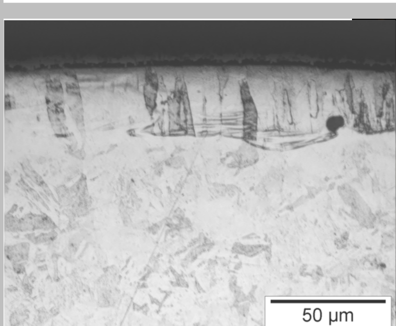
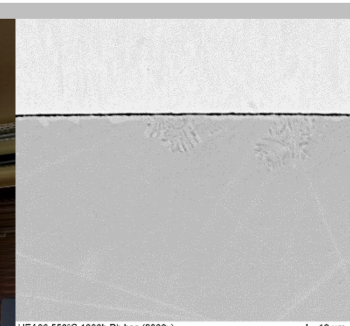
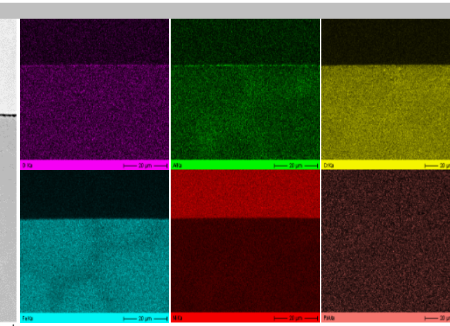
Karlsruher Institut für Technologie

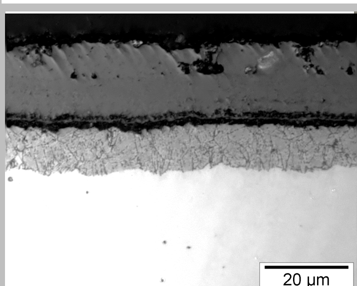
DEVELOPMENT OF ALUMINA FORMING MATERIALS FOR CORROSION MITIGATION IN HEAVY LIQUID METAL COOLED NUCLEAR REACTORS

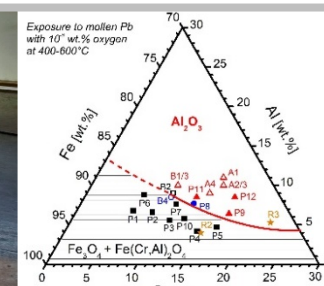
A. Weisenburger, H. Shi, A. Jianu, A. Heinzel, R. Fetzer, W. An, S. Schlabach, V. Szabo and G. Müller *– KIT*

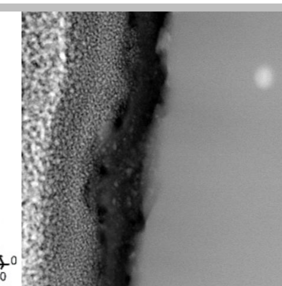






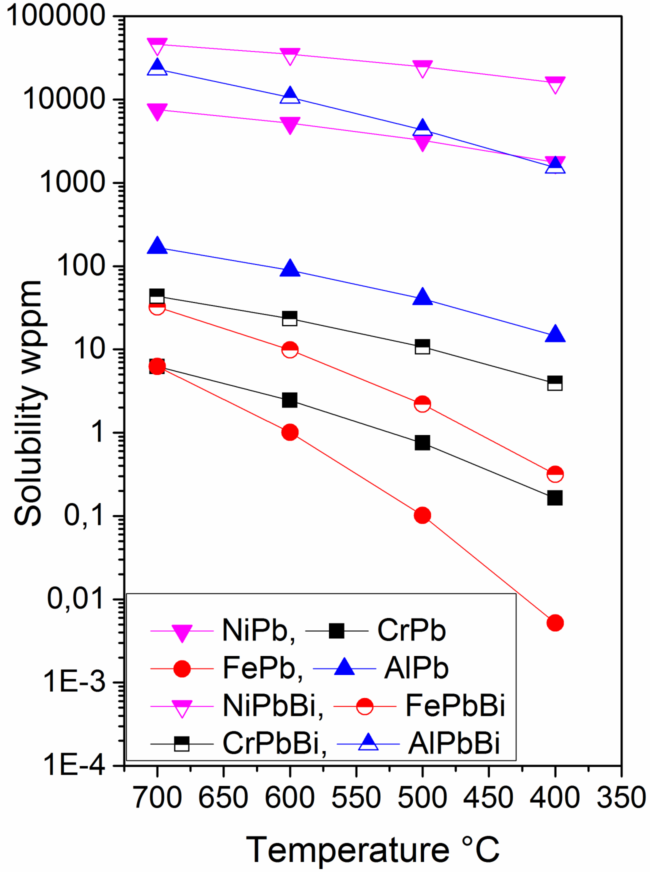




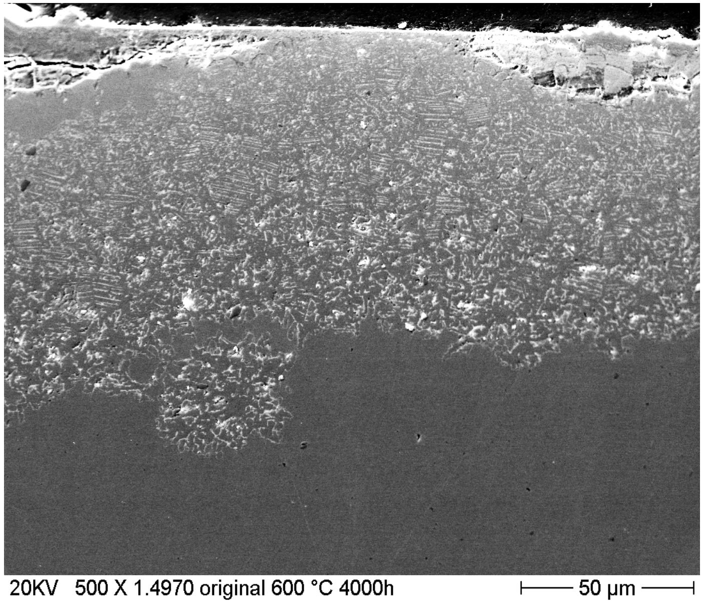


Steel corrosion in liquid Pb-alloys

Solubility of elements in Pb/PbBi ➔ Dissolution attack - corrosion



1.4970 steel exposed to LBE at 600°C



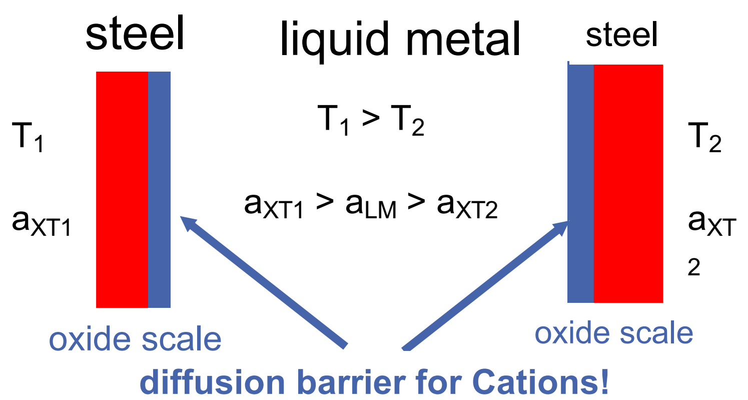
Way Out: insoluble materials (W, Mo, .., ceramics)

or

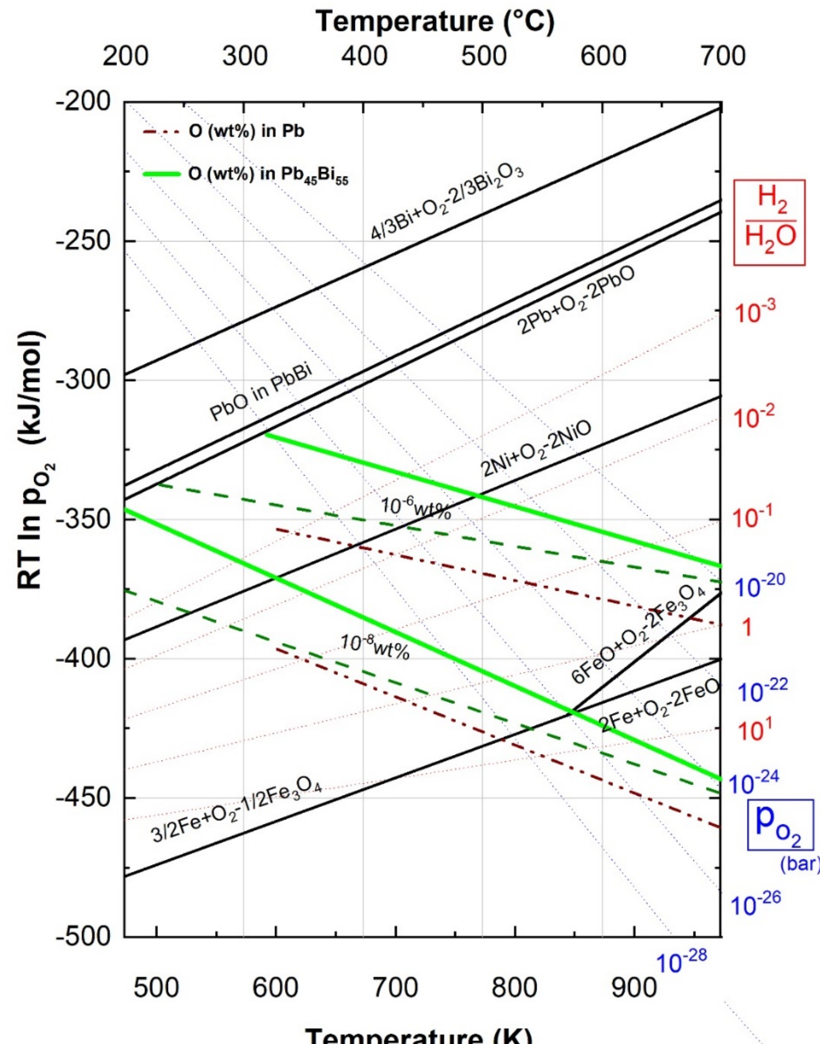
like e.g. in atmospheric conditions – protection by oxide scales growing in the media

Mitigation of steel corrosion in liquid Pb-alloys

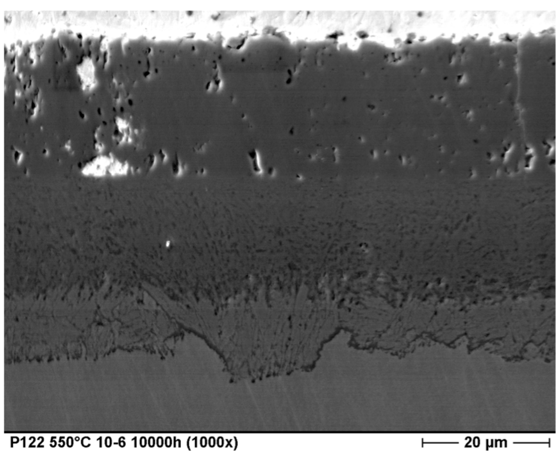
Way out:
Oxide scale on the steel surface prevent the dissolution



Ellingham diagram



f/m steel at 550°C in LBE

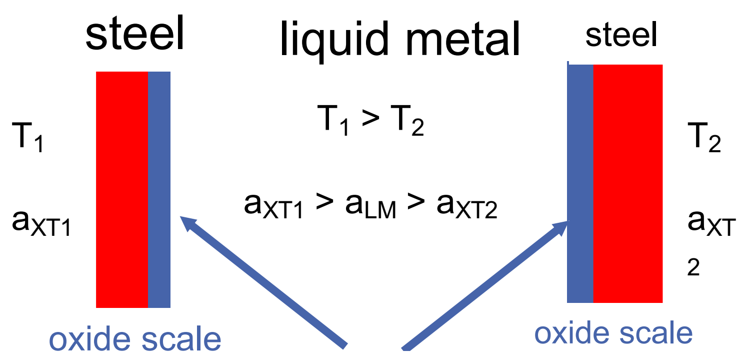


? more stable Oxides – larger enthalpy of oxide formation?

Slow diffusion of elements through scale

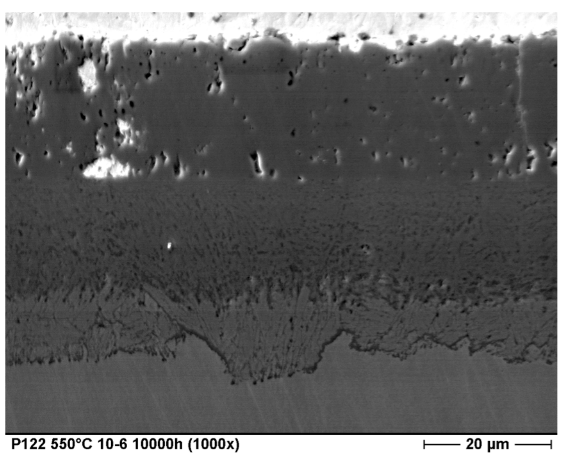
Mitigation of steel corrosion in liquid Pb-alloys

Way out:
Oxide scale on the steel surface prevent the dissolution



diffusion barrier for Cations!

f/m steel at 550°C in LBE



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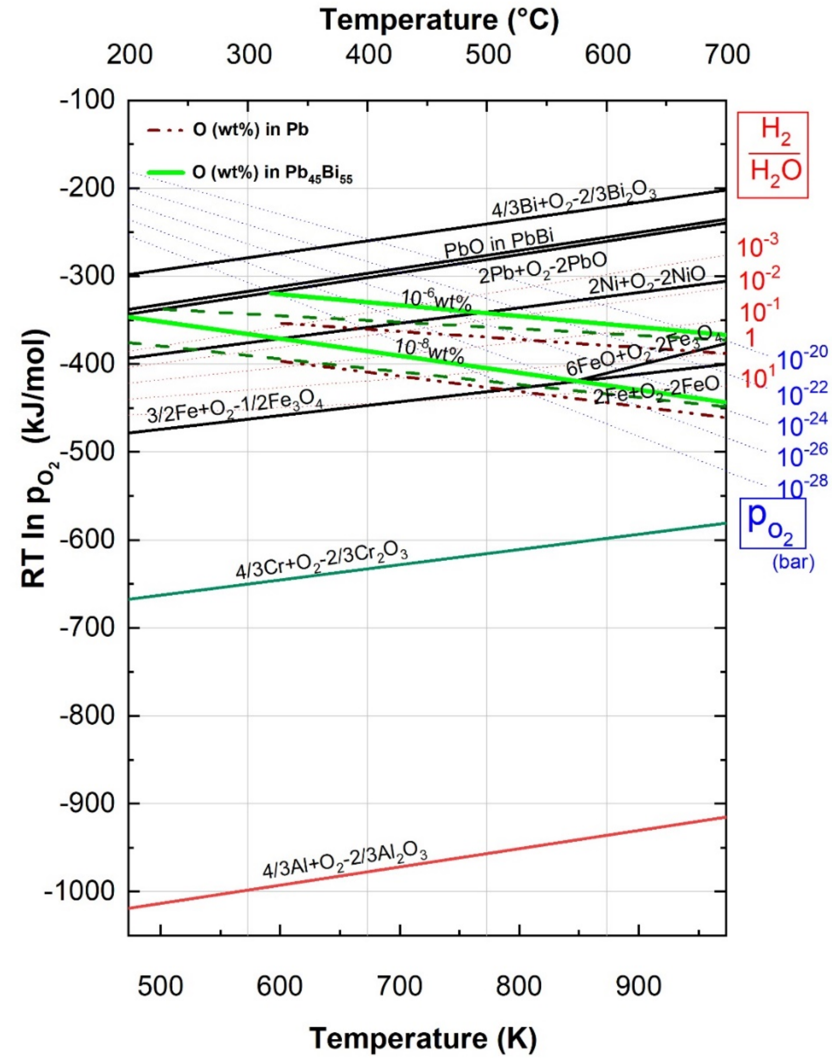
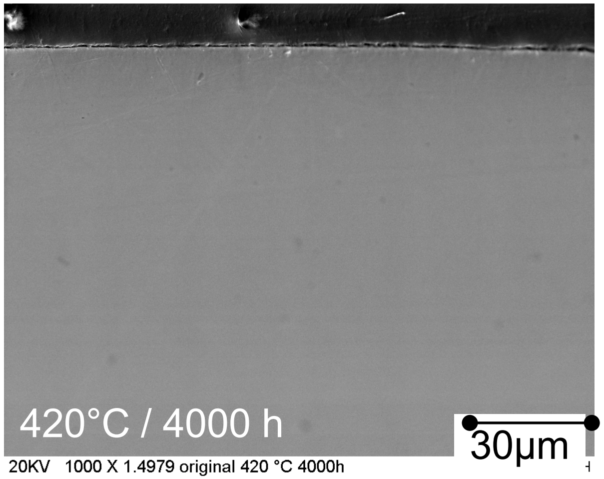
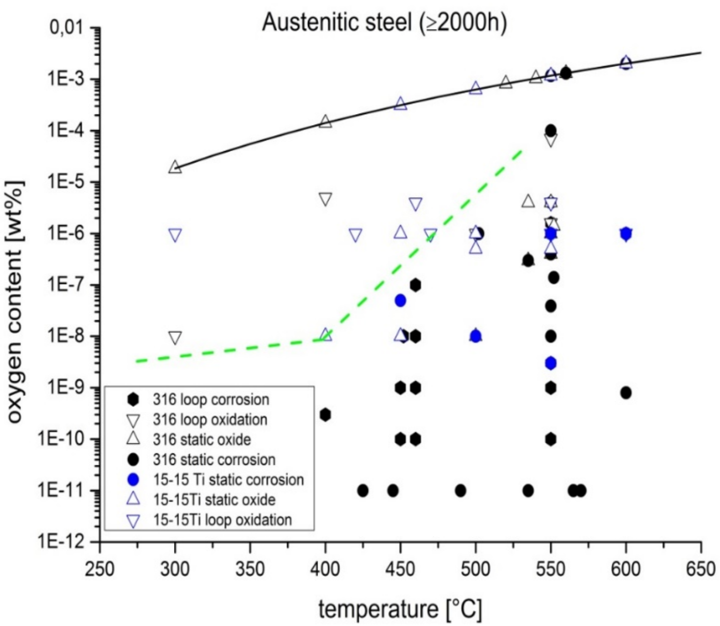
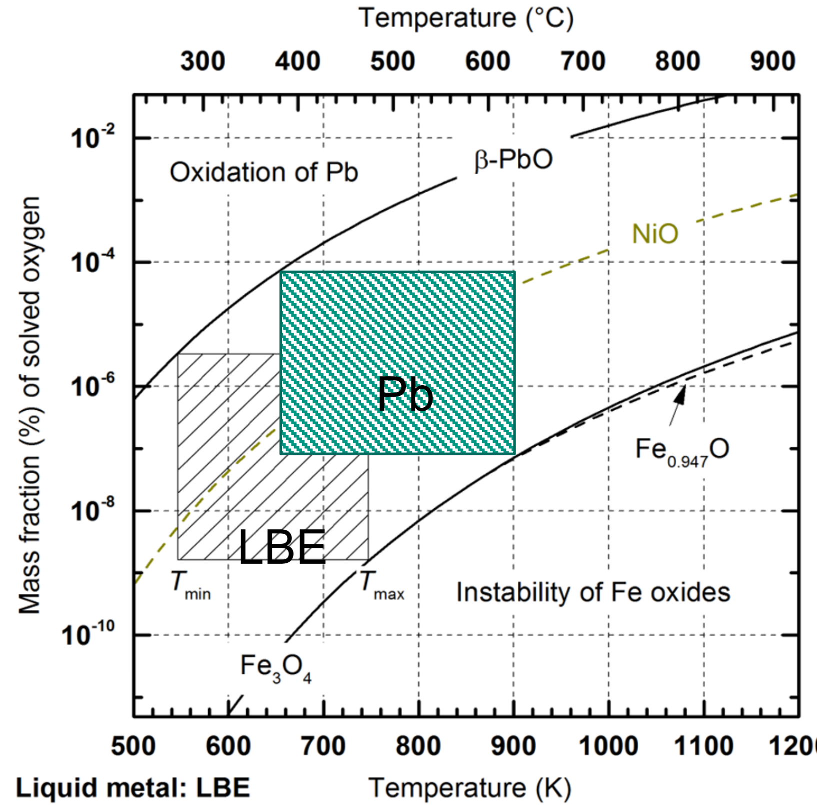


Steel corrosion in liquid Pb-alloys





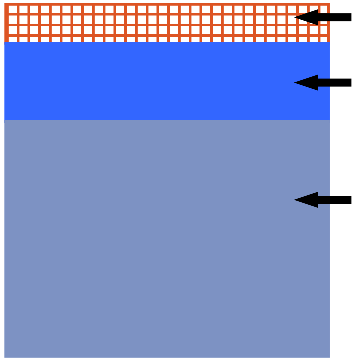


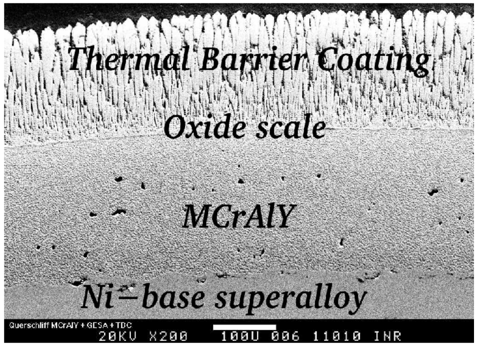
OECD Liquid metal handbook (2015)

Austenitic steels can be used up to 450°C
Oxygen content $>10^{-7}$wt% required
➔ Higher T or lower oxygen content

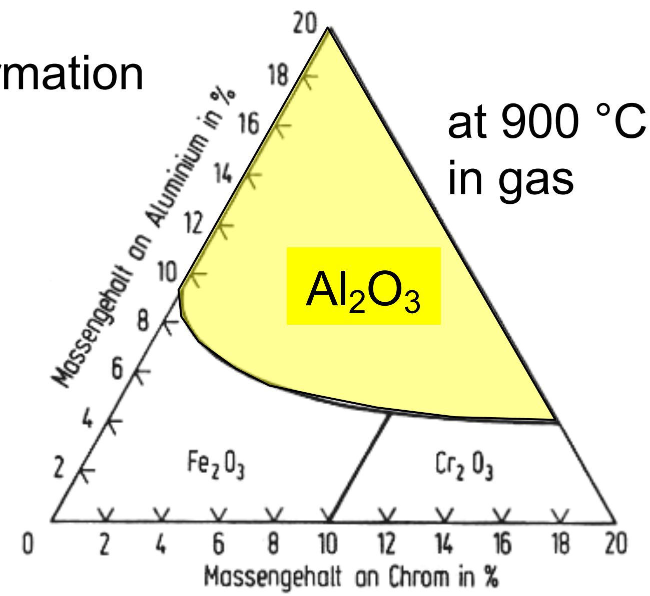
➔ Advanced mitigation strategies

In-situ formed Al_2O_3 as protective oxides scale





Oxide map of FeCrAl - oxide



at 900 °C
in gas

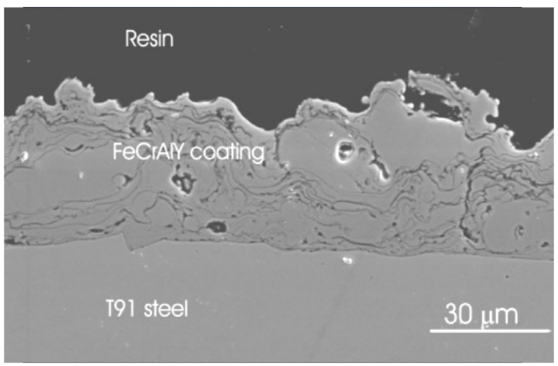
Al_2O_3 is very stable oxide - standard free energy of formation
Diffusion in Al_2O_3 very slow
- ➔ slowly growing oxide scale
- ➔ perfect barrier

No interaction with Pb-alloys
Reservoir layer – self healing
Not a coating: either **surface alloy** or **bulk**
Proven at other high temperature applications

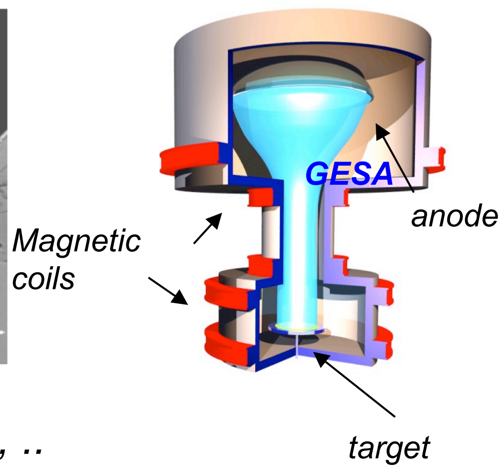
Al - containing surface alloys

The procedure consists in two steps:

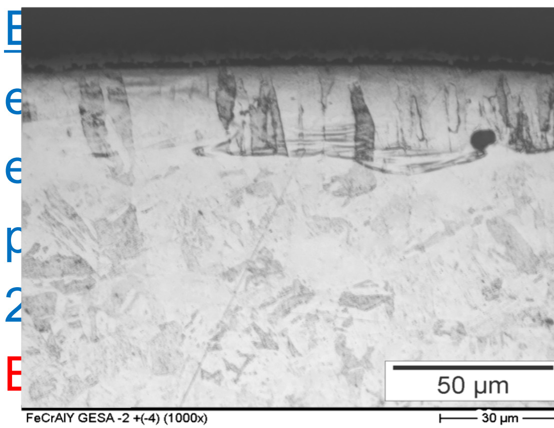
(i) coating the surface steel with Al or Al containing alloy (Fe-Cr-Al system)
(ii) melting the coating and the surface layer of the steel *using intense pulsed electron beams* (*GESA process* – Karlsruhe Institute of Technology).



LPPS, VPS, E-beam PVD, ..



E
e keV
e W/ cm²
p : 1 -
2
E m

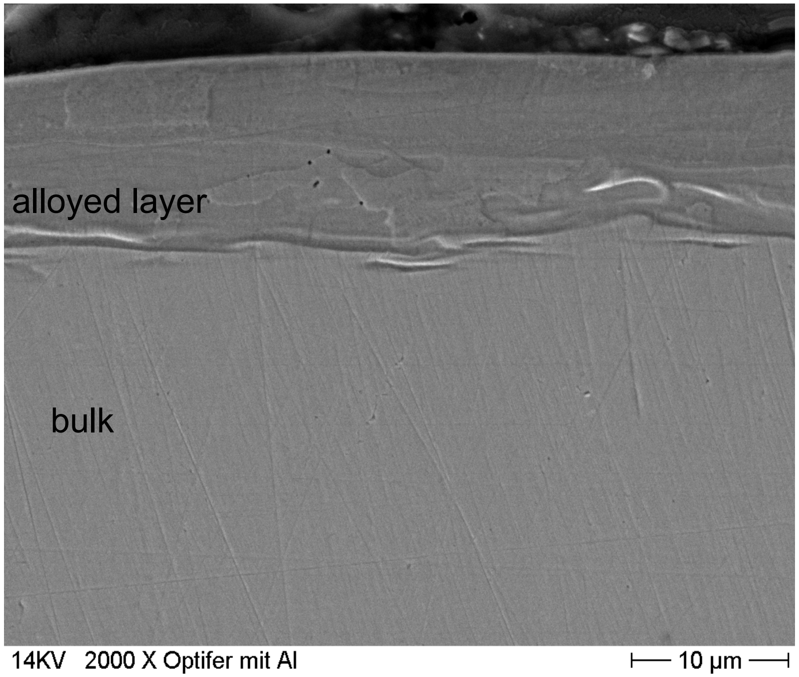


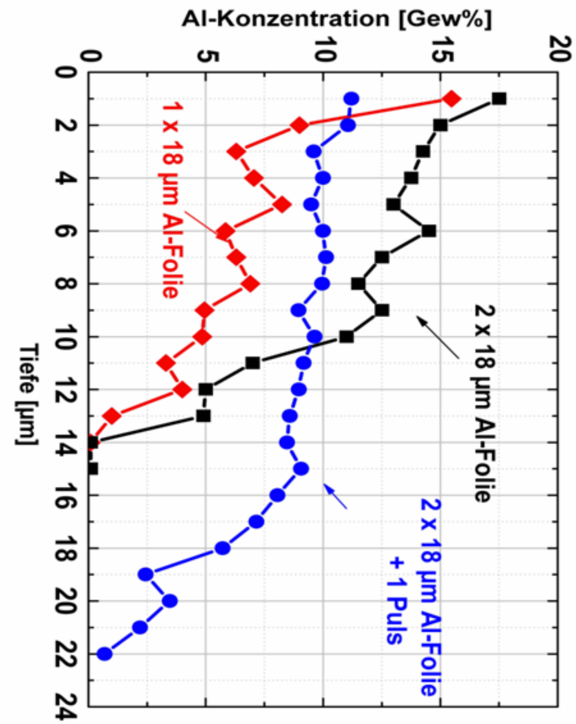
GESA treatment leads to:

metallic bonding – pore removal – surface smoothening and reduced Al content

Steel surface alloying with Al (GESA treatment)

Cross section of alloyed layer





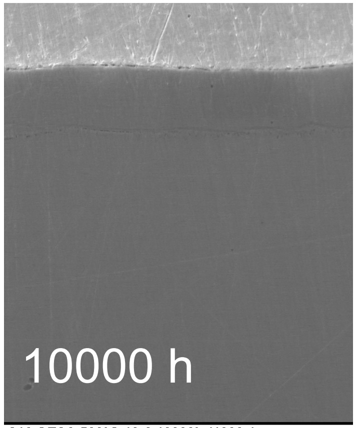
Surface alloying by turbulent mixing

Al content in surface layer can be adjusted by adapting the GESA process

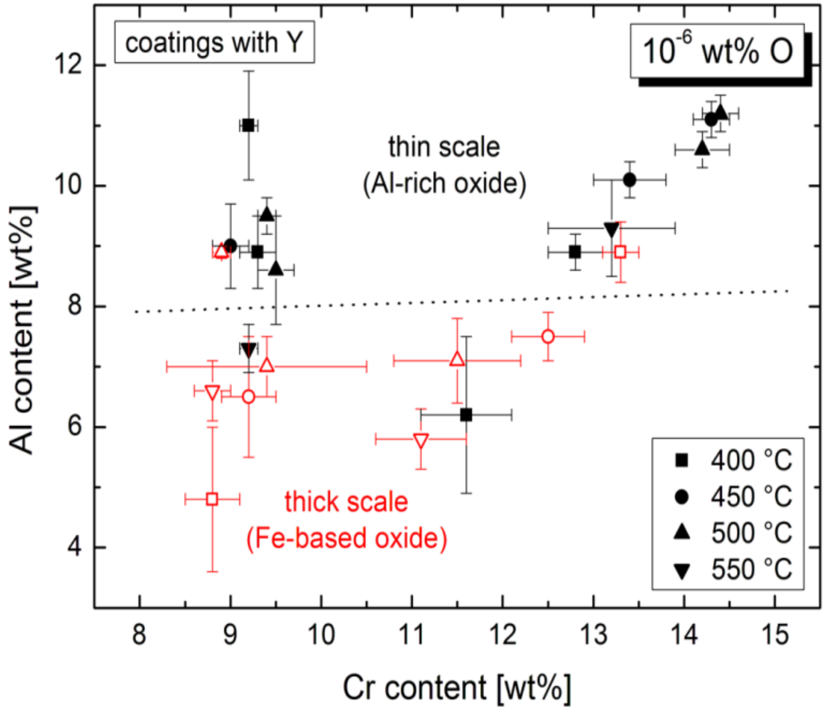
Coating + GESA treatment parameters

Pb/PbBi compatibility of Al surface alloyed steel at optimal oxygen concentration 10^{-6} wt%

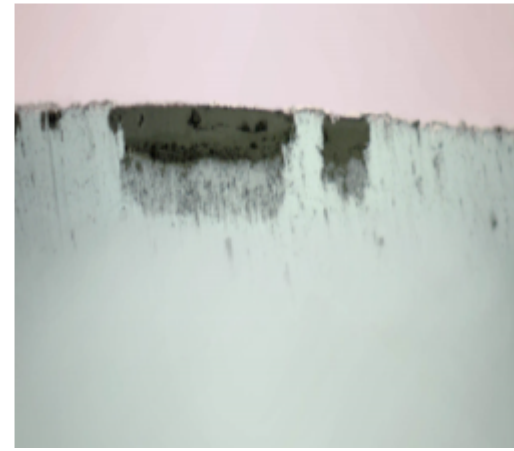
500°C



316 GESA 500°C 10-6 10000h (1000x)



550°C



Up to 600°C and 1 corrosion attack and no visible oxidation. Fe12Cr7Al

Thin alumina scales protect the surface alloyed steel.

n at 550°C Al< 4wt%

➔ „normal Fe-based scales

➔ ?optimum Al/Cr content?

➔ Bulk FeCrAl to answer this question

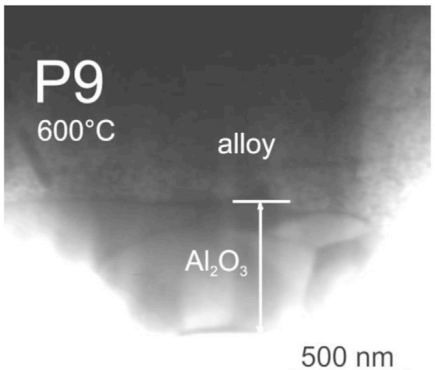
R. Fetzer, G. Mueller, W. An, A. Weisenburger, Metal surface layers after pulsed electron beam treatment *Surf. Coat. Tech.* 258, 549 (2014) doi.org/10.1016/j.surfcoat.2014.08.039

R. Fetzer, A. Weisenburger, A. Jianu, G. Müller, Oxide scale formation of modified FeCrAl coatings exposed to liquid lead, *Corros. Sci*. 55, 213-218 (2012) https://doi.org/10.1016/j.corsci.2011.10.019

Alumina forming steels - Bulk FeCrAl +RE

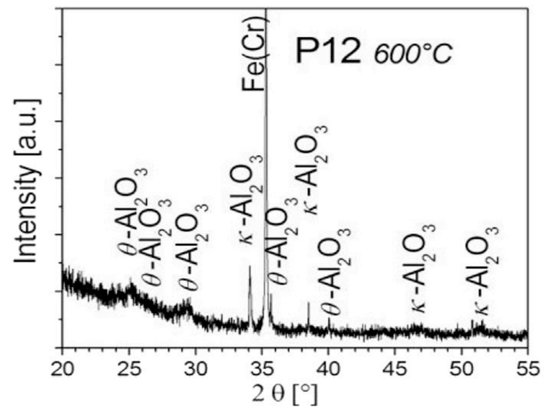
Influence of Cr Al content plus RE on the corrosion behavior (400-600°C) in Pb

Fe-(6.2–16.9)Cr-(4.2-8.8)Al

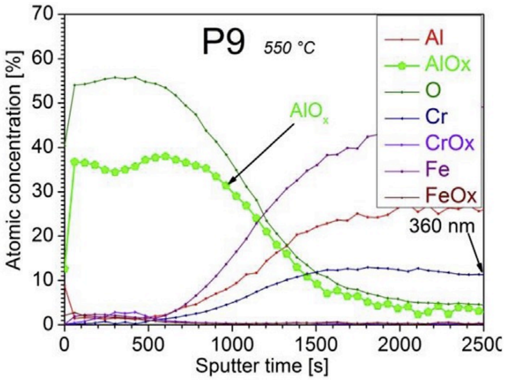


b)

a)



c)

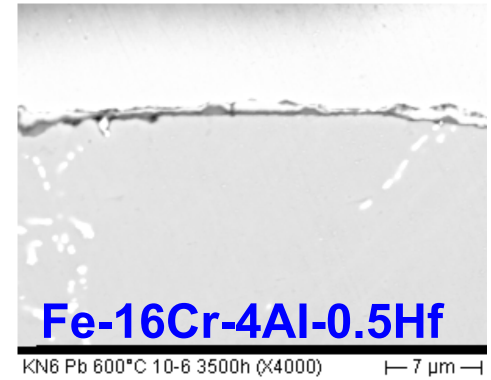


b)

formation of thin Al-oxide scale

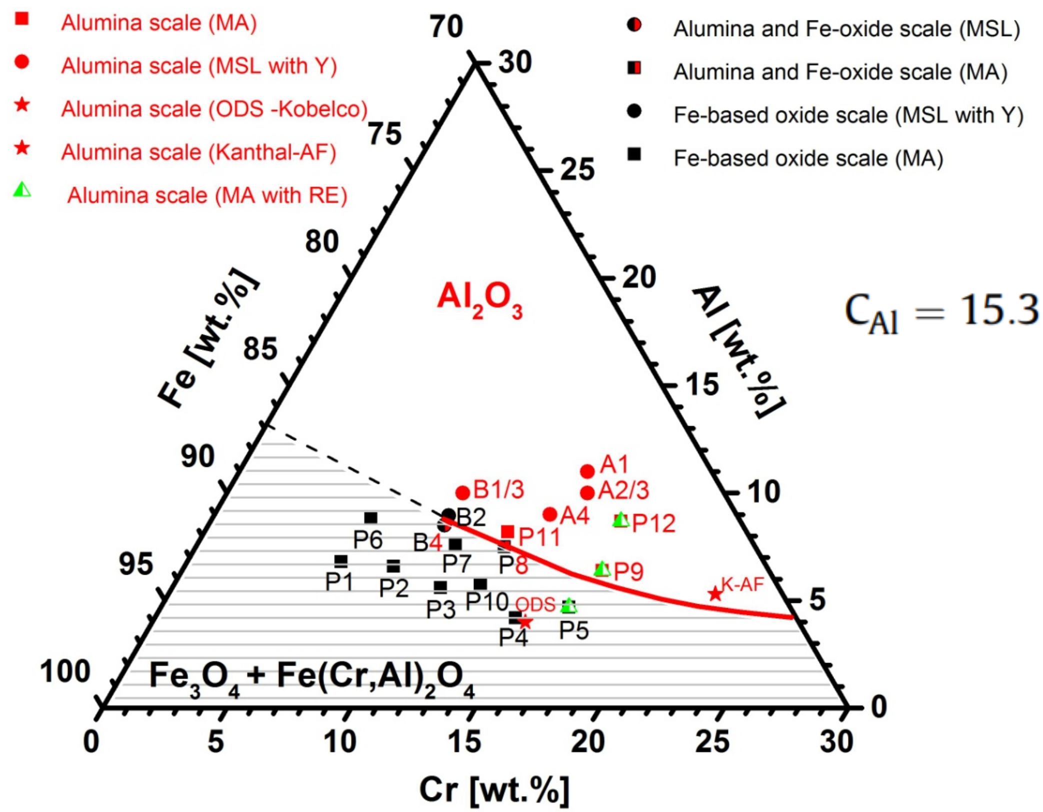
Gracing incident XRD
Cr/Al ratio **16Cr/6Al** required for alumina formation
Mainly transition aluminas no α–Alumina

Fe-16Cr-(4, 6, 8) Al-0.5Y, Zr, Hf, Mo



Reactive elements like Y, Zr, Hf foster the alumina formation

Oxide map of FeCrAl+RE in Pb-alloys between 450 and 600°C – oxygen 10^{-6}wt%



$$C_{Al} = 15.3 - 0.81(C_{Cr}) + 0.0156(C_{Cr})^2 \text{ [wt.\%]}$$

Al_2O_3 formation at entire temperature range requires a certain Al, Cr ratio

Reactive elements like Y, Zr, Hf foster the alumina formation

Both surface alloyed and bulk FeCrAl can protect the steels in Pb up to 750°C

A. Jianu, R. Fetzer, A. Weisenburger, S. Doyle, M. Bruns, et al., Stability domain of alumina thermally grown on FeeCreAl-based model alloys and modified surface layers exposed to oxygen containing molten Pb, J. Nucl. Mater. 470, 86 (2016) doi.org/10.1016/j.jnucmat.2015.12.009

Alumina forming austenitic steels - AFA

Elements	Range(wt.%)	Role
Ni	20~32	stabilize austenite
Al	2~5	oxidation resistance
Cr	12~16	third element effect

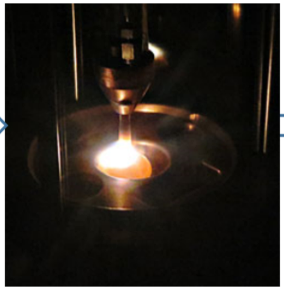
1st generation AFA-austenitic alloys:
$FeCr_{12\sim16}Al_{2.5\sim4}Ni_{20\sim29}$

2nd generation AFA-austenitic alloys:
$FeCr_{14\sim16}Al_{2.5\sim4}Ni_{20\sim29}$ + Y + Nb

Metal powder

Arc melter

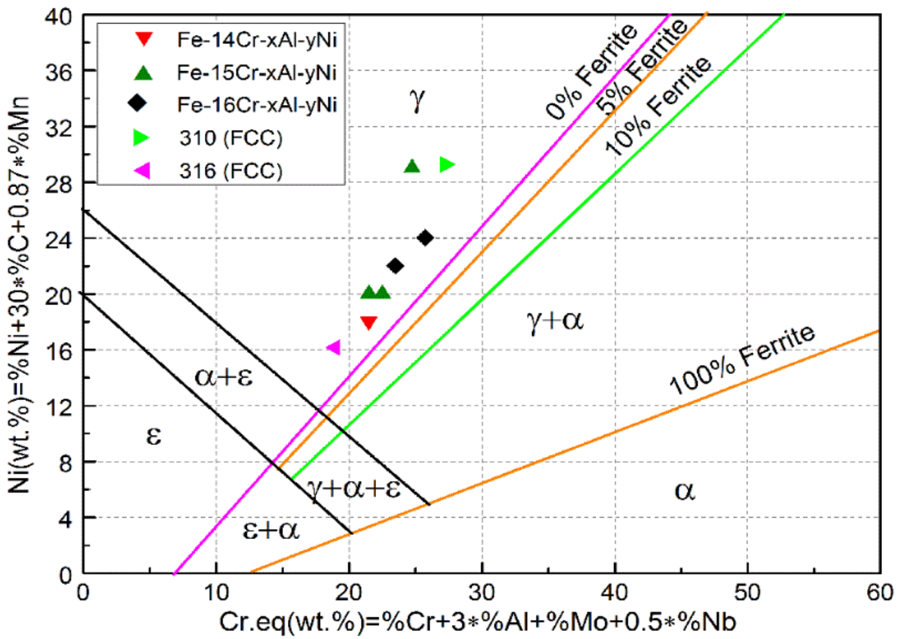
heat treatment (quarz glas capsule)
1250°C 2h – rapid cooling in water



A. Weisenburger et. al.

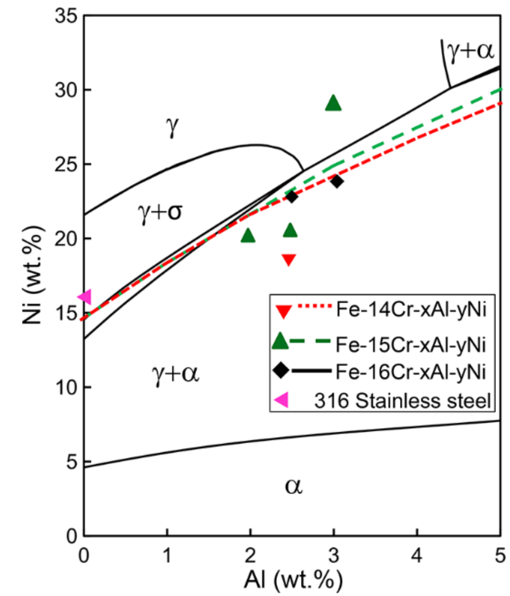
AFA alloy design

Schaeffler diagram of AFA model alloys with Y and Nb



AFA: Schaeffler constitution diagram show the phase at room temperature

Calculated phase diagrams for model Fe-(14,15,16)Cr-xAl-yNi+Y+Nb alloy system at 600°C



AFA: Phase prediction at 600°C (thermal-calc, TCFE 7 database)

A. Weisenburger et. al.

2nd generation of AFA – KIT

Based on 1st results - simple model alloys

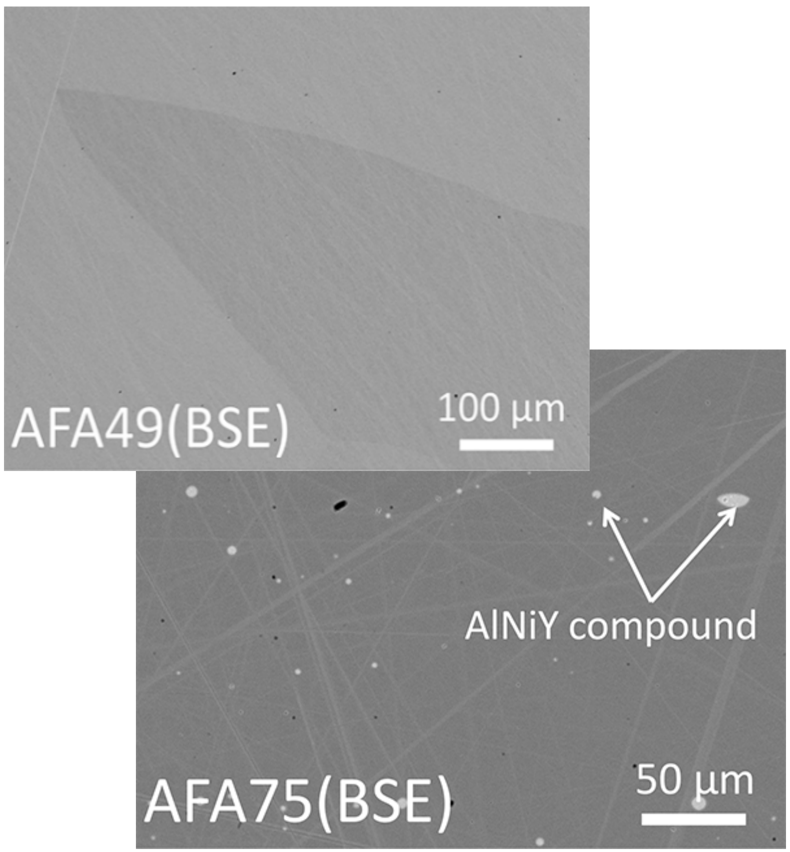
➔ to evaluate minimum Al and Cr content required, maximum Ni content allowed – Phases are measured after heat treament

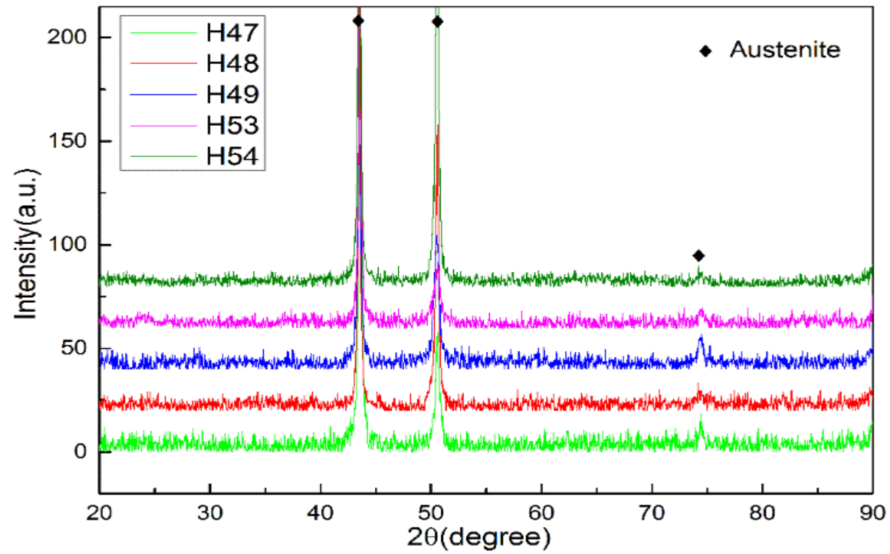
Code	Nominal composition	Cr	Al	Ni	Fe
AFA45	Fe-14Cr-3Al-20Ni	14.4	2.8	19.5	Balance
AFA46	Fe-16Cr-2.5Al-20Ni	16.6	2.3	19.6	Balance
AFA47	Fe-16Cr-3Al-20Ni	16.6	2.7	21.7	Balance
AFA48	Fe-12Cr-4Al-22Ni	12.2	4.0	21.3	Balance
AFA49	Fe-14Cr-4Al-22Ni	14.4	4.2	21.2	Balance

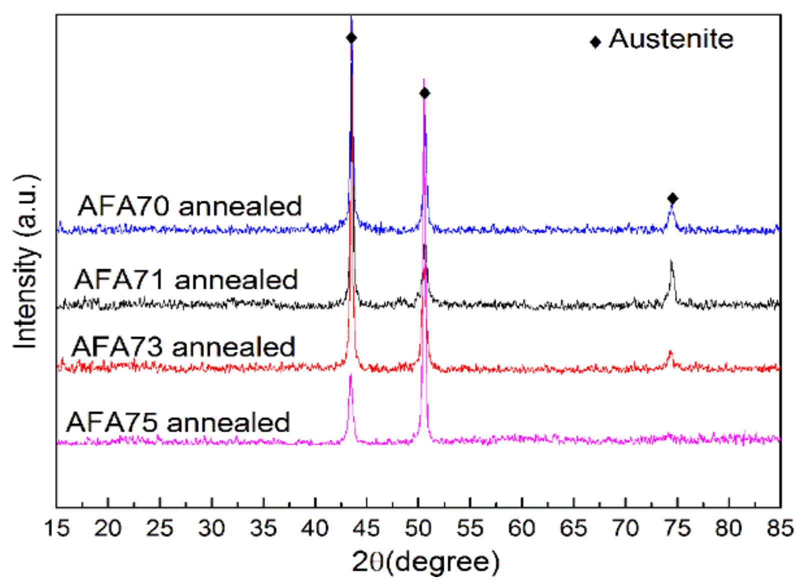
Code	Nominal compositions	Al	Cr	Ni	Nb	Y	Fe
AFA70	Fe-14Cr-2.5Al-18Ni-0.5Y	2.7	14.7	17.9	--	0.4	Balance
AFA71	Fe-15Cr-2.5Al-20Ni-0.5Y	2.5	15.4	19.9	--	0.5	Balance
AFA72	Fe-16Cr-2.5Al-22Ni-0.5Y	2.5	15.4	21.8	--	0.5	Balance
AFA73	Fe-15Cr-2Al-20Ni-0.5Y-1.5Nb	2.1	15.4	22.0	1.3	0.5	Balance
AFA74	Fe-15Cr-3Al-29Ni-0.5Y-1.5Nb	4.3	15.5	27.9	1.1	0.5	Balance
AFA75	Fe-16Cr-3Al-24Ni-0.5Y-1.5Nb	3.1	15.7	24.1	1.68	0.7	Balance

1st and 2nd generation of AFA – after annealing

- FCC is the only phase after annealing.
- Homogenized chemical compositions.
- Large grain size(>300μm)







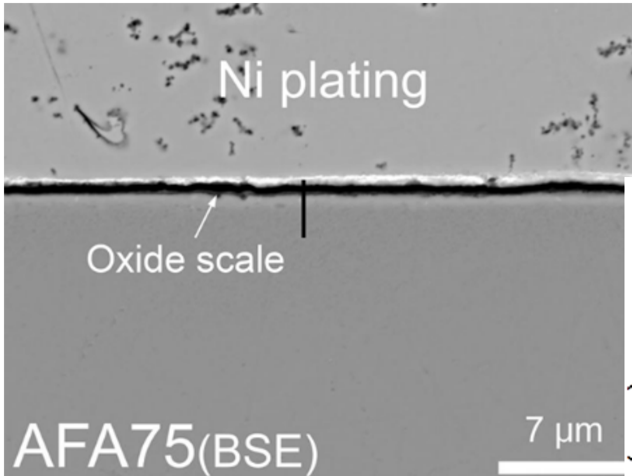
Overview on corrosion behaviour in Pb at 550°C and 600 °C of AFA model alloys

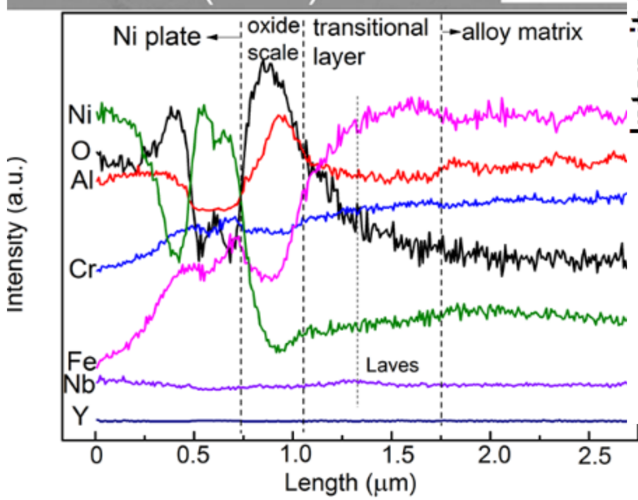
Code	Chemical composition (wt.%)	550 °C	600 °C
AFA45	Fe-14.4Cr-2.8Al-19.5Ni	🙂	☹️
AFA46	Fe-16.6Cr-2.3Al-19.6Ni	🙂	🙂
AFA47	Fe-16.6Cr-2.7Al-21.7Ni	🙂	☹️
AFA48	Fe-12.2Cr-4Al-21.3Ni	☹️	☹️
AFA49	Fe-14.4Cr-4.2Al-21.2Ni	☹️	☹️
AFA50	Fe-16.5Cr-2.5Al-21.4Ni	🙂	🙂
AFA51	Fe-12.3Cr-4.3Al-23.3Ni	☹️	☹️

All alloys with less than 15wt% Cr failed at least at 600°C

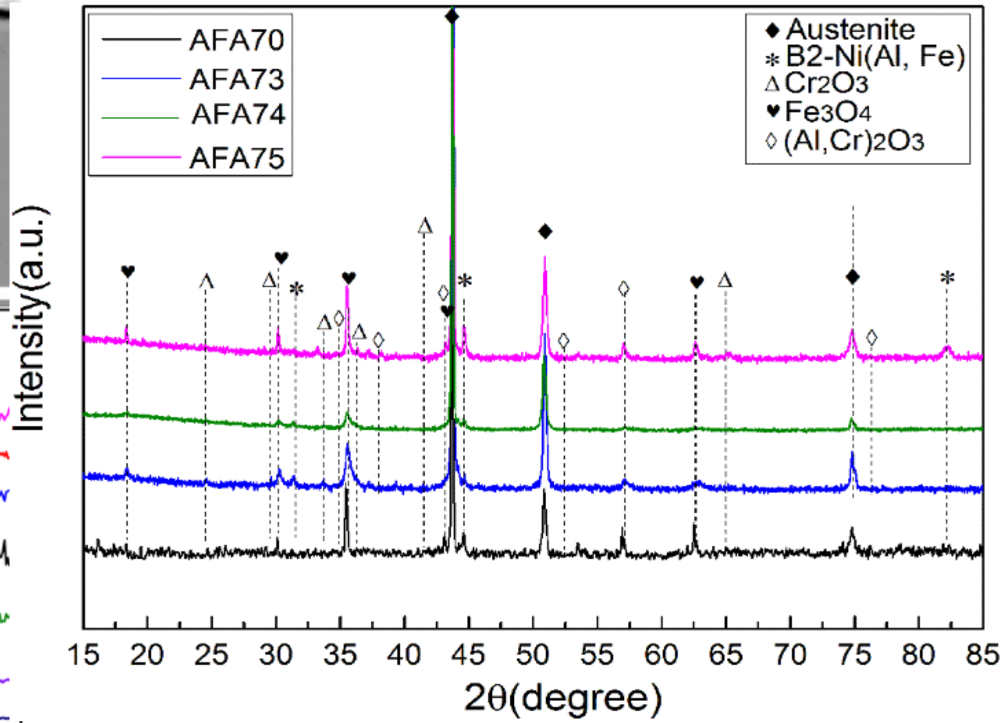
Code	Chemical compositions (wt.%)	1000 h	2000 h
AFA70	Fe-14.7Cr-2.7Al-17.9Ni-0.4Y	🙂	🙂
AFA71	Fe-15.4Cr-2.5Al-19.9Ni-0.5Y	🙂	🙂
AFA72	Fe-15.4Cr-2.5Al-21.8Ni-0.5Y	😐	🙂
AFA73	Fe-15.4Cr-2.1Al-22Ni-0.5Y-1.3Nb	🙂	🙂
AFA74	Fe-15.5Cr-4.3Al-27.9Ni-0.5Y-1.1Nb	🙂	🙂
AFA75	Fe-15.7Cr-3.1Al-24.1Ni-0.7Y-1.68Nb	🙂	🙂

Exposure of Y and Nb containing AFA model alloys to Pb at 600°C for 2000h - stagnant 10^{-6}wt% oxygen



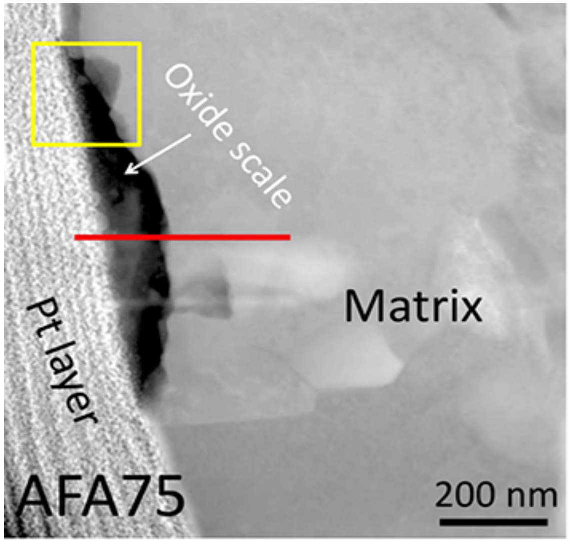


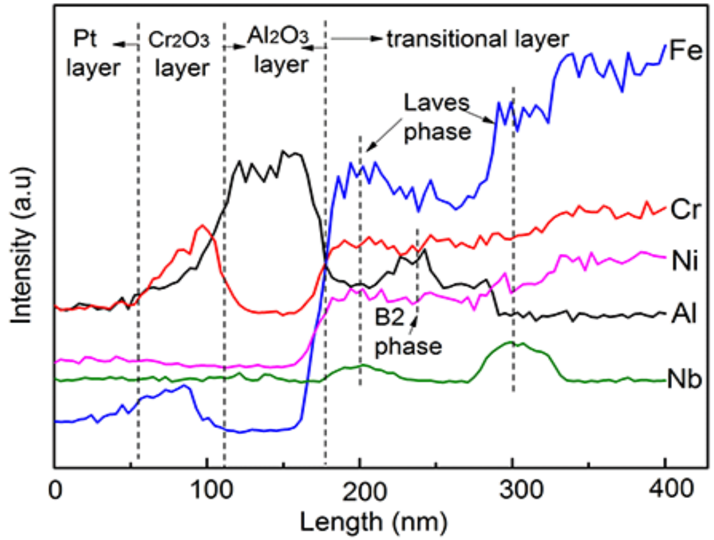
AFA75 Fe-16Cr-3Al-24Ni-0.5Y-1.5Nb



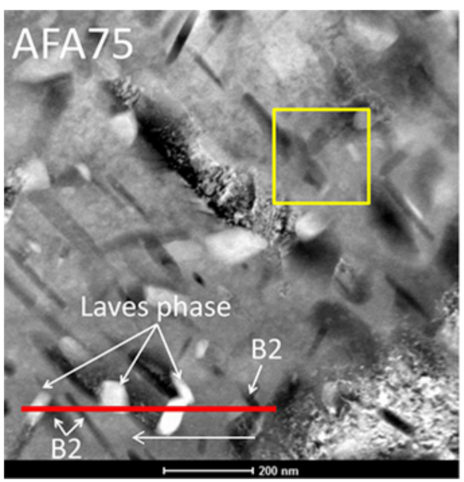
Thin Al-rich oxide scales $(Al,Cr)_2O_3$

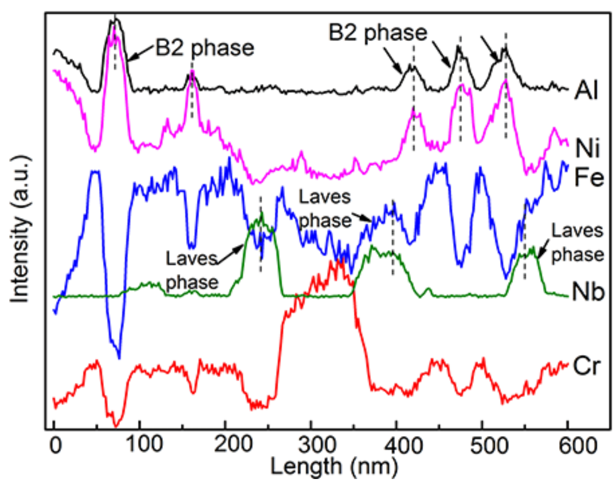
TEM investigation of AFA 75 after 2000h at 600°C





Thin Cr-oxide layer followed by Al-Oxide scale - < 50nm after 2000h





Matrix - precipitates:

Dark: Al, Ni - B2 phase
Bright: Nb rich Laves

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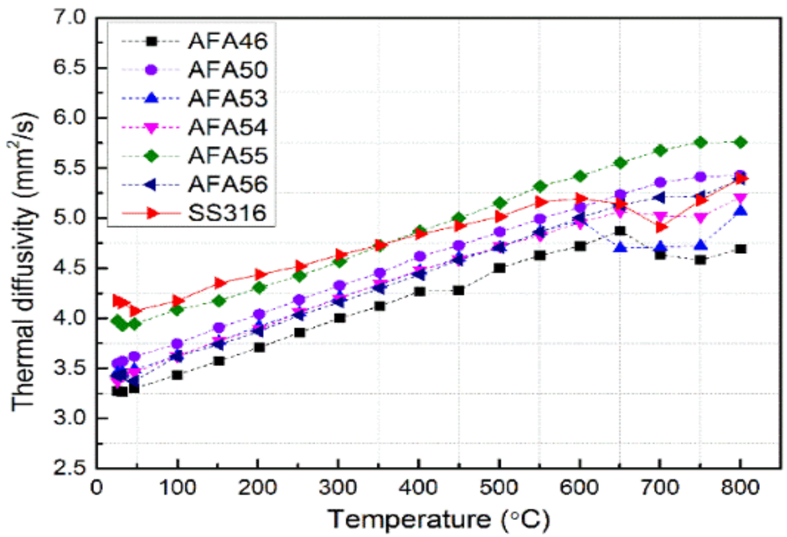
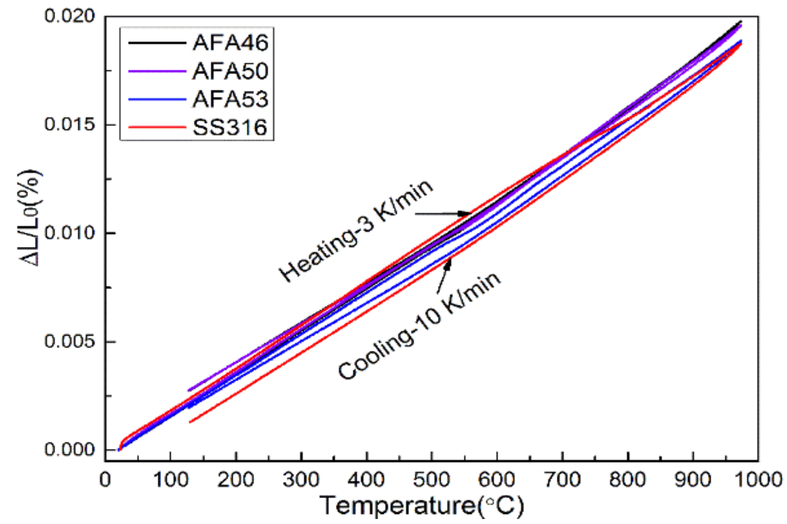
KIT - Thermal properties – first brief look





- *Thermal expansion coefficient* similar for all tested AFA and similar to 316
- *Thermal diffusivity* similar to 316
  - some show decrease of thermal conductivity for even higher temperatures
    - further examinations and explanations required

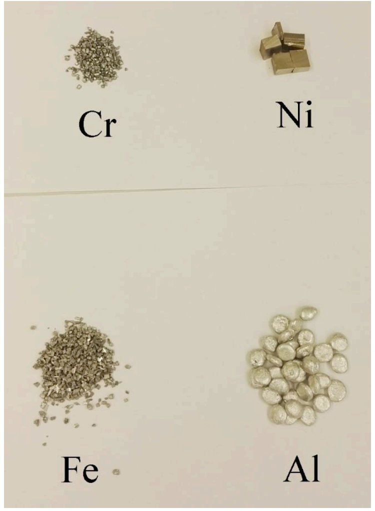
HEA Alloys design & manufacturing & 1st analysis

High entropy alloys: $FeCr_{20\sim30}Al_{3\sim6}Ni_{20\sim37}$

	Valence electron concentration VEC	Atomic size difference δr	Mix enthalpy ΔHmix
FCC	>7.8	<6.6	-10KJ/mol<ΔH<5KJ/mol
BCC	<6.87	<6.6	-10KJ/mol<ΔH<5KJ/mol

Element X concentration: 5 mol.% < X% < 35 mol.%

Metal powder



Arc melter

$$\Omega = \frac{Tm \cdot \Delta S_{mix}}{|\Delta H_{mix}|}$$

estimate the high-entropy solid-solution formation value > 1.1

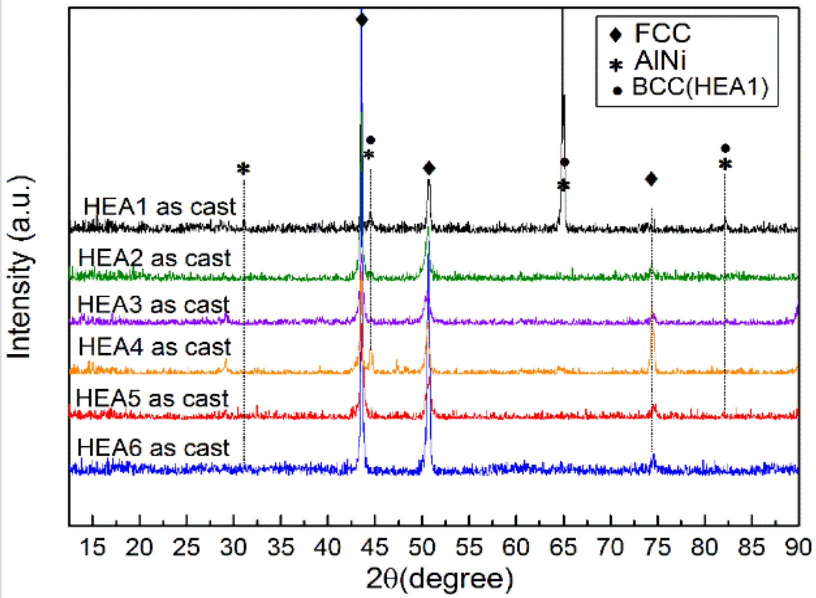
No further heat treatment – all results in as produced status

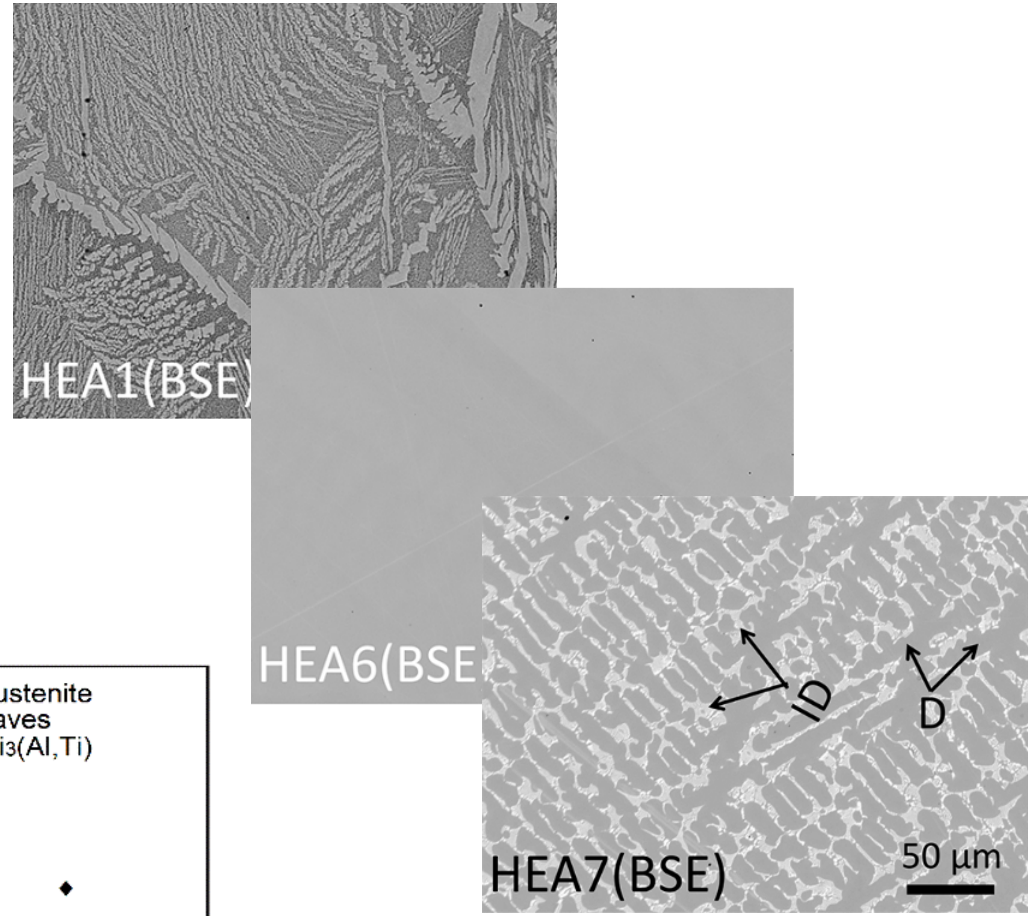
Design of HEA

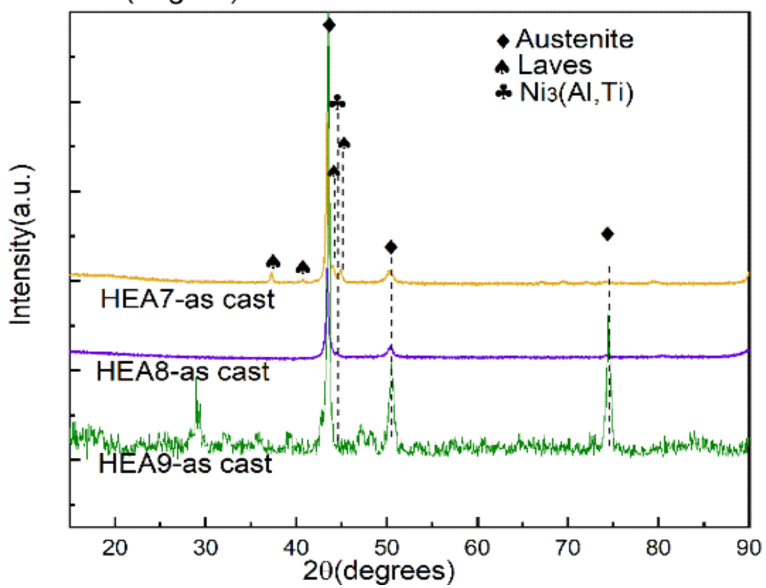
Code	Chemical formula	ΔHmix	VEC	δr	Ω	Predicted Phase
HEA1	$Al_{0.32}CrFeNi_{0.9}$	-8.62	7.56	4.44	2.28	SS (FCC) +IM
HEA2	$Al_{0.3}Cr_{0.68}FeNi$	-8.29	7.75	4.41	2.31	SS (FCC) +IM
HEA3	$Al_{0.26}Cr_{0.68}FeNi$	-7.87	7.76	4.22	2.43	SS (FCC) +IM
HEA4	$Al_{0.36}Cr_{0.68}FeNi$	-8.87	7.62	4.74	2.18	SS (FCC) +IM
HEA5	$Al_{0.18}Cr_{0.74}FeNi$	-6.84	7.89	3.54	2.76	SS (FCC)
HEA6	$Al_{0.23}Cr_{0.68}FeNi$	-7.55	7.85	4.02	2.52	SS (FCC)
HEA7	$Al_{0.24}Cr_{0.6}Fe_{0.9}NiNb_{0.15}$	-10.92	7.71	4.83	1.98	SS (FCC) +IM
HEA8	$Al_{0.25}Cr_{0.69}FeNiTi_{0.16}$	-11.18	7.62	5.27	1.89	SS (FCC) +IM
HEA9	$Al_{0.25}Cr_{0.69}FeNiCu_{0.16}$	-5.45	7.95	4.02	3.82	SS (FCC)

VEC of HEA 1 to 4 and HEA 7 to 9 : FCC + 2nd phase
HEA 5,6 single phase fcc,
δr is always below the critical value for both fcc and bcc HEA

Microstructure of as cast HEA







HEA 1 4 FCC + AlNi
HEA 5, 6 single phase FCC
HEA7 - 8 FCC + Laves + Ni_3(Al, Ti)

EXPOSURE in Pb at 600°C for 1000h - HEA

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General corrosion resistance of HEA - exposed in stagnant molten Pb at 600°C with 10^{-6} wt.%O_2 for 1000h

Code	Nominal composition	550 °C	600 °C
HEA1	$Al_{0.32}CrFeNi_{0.9}$		
HEA2	$Al_{0.3}Cr_{0.68}FeNi$		
HEA3	$Al_{0.26}Cr_{0.68}FeNi$		
HEA4	$Al_{0.36}Cr_{0.68}FeNi$		
HEA5	$Al_{0.18}Cr_{0.74}FeNi$		
HEA6	$Al_{0.23}Cr_{0.68}FeNi$		
HEA7	$Al_{0.24}Cr_{0.6}Fe_{0.9}NiNb_{0.15}$		
HEA8	$Al_{0.25}Cr_{0.69}FeNiTi_{0.16}$		
HEA9	$Al_{0.25}Cr_{0.69}FeNiCu_{0.16}$		

- Samples surface with only a little bit Pb attaching, indicating the formation of oxide scale
- HEA 9 -Pb adherent – scale spallation but no dissolution

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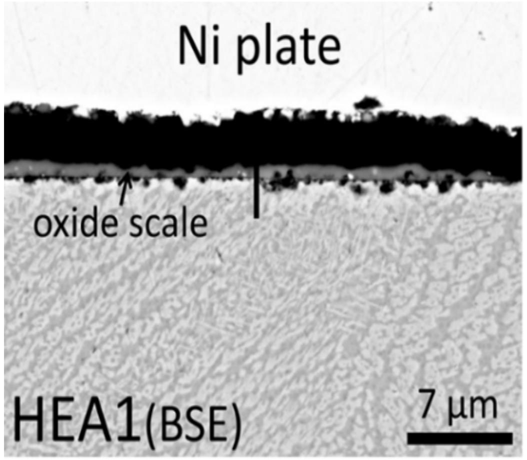
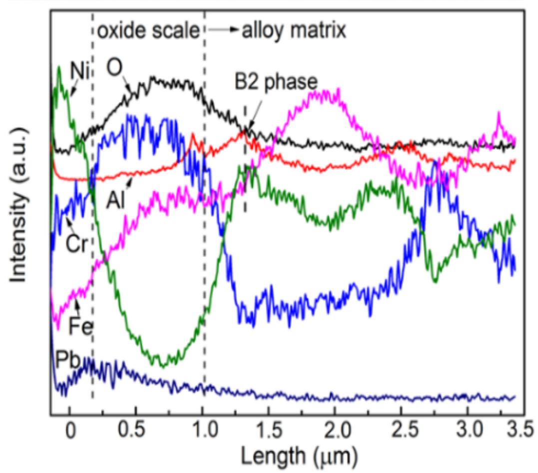
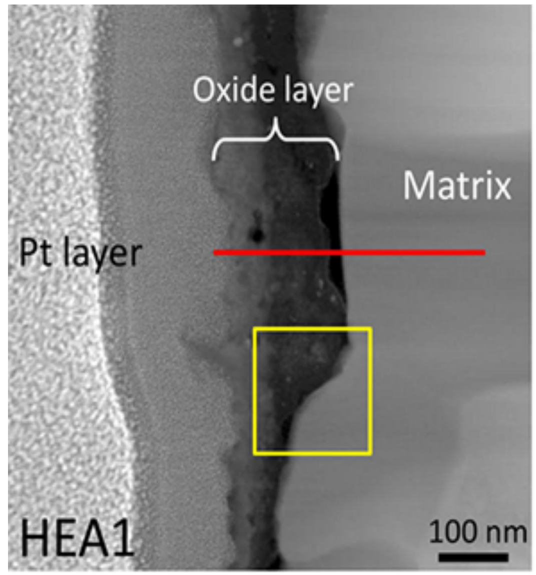
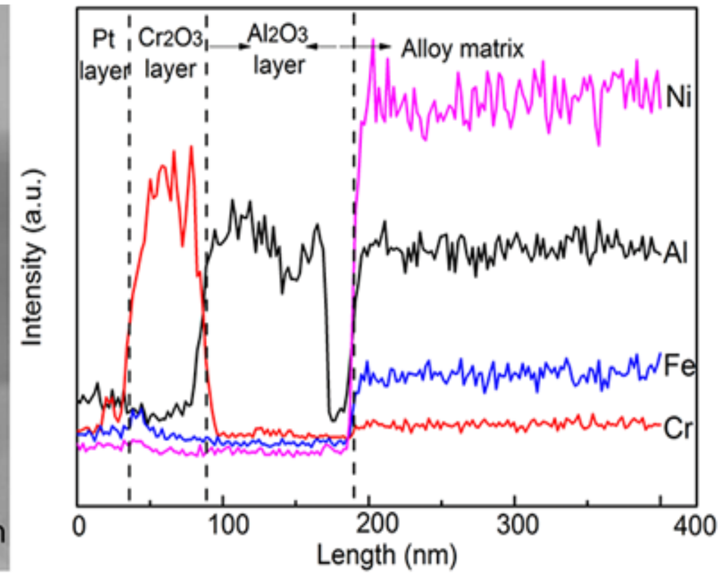
HEA - 1000h at 600°C in Pb 10^{-6}wt% oxygen



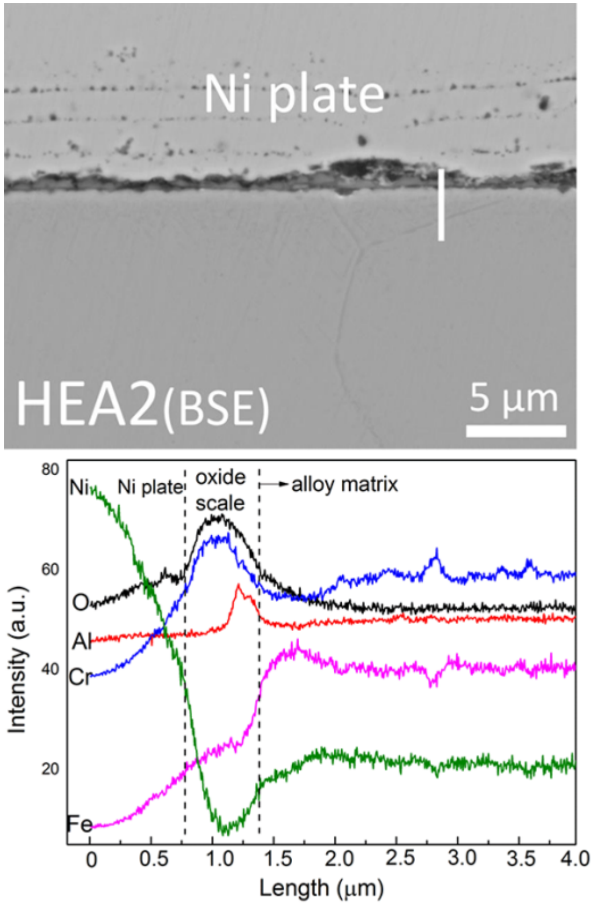


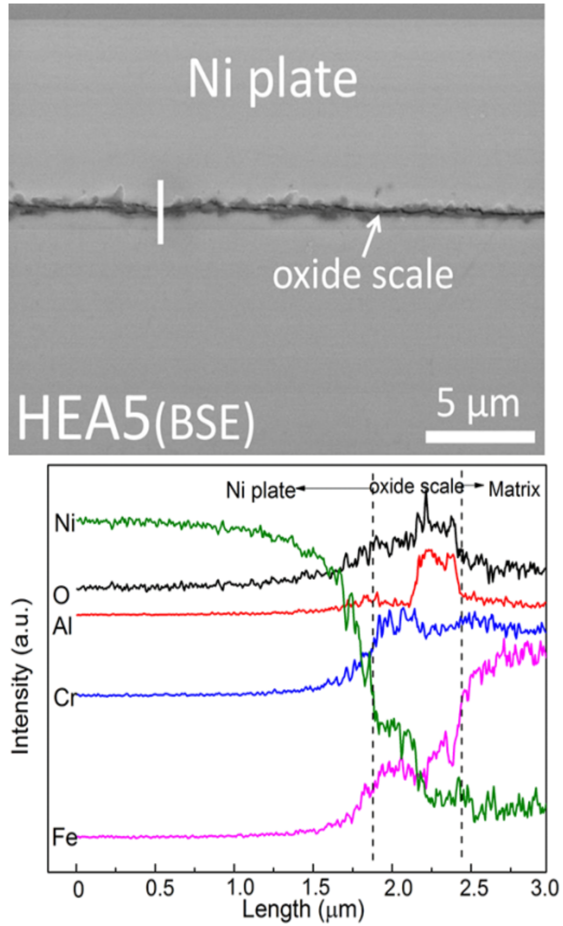




All specimens besides the Cu containing show the formation of a protective oxide scale mainly AlCr rich.

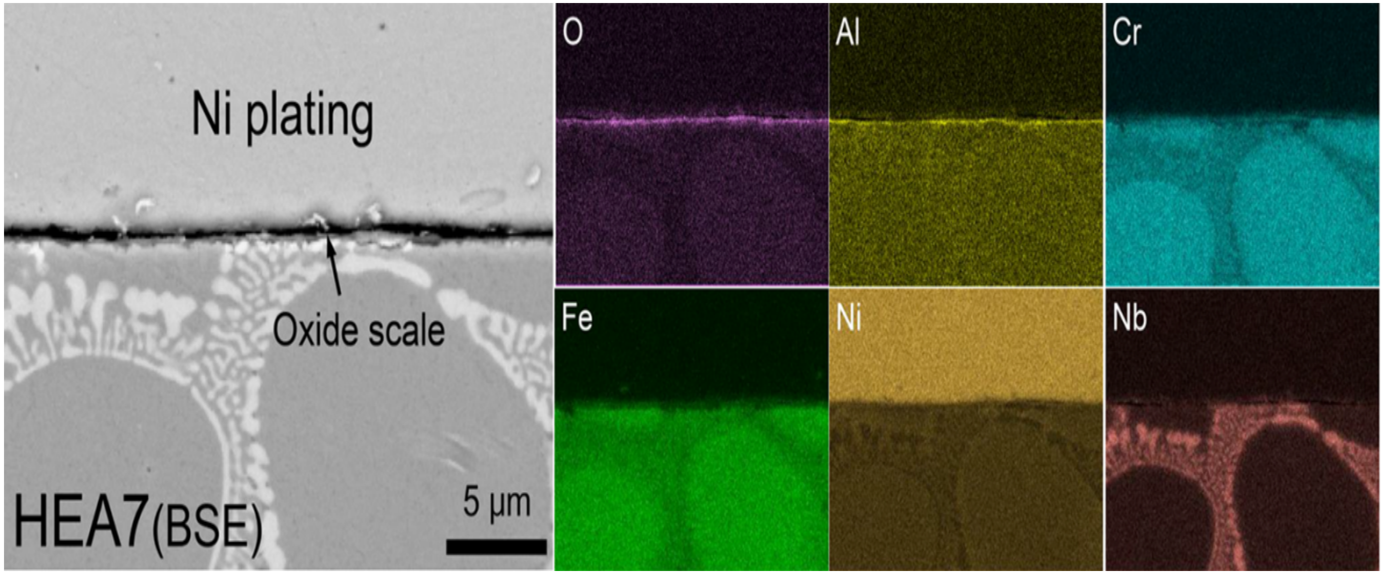
HEA - 1000h at 600°C in Pb 10^{-6}wt% oxygen





All specimens besides the Cu containing show the formation of a protective oxide scale mainly AlCr rich.

HEA - 1000h at 600°C in Pb 10^{-6}wt% oxygen



Continues thin Al rich oxide scale protects the HEA.

Thin Al/Cr Oxide scales were also detected on the laves phase of HEA 7.

Laves Phase contain 17 at% Nb and 7at% Al

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Microstructure stability of HEA after exposure to Pb at 600°C

Code	Phase transformation	Second phase coarsening or precipitates
HEA1	N	N
HEA2	N	N
HEA3	N	Y (at 600 °C)
HEA4	N	N
HEA5	N	Y
HEA6	N	Y (at 600 °C)
HEA7	N	N
HEA8	Y	Y

Beside HEA 8 (containing Ti) all are phase stable
HEA 1,2,4,7 so not show coarsening or precipitation either

Summary Outlook

There are options to overcome the temperature limit

All the approaches are suitable advanced corrosion mitigation strategies
Temperature > 600°C in Pb, PbBi feasible

Issues: Al-Surface alloys using GESA process – reproducibility and reliability
and
Bulk alumina formers, FeCrAl, AFA and HEA – influence of minor elements (C, RE, ..), production route – large scale,

None of these is yet fully characterized
None of these is ready now – coatings and surface alloys more advanced
AFA and HEA require "real" metallurgical processing – at time 1st metallurgical processed AFA are in our LAB – exposure test up to 750°C are performed – evaluation of exposed specimens started

All require more R&D

H2020 project GEMMA
EERA-JPNM PP – ALCORE – focus on Alumina forming alloys
- HEAFNA – HEA for nuclear applications