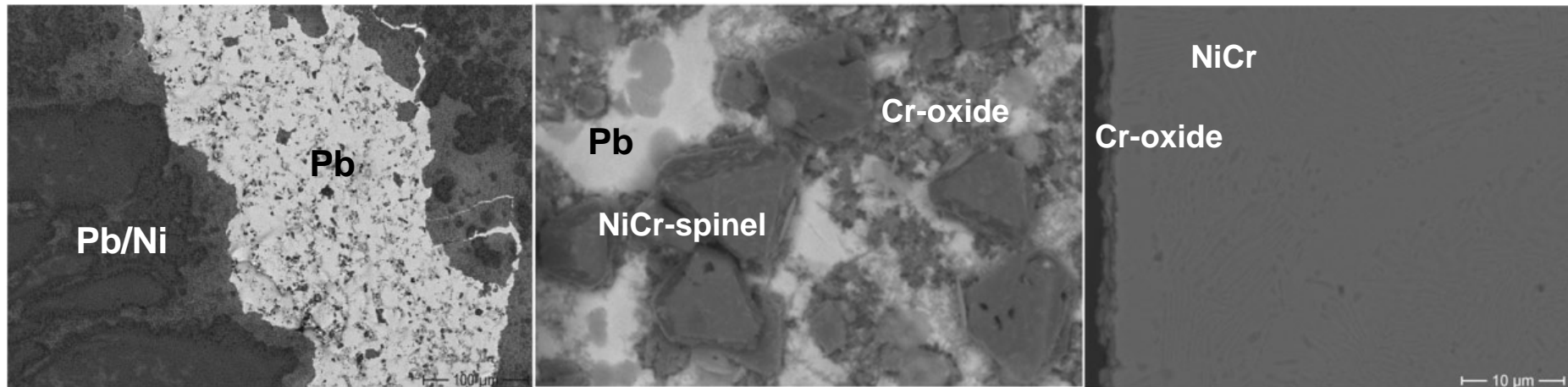


Oxidation and dissolution of binary Ni-Cr and ternary Ni-Cr-Al alloys in stagnant liquid lead at 750°C

O. Picho, C. Schroer, V. Trouillet and J. Konys



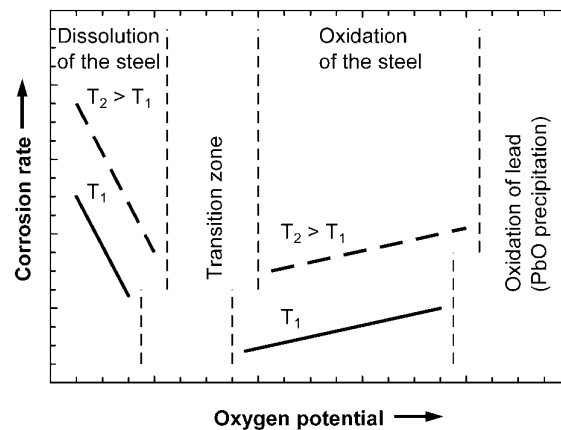
Application of Lead Technology to Subcritical (ADS) and Critical (LFR) Nuclear Systems/Reactors

LFR

- One of the concepts for the 4th generation of nuclear power plants (Gen IV)
- In the long-term, Pb as primary coolant at maximum 800°C
- Short- to mid-term: Pb- or LBE-cooled at 450 – 550°C

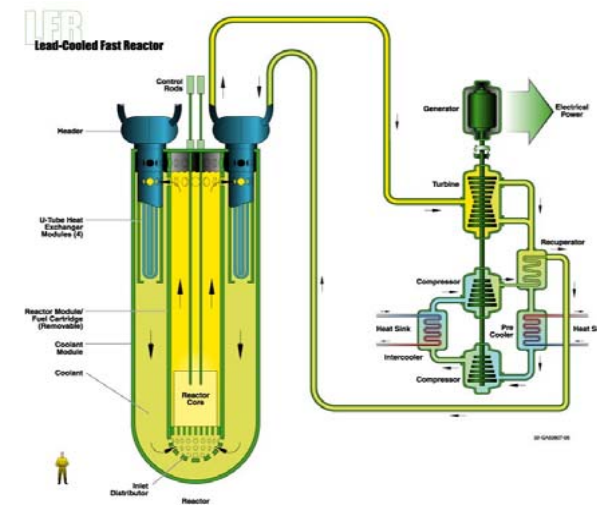
Corrosion of structure materials/ steels

- Dissolution of steel constituents
- Minimized by adding oxygen to liquid metal/ oxidation



ADS

- Transmutation of nuclear waste
- Power generation
- Liquid lead (Pb) or lead-bismuth eutectic (LBE) as spallation target and primary coolant
- Maximum temperature, typically
- 450 – 550°C



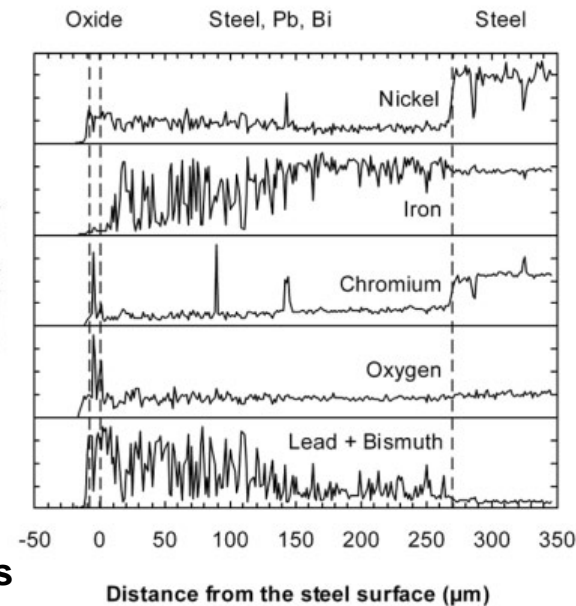
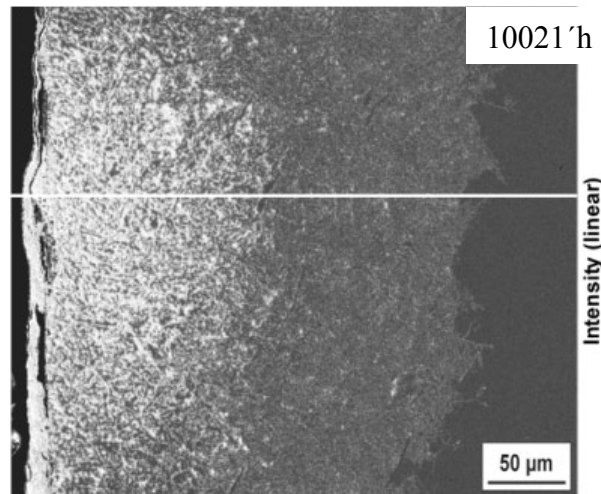
Motivation

At $T > 600^\circ\text{C}$ *Ni-based alloys* because of appropriate thermomechanical properties

BUT:

- Selective leaching of Nickel
- Penetration of liquid Pb into the material

Fe12Cr16Ni-316L Steel



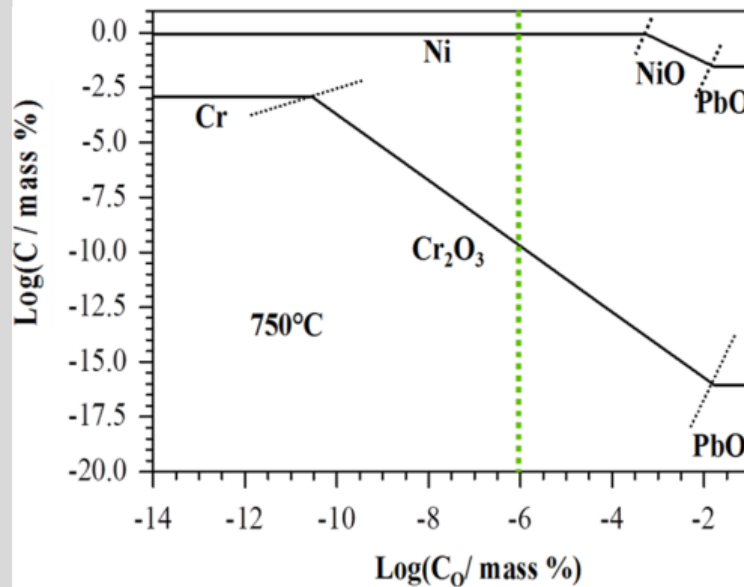
$T = 550^\circ\text{C}$, $c_{\text{O}} = 1.6 \times 10^{-6} \%$, $v = 2 \text{ m/s}$

Which Cr-content can suppress Ni-dissolution ?

Material

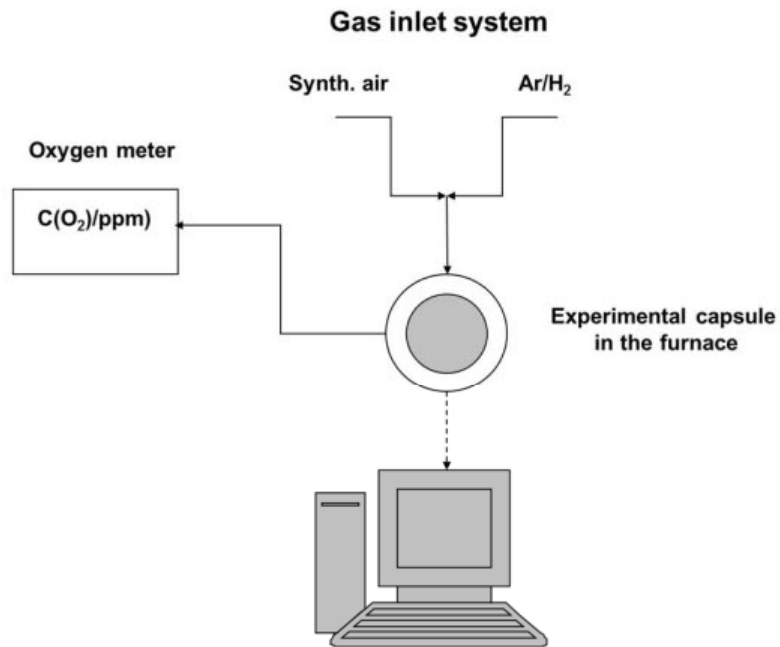
Elements	Ni	Ni25Cr	Ni30Cr	Ni35Cr	Ni48Cr	Ni35Cr1Al	Ni35Cr3Al	Ni35Cr5Al
Ni (mass%)	99,9	74,36	69,36	64,43	52,39	63,74	61,74	60,31
Cr (mass%)		25,33	30,35	35,25	48,01	35,10	35,20	34,64
Al (mass%)		0,31	0,29	0,32	0,30	1,10	3,05	5,04
Ti (mass%)					0,30			

Experimental conditions



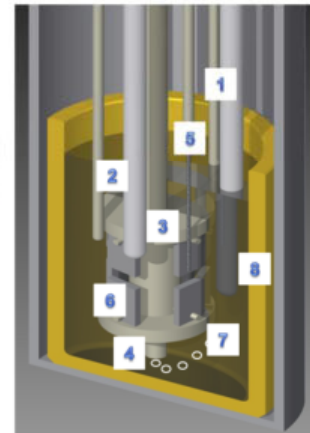
- **Static liquid lead** at 750°C - as basic for modelling of corrosion behavior
- **Co=10⁻⁶ mass %** - corresponds to typical reactor operating conditions

Corrosion test apparatus



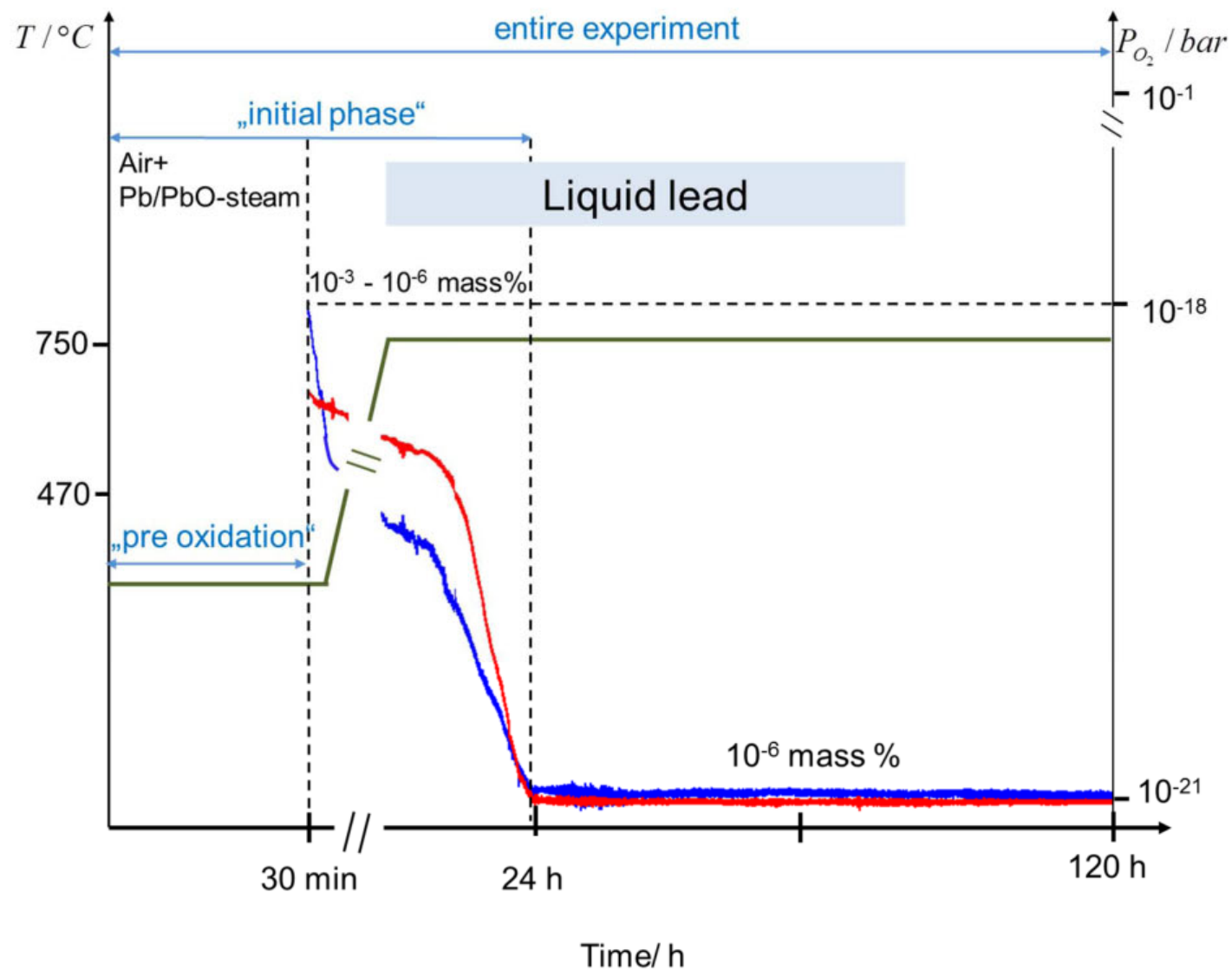
Data acquisition

- oxygen potential ($U_{1,2}/V$)
- temperature ($T_{1,2}/^{\circ}C$)



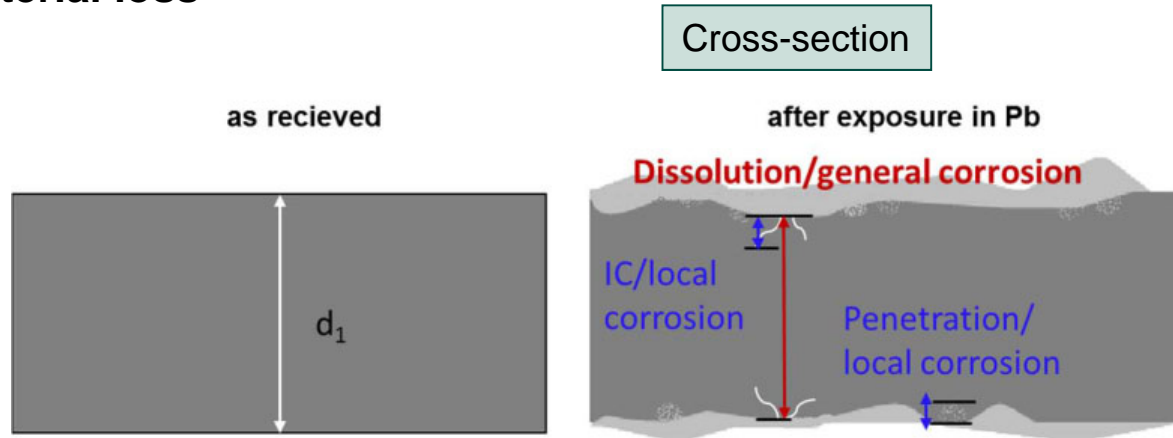
1. O₂ - sensor + thermocouple on the 1st level
2. O₂ - sensor + thermocouple on the 2nd level
3. Sample holder (Al₂O₃)
4. Gas bubbling tube (Al₂O₃)
5. Mo-electrode
6. Specimens (15x10x2 mm)
7. Oxygen containing liquid lead
8. Crucible (Al₂O₃)

Experimental procedure



Quantification of specimens bevor and after tests

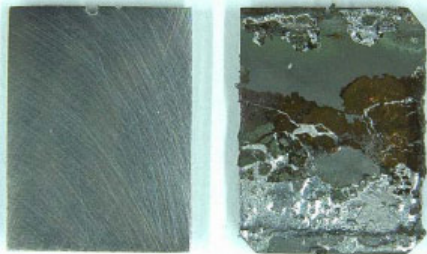
Material loss



$$\Delta x = (d_1 - d_2) / 2$$

Surface

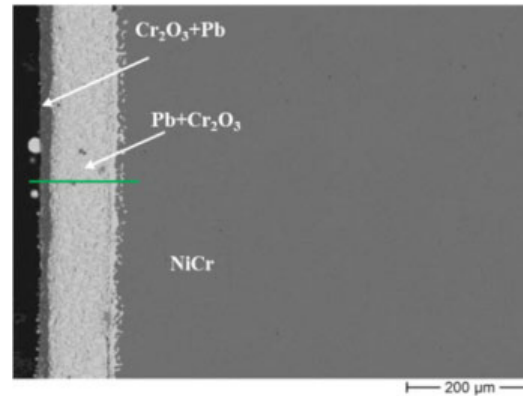
XPS	SEM/EDS
<ul style="list-style-type: none"> „pre oxidation“ 30 min 	<ul style="list-style-type: none"> „Initial phase“/ 24 h 120 h



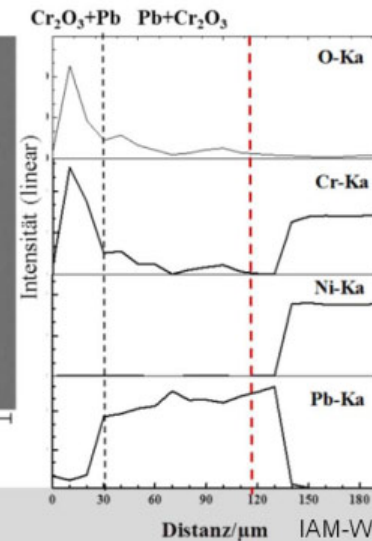
Cross-section

SEM/EDS

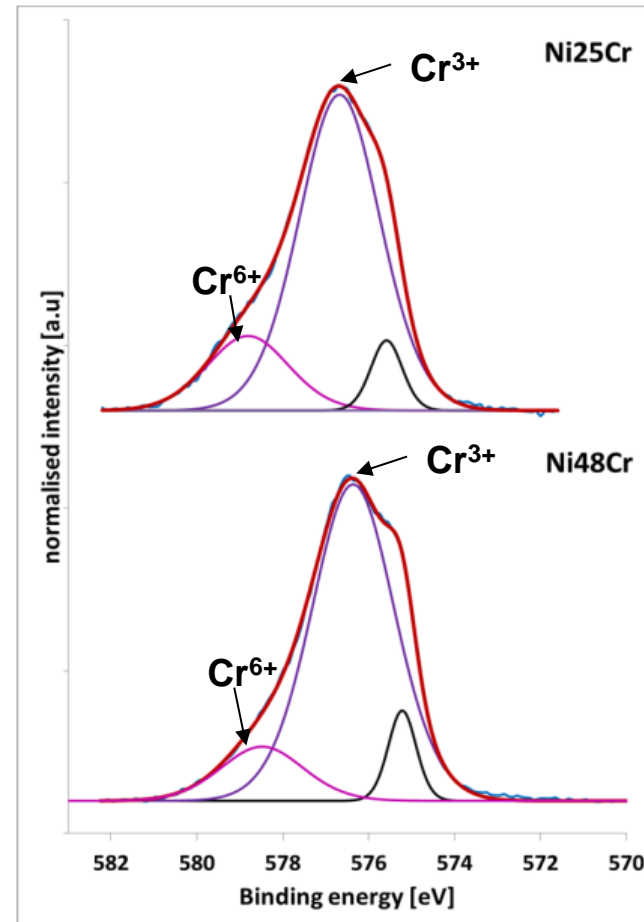
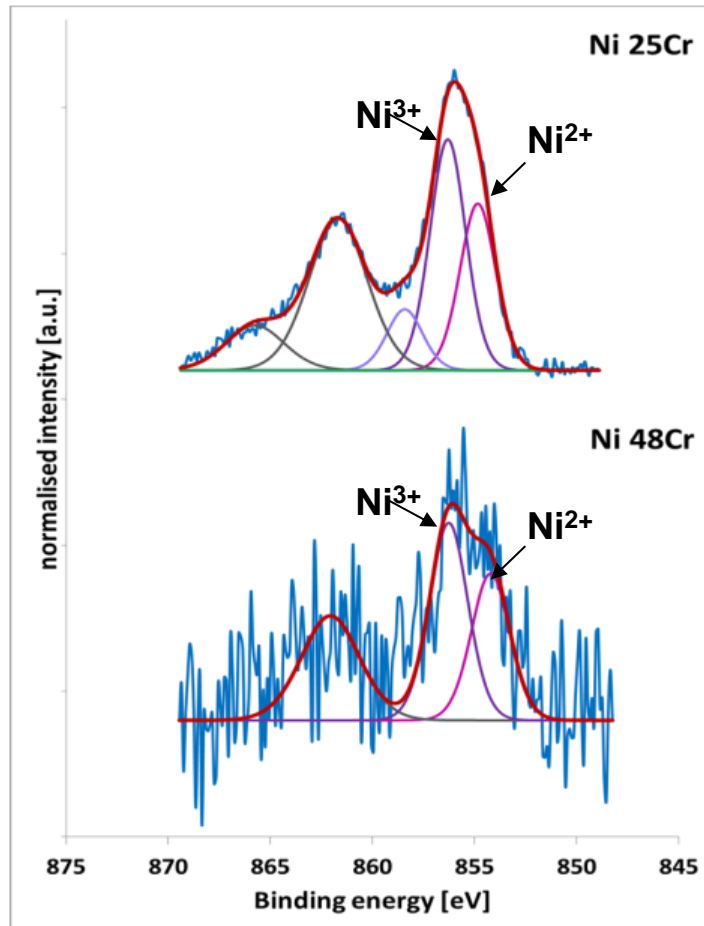
- „Initial phase“/24 h
- 120 h



Cross-section



XPS-Analysis from binary Ni-Cr-alloys with 25 and 48 mass% of Cr



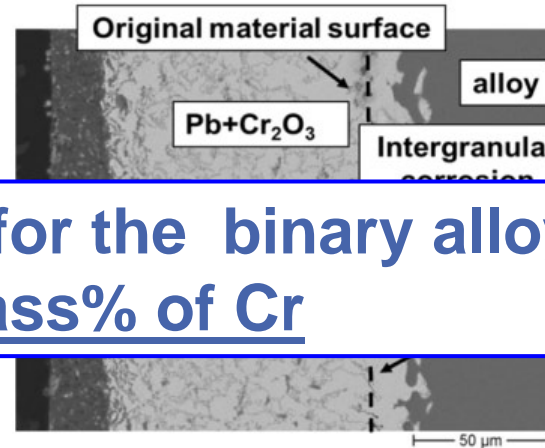
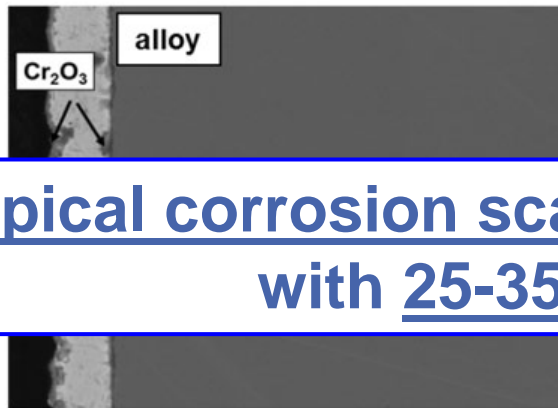
- Ni25Cr has higher concentration of Ni-Oxide on the material surface
- Both materials provide a thin Cr-oxide film

Binary Ni-Cr alloys

Ni30Cr

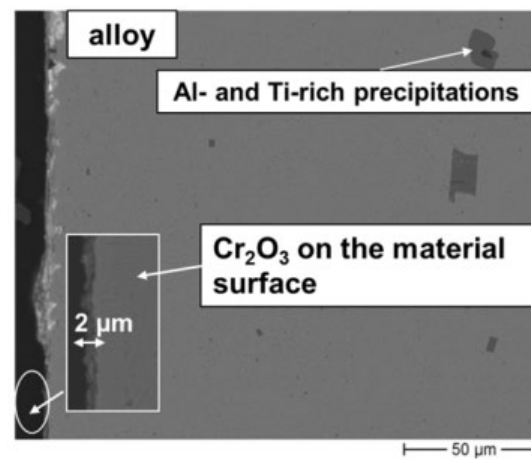
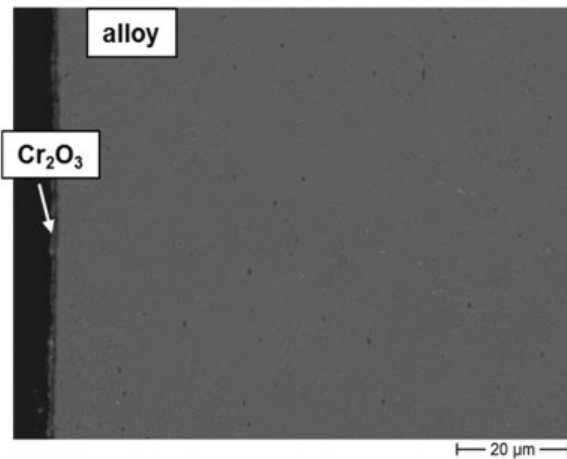
Initial Phase/ 24 h

120 h

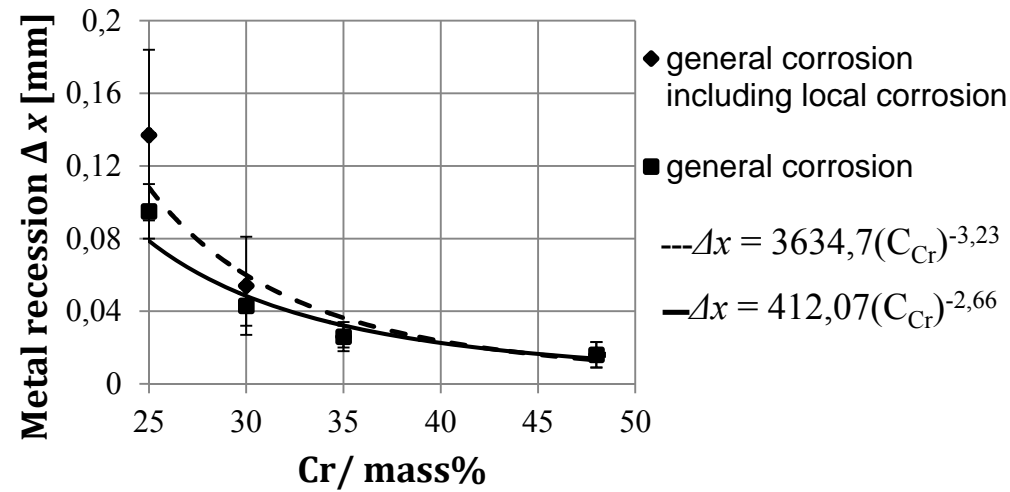


Typical corrosion scale for the binary alloys with 25-35 mass% of Cr

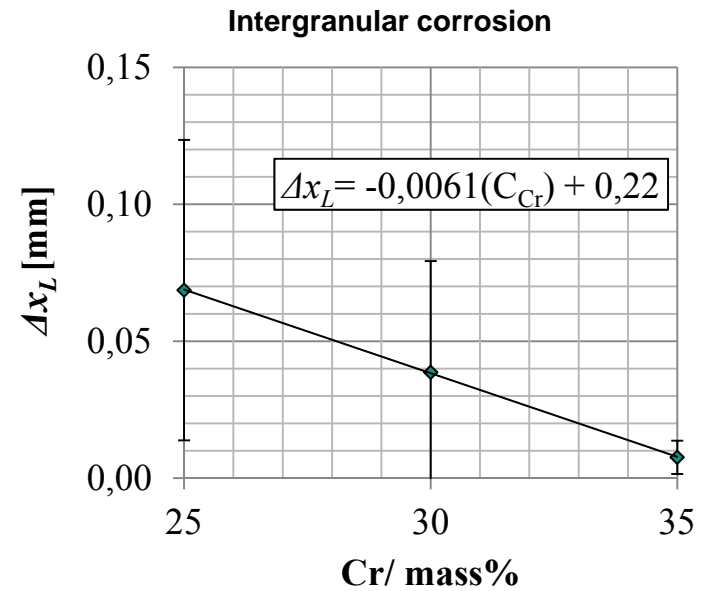
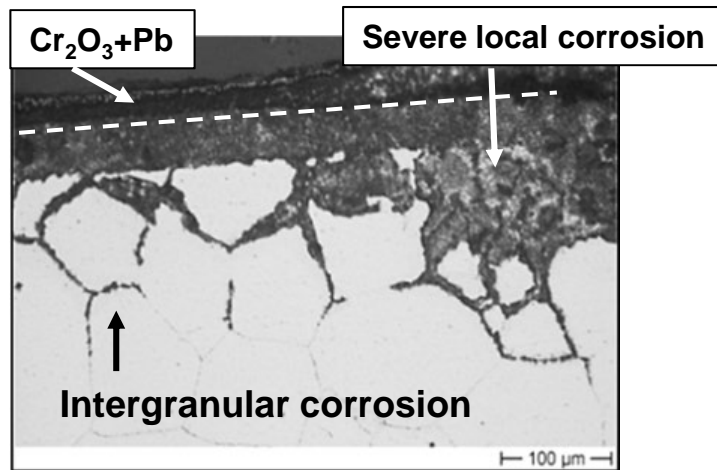
Ni48Cr



Material degradation



Ni25Cr



Analysis of oxidation and dissolution behavior of binary NiCr-alloys

Cr-Oxidation

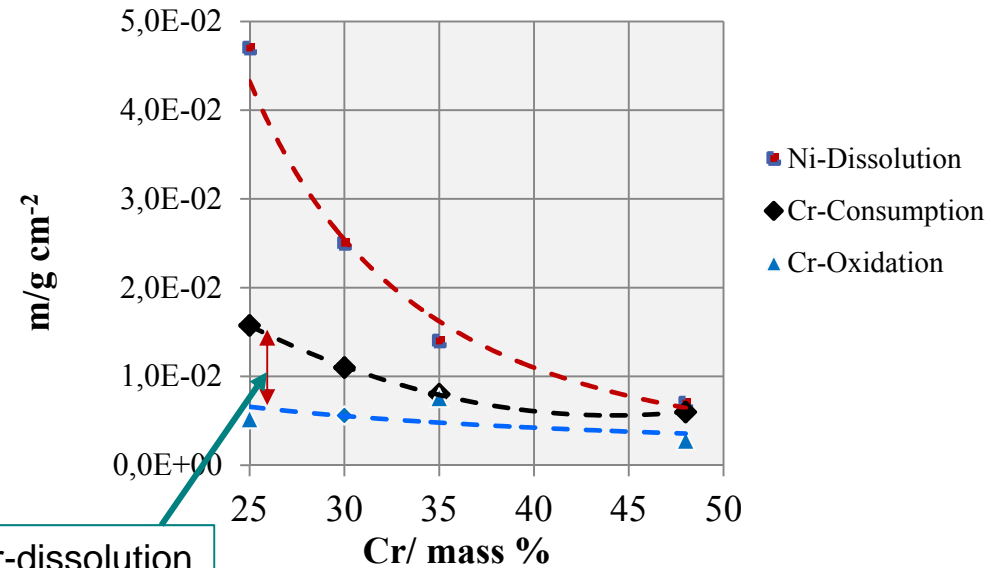
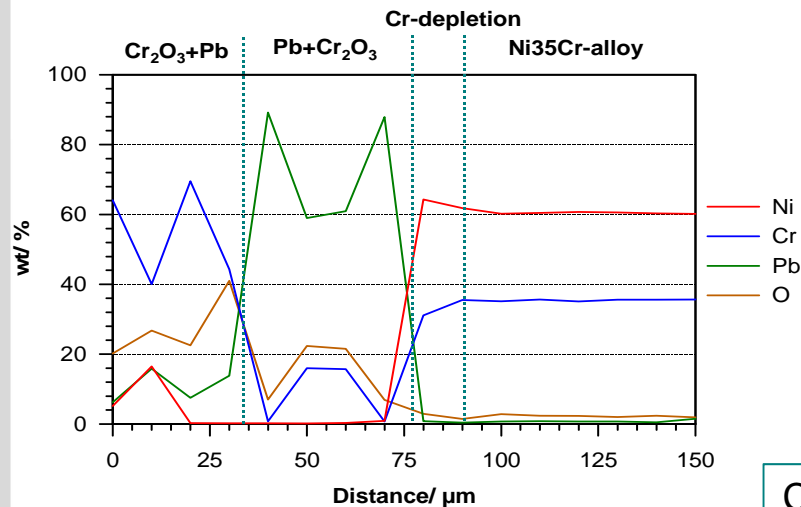
$$m_{Cr_{depletion}} / \frac{g}{cm^2} = \rho_{NiCr} (\chi_{Cr}^0 - \chi_{Cr}^*) x_{deplet}$$

$$m_{Cr_{consumption}} / \frac{g}{cm^2} = \rho_{NiCr} \chi_{Cr}^0 x_{consum}$$

$$m_{Cr_{oxidation}} / \frac{g}{cm^2} = \rho_{Cr_2O_3} \chi_{Cr_2O_3} x_{oxide}$$

Ni-Dissolution

$$m_{Ni_{dissolution}} / \frac{g}{cm^2} = \rho_{NiCr} \chi_{Ni}^0 x_{dissolved}$$

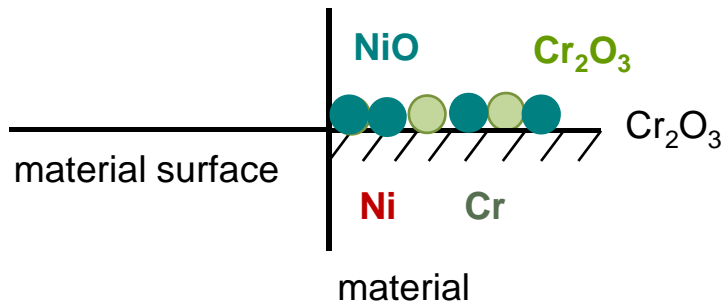


Cr-dissolution

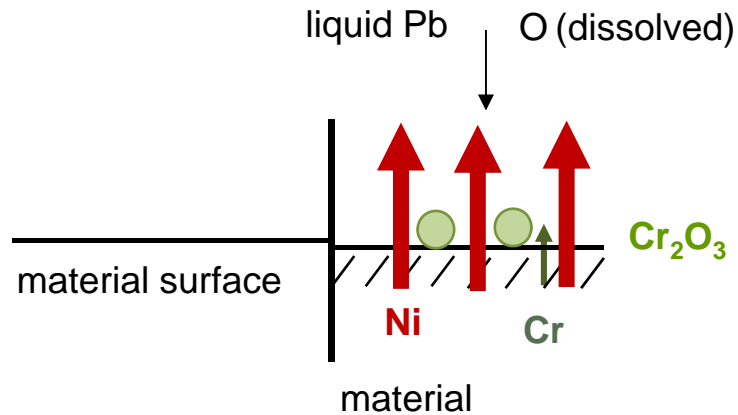
Corrosion mechanism of binary Ni-Cr-alloys

Ni25-35Cr

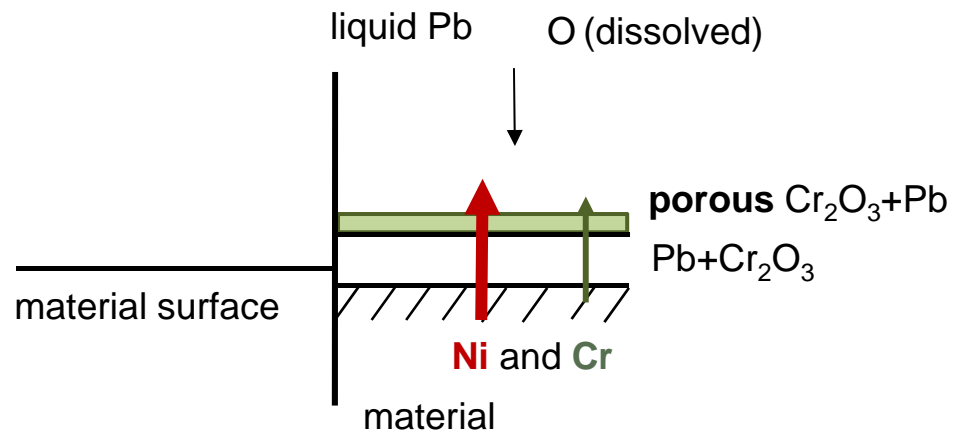
after „pre oxidation“



start of „initial phase“



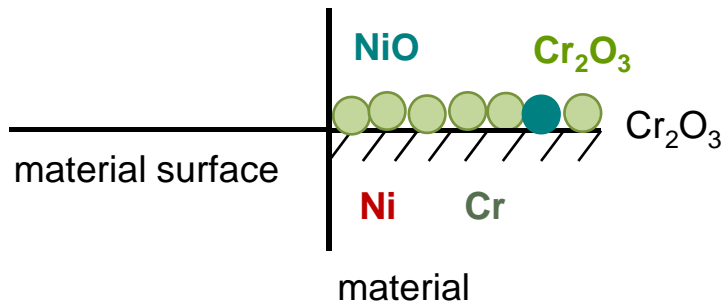
Finish of entire experiment



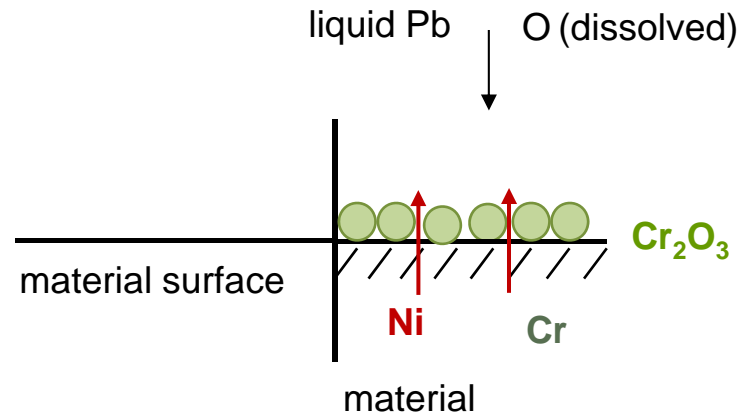
Corrosion mechanism of binary Ni-Cr-alloys

Ni48Cr

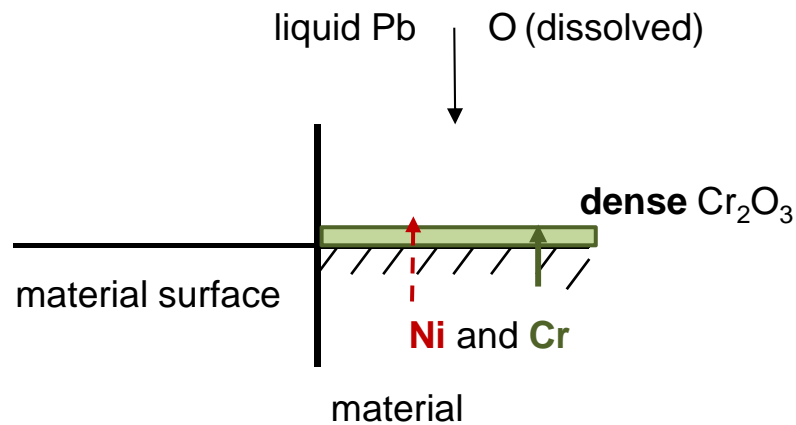
after „pre oxidation“



start of „initial phase“



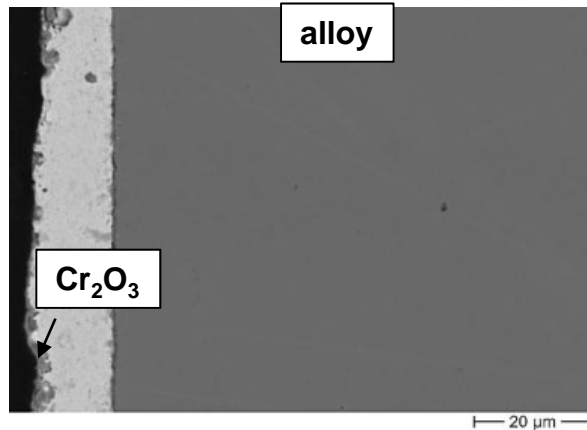
Finish of entire experiment



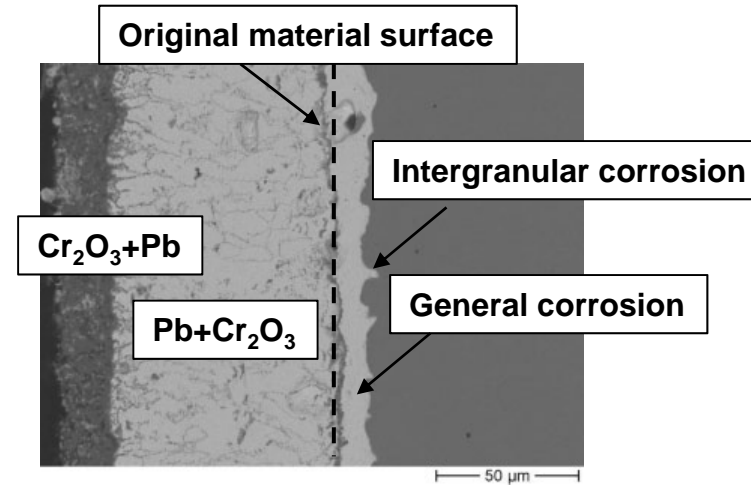
Ternary Ni35Cr1-5Al alloy

Ni35Cr

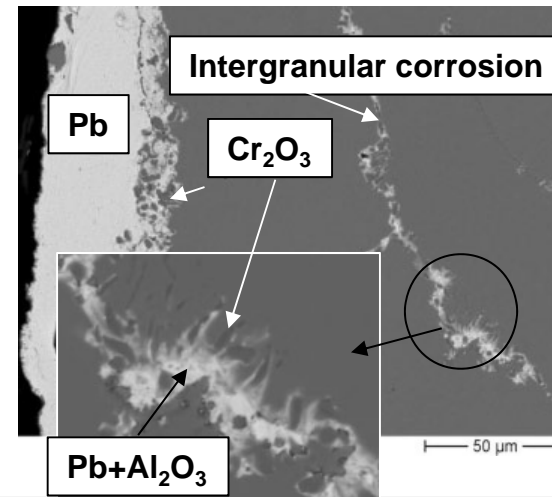
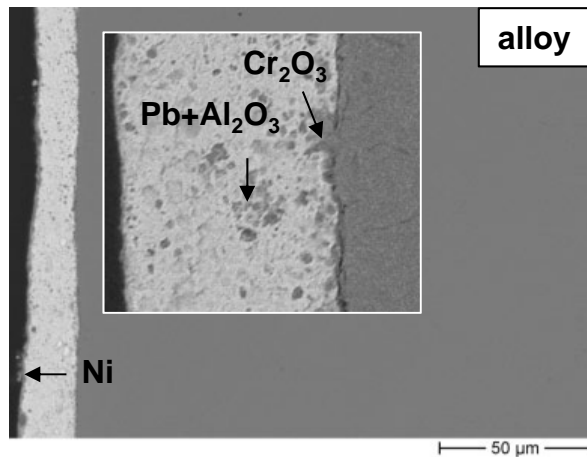
Initial Phase/ 24 h



120 h



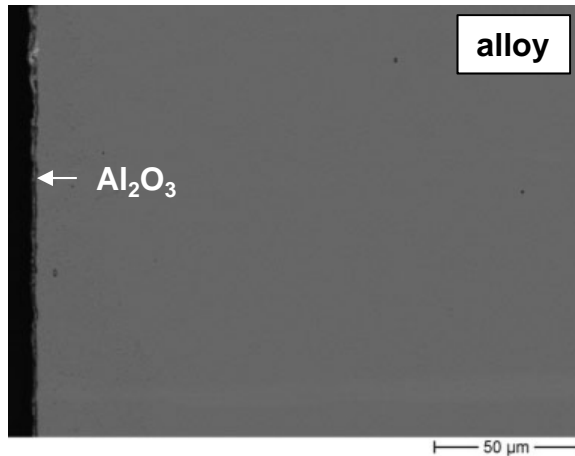
Ni35Cr1Al



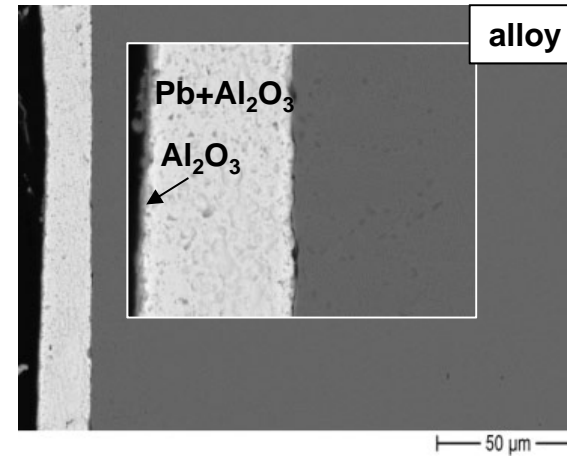
Ternary Ni35Cr1-5Al alloy

Ni35Cr3Al

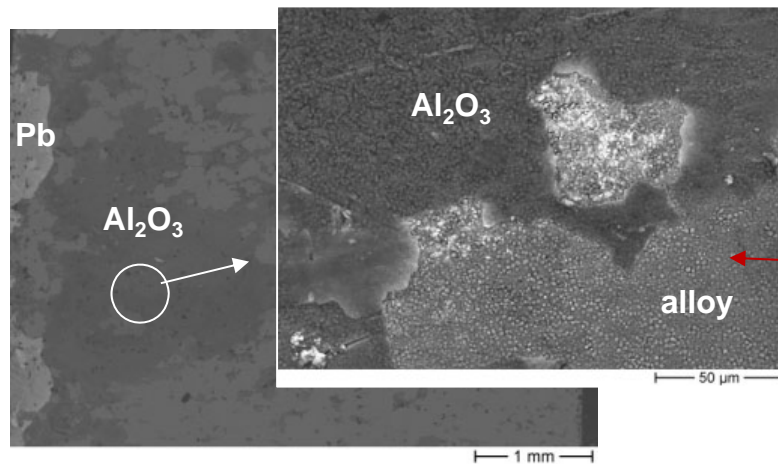
Initial Phase/ 24 h



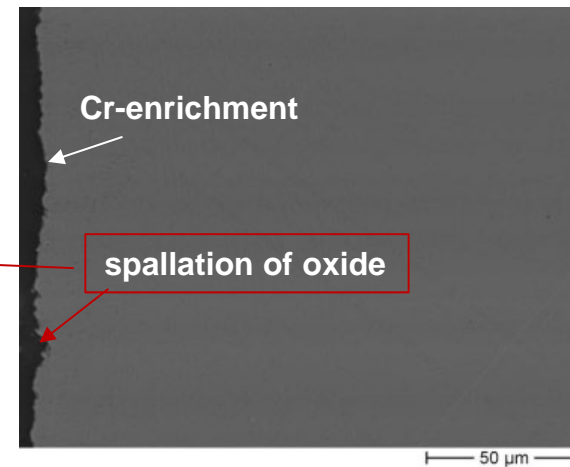
120 h



surface/ 120 h



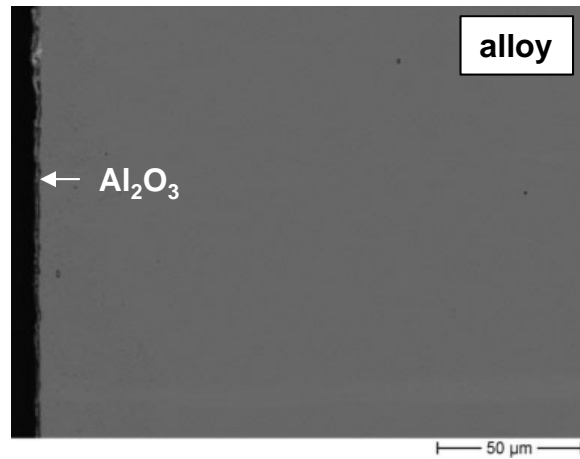
120 h



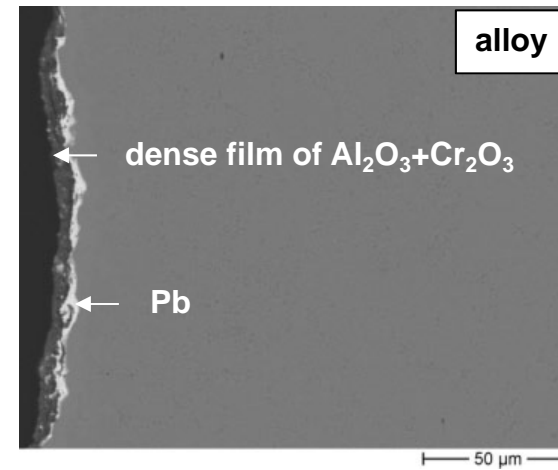
Ternary Ni₃₅Cr₁₋₅Al alloy

Ni₃₅Cr₅Al

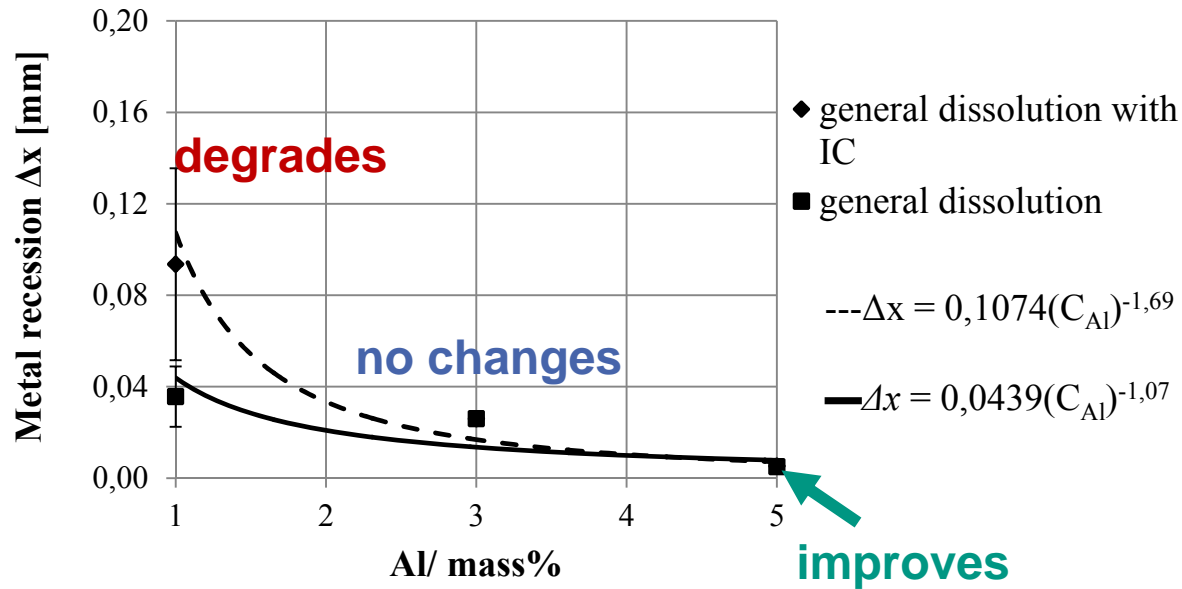
Initial Phase/ 24 h



120 h



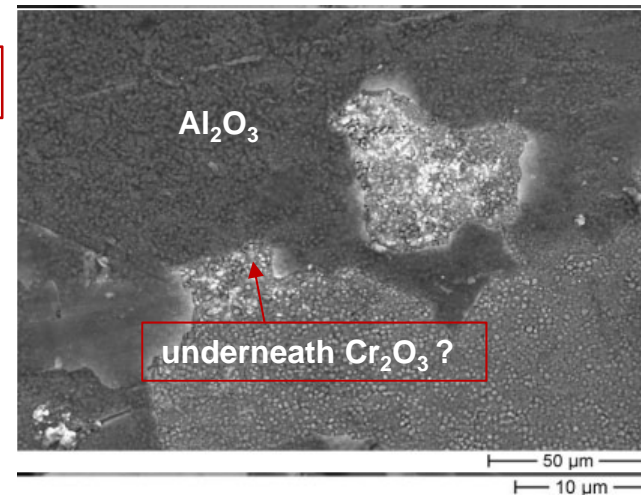
Material loss depending on Al-content



Obstruction of Cr-oxidation on the material surface

+

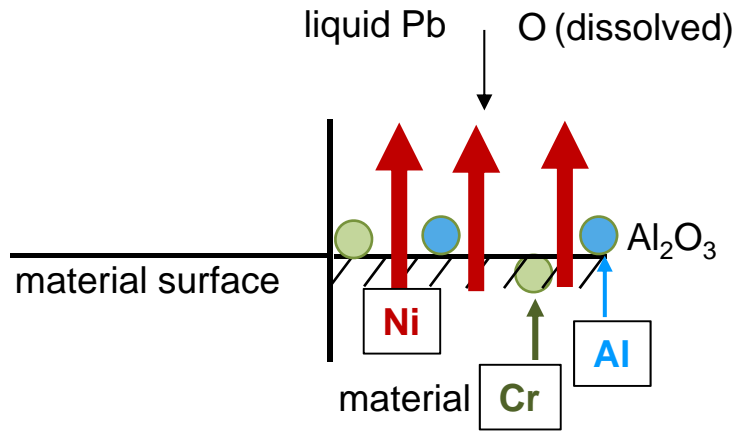
Low adhesion of oxide film



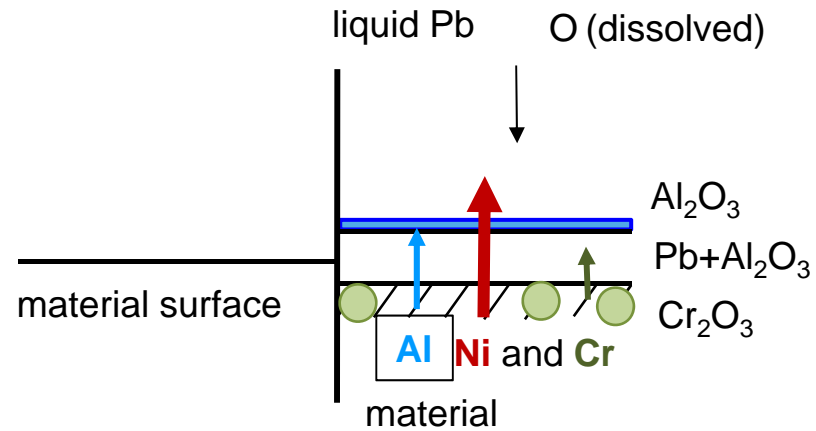
Corrosion mechanism on ternary Ni35Cr-alloys

Ni35Cr1-3Al

start

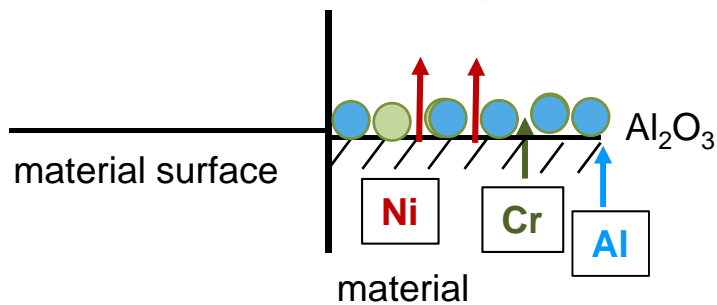


finish

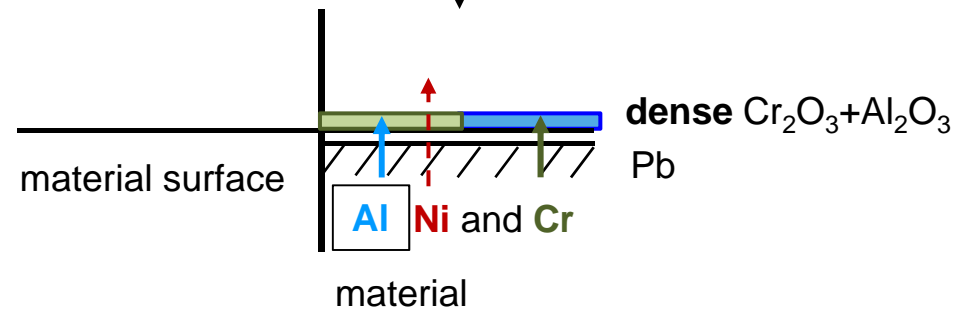


Ni35Cr5Al

liquid Pb O (dissolved)



liquid Pb O (dissolved)



Conclusions

1. The significant corrosion of binary (Ni25-35Cr mass%) and ternary Ni-Cr-alloys (1-3 mass%) could be explained by:
 - a) formation of porous oxide film away from material surface
 - b) intergranular corrosion
 - c) spallation of oxide film
2. This is supported by high Ni and Cr-dissolution instead of only oxidation of Cr. Also addition of less noble Al leads to a decrease of Cr-oxidation, but the Al-content is not high enough to form stable Al_2O_3 .
3. Increasing of Cr (48 mass%) and Al-content (5 mass%) improves corrosion performance with respect to close position of the dense oxide layer to the material surface.
4. Controlling of dissolution process (reduction of metal recession) by addition of alloying elements is a main issue for further investigation of both materials.

Thanks for your attention

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Programme within the cross-cutting project
GETMAT (contract no.FP7-212175) is
gratefully acknowledged.