15th of May 2017

Materials for extreme conditions: High temperature corrosion and steel design

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High Temperature Oxidation and Corrosion

Basically very simple:
For a given environment, the metal should form either a **protective oxide** or **no reaction at all**.

Or in other words:
Kinetics (slow) or
Thermodynamics (immunity)

Oxidation kinetics

Important Properties for an oxide scale:

Transport properties (ionic, electronic, atomic and gaseous)
-Defect type and concentration

Mechanical properties of the oxide/metal
- Low stresses, PBR, thermal expansion, adhesion

Melting point and vapour pressure

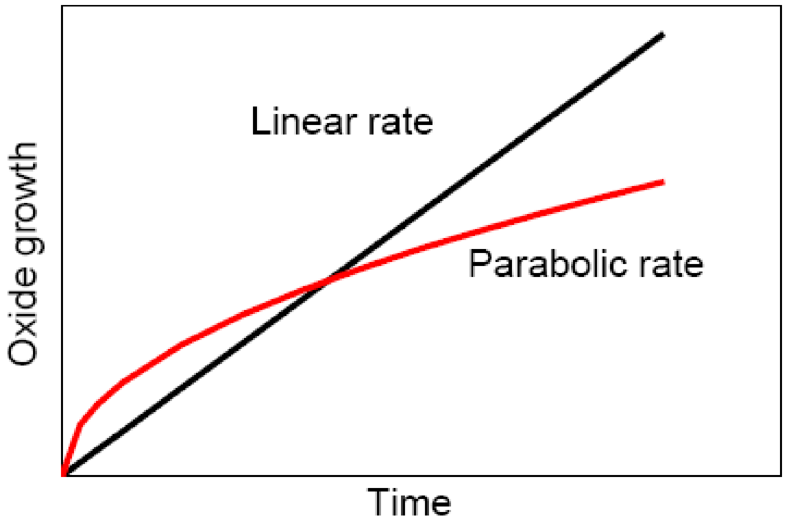
Balanced oxide growth, adherent oxide with low population of macro defects (porosity, cracks)

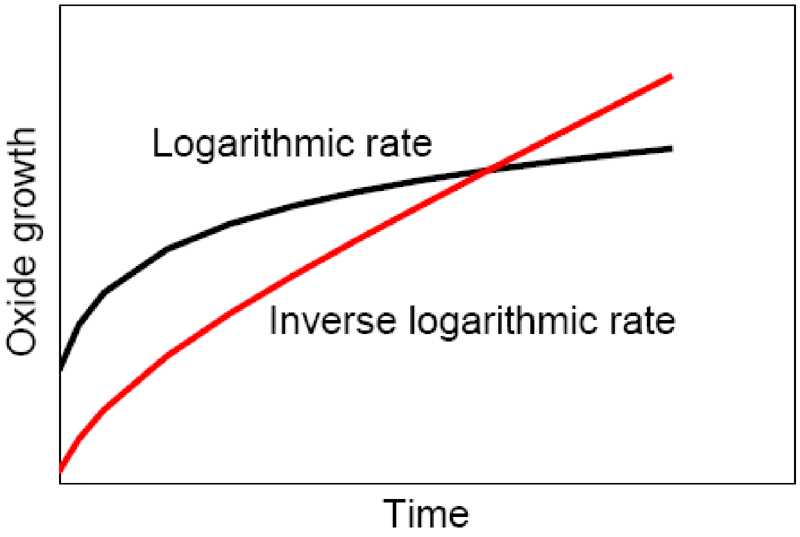
The ideal high temperature oxide:

- One oxide phase, thermodynamically stable in a wide range of temperatures and oxygen partial pressures.
- High melting point (both substrate and formed oxide)
- Low vapor pressure of the oxide (and metal substrate).
- Balanced oxide growth, i.e. oxygen ion inward diffusion should be balanced with metal ion outward diffusion $\Rightarrow$ no porosity and no cracks.
- Not too large volume change when the metal oxide forms (PBR)
- Thermal expansion of the oxide should be close to that of the metal substrate.
- Low concentration/density of intrinsic, extrinsic, point and extended oxide defects.
- $\Rightarrow$ Low diffusion coefficients for oxide ions and metal ions in the oxide.

$\Rightarrow$ Slow growing adherent oxide (parabolic growth)

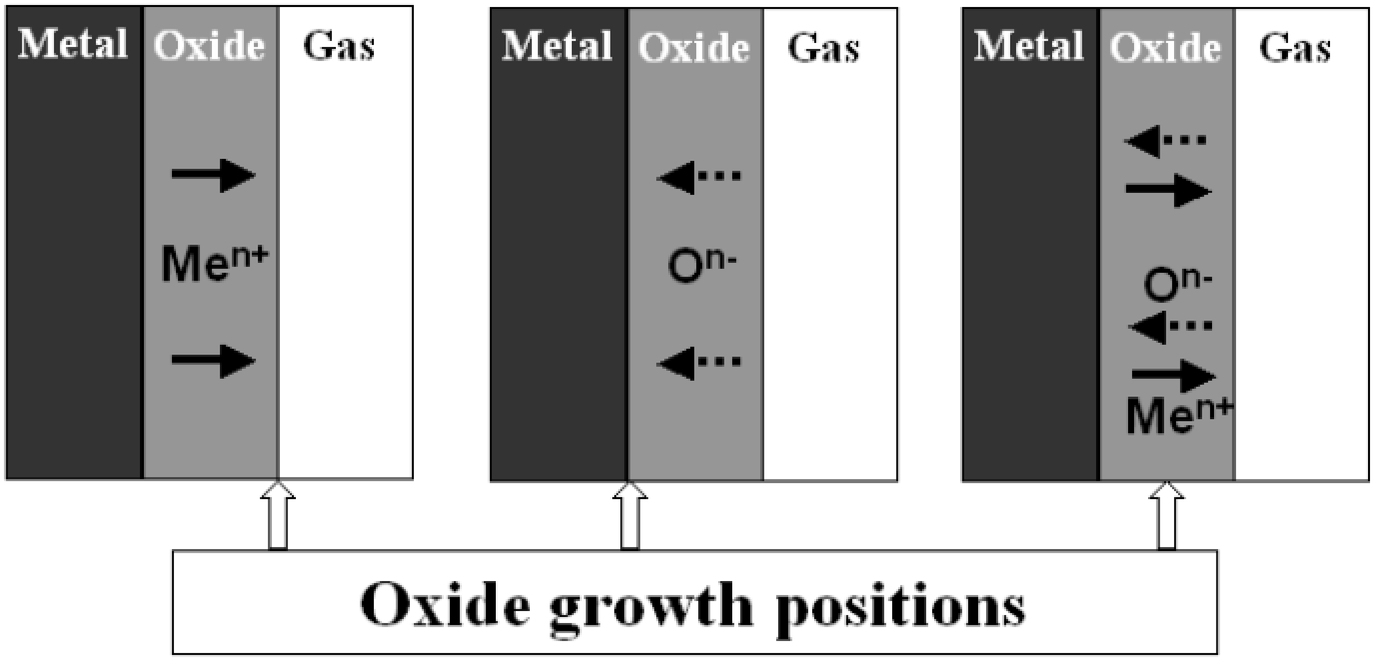
Oxidation kinetics





Parabolic rate: $x^2 = k_p t$, where k_p is the parabolic rate constant. It indicates a uniform thermal diffusion process through a growing scale (Wagner theory).

Oxide growth and kinetics



”If cations move sufficiently to avoid development of stress and anions move in sufficiently to avoid the development of cavities and porosity, a highly resistant film should develop” U.R. Evans 1963.

Then the interesting question rises how to realize the simultaneous movements in both directions? (Answer: RE)

Chromium oxide hydroxide evaporation

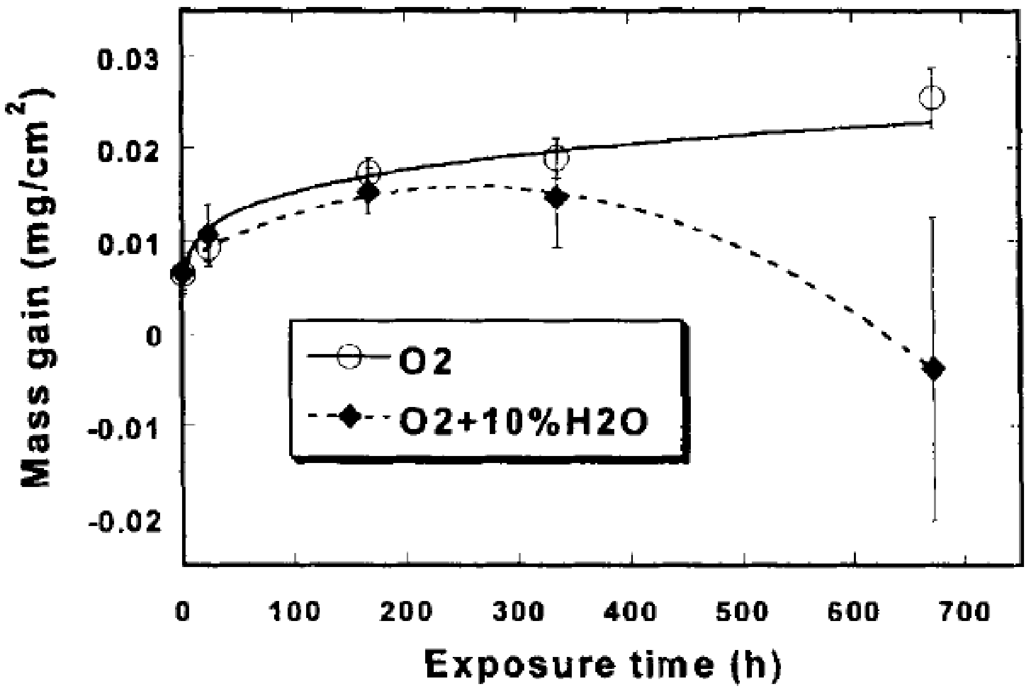
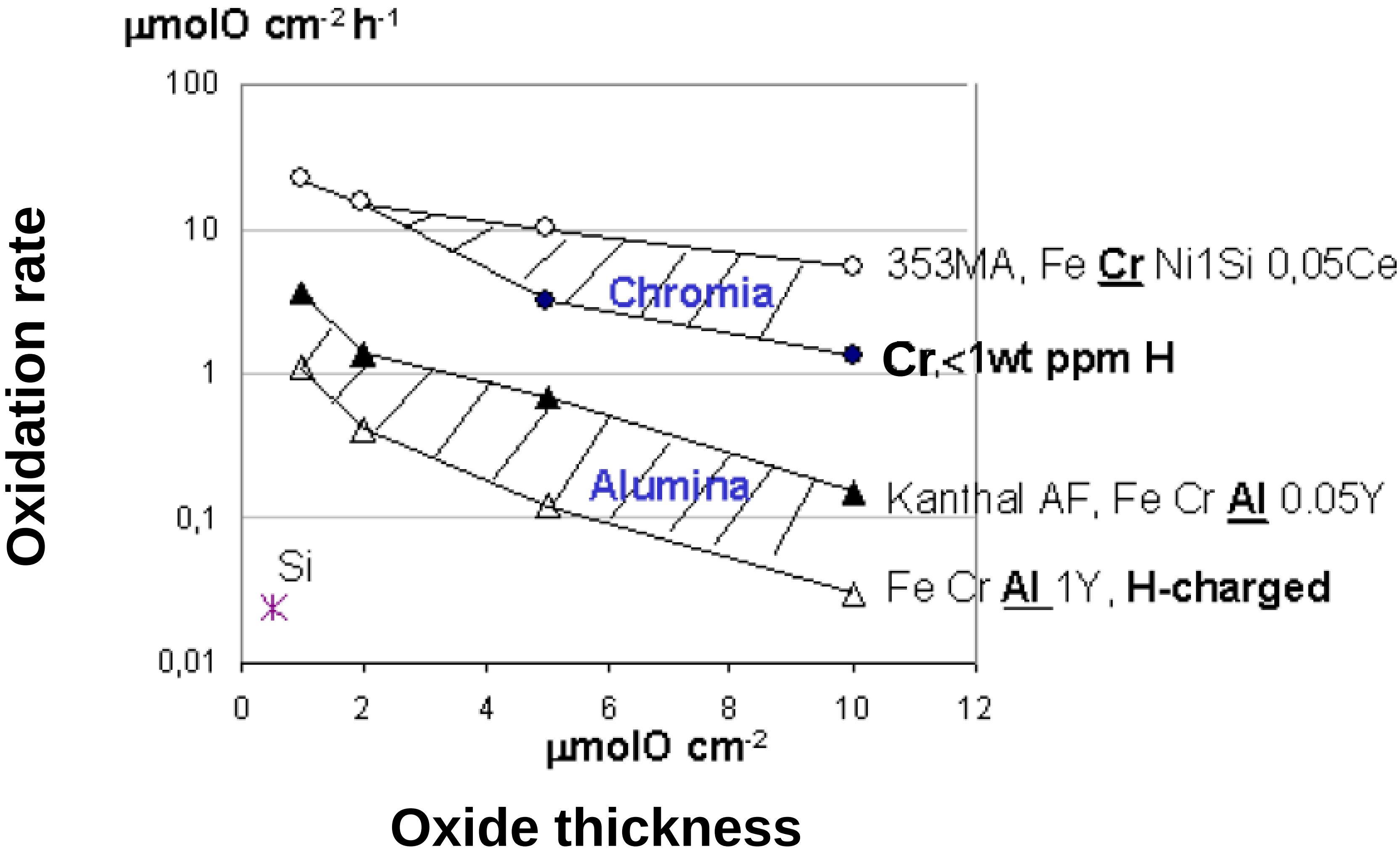


Fig. 2. Weight gain curves of 304L steel exposed at 873 K in pure O_2 and with addition of 10% H_2O vapor.

Evaporation represent one serious weakness of chromia forming stainless steels such as AISI 304L and 316L

$$\tfrac{1}{2}Cr_2O_3(s) + \tfrac{3}{4}O_2(g) + H_2O(g) \leftrightarrow CrO_2(OH)_2(g)$$

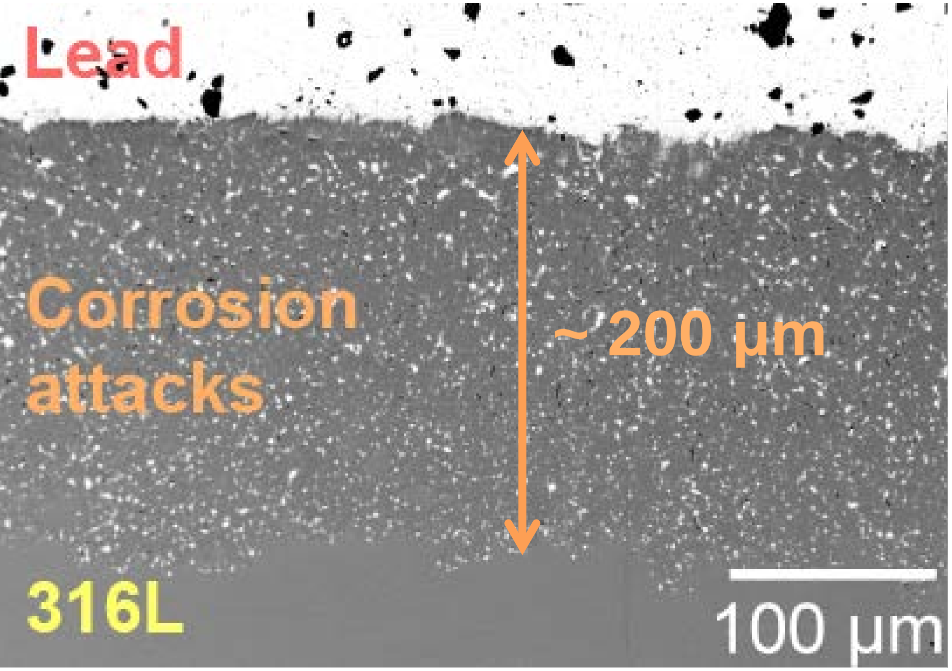
Overview of protective oxides at 900°C



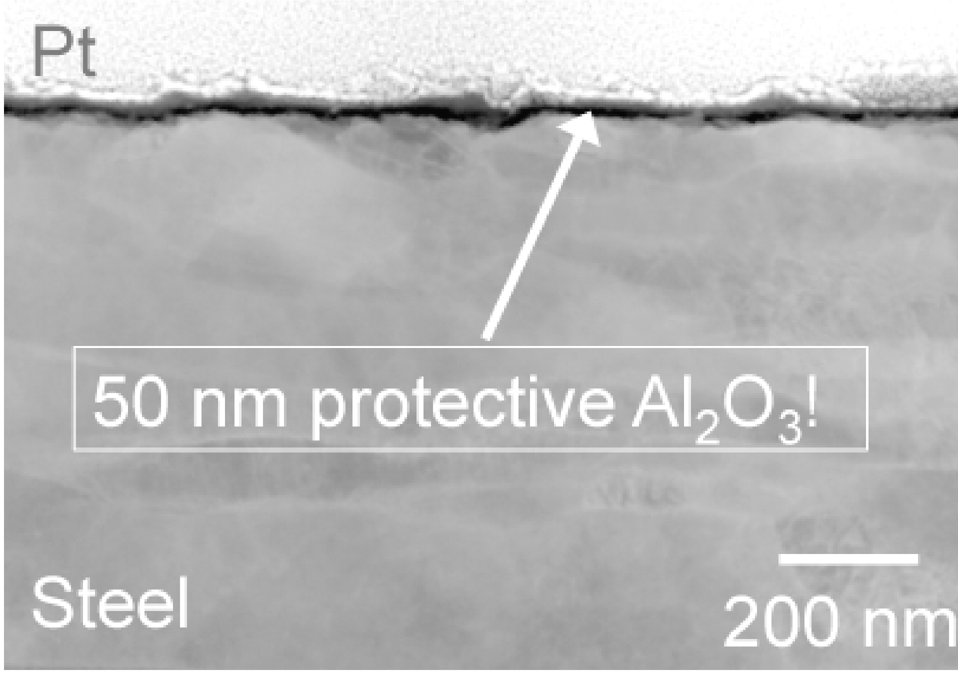
Chromia vs Alumina forming steels

Exposure in liquid lead 10.000h @ 550° C, 10^{-7} wt. % dissolved oxygen

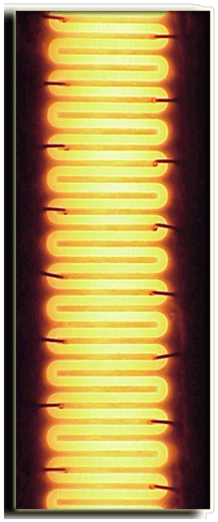
Cr_2O_3 forming steel (316L)



Al_2O_3 forming steel (Kanthal APMT)



FeCrAl-alloys, alumina (Al_2O_3) forming steels



- Ferritic FeCrAl alloys, a Swedish invention (Hans von Kantzow, patented 1926)

- Marketed by Sandvik Heating Technology AB (Kanthal AB)

- Mainly used in heating elements and wires

- Commonly used at high temperatures (900-1300 °C)

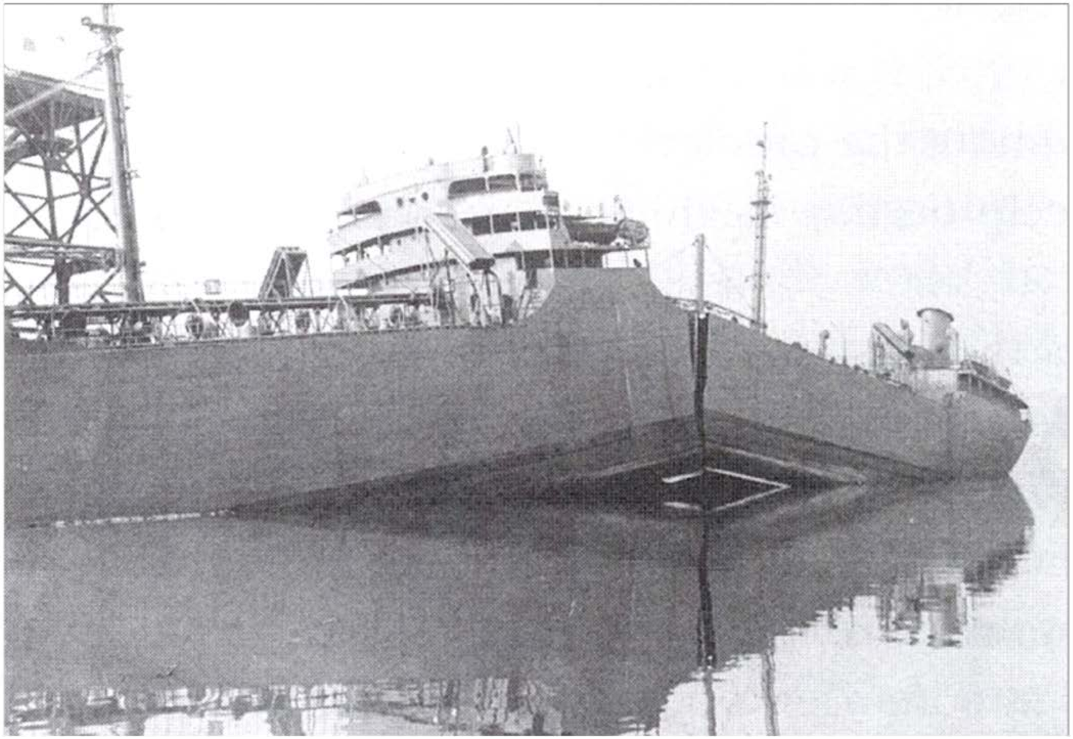
- **Fe**-(15-25)**Cr**-(3-6)**Al**

KANTHAL

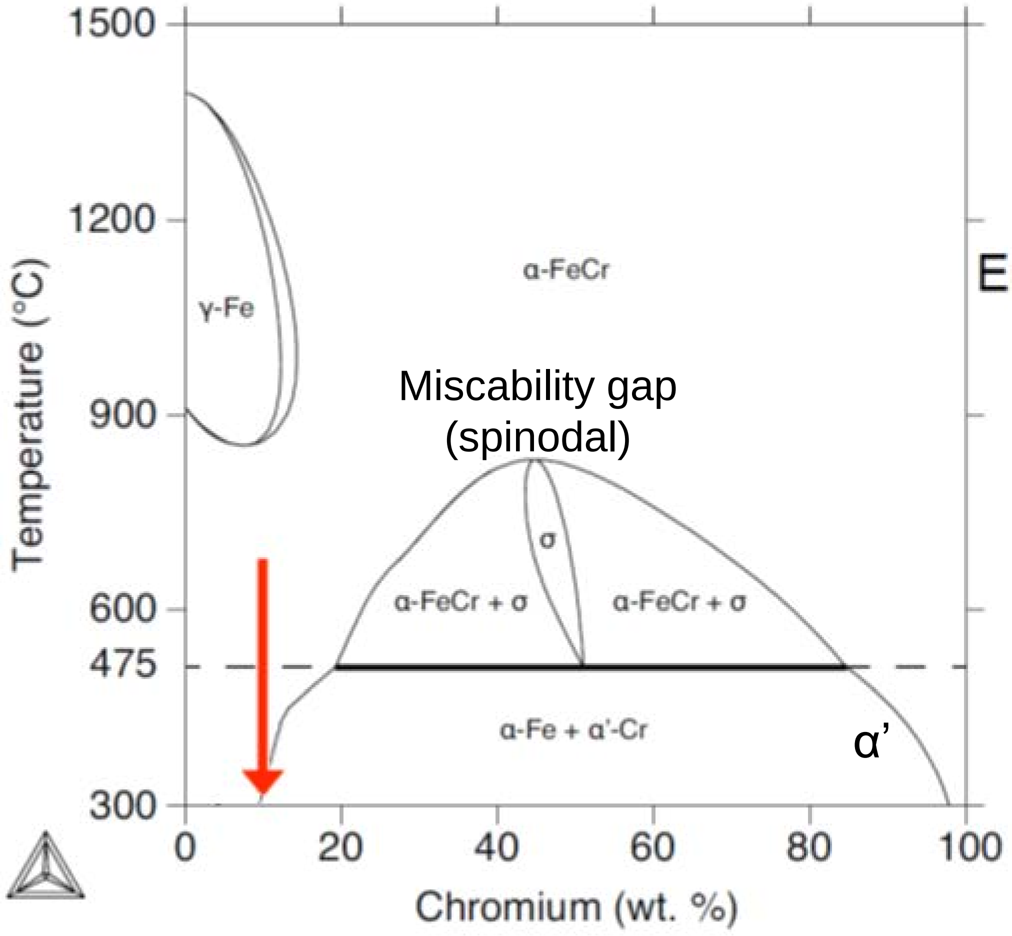
SANDVIK

Why not use FeCrAl alloys in all high temperature extreme environment?

Embrittlement



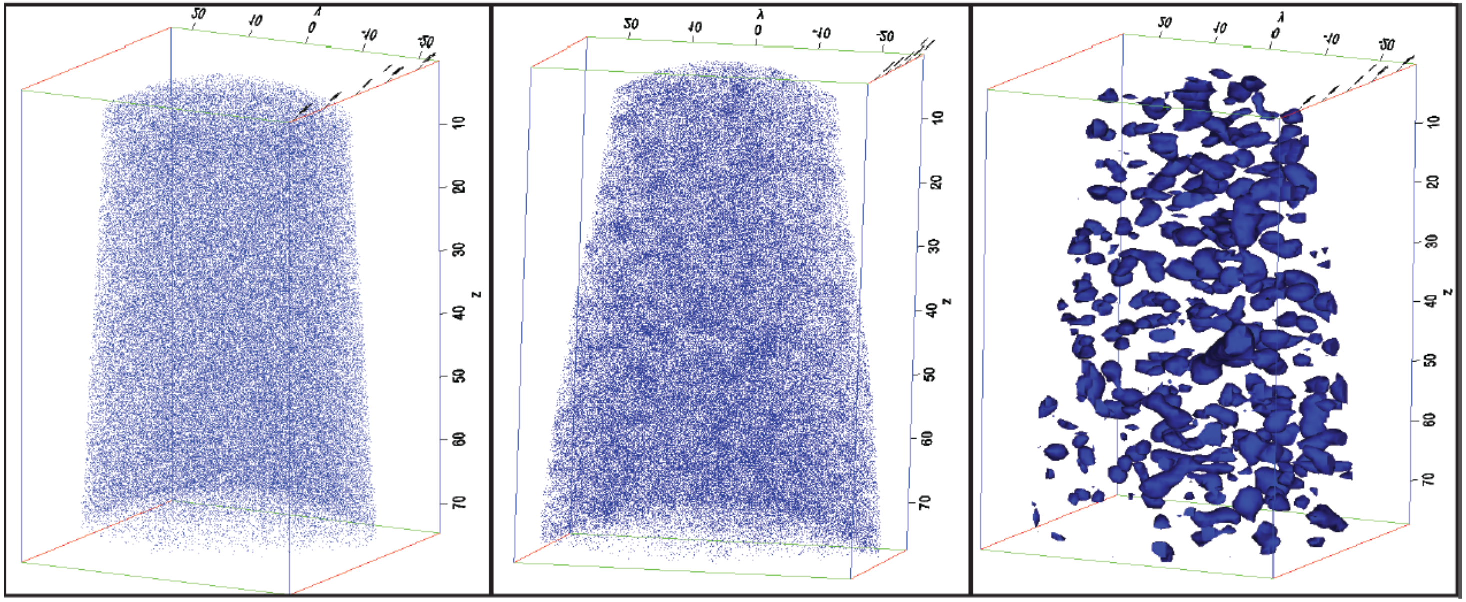
Embrittlement in ferritic Fe-Cr and FeCrAl steels



Embrittlement resistance at 10 wt.% Cr?

Al-alloying in steels supresses α’-formation

APT reveals the nm-sized Cr-rich α' particles



10Cr-(4-8)Al
10,000 h, 500 °C

21Cr-5Al
48 h, 475 °C

c_{Cr}>30%

Atom probe tomography (50 x 50 x 70 nm)

Effect of reactive element additions

REACTIVE ELEMENTS

Y, Zr, Hf, Ce, La, Th, Ti, (Nb)

<<1 wt%

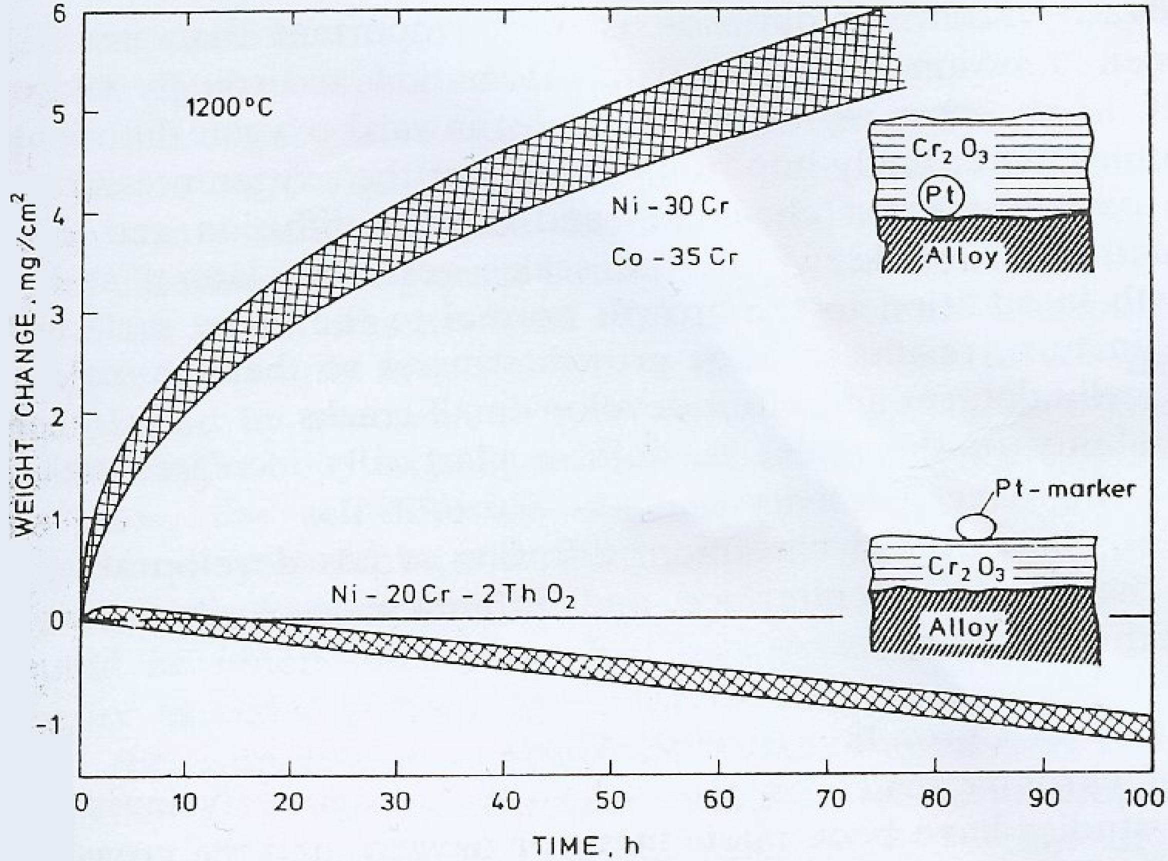
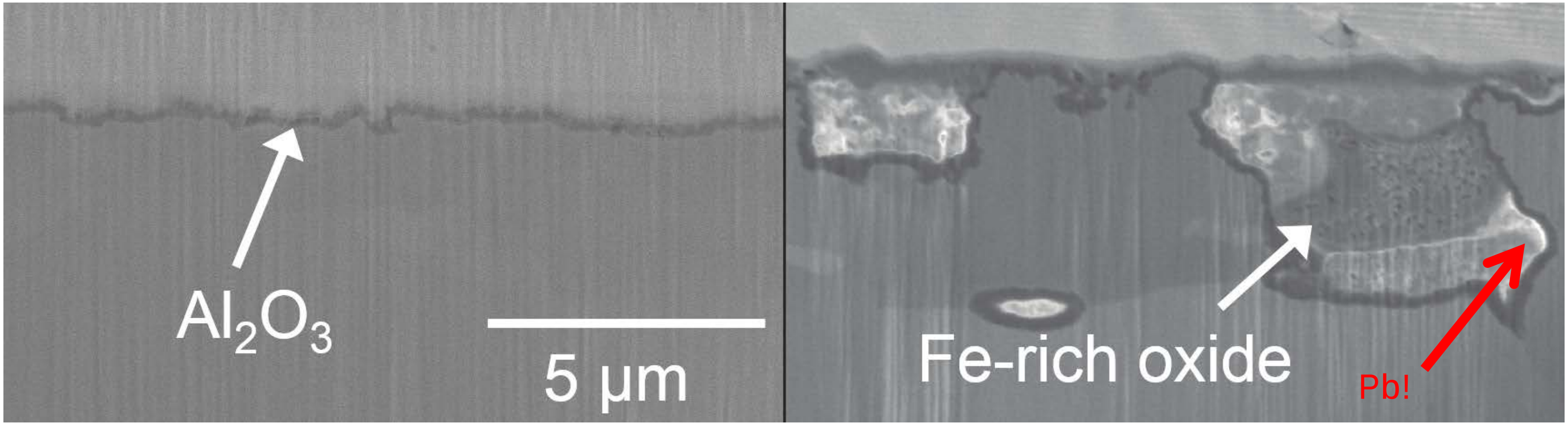


Fig. 12.9. Comparison of the oxidation of Ni–30 wt.%Cr, Co–35 wt.%Cr and TDNiCr (Ni–20 Cr–2 vol.%ThO_2) at 1200 °C. (Results of Giggins and Pettit[35] and Kofstad and Hed.[36])

Effect of reactive element additions

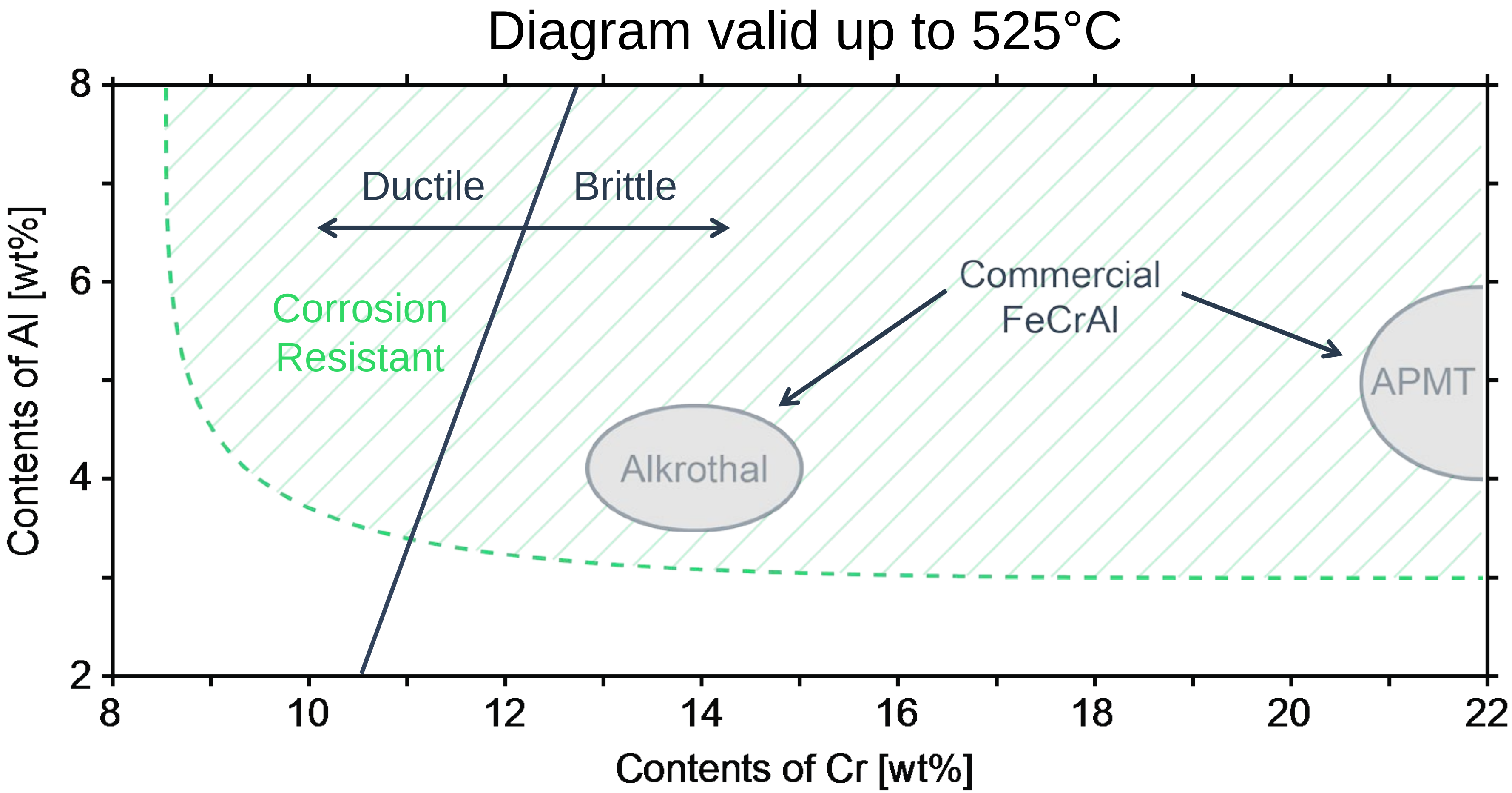


Fe10Cr6Al with RE

Fe10Cr6Al without RE

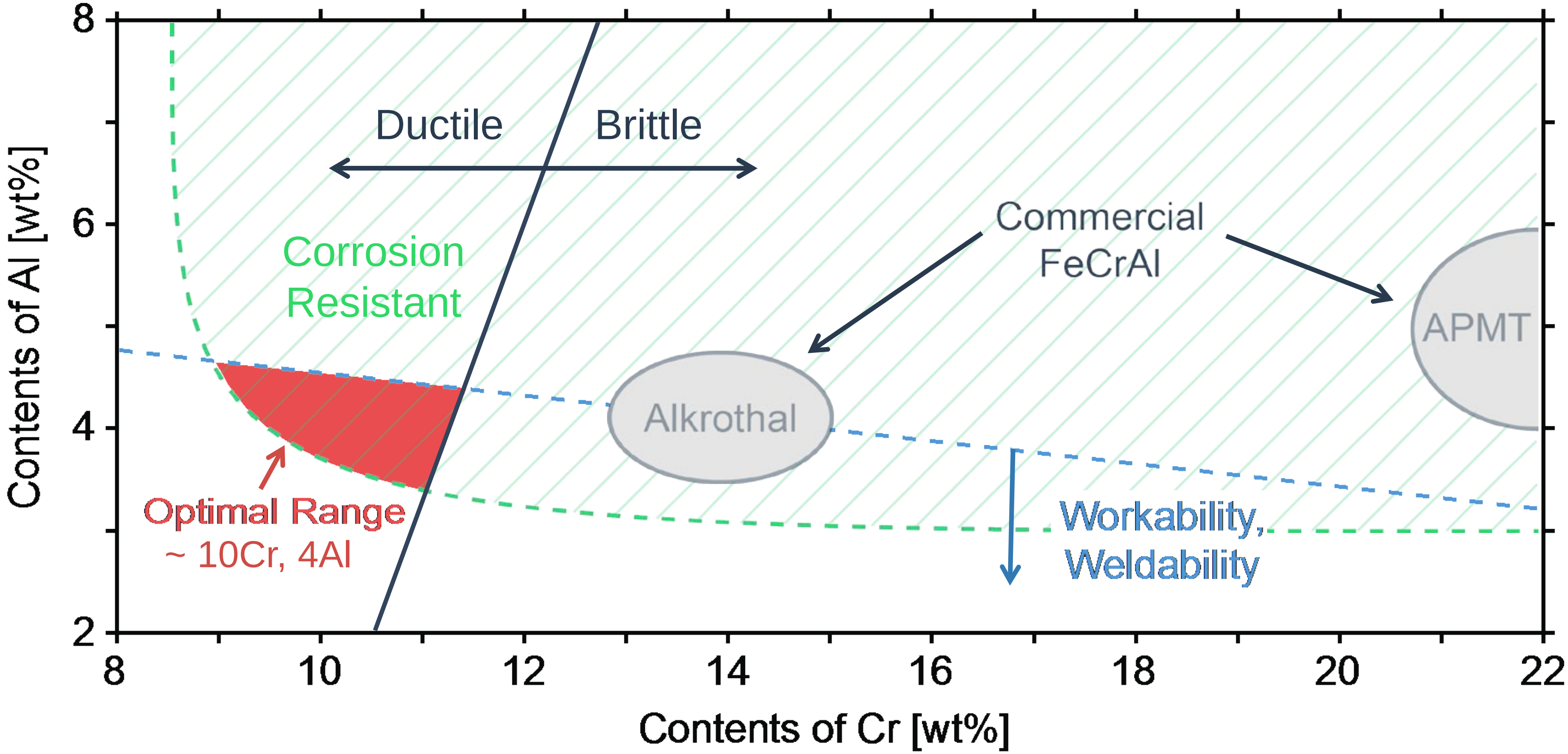
*RE: 0.07 wt.% **Ti** & 0.08 wt.% **Zr***

New FeCrAl construction materials



New FeCrAl construction materials

Diagram valid up to 525°C

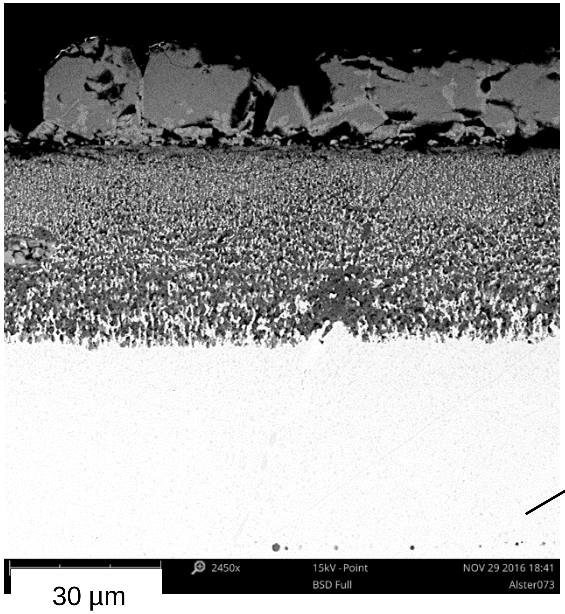


Examples of oxidation and corrosion behaviour in extreme environments

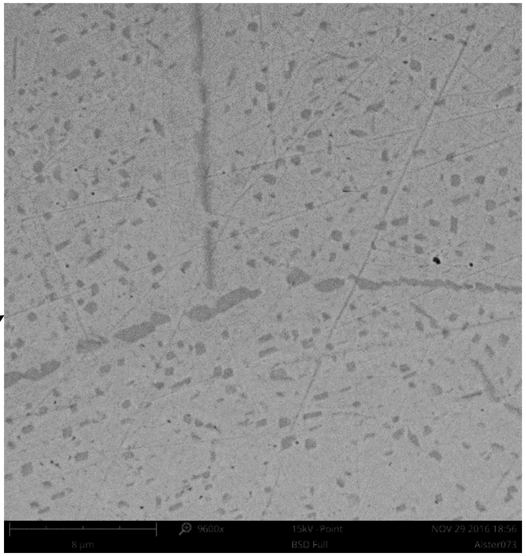
Exampel of corrosion attack in molten Li_2CO_3-Na_2CO_3-K_2CO_3

SEM cross section
Stainless steel 347H
chromia former

Gas flow, CO_2 20ml/min
Temp: 750°C
time: 741 hrs



Thick unprotective Fe-oxide and internal oxidation. Carburized metal underneath

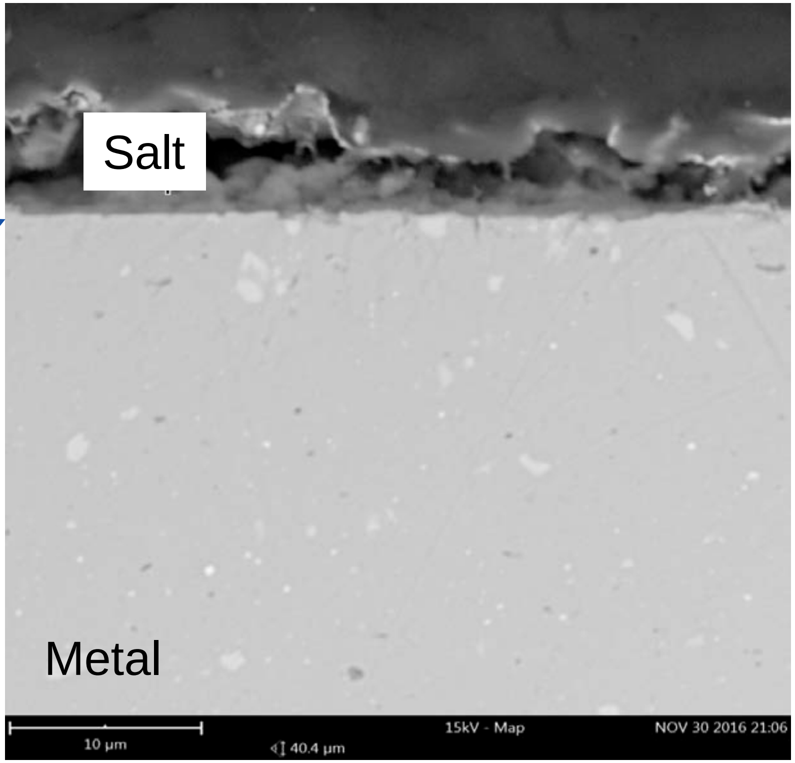


Detail of carburized metal

Exampel of corrosion attack in molten Li_2CO_3-Na_2CO_3-K_2CO_3

SEM cross section
APMT (FeCrAl)
alumina former

Thin oxide layer

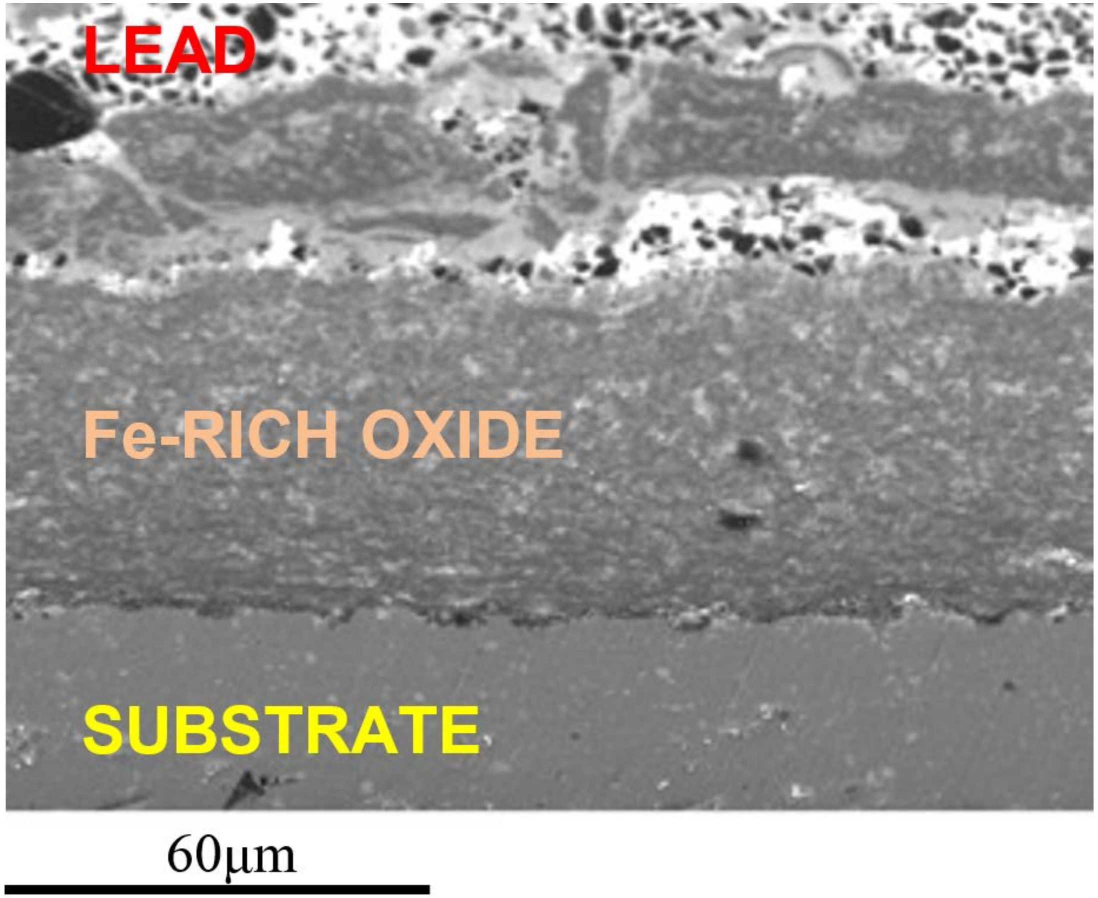


Gas flow, CO_2 20ml/min
Temp: 750°C
time: 741 hrs

Kanthal APMT forms a thin protective alumina scale.

No other commercial alloy “survives” in molten carbonate @ 750°C!

Expsure in liquid lead for 3 month @ 750°C

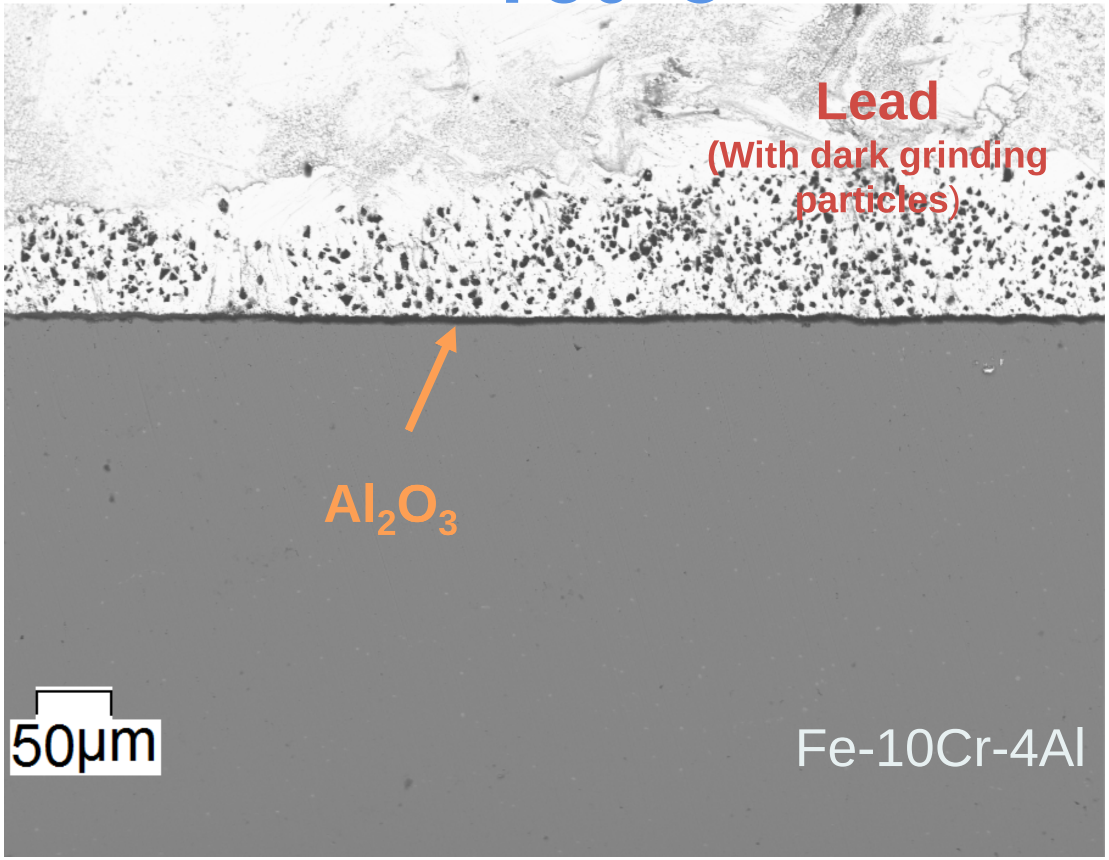


10^{-6} wt% O in liquid lead

Commercial FeCrAl, APMT (Fe-22Cr-5.5Al-3Mo)

BSE – Backscatter Electron Microscopy

Expsure in liquid lead for 3 month @ 750°C

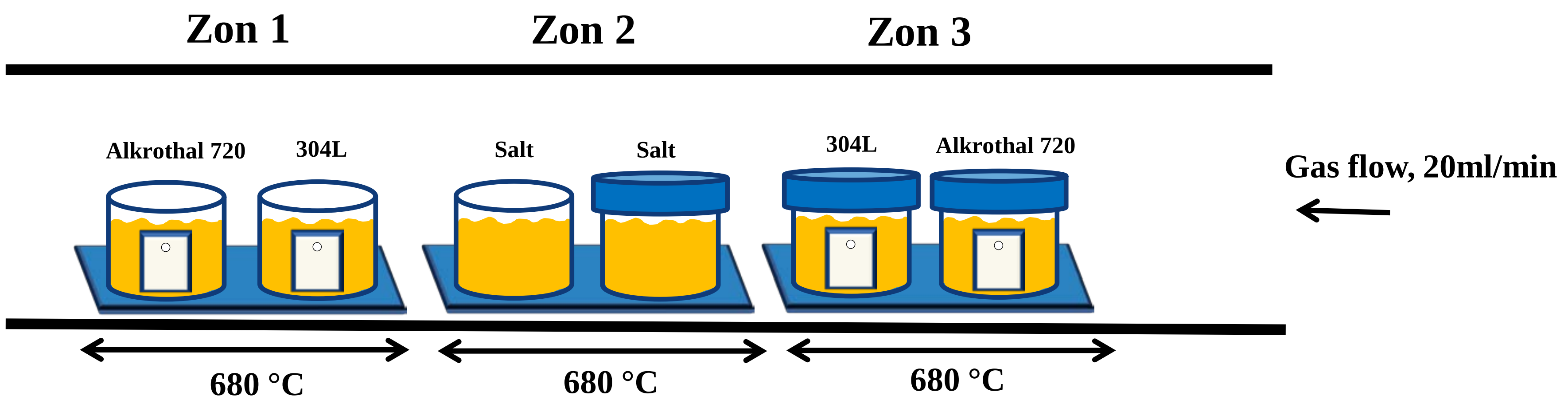


Optimized 10Cr-4Al-RE, virtually unaffected in liquid lead @ 750°C – world record!

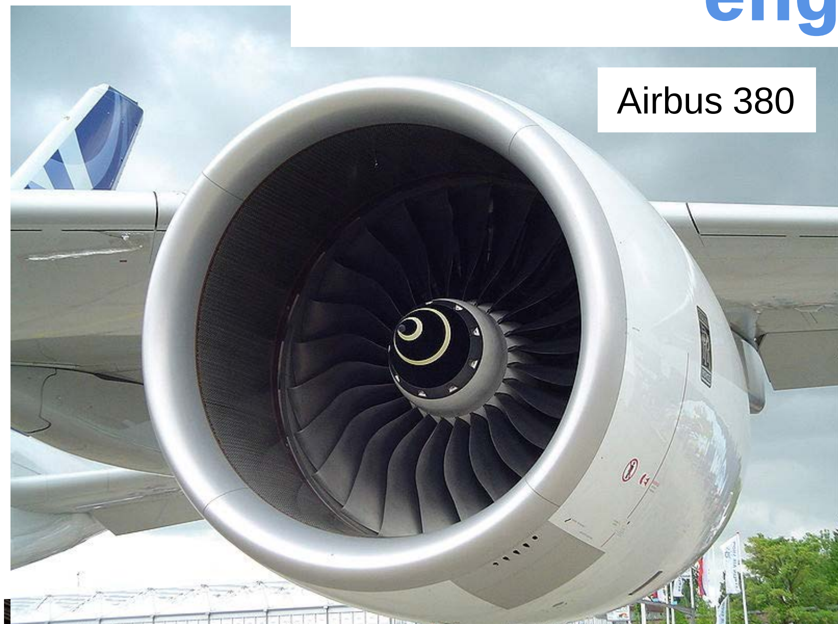
BSE – Backscatter Electron Microscopy

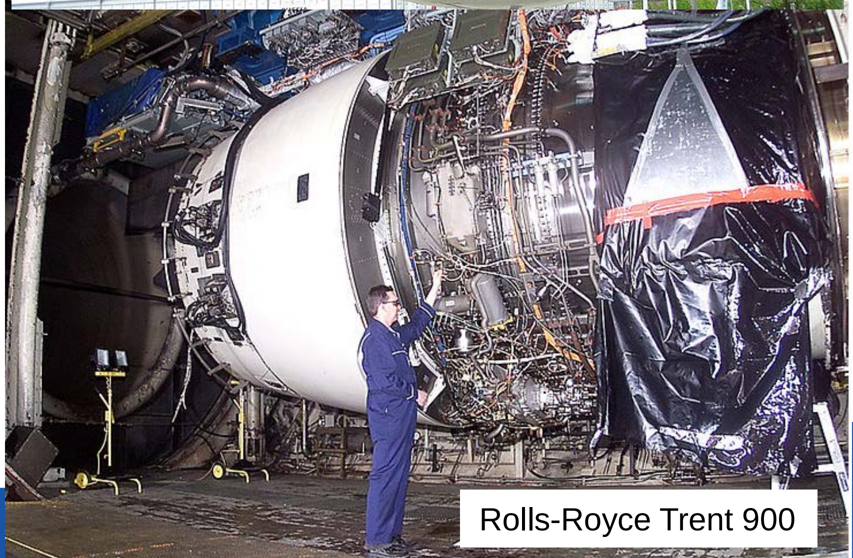
Tube furnace setup for exposure in nitrate and carbonate salt

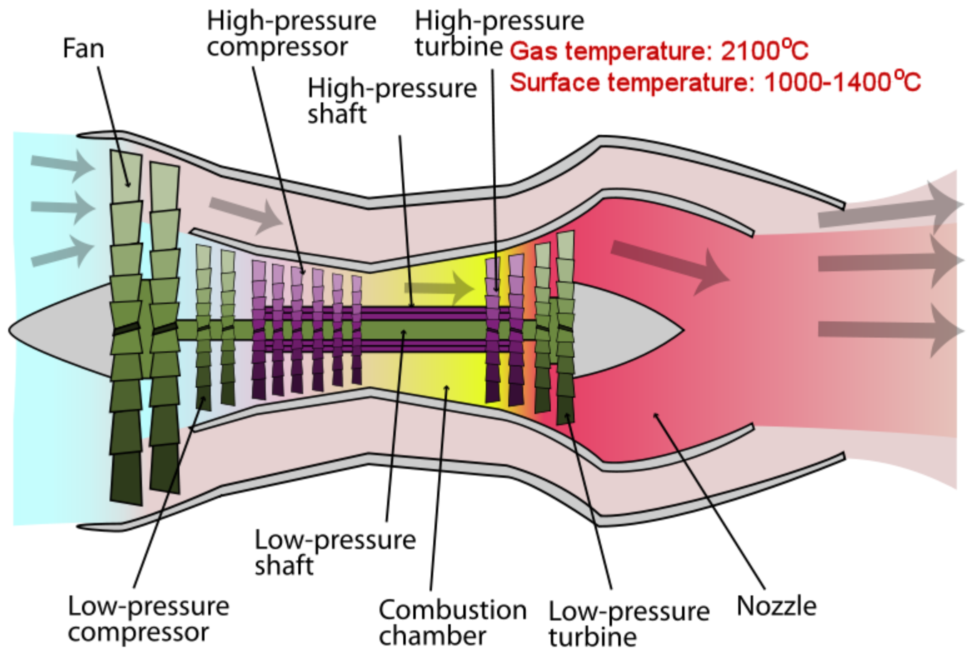
Temperature: 550 - 750°C
Gases: syntetic air or CO_2 depending on salt type



The Jet Engine – a high temperature engineering callange



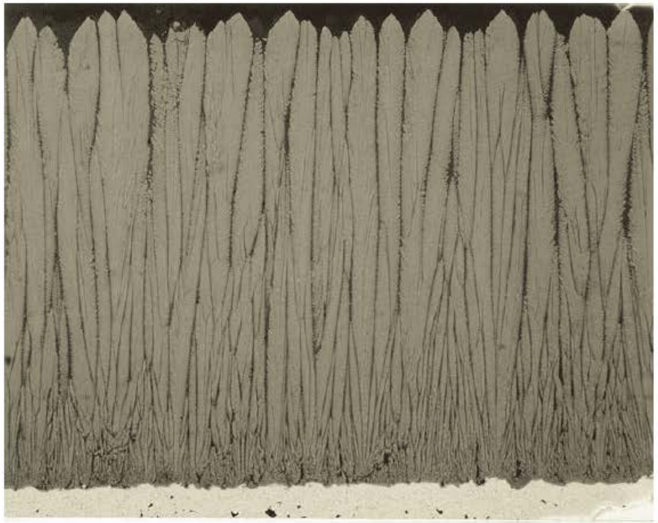




Single crystal Ni-base alloys with NiCoCrAlY-coatings and Thermal Barrier Coatings,TBC (Al_2O_3 and ZrO_2 as protective oxides)

Rolls Royce turbine blade coatings

A plasma-sprayed TBC



An EB-PVD TBC

Thermal Barrier Coating:
YSZ,
Yttria Stabilized ZrO_2

Surface and Coatings Technology, Volumes 151-152, 1 March 2002, Pages 383-391

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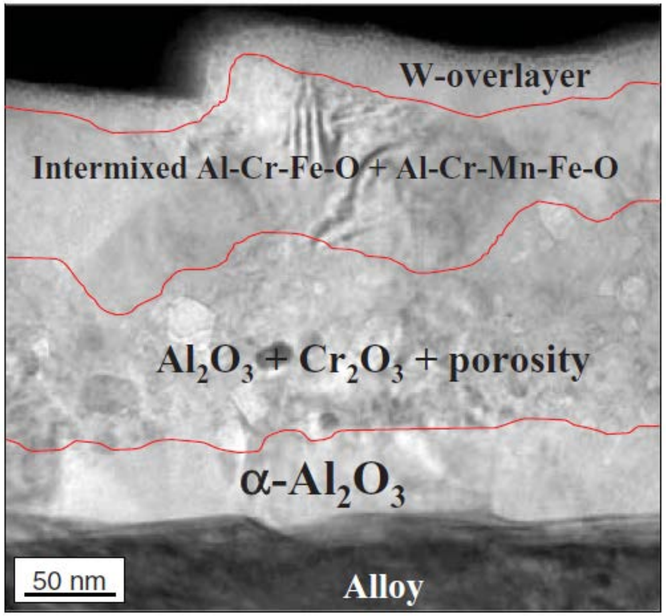
Alumina Forming Austenites

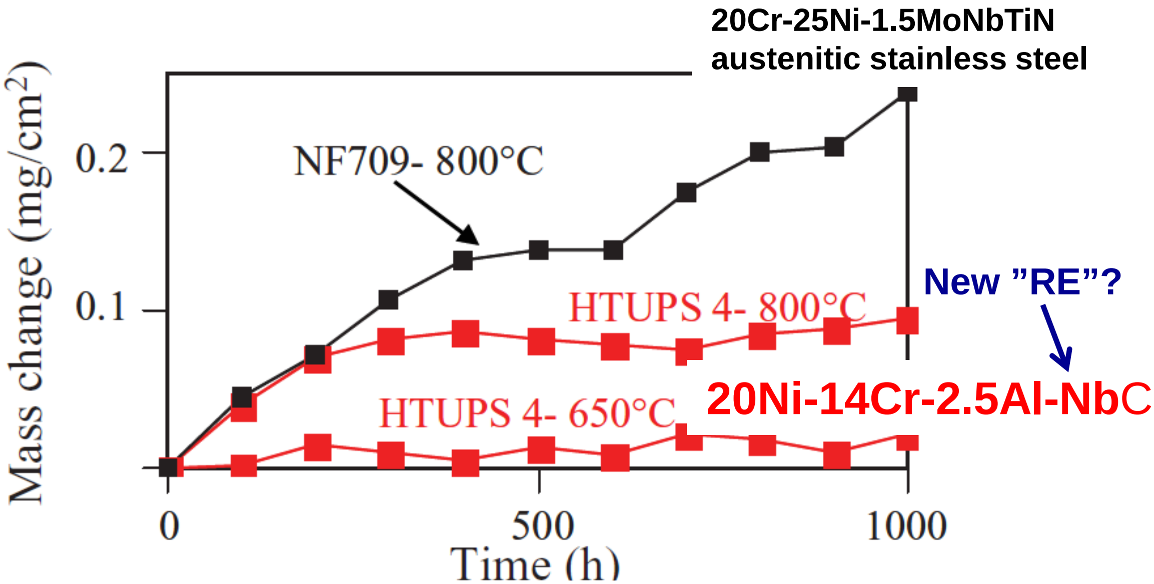
AFA

Steels with excellent oxidation resistance AND good high temperature mechanical properties

Creep-Resistant, Al_2O_3-Forming Austenitic Stainless Steels
Y. Yamamoto, *et al.*
Science **316**, 433 (2007);
DOI: 10.1126/science.1137711

" .... The smaller amounts of aluminum permitted stabilization of the austenitic matrix structure and made it possible to obtain excellent creep resistance. Creep-rupture lifetime exceeding 2000 hours at 750°C and 100 megapascals in air, and resistance to oxidation in air with 10% water vapor at 650° and 800°C, were demonstrated."





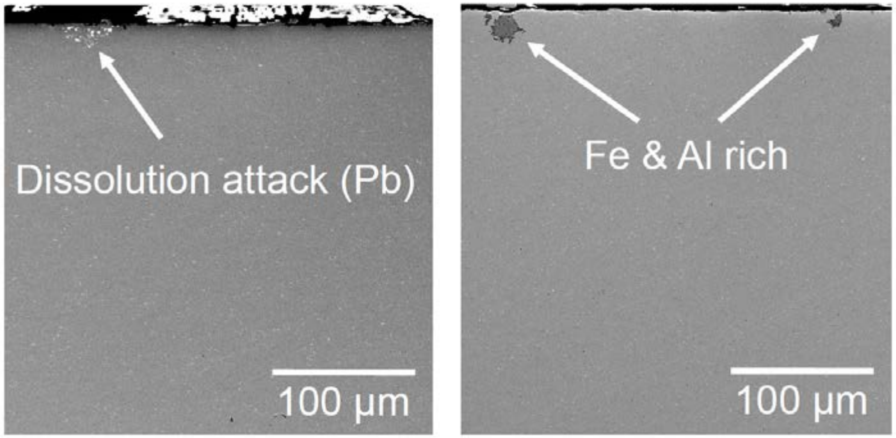
Oxidation kinetics in air + 10% H_2O

Experimental AFA for LFR (KTH/GEMMA)

Alloy	Fe	Ni	Cr	Al	C	Nb	Mo	Mn
20 Ni AFA	Bal.	**20**	**14**	**2.5**	0.08	0.9	2.5	1.6
14 Ni AFA	Bal.	**14**	**14**	**2.5**	0.08	0.9	2.5	1.6

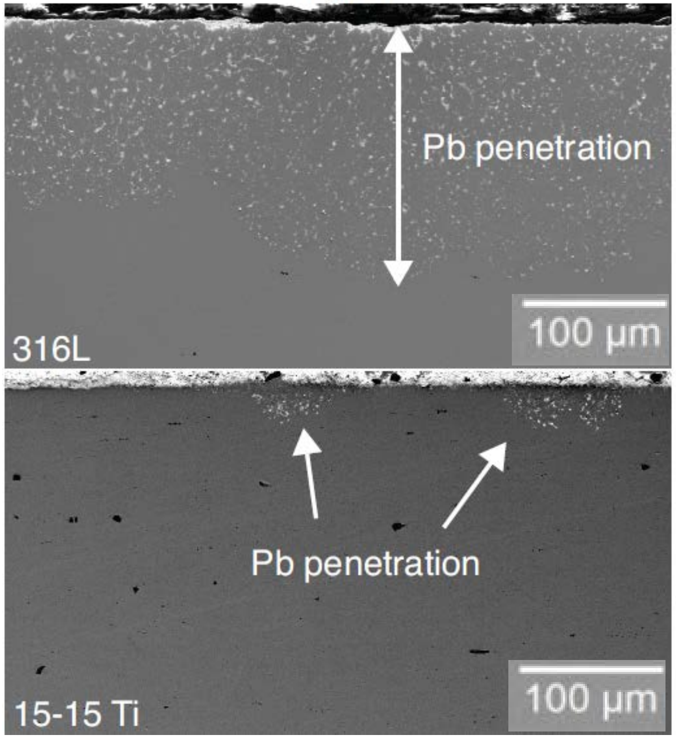
→ 550 °C → up to 1 year → 10^{-7} wt. % O

Corrosion resistance of AFA alloys

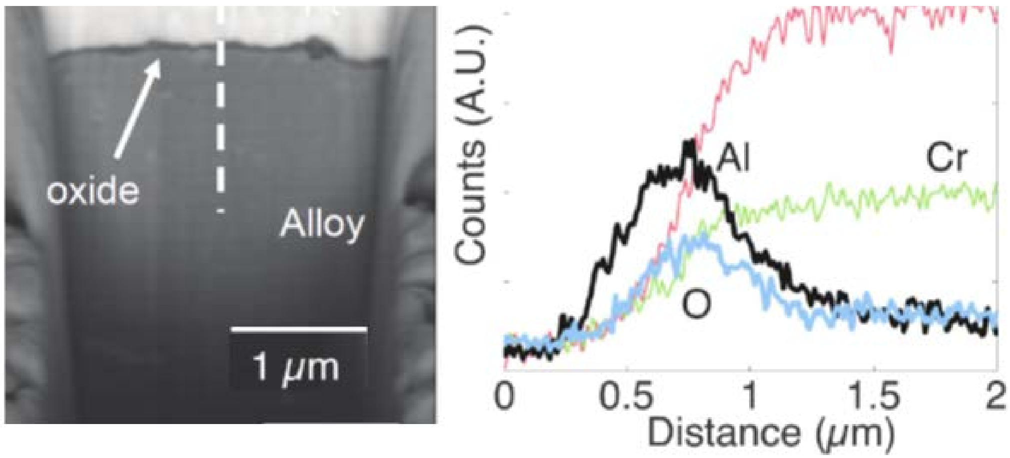


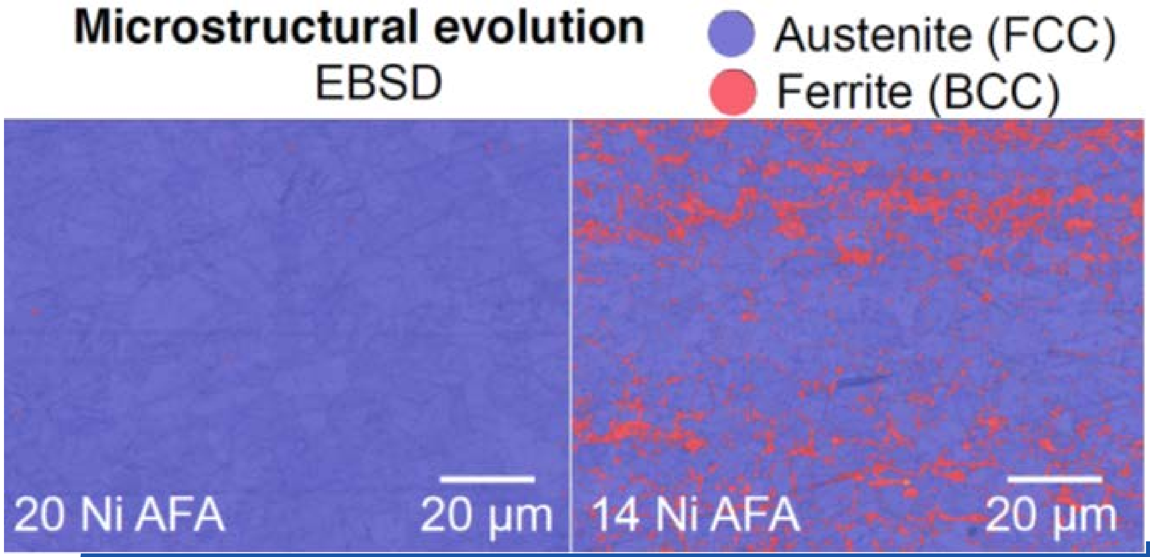
20 Ni AFA 14 Ni AFA

Reference steel samples



Experimental AFA for LFR





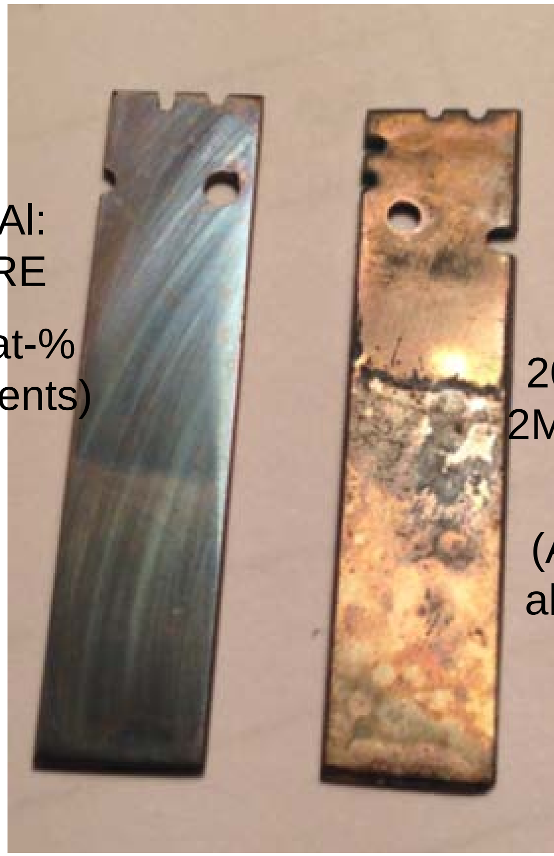
The chromia forming 15Cr/15Ni-Ti type of cladding steel has the potential to be ”upgraded” to an AFA grade.

Thus combining excellent corrosion resistance with good mechanical properies and irradiation resistance.

Overview: Different alloys exposed one year in liquid lead at 550^{O}C

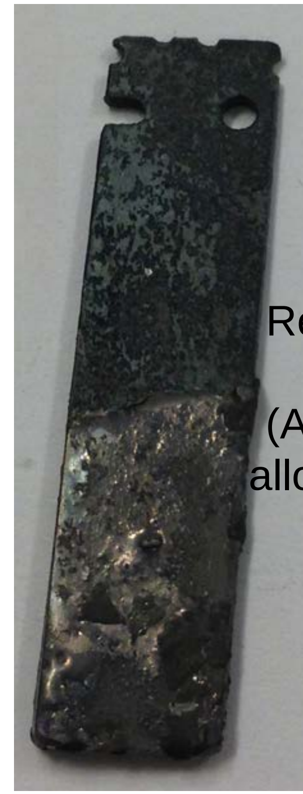
New FeCrAl:
10Cr-4Al-RE

(Around 18 at-% alloying elements)



AFA
20Ni-14Cr-2.5Al-2Mn-2.5Mo-0.9Nb-0.08C

(Around 45 at-% alloying element)



Reference steel:
AISI 316L
(Around 40 at-% alloying elements)

Summary/Conclusions

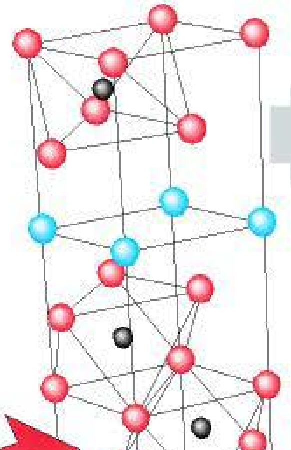
Steel type:	Weakness:
Chromia forming steels (FCC, BCC)	No protective oxide in extreme environments
Commercial FeCrAl alloys (BCC)	Spinodal decomposition, α'-embrittlement
New Fe10Cr-4Al (BCC)	Creep properties?
AFA-steels (FCC)	Structure stability at intermediate temp.?

The excellent oxidation resistance and self-healing properties of the alumina forming FeCrAl and AFA alloys opens up for technological breakthrough in energy production, such as next generation nuclear (Gen IV) and thermal solar power (CSP's).

Titankiselkarbid, Ti_3SiC_2 (Alumina former: Ti_2AlC)

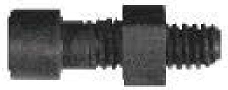
Nytt supermaterial med unika egenskaper hämtade från såväl metaller som keramer:

- Leder utmärkt värme och elektricitet.
- Klarar snabba värmechocker och hårda slag.
- Motstår nötning och har liten friktion.
- Tål kemiska angrepp och höga temperaturer (2 000°C).
- Är plastiskt och lätt att bearbeta med traditionella verkstadsmetoder.
- Är lätt och styvt.



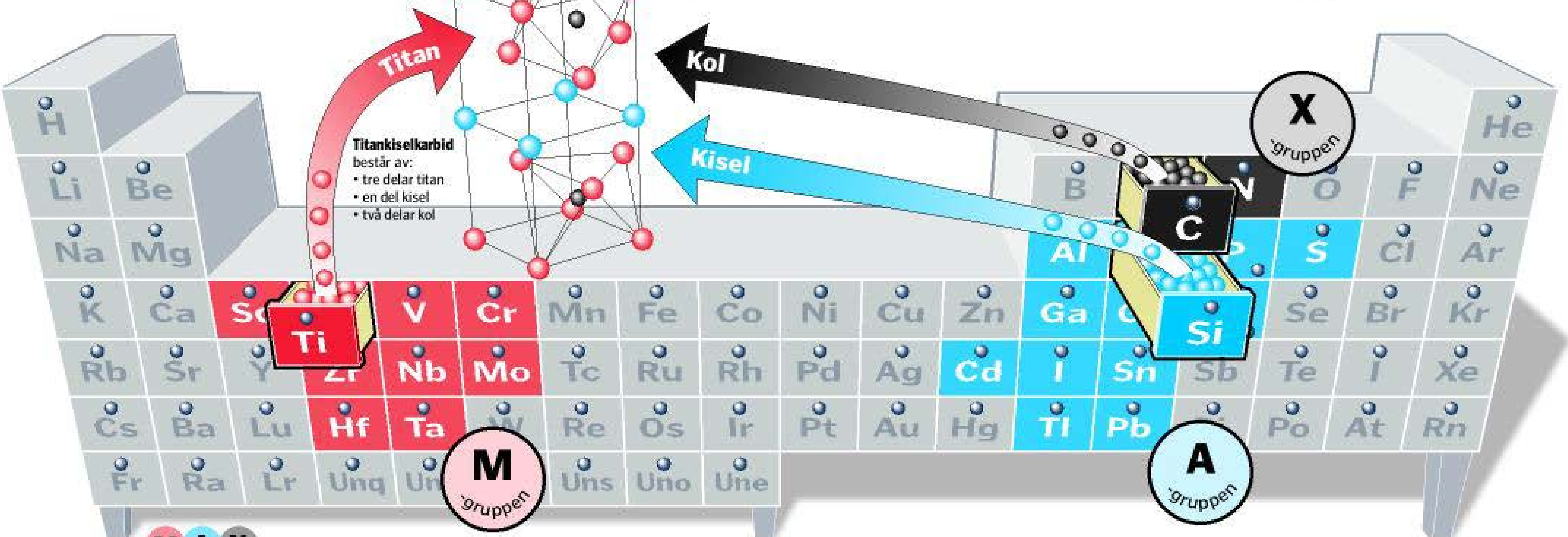
Atomerna bildar ett nanolaminatet som gör materialet starkt.

Den värmetåliga keramen kan tillverkas i allehanda former och som råmaterial för...



...vidare verstadsbearbetning...

...eller för tunna ytskikt med goda elektriska egenskaper på kontakter.



MAX -materialet

är känt sedan flera decennier, men det var först vid ett "misslyckat" experiment för åtta år sedan som den amerikanske materialforskaren Michel Barsoum kunde framställa det i ren form. "MAX" står för de tre ämnen som ingår i materialet. "M" är tidiga övergångsmetaller, "A" är atomer ur periodiska systemets A-grupp och "X" är kol eller kväve.

Ett atomslag ur vardera gruppen ingår i MAX-materialen, som således finns inga många varianter. Ett sextiotal av dem ärframställda i labbskala, men endast ett fåtal är närmare undersökta. Kanthal har bland annat ersatt kislet i Barsoums titan-kisel-karbid med aluminium för att tåla högre temperaturer.

THANK YOU FOR YOUR ATTENTION!

If you like the to have a PDF copy of the presented materiel, send an e-mail to:

szakalos@kth.se