

Oxidation of Alumina-forming ODS Alloys

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Outline of the Presentation

- **Introduction – factors affecting the oxidation of ferritic stainless steels**
- **Scale growth**
- **Scale adhesion**
- **Breakaway effects**
- **Improvements that can be made to mitigate degradation due to oxidation**

Major constituents of some commercial FeCrAl alloys

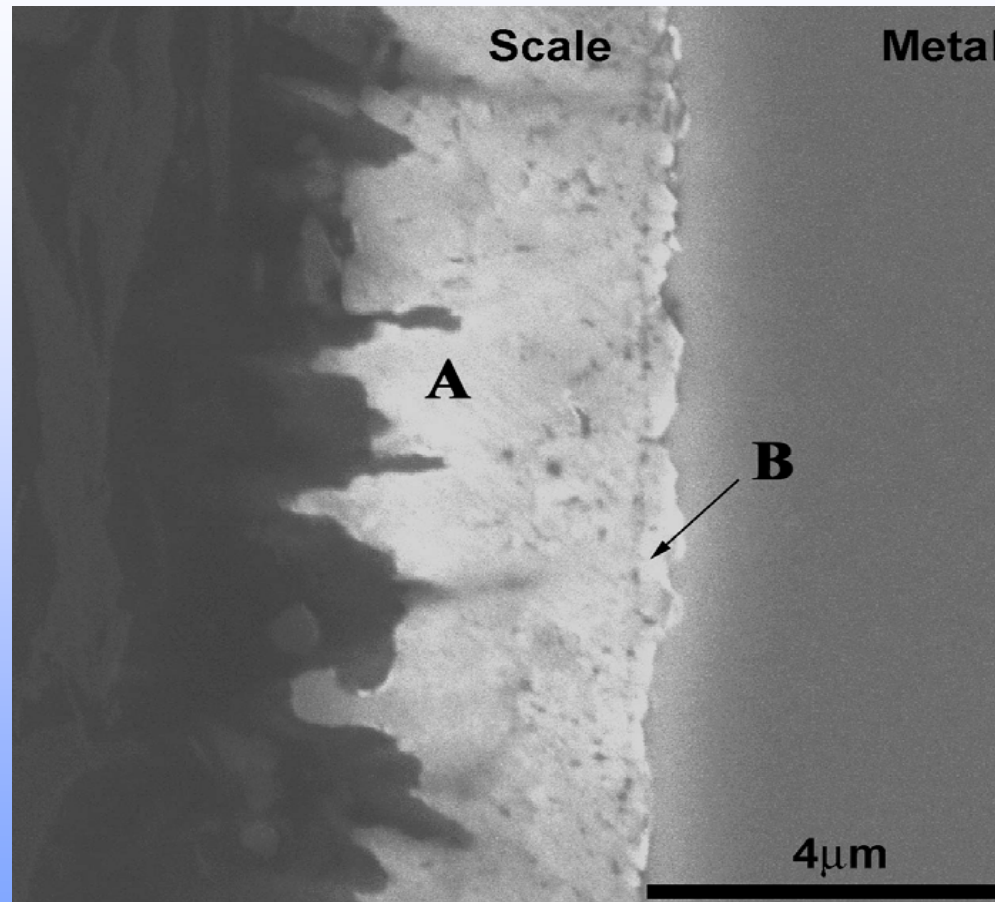
Alloy	Wt%		Ppm					balance Fe	
	Al	Cr	Y	Hf	Zr	Ti	Si	Y ₂ O ₃	
Aluchrom YHf	5.5	20.0	480	405	320	99	2900	0	
Kanthal AF	5.2	21.0	340	3	580	940	1900	0	
Kanthal APM	5.9	21.0	200	200	1000	200	-	0	
MA956 (ODS)	4.6	20.0	0	-	-	5000	-	5000	
PM2000 (ODS)	5.9	21.0	0	-	-	4100	-	5000	



Scale Growth

- **Want to form protective, stable α - alumina scale as soon as possible**
- **Subsequent oxide growth should be as slow as possible to conserve aluminium supply**
 - **Pre treatment of alloy to ensure formation of α -alumina scale**
 - **Use reactive element additions to control scale growth rate**
 - **Add a non-ODS layer to minimize lack of compliance between oxide and substrate**
 - **Start with more aluminium in base alloy**

Scale cross-section



50 μm foil Aluchrom YHf 3000h at 900°C

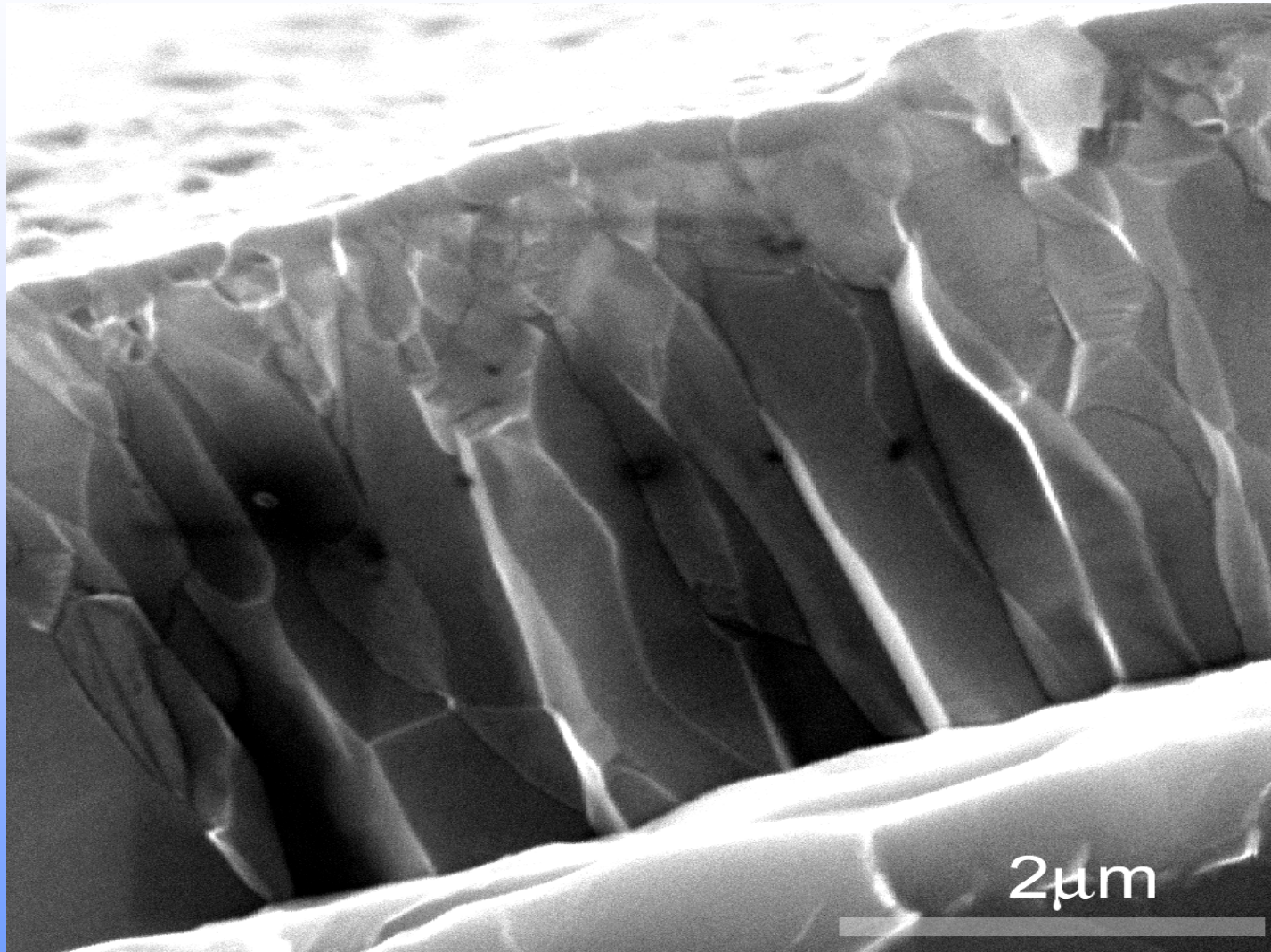
A – initially formed outward growing transient alumina

B – inward growing α -alumina



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Columnar growth of alumina



**Model FeCrAlY alloy oxidised
for 500 h at 1200°C**

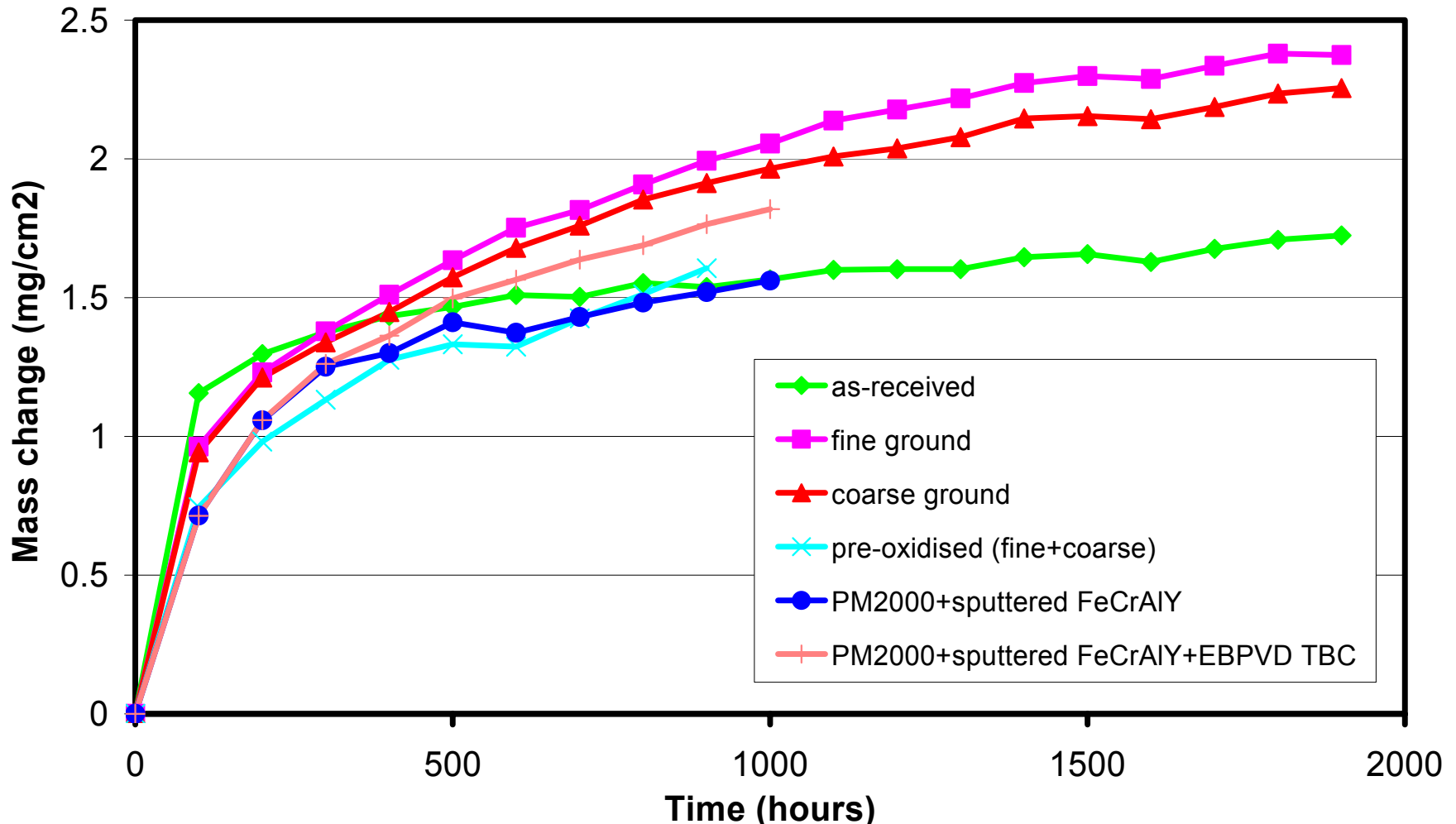


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Scale Growth

- Can preoxidise alloys at $T > 1000^{\circ}\text{C}$ to ensure that α -alumina results – but ‘waste’ aluminium
- Work by Quadakkers et al has shown that gas annealing at 1200°C in an $\text{Ar} + 4\%\text{H}_2 + 2\%\text{H}_2\text{O}$ mixture quickly gives an excellent protective scale for many alloys
- Although alloys with more than 6% Al have low ductility, extra Al can be incorporated into the finished components by a gas phase reaction followed by a diffusion treatment.
- Can modify the surface layer of the alloy by mechanical treatment or add an overlayer
- Additions of a ‘soft’ FeCrAl layer to ODS alloys appears to have a beneficial effect.





Mass change data from PM2000 slow cycle / 'isothermal' exposures
in combustion gas at 1200°C





PM2000
+ sputtered FeCrAlY
+ EBPVD TBC

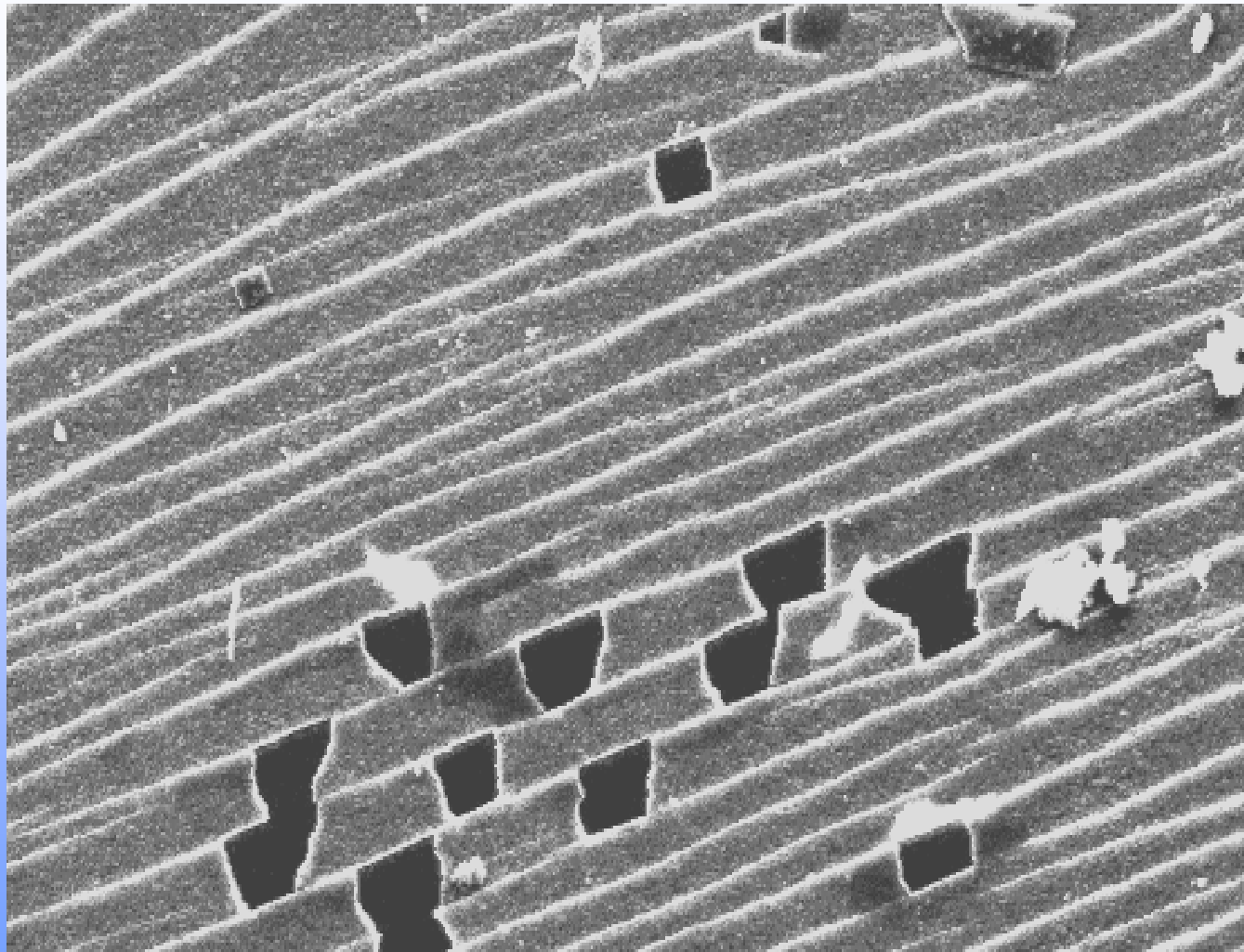
500 hours at 1200°C in combustion gas
(N₂+14%O₂+3.2%CO₂+1%Ar+5%H₂O)



Scale Adhesion

- **Presence of reactive elements such as yttrium, hafnium and titanium help scale adhesion**
- **Reactive elements also act as scavengers for tramp elements such as sulphur, which otherwise segregate to metal - oxide interface and affect adhesion**
- **Even carbon can form chromium carbides at the scale metal interface, although may be tied up with titanium, for example**
- **The build up of oxide growth stresses or accumulation of point defects at the scale metal interface can also affect adhesion**

Fe-20Cr-5Al with S<5ppm, oxidised at 1060°C for 4.5h

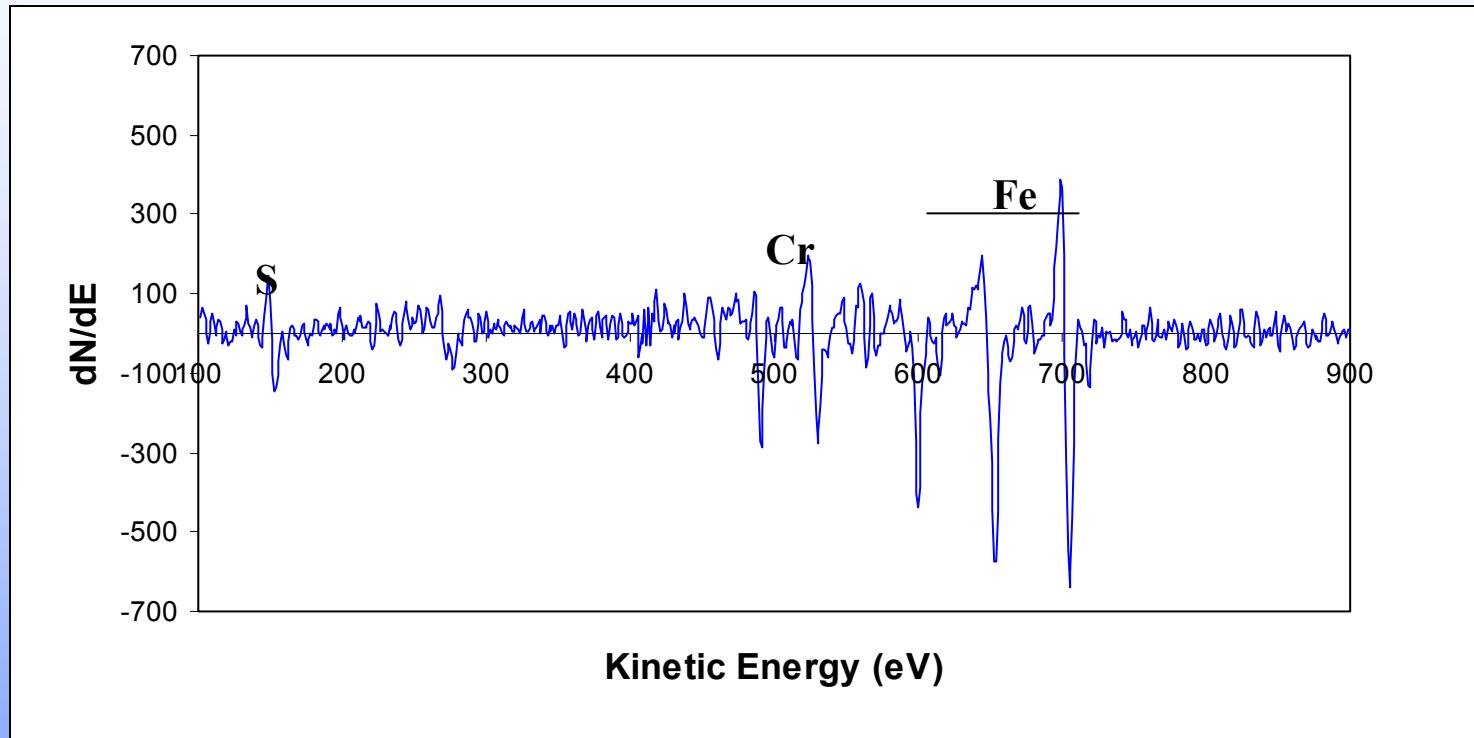


10 μ m

In-situ bending
experiment



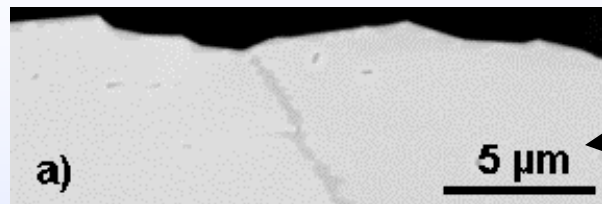
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**Auger spectrum, Fe-20Cr-5Al with S<5ppm,
oxidised at 1060°C for 4.5h (in-situ bending experiment)**



Oxidation of an FeCrAlY alloy with 530ppm carbon at 1200°C



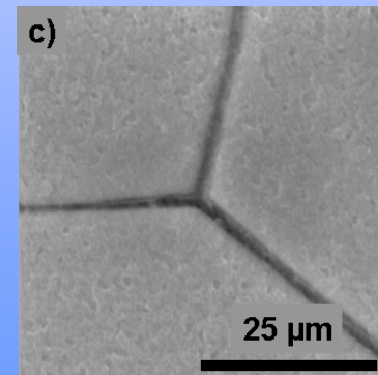
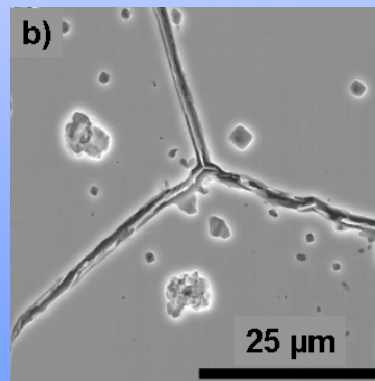
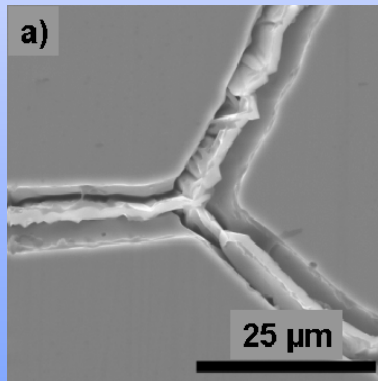
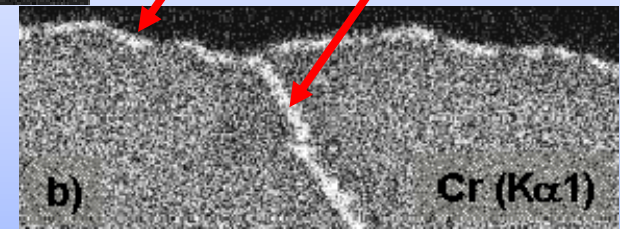
Alumina scale

Substrate

Kochubey, Naumenko et al (2006)



Cr present at the metal - oxide interface as well as the grain boundary

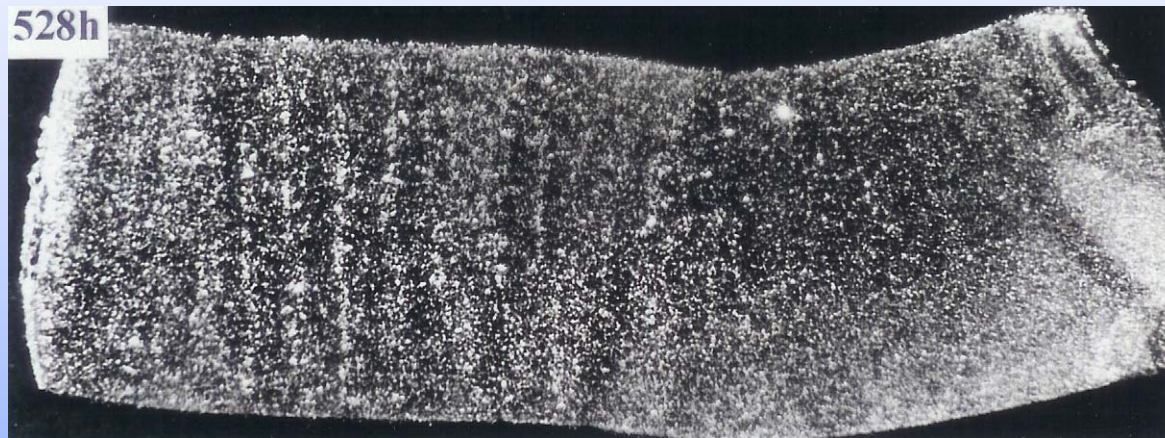


Carbide growth at different cooling rates:
(a) furnace cooled, (b) air cooled, (c) liquid N₂ quenched



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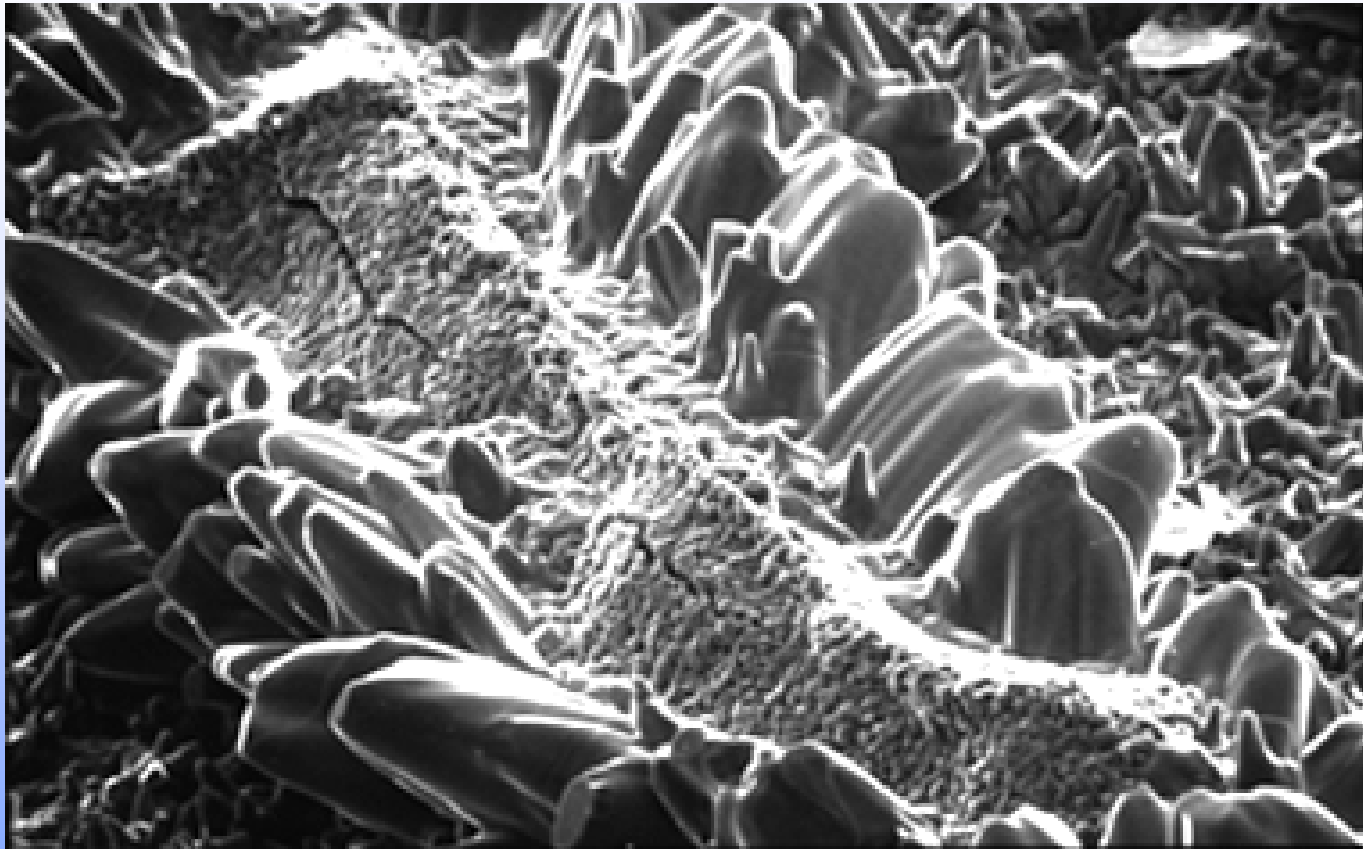
Distortion of parallel sided coupon of Fe-20Cr-5Al alloy after oxidation for 528 h at 1050°C



Breakaway Effects

- **Lack of aluminium in sufficient quantities to reheat protective alumina scale that has fractured can lead to growth of voluminous iron and chromium rich oxides**
- **Iron/chromium scale then formed offers little protection and sample quickly goes into “breakaway” oxidation**
- **Related to the amount of aluminium remaining in the sample and the size of the aluminium reservoir**



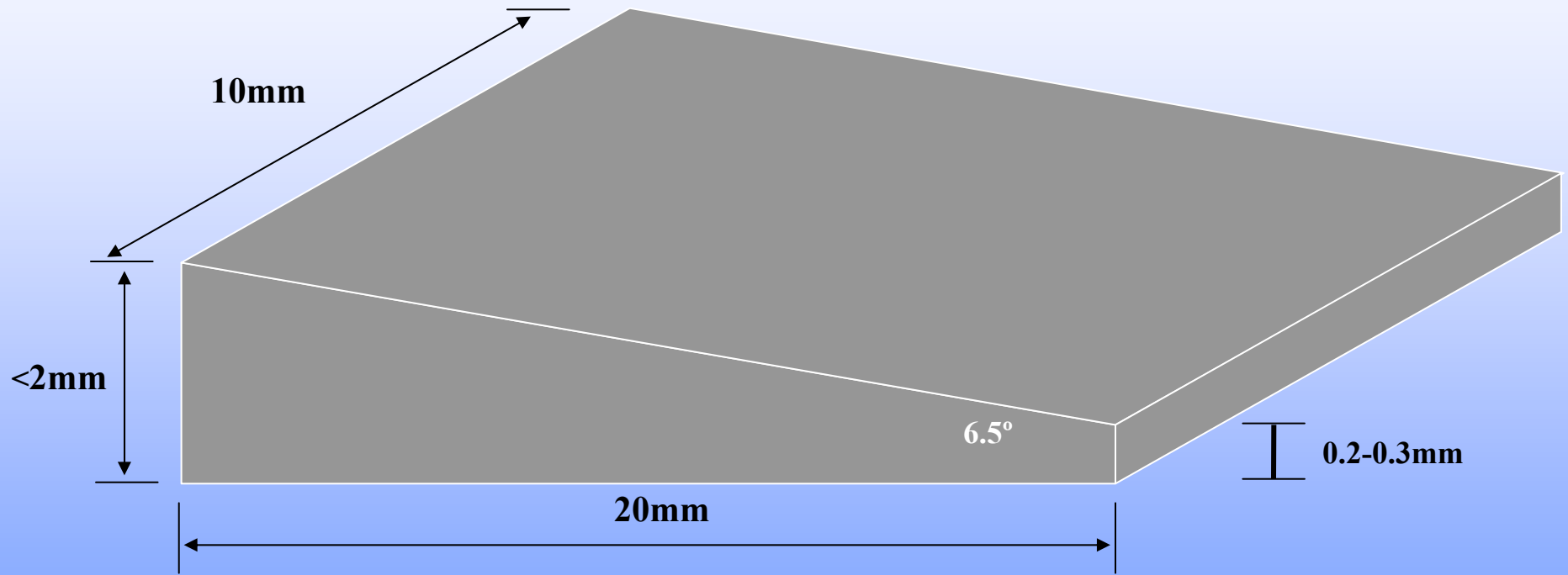


100 μ m

SEM image of breakaway oxidation in PM2000, oxidised at 1300°C for 140h containing critical remnant aluminium concentration



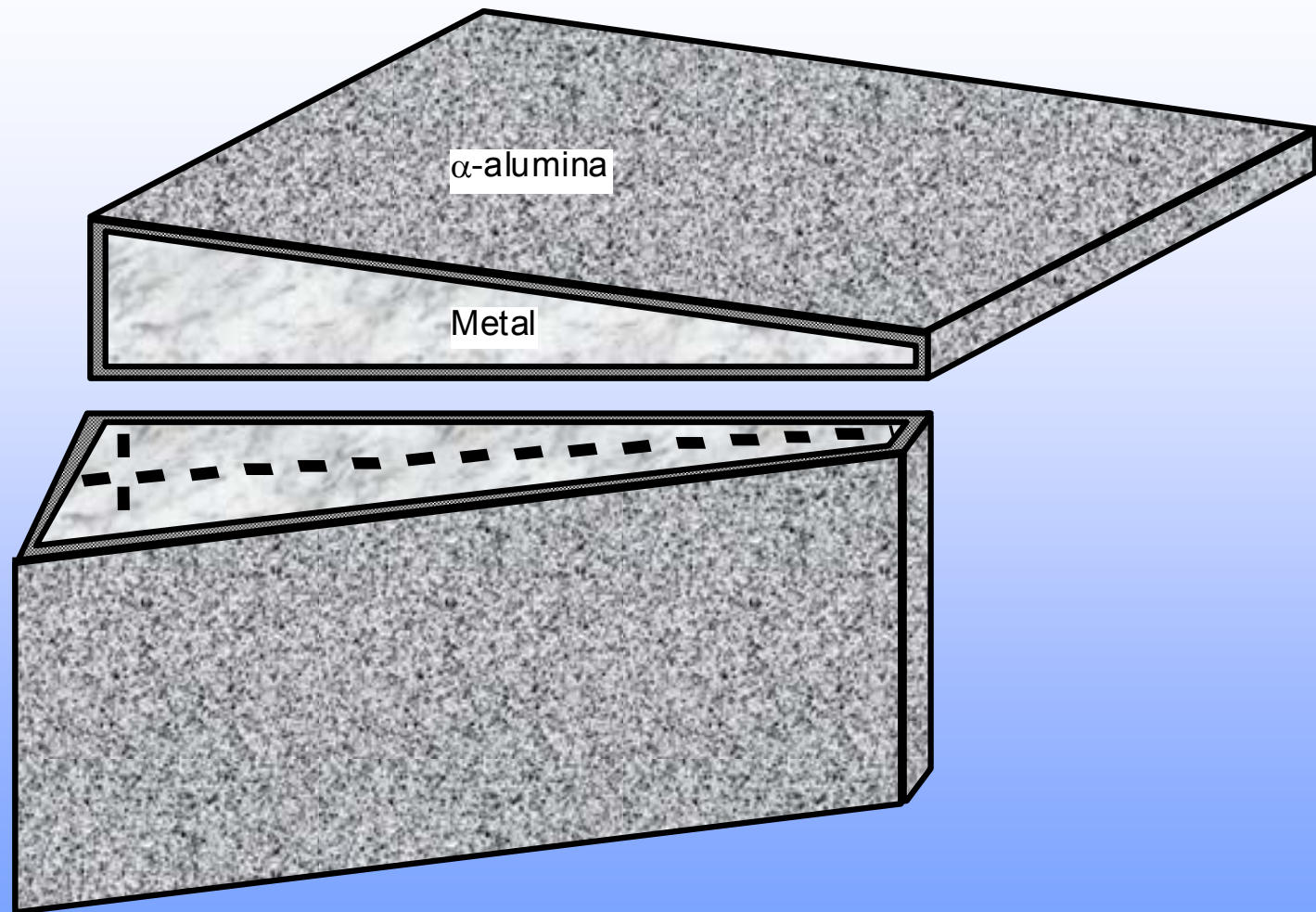
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Taper section sample geometry

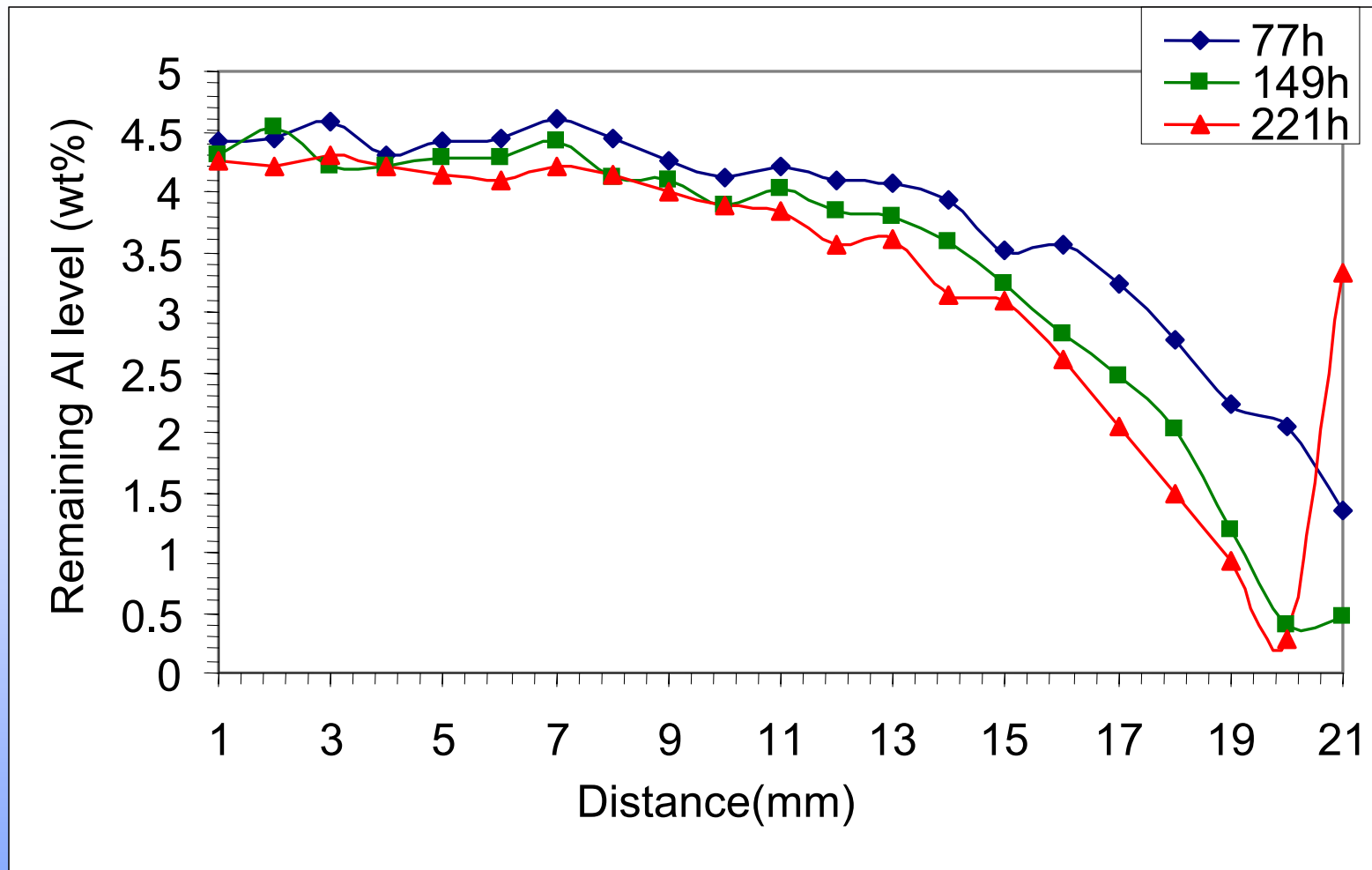


MA956 oxidised at 1350°C for 24h.



A schematic diagram showing the cut face from which elemental profiles were recorded during the microprobe analysis.

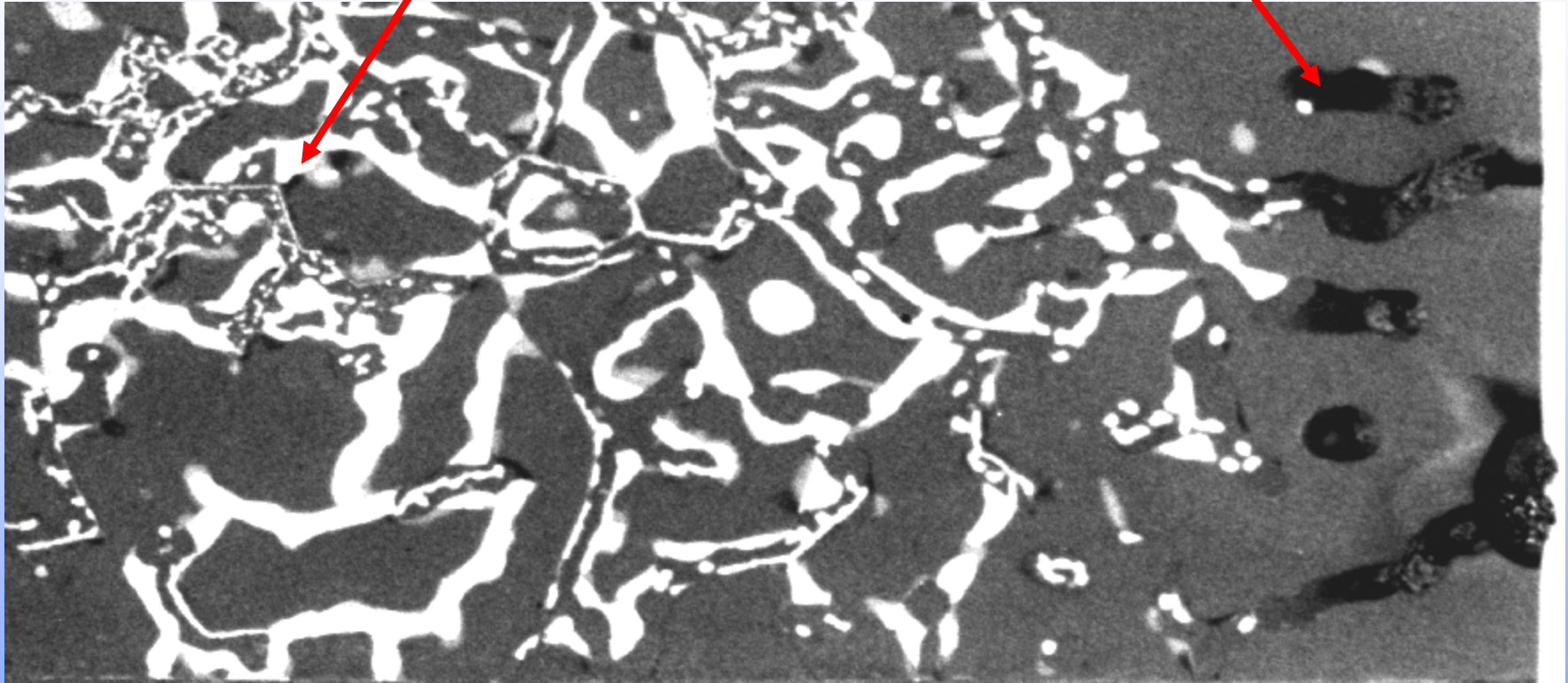




Al profiles along wedges of Kanthal APM alloy, oxidised at 1350°C for three different times.

Spallation

Breakaway Oxidation

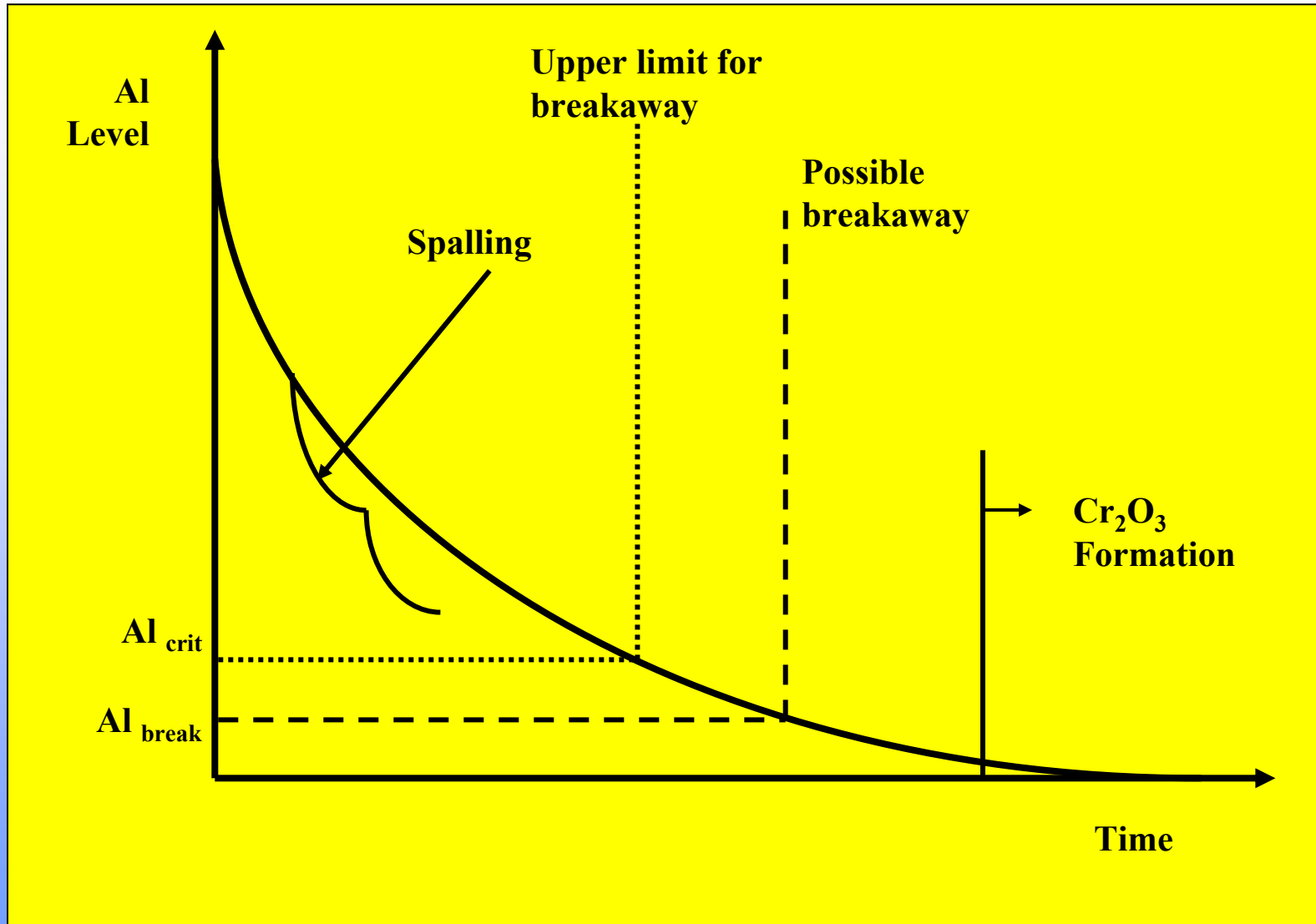


5mm

**Wedge-shaped sample of an FeCrAl model alloy
oxidised at 1300°C for 96h in laboratory air.**

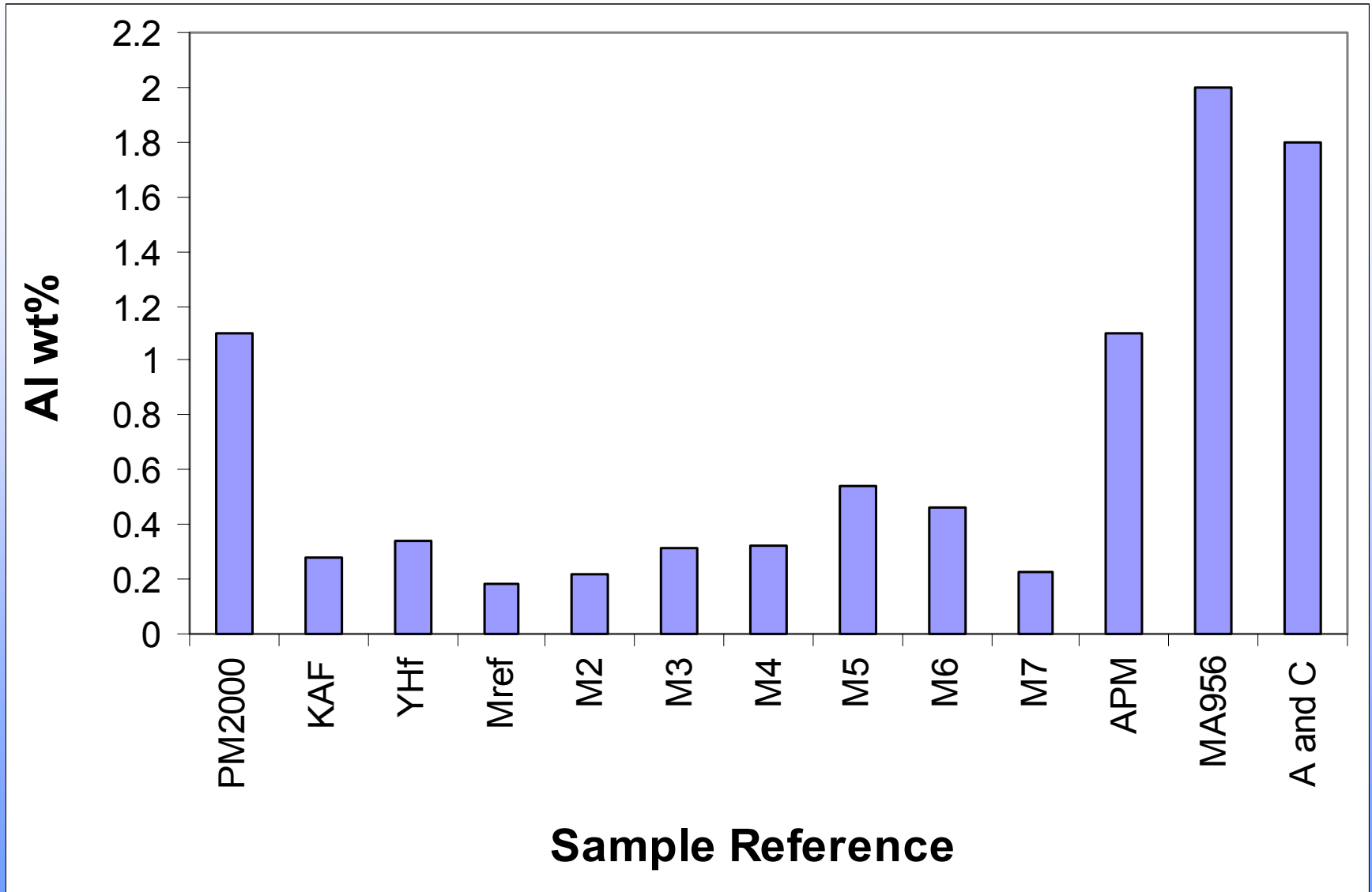


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After H. E. Evans et al

Remnant Al content at onset of breakaway (1200°C)



Control of Oxidation of ODS Alloys

- **Gas annealing at 1200°C in an Ar + 4% H_2 + 2% H_2O mixture quickly forms an excellent protective α -alumina scale for some alloys.**
- **Incorporate more than 6% Al into the finished components by a gas phase reaction followed by a diffusion treatment may prolong lifetime.**
- **Addition of a 'soft' FeCrAl layer to ODS alloys may have a beneficial effect on the control of scale spallation.**
- **Sufficient quantities of reactive elements and titanium are needed to control any tramp elements and excess carbon which may be present.**

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