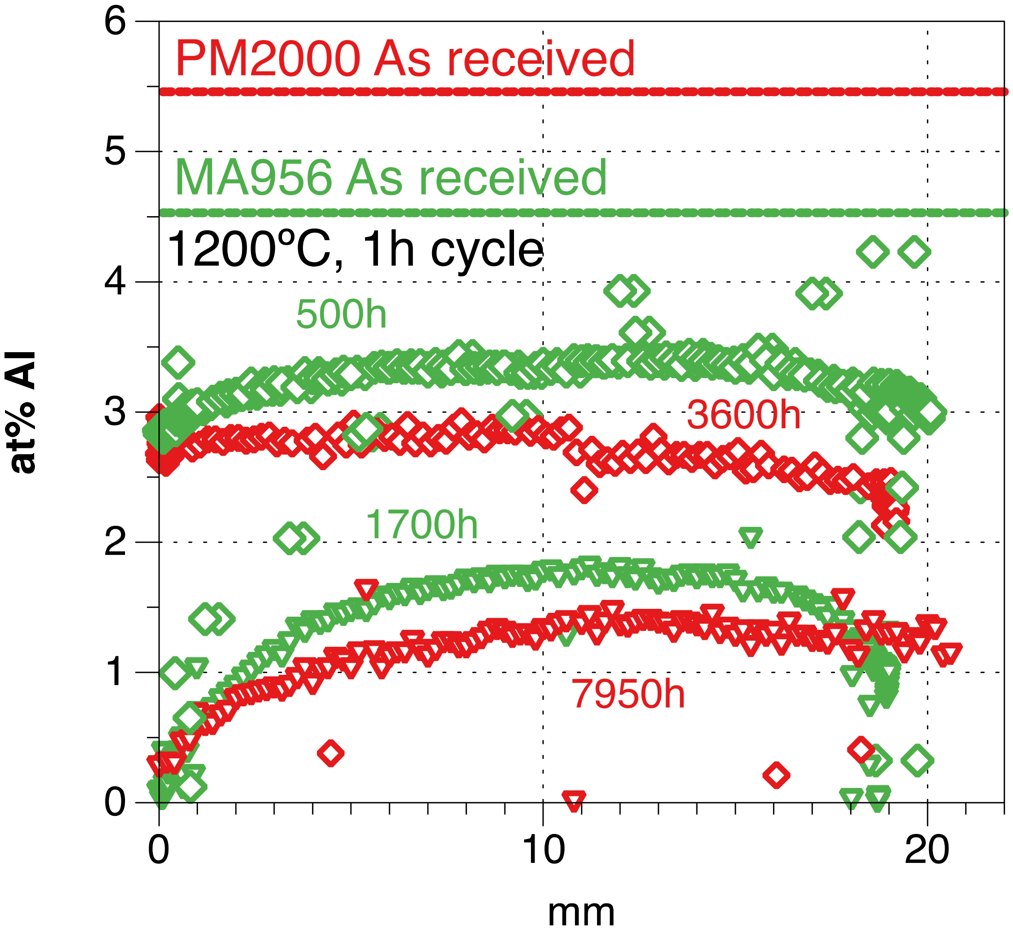
Specimen mass change not reliable for parameters determination





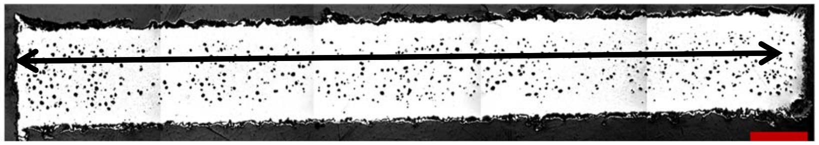
- Oxide flakes remain attached to the specimens leading to higher mass data
- Use of total mass gain for 100h cycle with specimens in crucible
- Measurement of Al content $\iiint_V \rho \cdot C_{Al}\, dV$ for interrupted tests

Determination of model parameters from measurement of Al in interrupted specimens



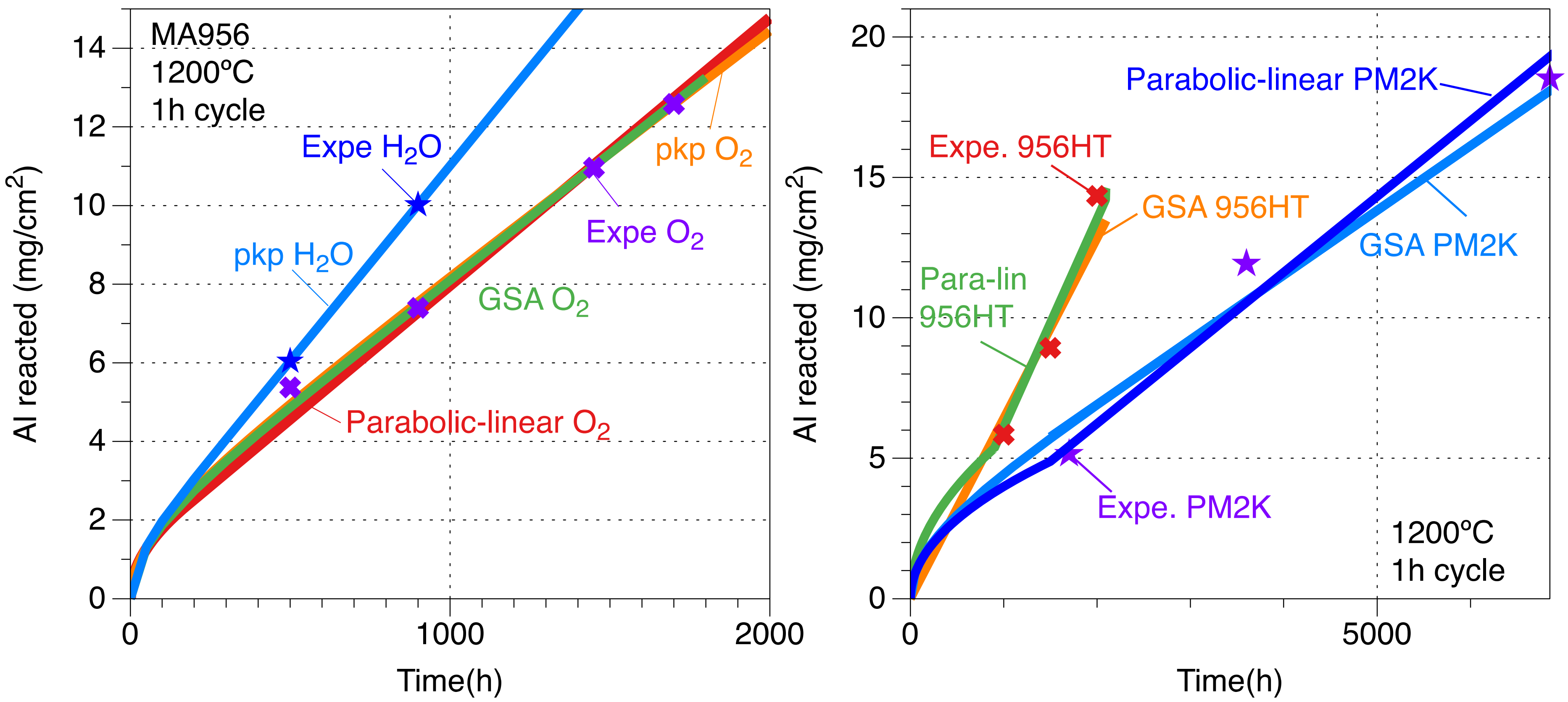
Al remaining content was measured for MA956, MA956HT and PM2K after after various exposure time

specimen cross-section



Al measurement by electron microprobe (EPMA)

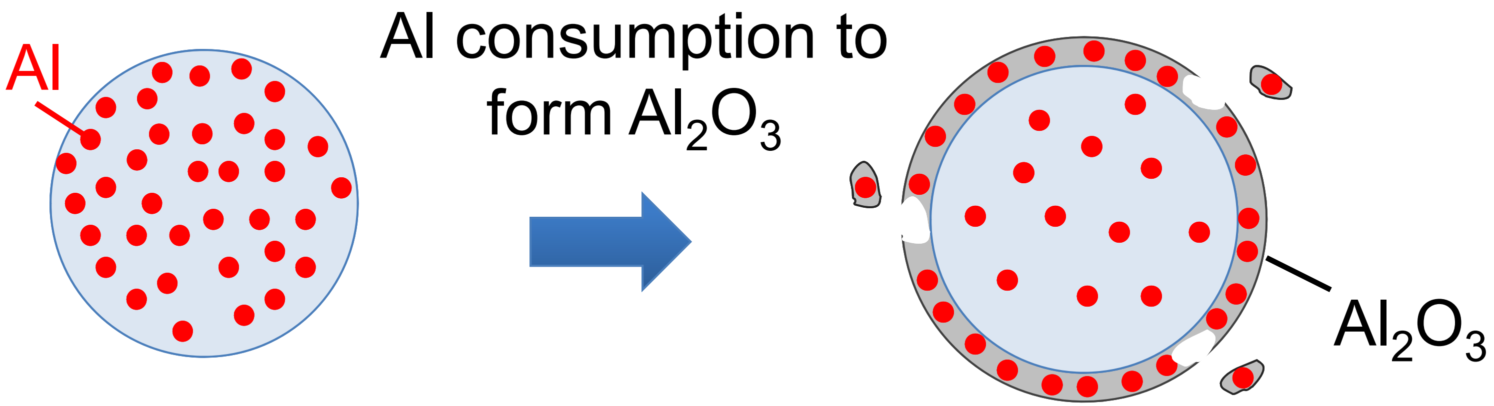
Good fit for 956, 956HT & PM2K with all models & ~linear Al consumption rate



Linear consumption rate 3 times slower for PM2K

Linear consumption rate 50% faster in H_2O for MA956

Lifetime Model based on Al consumption down to critical Al content



S: Surface area
V: Volume

$$S \cdot F_{Al}(t_b) = \rho \cdot V \cdot C_{Al0} - \iiint_V \rho \cdot C_{Alb}\, dV$$

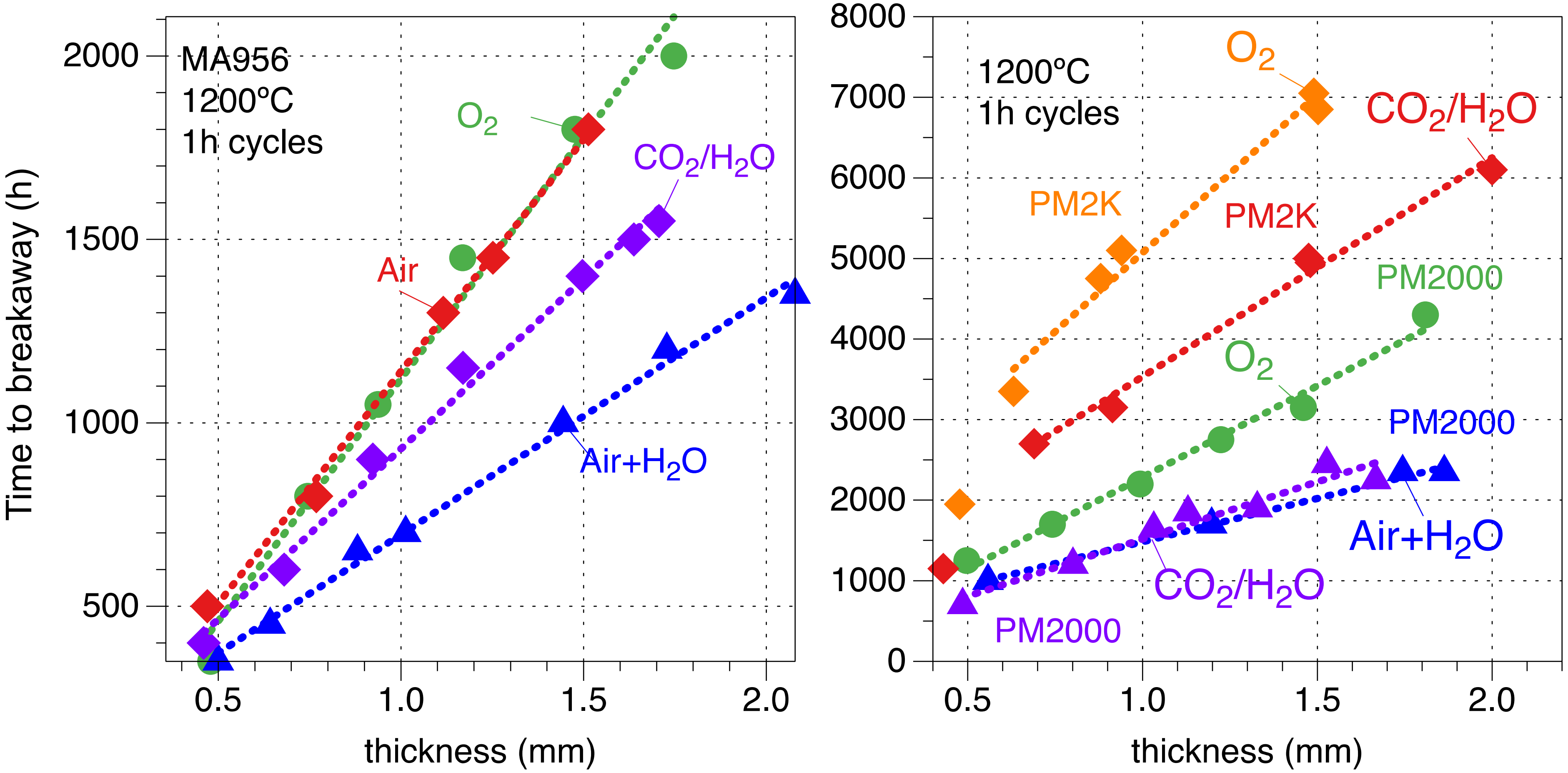
Done

Next

Al consumption $F_{Al}(t)$
due to cyclic oxidation

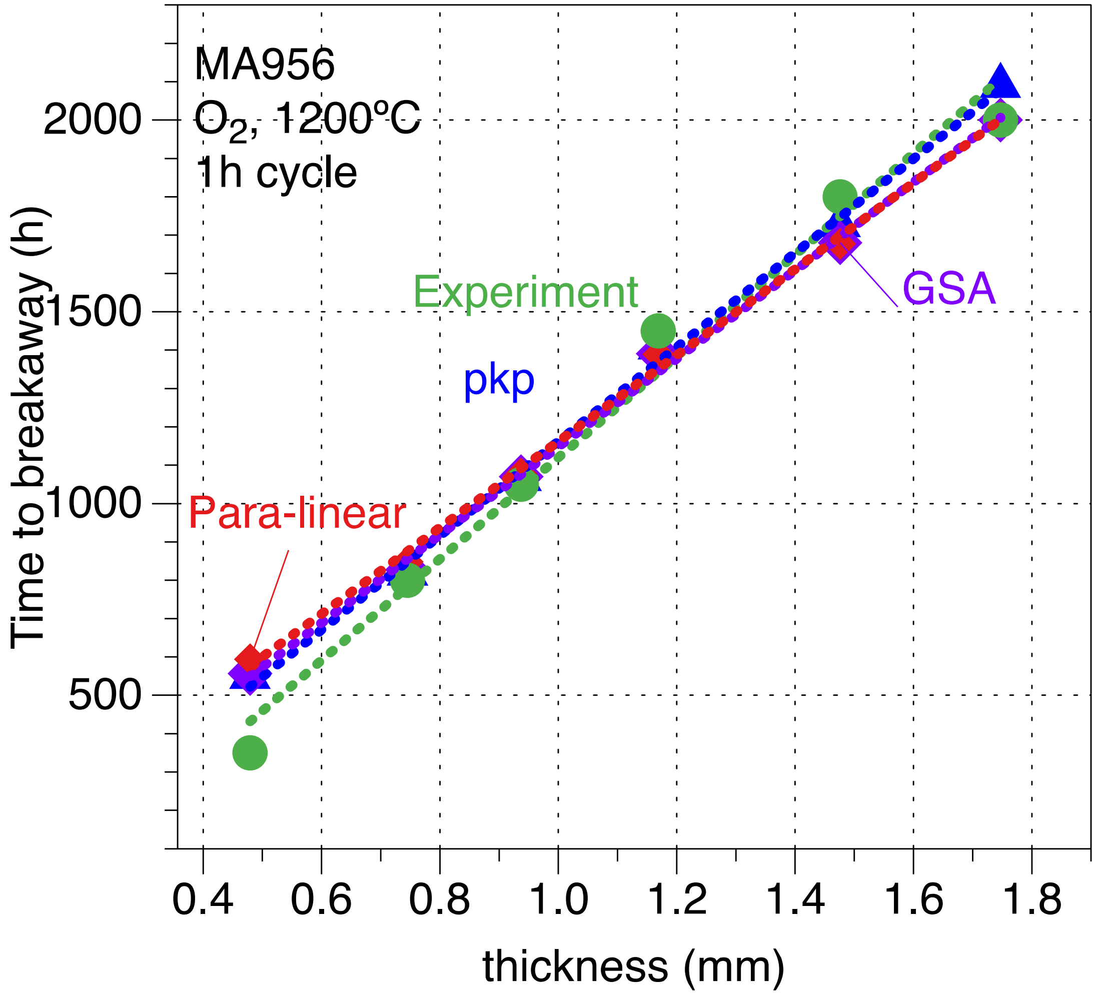
Critical Al content

Use of time to breakaway data to calculate Al content at breakaway



Tests with specimen thickness varying from 0.5 to 2mm

Good estimate with $C_{Alb\ average}$~1.5wt% for MA956, ~0.6wt% for PM2K



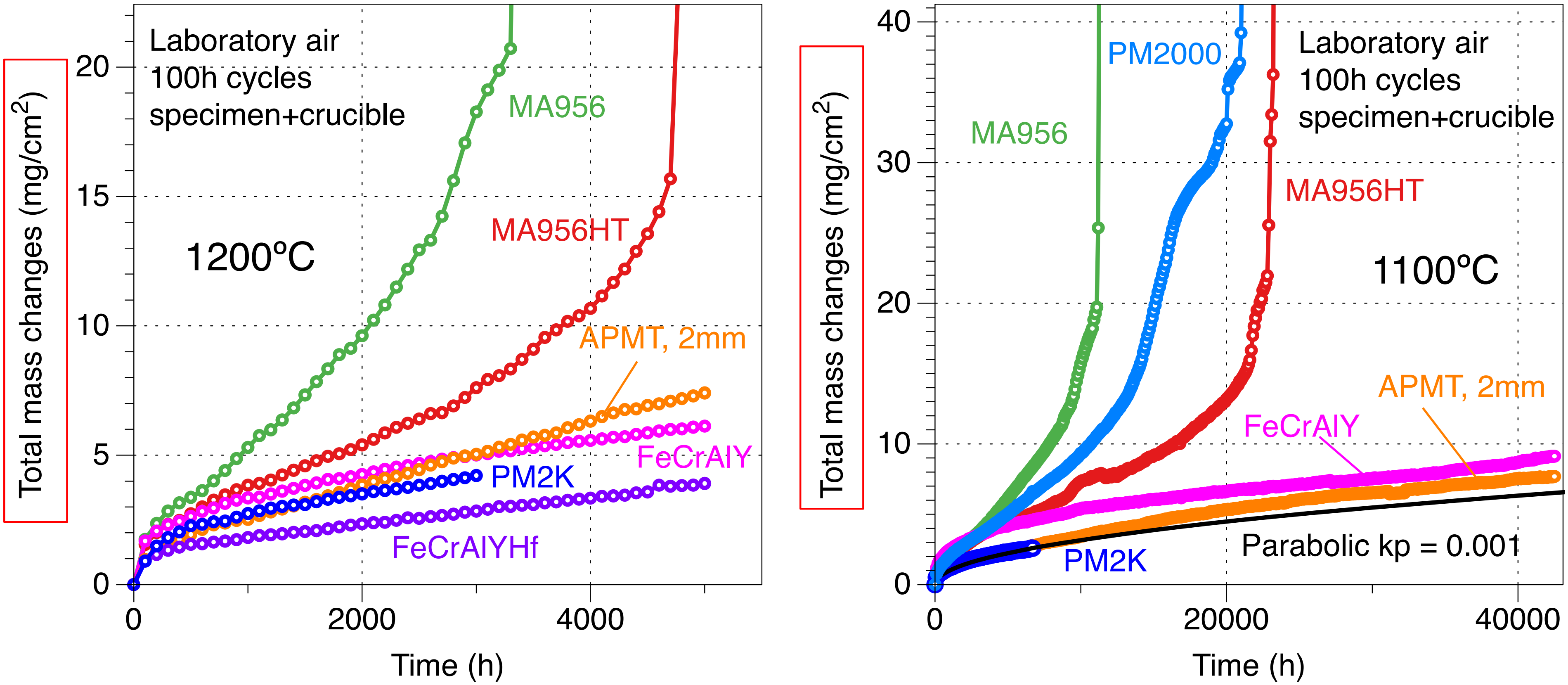
$$S \cdot F_{Al}(t_b) = \rho \cdot V \cdot C_{Al0} - \iiint_V \rho \cdot C_{Alb}\, dV$$

$$= \rho \cdot V \cdot C_{Alb\ average}$$

$$\boxed{F_{Al}(t_b) = \rho\,(C_{Al0} - C_{Alb\ average})\frac{V}{S}}$$

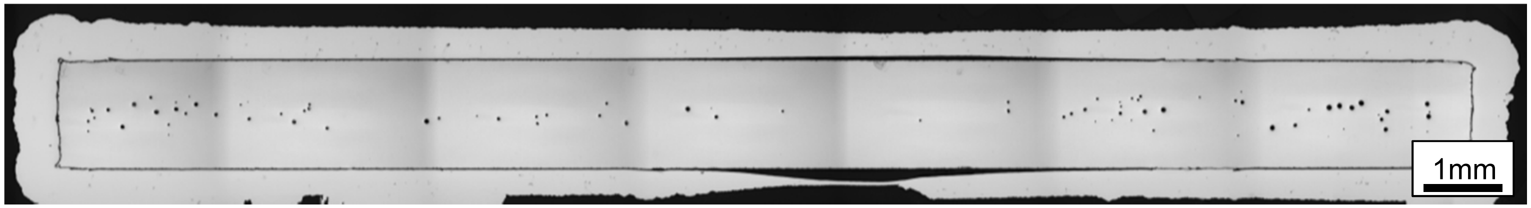
Linear ~cst ~thickness

100 cycle tests: very limited spallation for best alloys can lead to ~parabolic behavior over 40000h

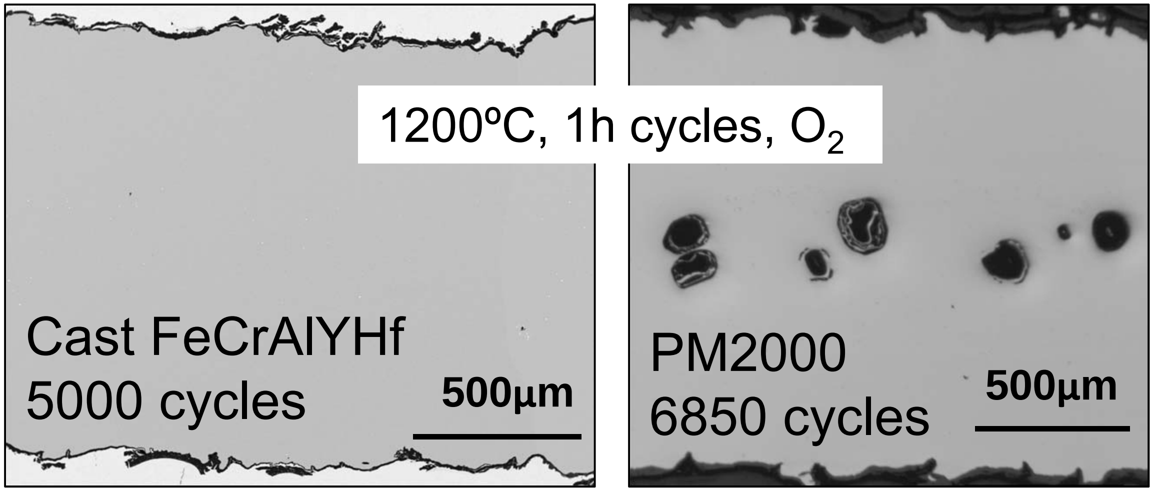


Very long parabolic regime for PM2K. Onset of spallation is key parameter for lifetime prediction (>100000h? at 1100ºC)

Porosity formation related to ODS fabrication & creep strength



1100° C 60, 100h cycle Porosity 0.38%



recrystallization at the surface decreases strength and can lead to surface deformation

- Acceptable porosity levels at 1100ºC?
- Macroscopic deformation of FeCrAlYHf not observed for PM2K

FY14 Milestones

- Properties of joints made by friction stir welding

Final characterization and mechanical testing of PM2000 and APMT in May. One paper submitted on PM2000 weld microstructure

- Lifetime model integrating effect of specimen geometry

One paper expected to be submitted in May 2014

-Milestone on creep-fatigue literature review

New FY15 project on creep fatigue

Conclusion

- Two industrial partners producing ODS powder and working on final commercial consolidated products

- New opportunities for ODS alloys: additive manufacturing, new NE interest

- FE ODS project has delivered key results for future use of ODS alloys:
  - Characterization of new fabrication and welding techniques
  - Long-term data and improved models to predict component lifetimes
  - Low level of impurities (S) key for great oxidation behavior

Acknowledgements

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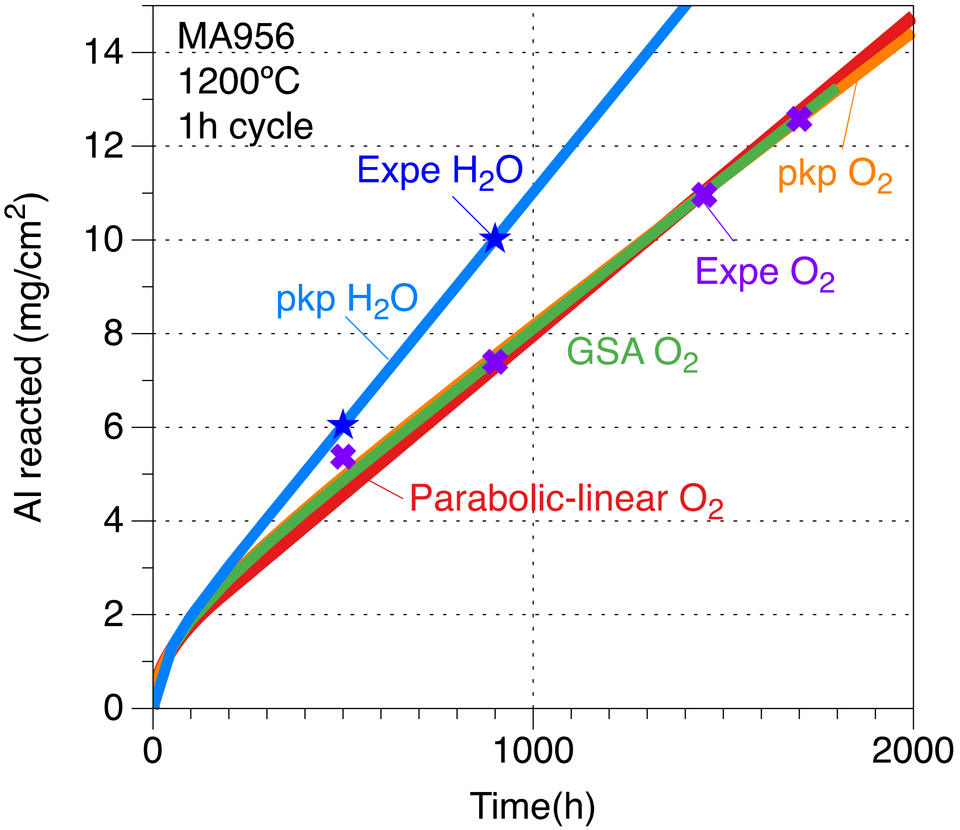
- B. Pint, P. Tortorelli, I. Wright, D. Hoelzer, K. Unocic for exciting scientific discussions

This research was sponsored by the U.S. Department of Energy, Office of Fossil Energy under the supervision of Vito Cedro III & Jason Hissam

Good fit for 956, 956HT & PM2K with all models & ~linear Al consumption rate



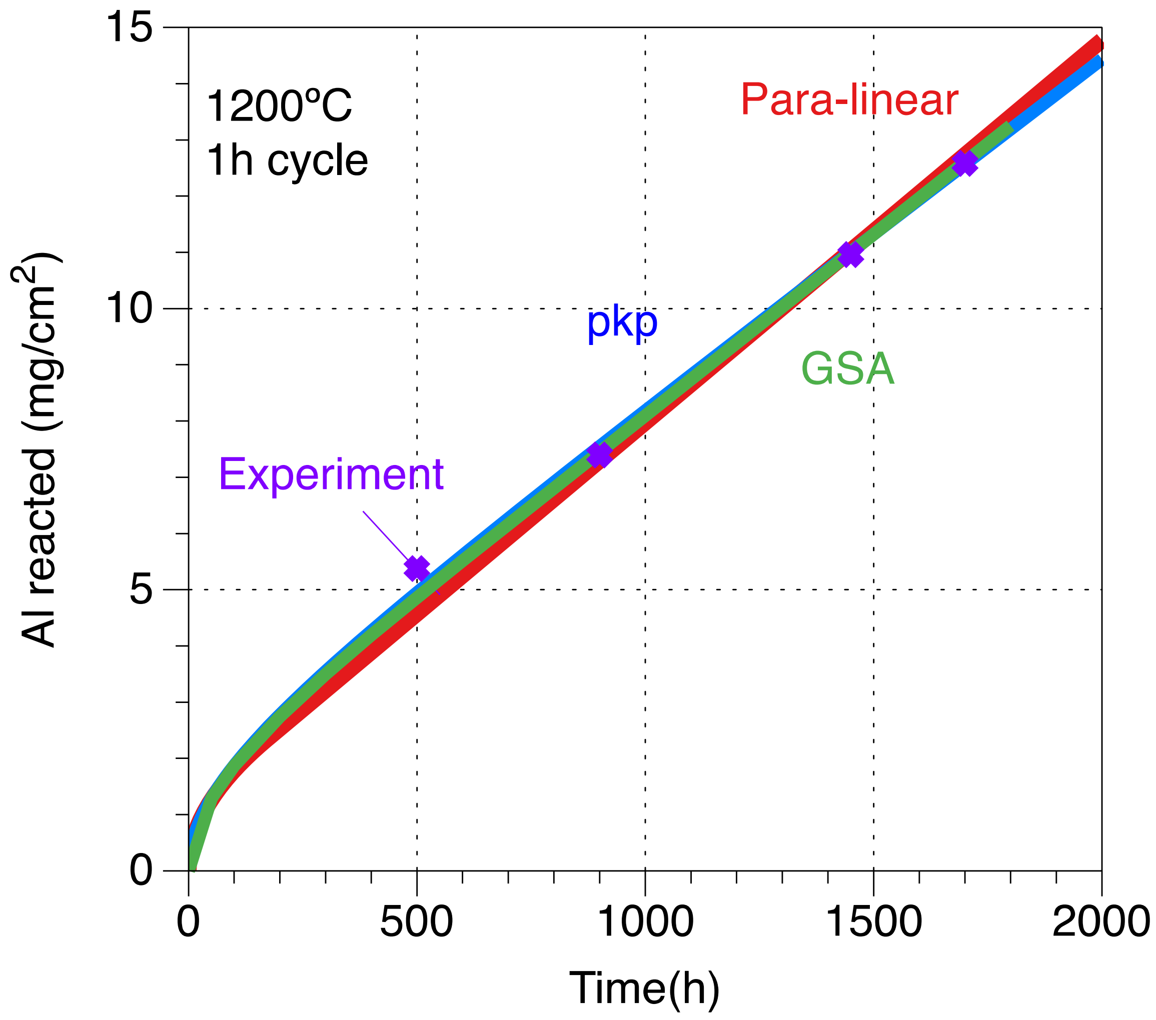
Smialek et al.

$$Slope = -(S_C - 1)\sqrt{Fa \cdot k_p \cdot \Delta t}$$

Linear slope depends on $Fa*k_p$ only

Good method to predict Al consumption rate but need specimen mass gain for correct Fa and k_p values

Good fit for MA956 with all models with similar quasi-linear curves



k_p from beginning of the cyclic curve with limited spallation

Parabolic-linear

a	0.00605
tp	169
kp	2.5200E-02

pkp

kp	0.0252
p	0.00154

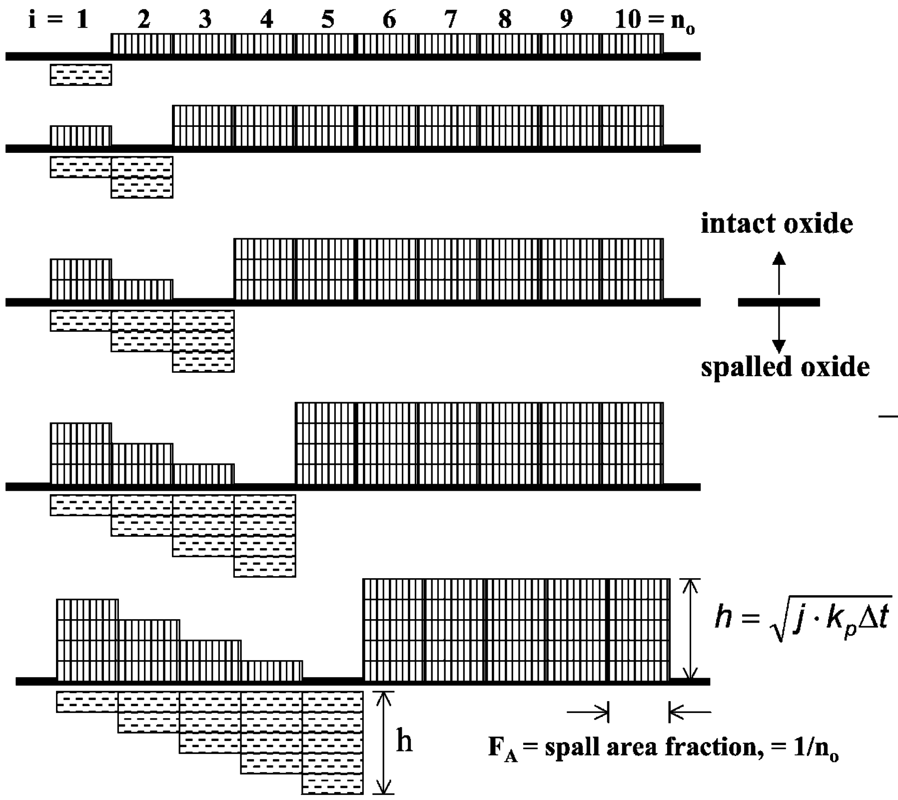
GSA

kp	0.0252
Fa	0.001305

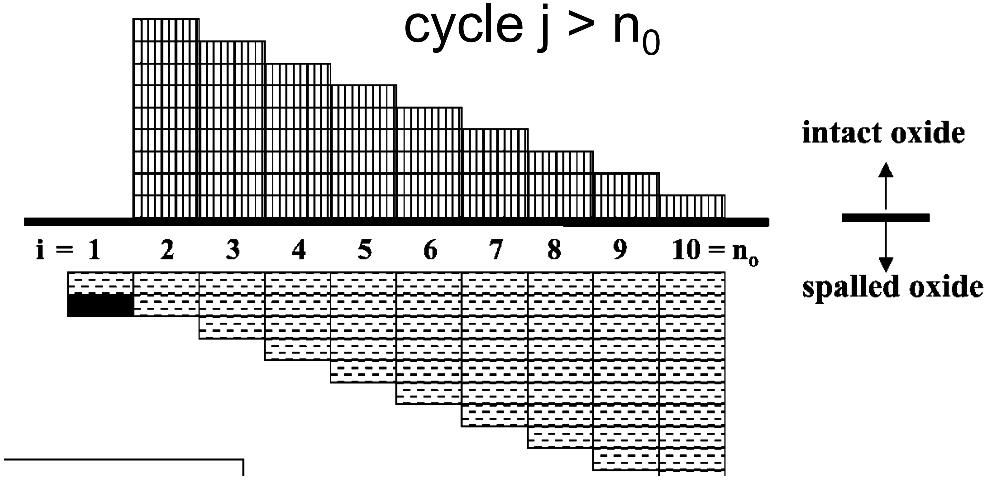
DICOSM GSA

Fa spall area fraction = $1/n_0$

cycle $j < n_0$



cycle $j > n_0$



linear specimen mass loss and Al consumption

Simple GSA relations:

$$\sum W^{\mathrm{GSA}}_{\mathrm{oxy,A}} = F_{\mathrm{A}}\sqrt{k_{\mathrm{p}}\Delta t}\left\{n_{\mathrm{o}} j^{1/2} + \frac{1}{3} j^{3/2}\right\}$$

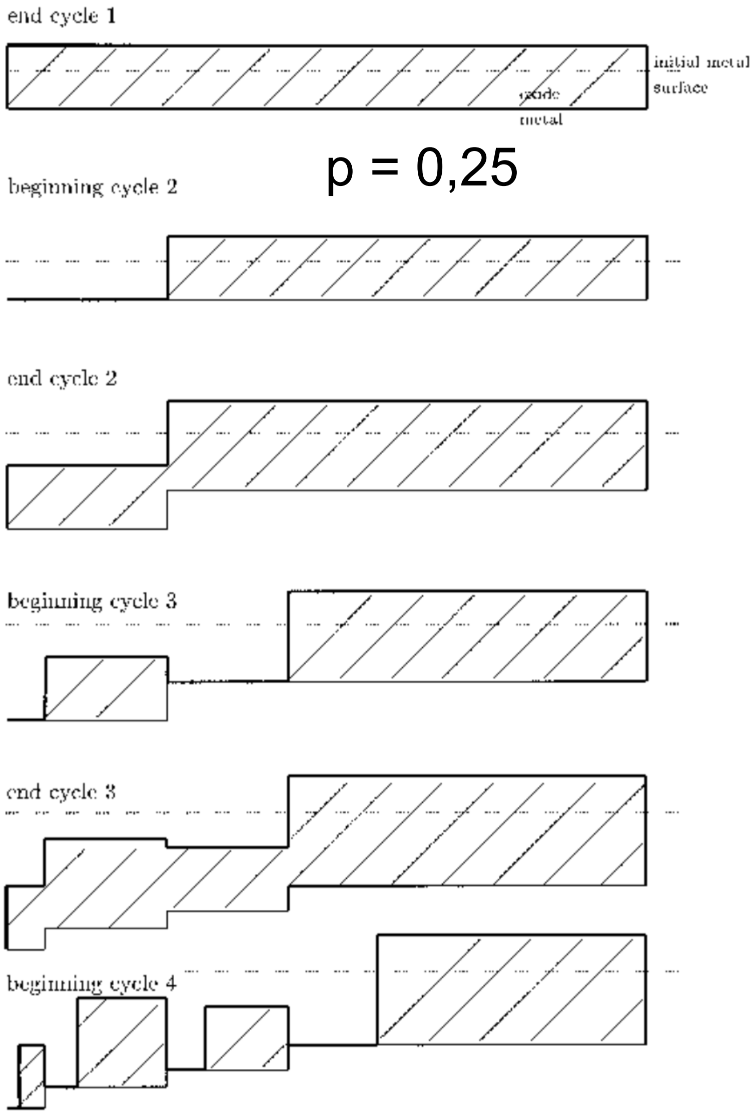
$$\sum W^{\mathrm{GSA}}_{\mathrm{oxy,B}} = F_{\mathrm{A}}\sqrt{k_{\mathrm{p}}\Delta t}\left\{j n_{\mathrm{o}}^{1/2} + \frac{1}{3} n_{\mathrm{o}}^{3/2}\right\}$$

$$\sum W^{\mathrm{GSA}}_{\mathrm{met}} = (S_{\mathrm{c}} - 1)\sum W^{\mathrm{GSA}}_{\mathrm{oxy}}$$

J.L. Smialek, Acta Mater. 51, 469–483 (2002)

pkp model

D. Poquillon & D. Monceau, Oxid. Met. 59, 409-431 (2003)



p = 0,25

Probabilistic approach, p = oxide scaling probability

ΔM_n : O mass gain during cycle n

$$\Delta M_n = A[pS_{n-2}(1-p) + B_{n-1}(1-p)]$$

$$A = \sqrt{kp\,\Delta t}$$

$$S_n(x) = \sum_{k=0}^{k=n}\left[x^k\left(\sqrt{k+1}-\sqrt{k}\right)\right]$$

$$B_n(x) = x^n\left(\sqrt{n+1}-\sqrt{n}\right)$$

Incremental calculation of ΔM_n

Collaboration with NE (lead) on new FeCrAl ODS alloys

Fusion: Use of ODS FeCrAl alloys for DCLL Blanket

- ODS FeCr are creep and radiation resistant but low compatibility with PbLi

- Development of ODS FeCrAl with low (<14Cr) to avoid α'-Cr embrittlement

- New ODS Fe12Cr5Al alloys with Y, Y+Zr and Y+Hf additions

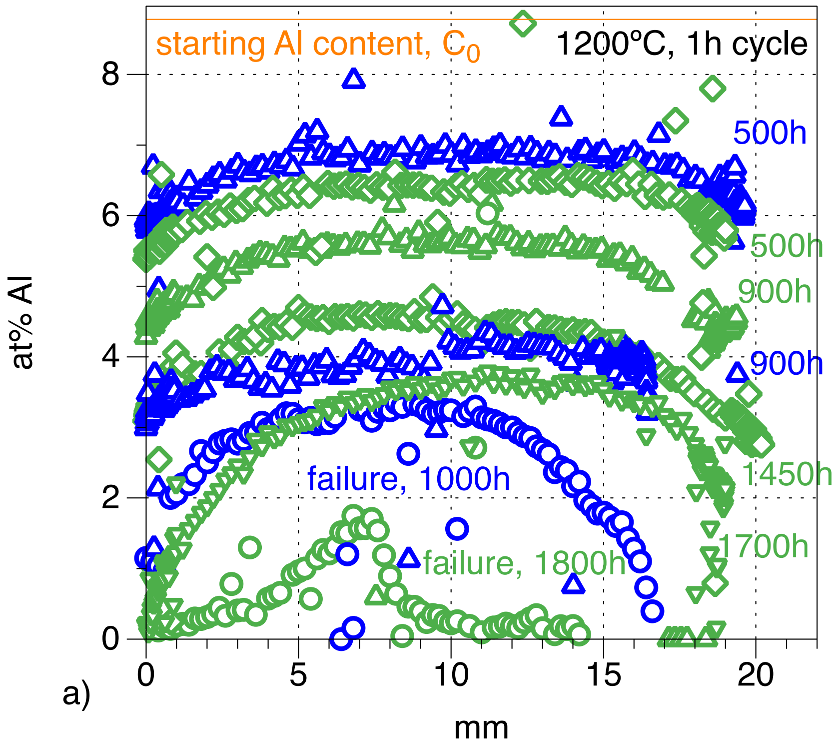
NE: Use of ODS FeCrAl alloys as fuel cladding material

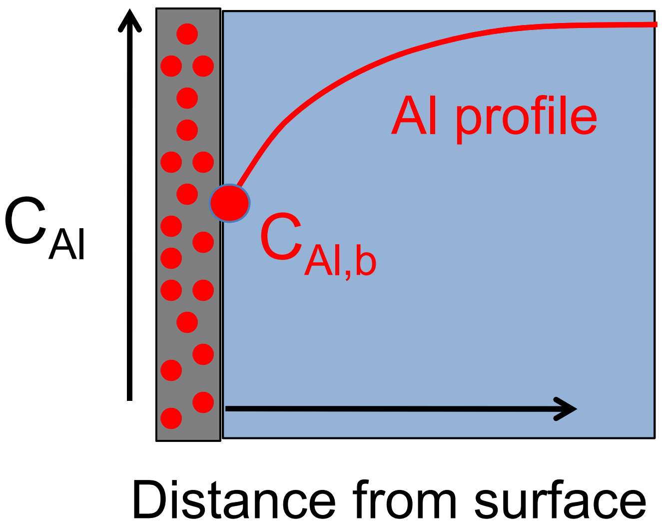
- Loss of coolant accident (LOCA) scenarios require materials that can withstand TºC>1200ºC-1400ºC for several hours

- Development of new ODS Fe-12-15Cr-4-5.5Al alloys with high temperature capability

- Team: B. Pint, D. Hoelzer, K. Unocic, T.S. Byun, S. Dryepondt

Better evaluation of critical Al concentration $C_{Alb\ average}$





- Al gradient in the alloy is related to specimen geometry
- Comparison between rectangular & cylindrical specimens
- Diffusion model to take into account the gradient

2-stage parabolic-linear model (wright)

1h cycle, 1200ºC, 500h

Limited spallation before reaching a critical oxide thickness

$t<t_p$

$$Mass\ Gain = \sqrt{kp\ t}$$

1h cycle, 1200ºC, 6850h

amount of spalled oxide = amount of oxide grown during 1 cycle

Linear mass decrease

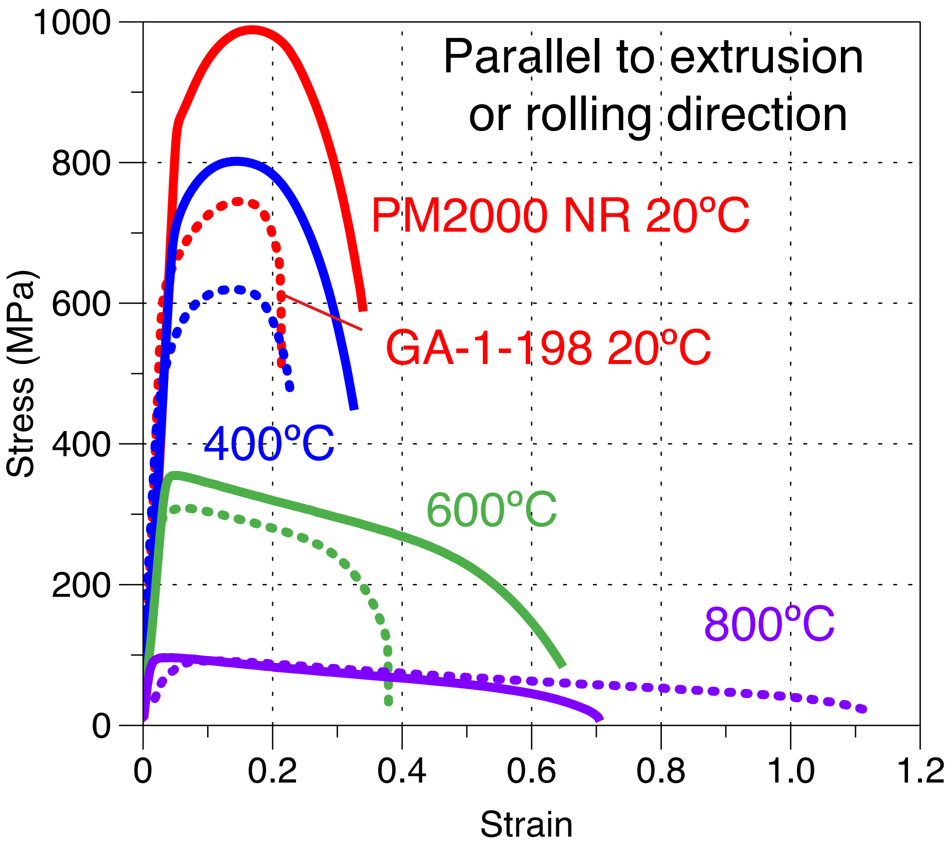
$t>t_p$

$$Mass\ Gain = k_p\left(t - t_p\right) + \sqrt{kp\ t_p}$$

Collaboration with Ames Lab

(I. Anderson, J. Rieken, A. Spicher)

New Fe-14.9Cr-12.4Al-0.9W-0.235Hf-0.185Y-0.12O GARS alloy



- Better tensile properties than previous GARS FeCr alloys

- Ball-milling at ORNL (D. Hoelzer) for 5h to improve microstructure & strength

- Oxidation testing at ORNL (B. Pint)