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

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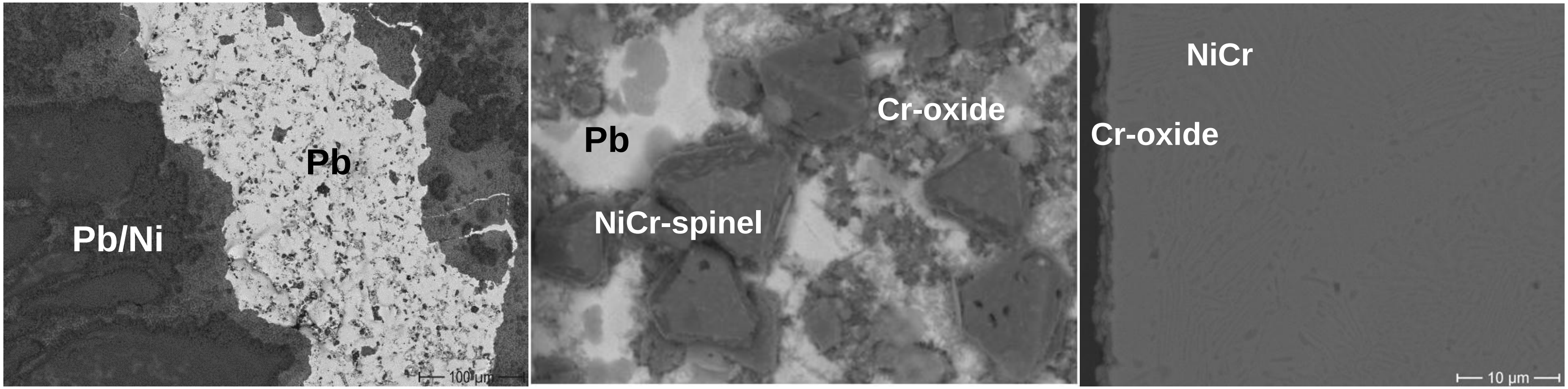


Application of Lead Technology to Subcritical (ADS) and Critical (LFR) Nuclear Systems/Reactors

Karlsruher Institut für Technologie

LFR

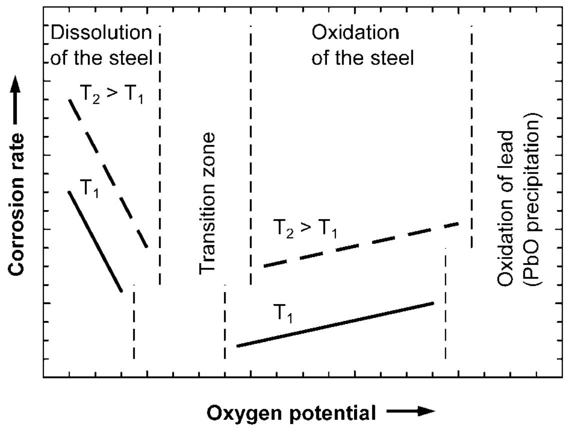
- One of the concepts for the 4th generation of nuclear power plants (Gen IV)
- In the long-term, Pb as primary coolant at maximum 800°C
- Short- to mid-term: Pb- or LBE-cooled at 450 – 550°C

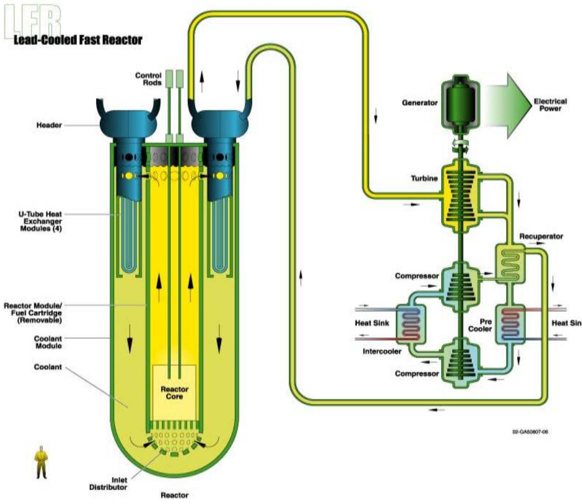
ADS

- 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

Corrosion of structure materials/ steels

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





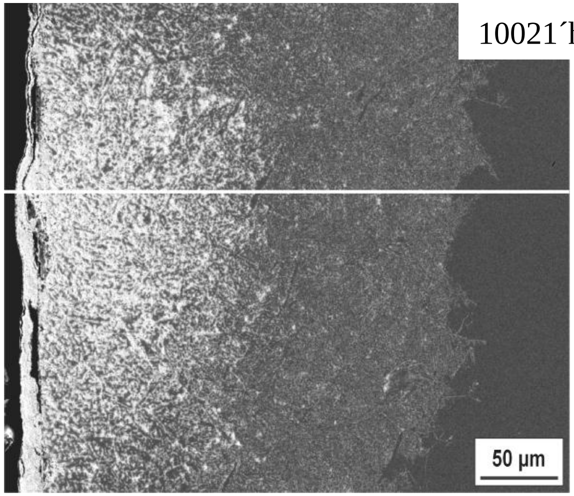
Motivation

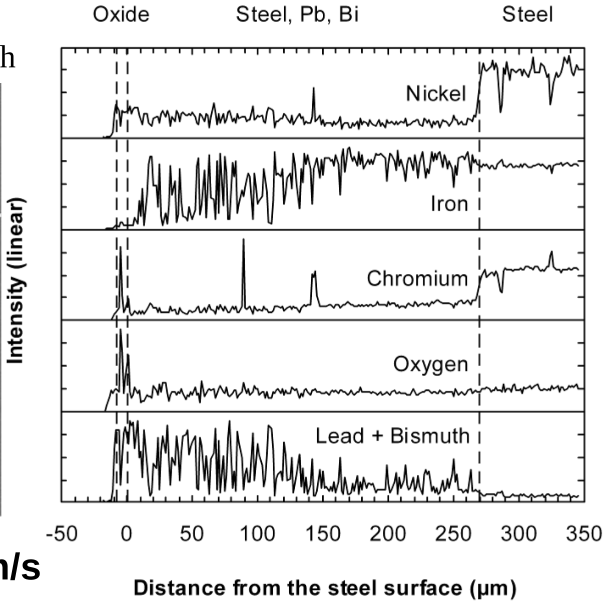
At T > 600°C Ni-based alloys because of appropriate thermomechanical properties

BUT:

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

Fe12Cr16Ni-316L Steel





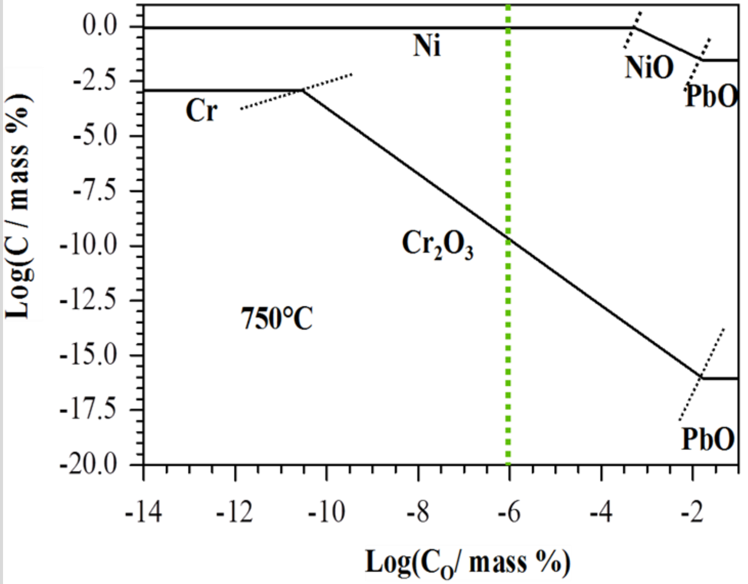
T= 550°C, $c_O = 1.6\times10^{-6}$ %, v = 2 m/s

Which Cr-content can suppress Ni-dissolution ?

Material

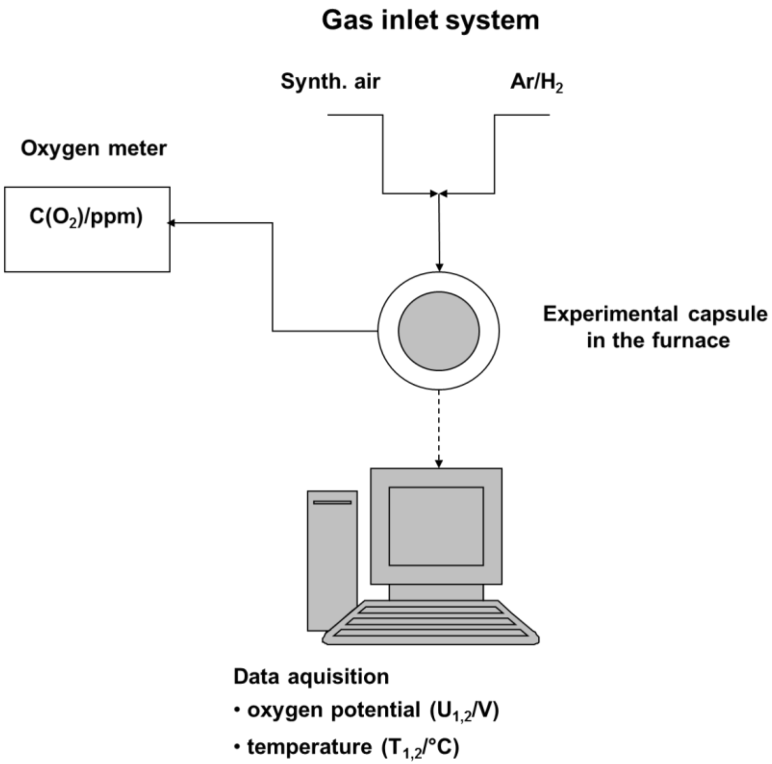
Elements	Ni	Ni25Cr	Ni30Cr	Ni35Cr	Ni48Cr	Ni35Cr1Al	Ni35Cr3Al	Ni35Cr5Al
Ni (mass%)	**99,9**	**74,36**	**69,36**	**64,43**	**52,39**	**63,74**	**61,74**	**60,31**
Cr (mass%)		**25,33**	**30,35**	**35,25**	**48,01**	**35,10**	**35,20**	**34,64**
Al (mass%)		0,31	0,29	0,32	0,30	**1,10**	**3,05**	**5,04**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



Gas inlet system

Synth. air

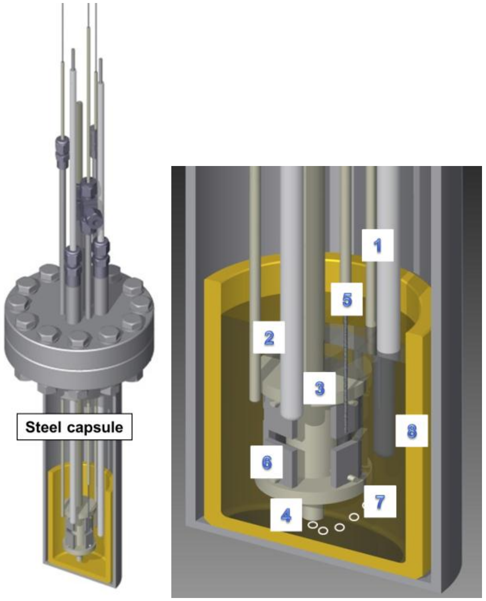
Ar/H_2

Oxygen meter

C(O_2)/ppm)

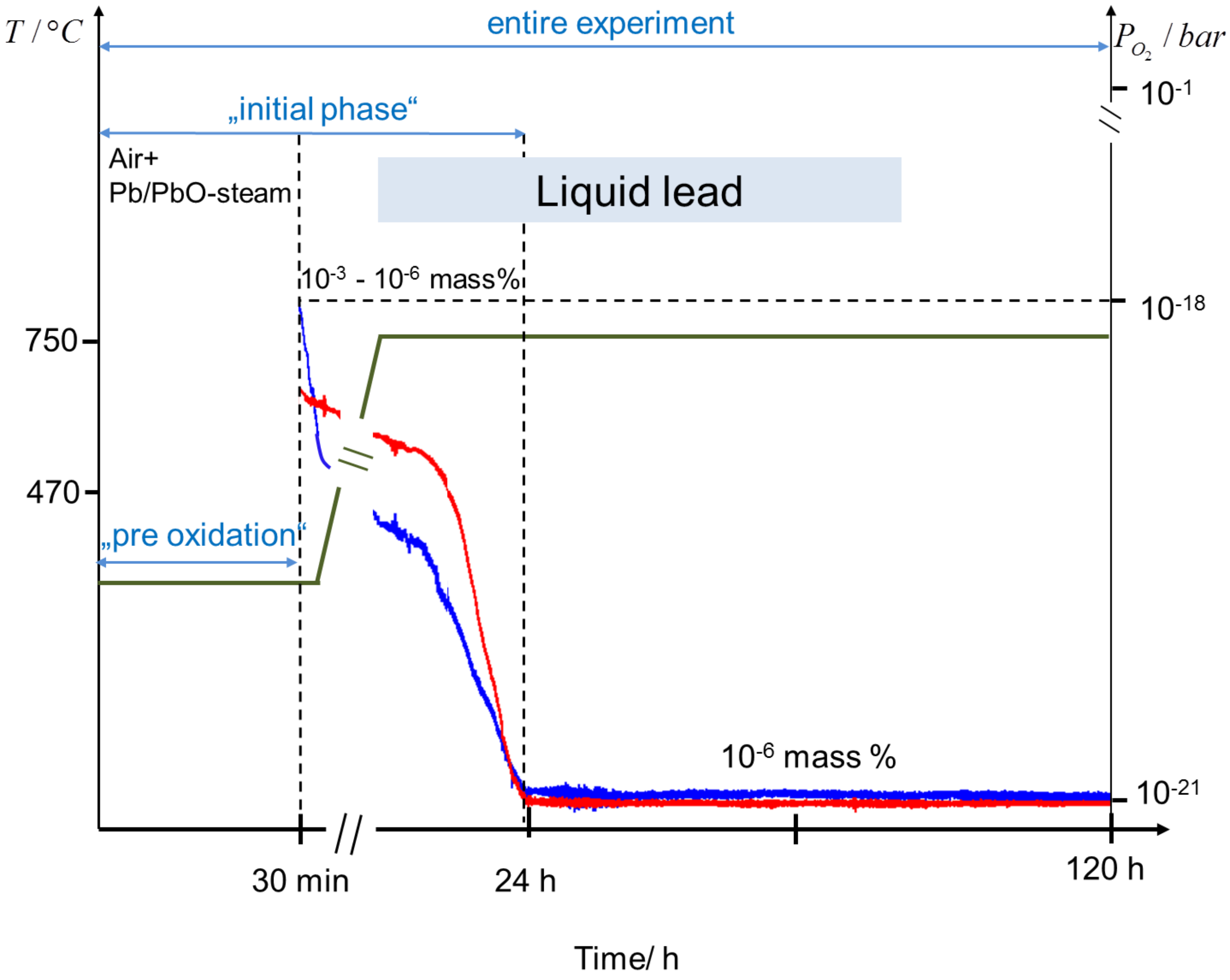
Experimental capsule in the furnace

Data aquisition
- **oxygen potential ($U_{1,2}$/V)**
- **temperature ($T_{1,2}$/°C)**



1. O_2- sensor +thermocouple on the 1st level
2. O_2- sensor +thermocouple on the 2nd level
3. Sample holder (Al_2O_3)
4. Gas bubbling tube (Al_2O_3)
5. Mo-electrode
6. Specimens (15x10x2 mm)
7. Oxygen containing liquid lead
8. Crucible (Al_2O_3)

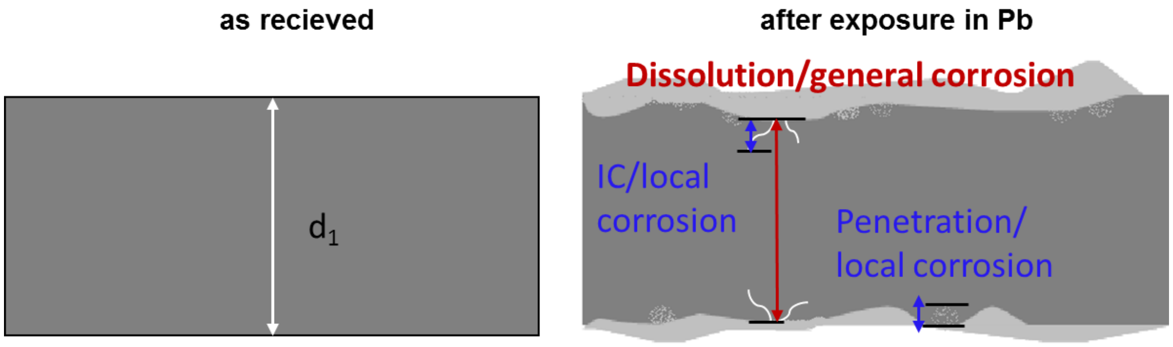
Experimental procedure



Quantification of specimens bevor and after tests

Material loss

Cross-section

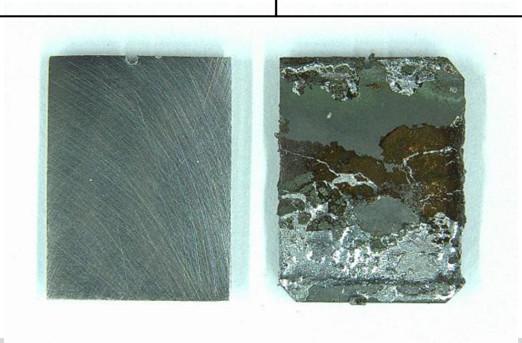


$\Delta x = (d_1 - d_2)/2$

d_2

Surface

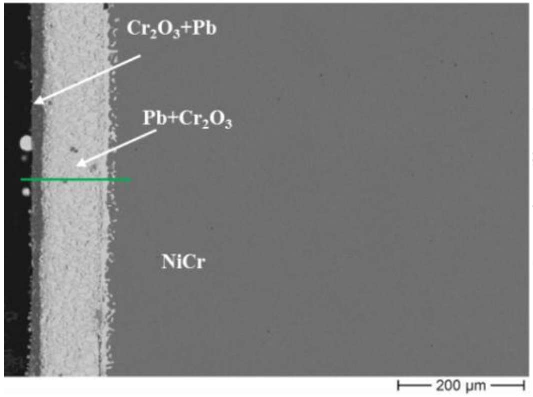
XPS	**SEM/EDS**
- „pre oxidation“ 30 min	- „Initial phase“/ 24 h - 120 h

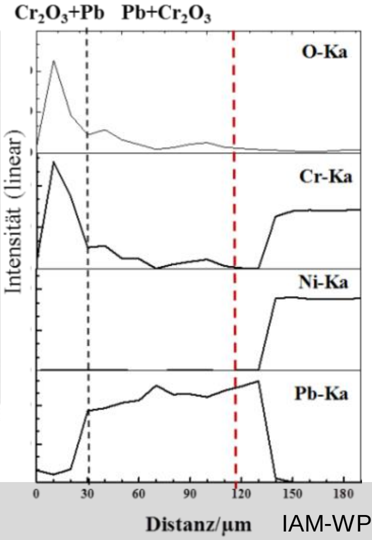


Cross-section

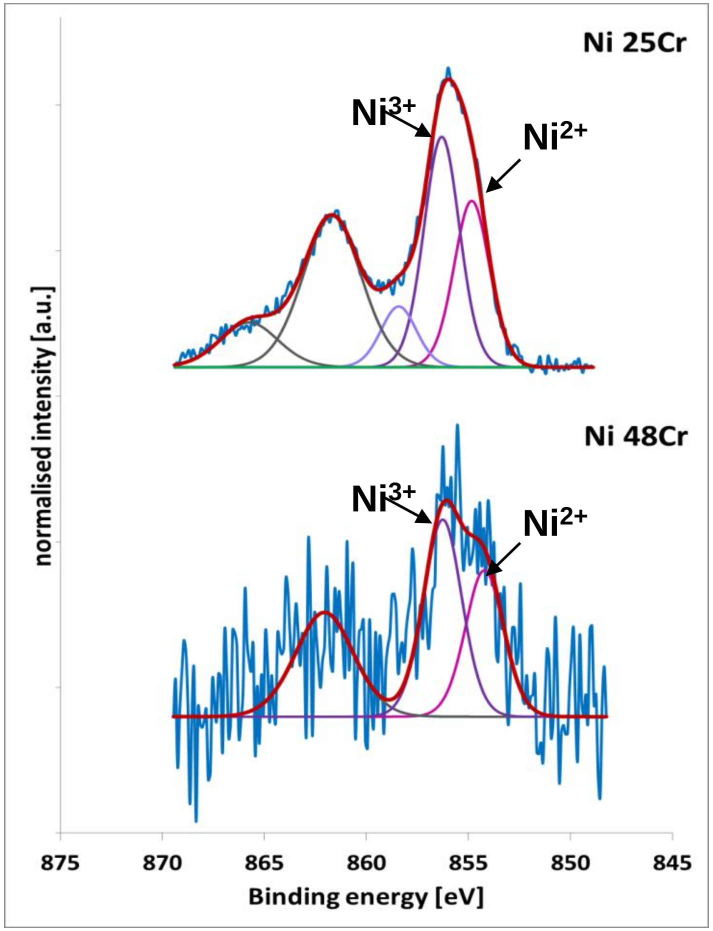
SEM/EDS

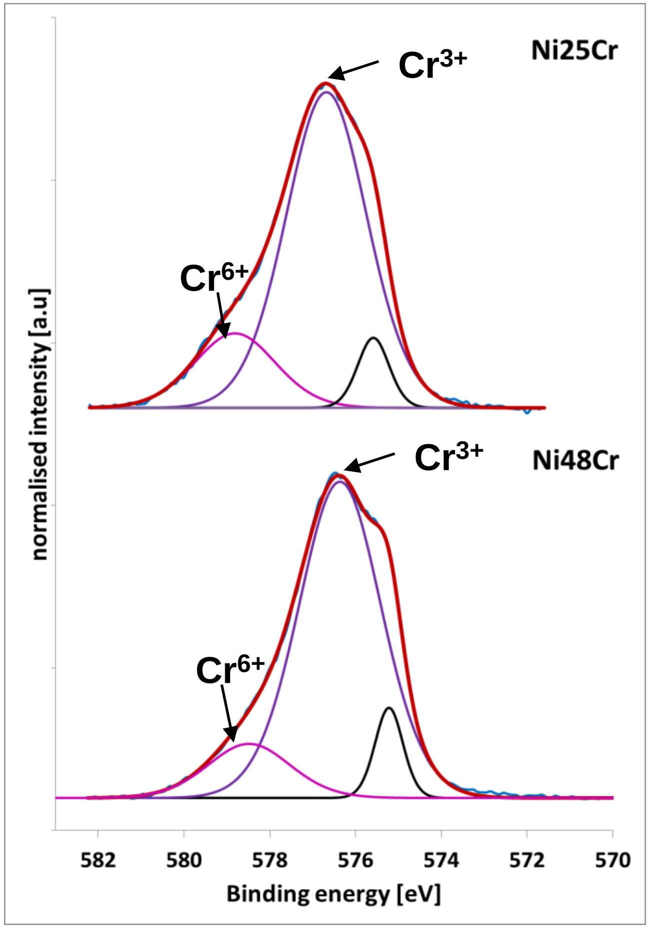
- „Initial phase“/24 h
- 120 h





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



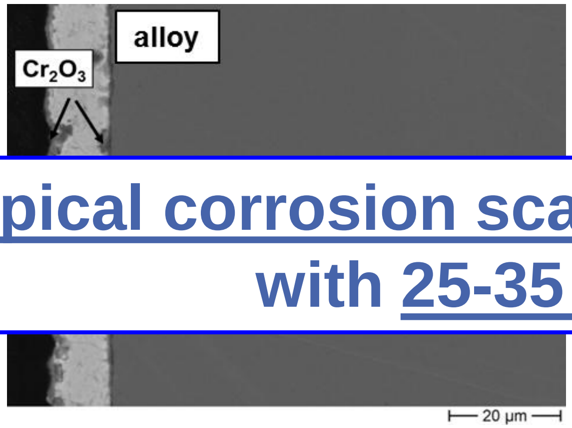


- Ni25Cr has higher concentration of Ni-Oxide on the material surface
- Both materials provide a thin Cr-oxide film

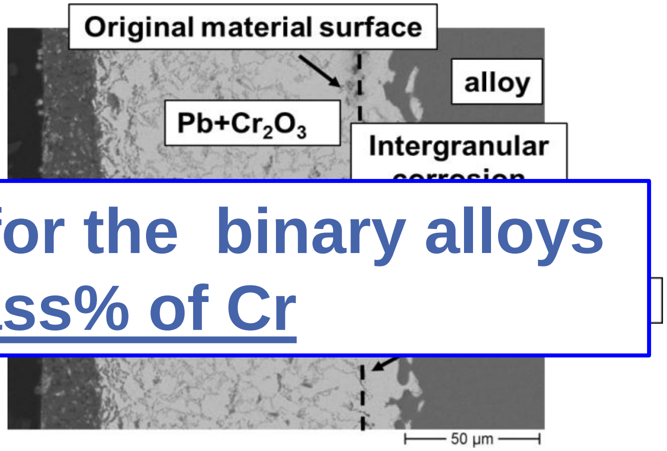
Binary Ni-Cr alloys

Ni30Cr

Initial Phase/ 24 h

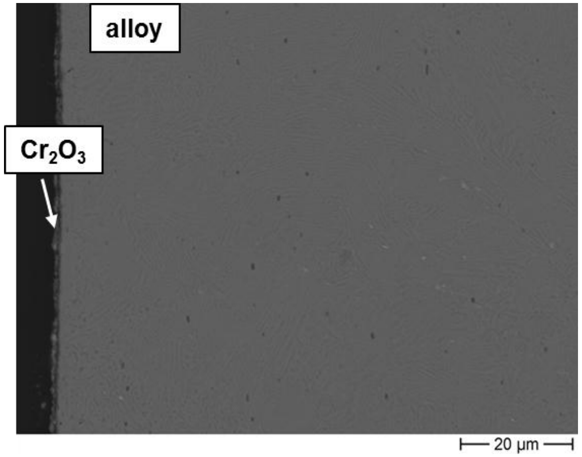


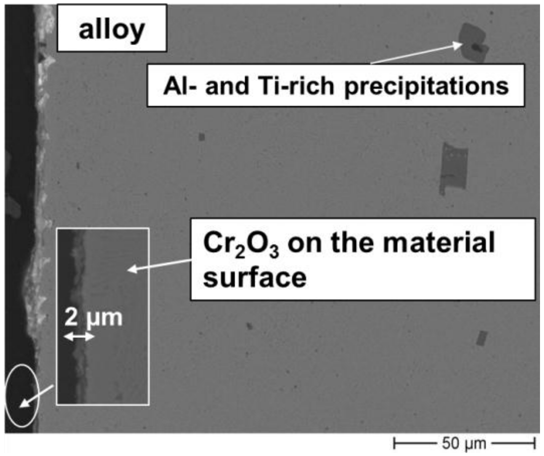
120 h



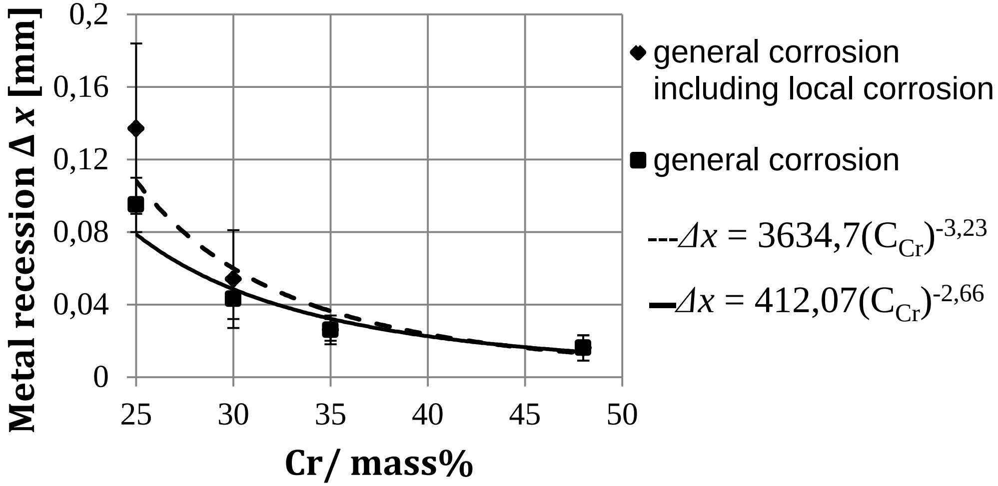
Typical corrosion scale for the binary alloys with 25-35 mass% of Cr

Ni48Cr

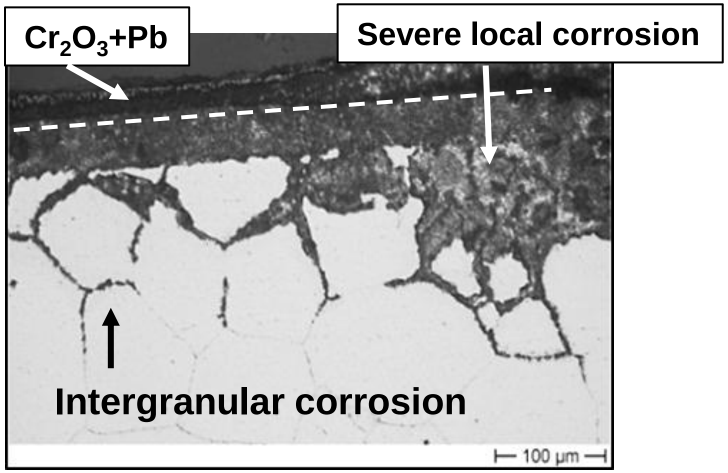


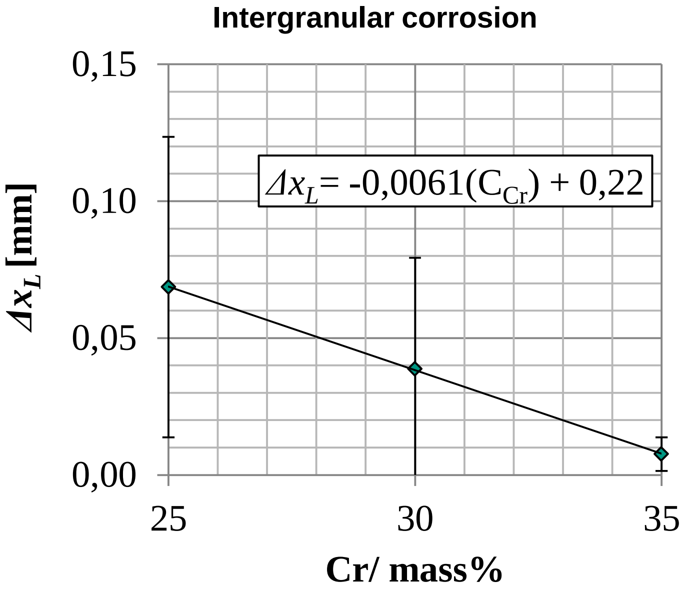


Material degradation



Ni25Cr





Analysis of oxidation and dissolution behavior of binary NiCr-alloys

Cr-Oxidation

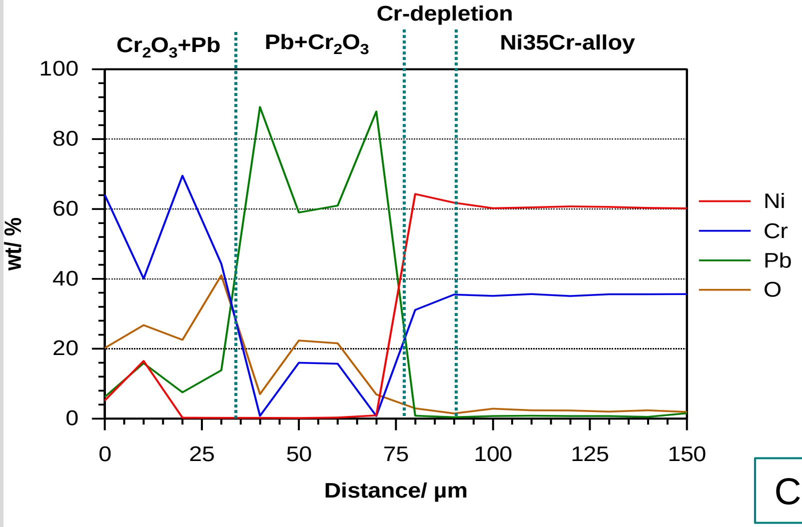
$$m_{Cr_{depletion}} / \frac{g}{cm^2} = \rho_{NiCr} (\chi^0_{Cr} - \chi^*_{Cr}) x_{deplet}$$

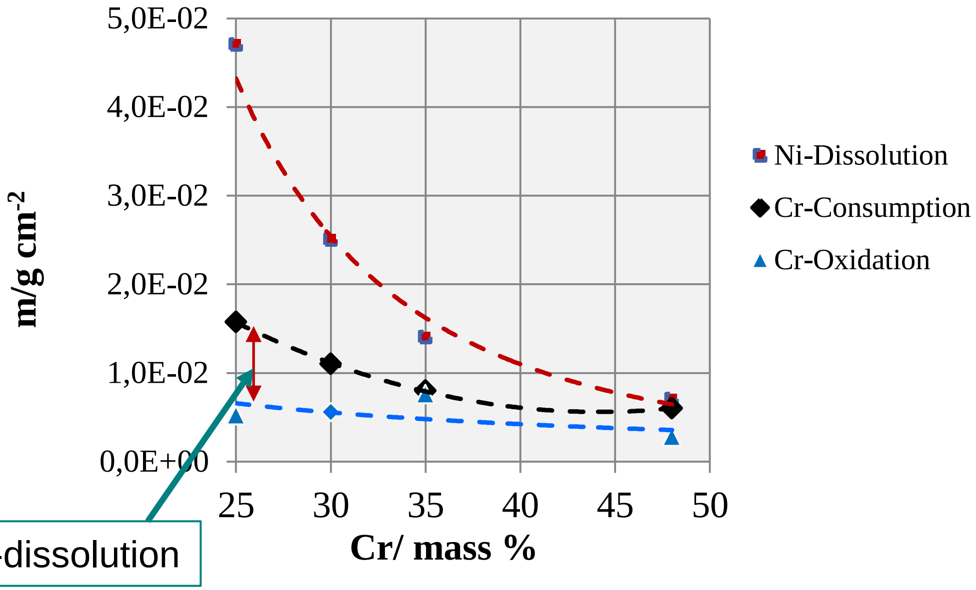
$$m_{Cr_{consumption}} / \frac{g}{cm^2} = \rho_{NiCr} \chi^0_{Cr} x_{consum}$$

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

Ni-Dissolution

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



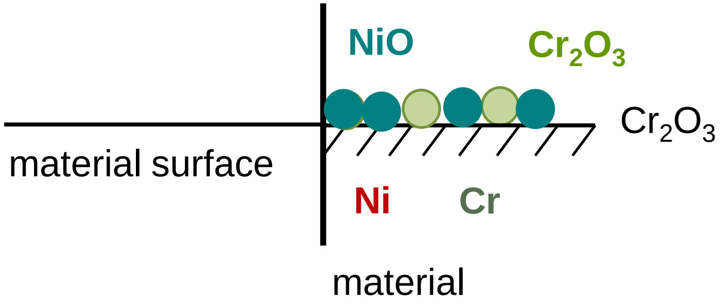


Cr-dissolution

Corrosion mechanism of binary Ni-Cr-alloys

Ni25-35Cr

after „pre oxidation“



NiO

Cr_2O_3

Cr_2O_3

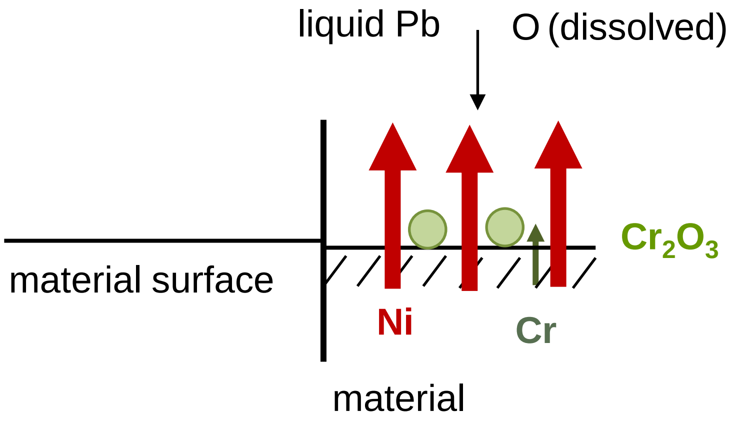
material surface

Ni

Cr

material

start of „initial phase“



liquid Pb

O (dissolved)

Cr_2O_3

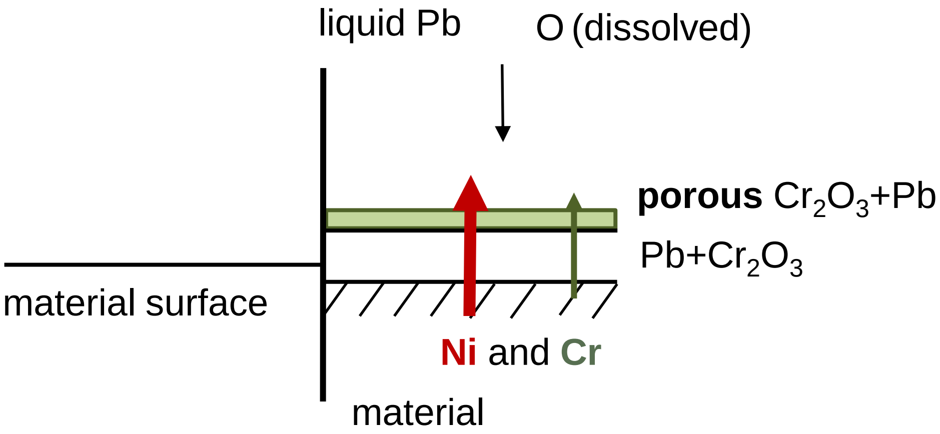
material surface

Ni

Cr

material

Finish of entire experiment



liquid Pb

O (dissolved)

porous Cr_2O_3+Pb

Pb+Cr_2O_3

material surface

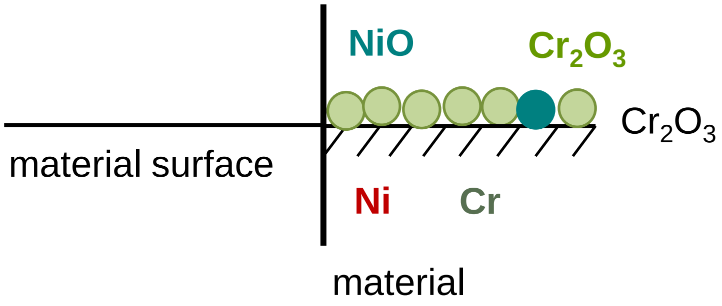
Ni and Cr

material

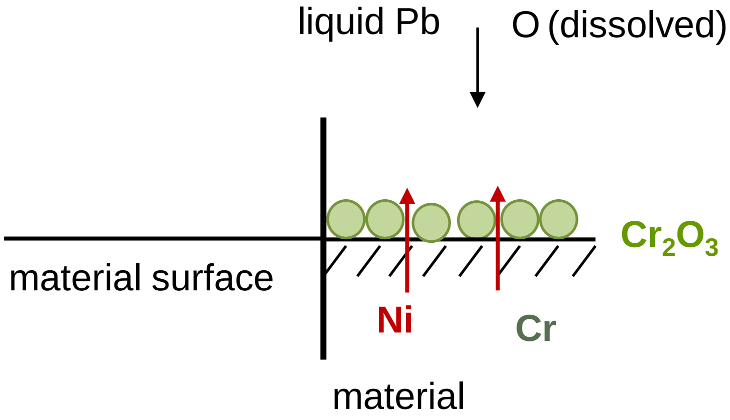
Corrosion mechanism of binary Ni-Cr-alloys

Ni48Cr

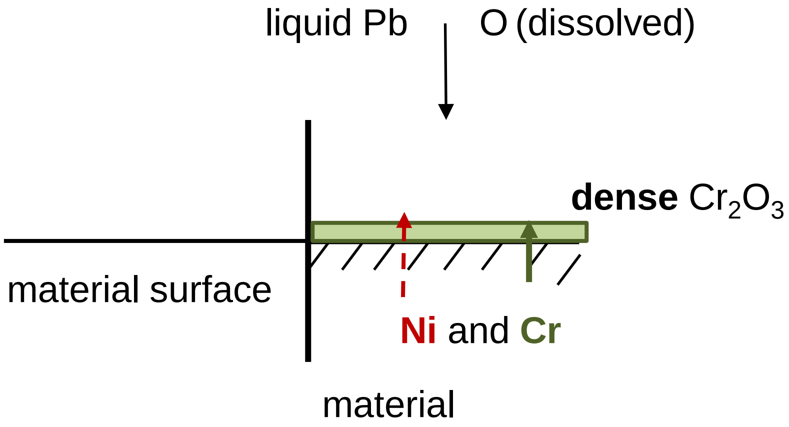
after „pre oxidation“



start of „initial phase“



Finish of entire experiment

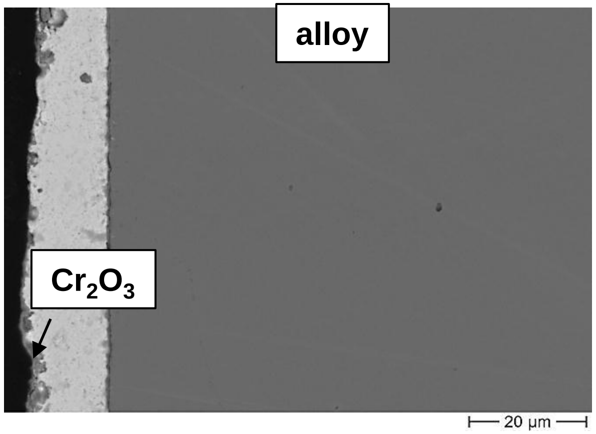


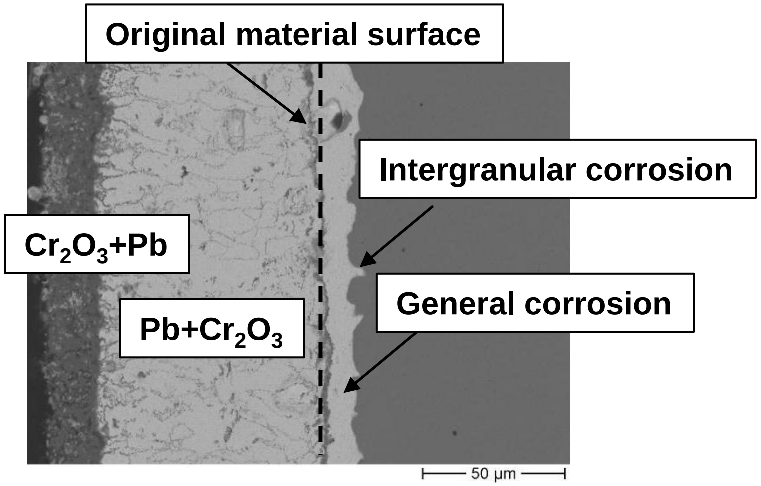
Ternary Ni35Cr1-5Al alloy

Ni35Cr

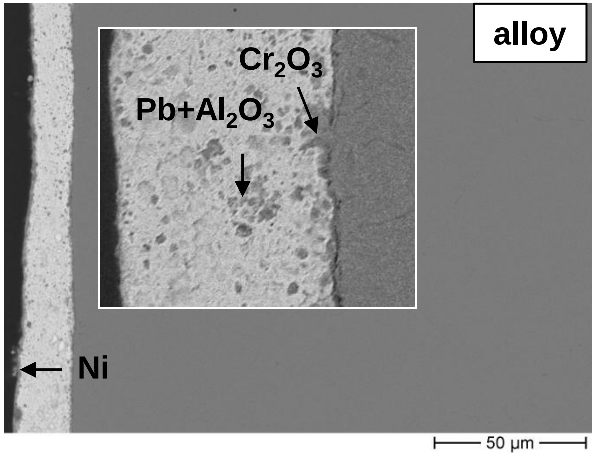
Initial Phase/ 24 h

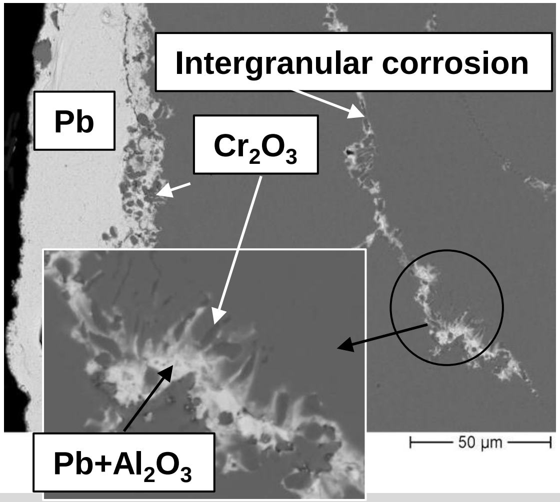
120 h





Ni35Cr1Al

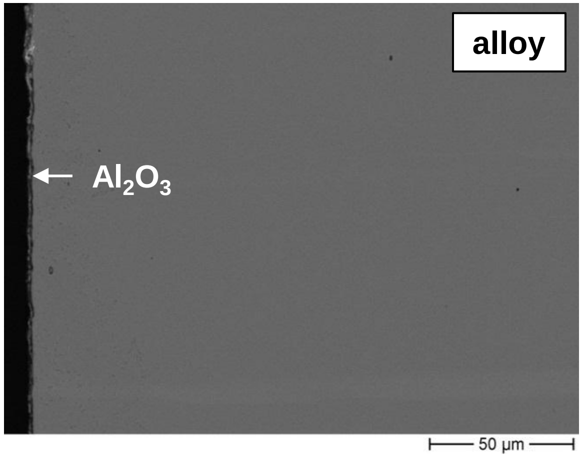




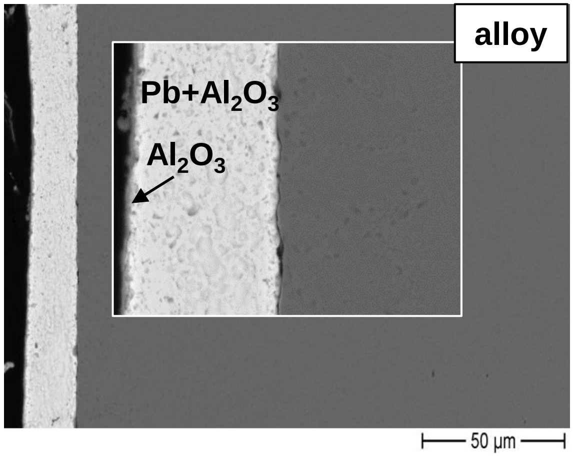
Ternary Ni35Cr1-5Al alloy

Ni35Cr3Al

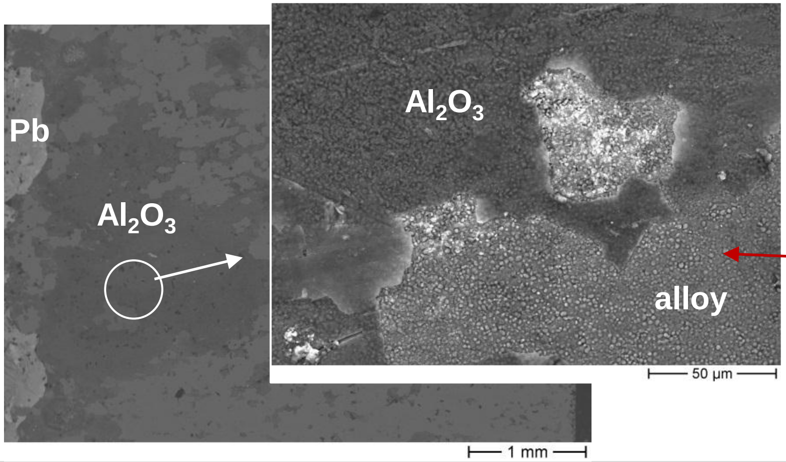
Initial Phase/ 24 h



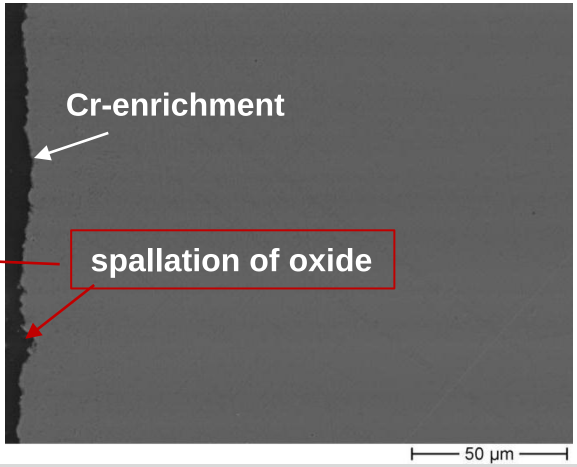
120 h



surface/ 120 h



120 h

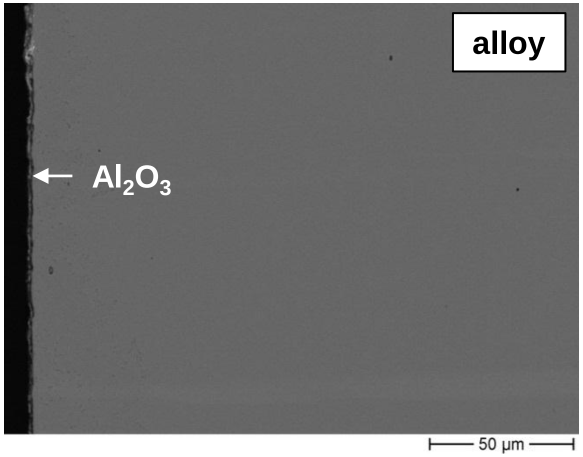


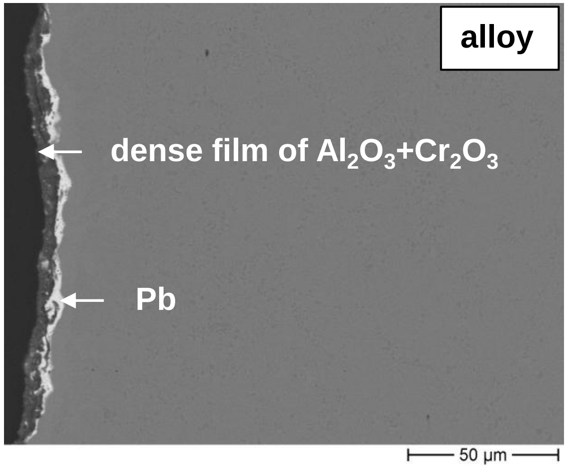
Ternary Ni35Cr1-5Al alloy

Ni35Cr5Al

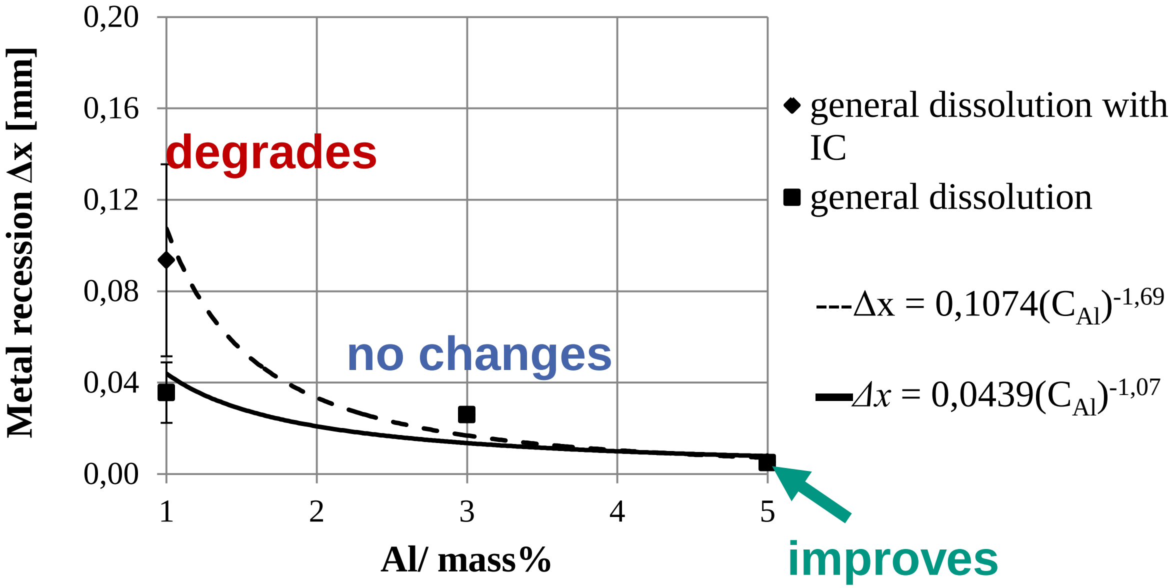
Initial Phase/ 24 h

120 h





Material loss depending on Al-content



---$\Delta x = 0{,}1074(C_{Al})^{-1{,}69}$

—$\mathit{\Delta x} = 0{,}0439(C_{Al})^{-1{,}07}$

degrades

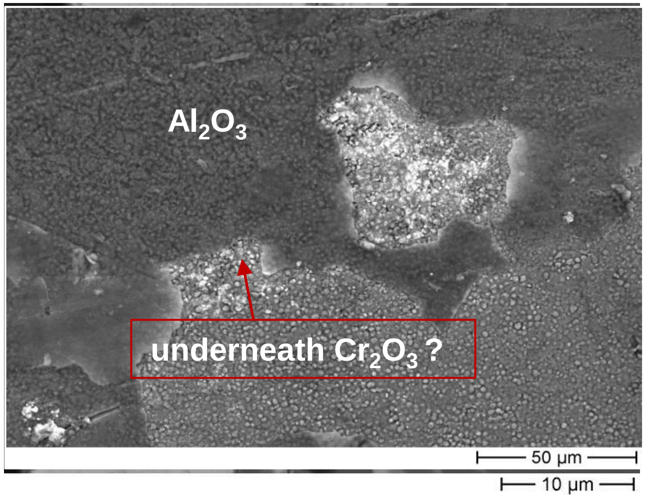
no changes

improves

Obstruction of Cr-oxidation on the material surface

+

Exfoliation of oxide film



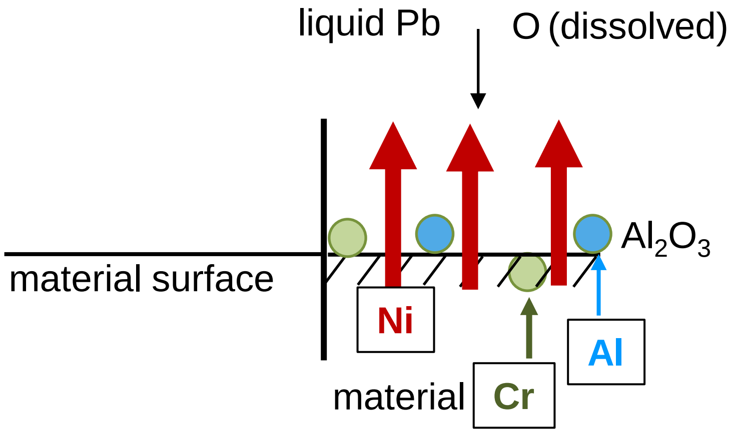
underneath Cr_2O_3 ?

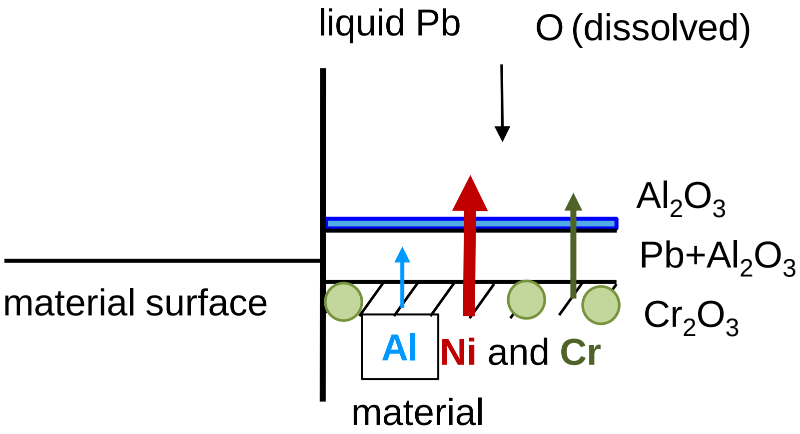
Corrosion mechanism on ternary Ni35Cr-alloys

Ni35Cr1-3Al

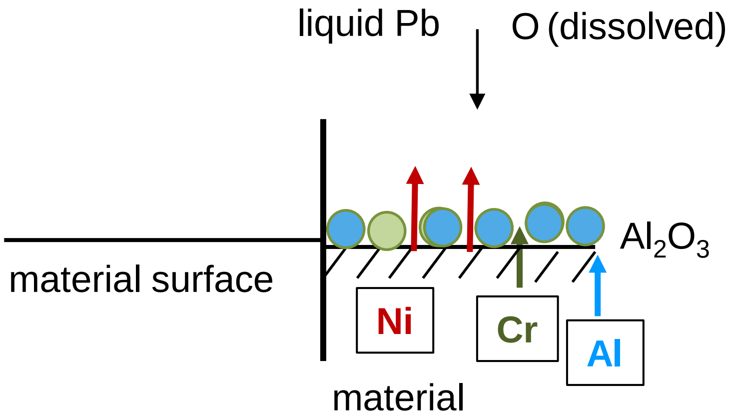
start

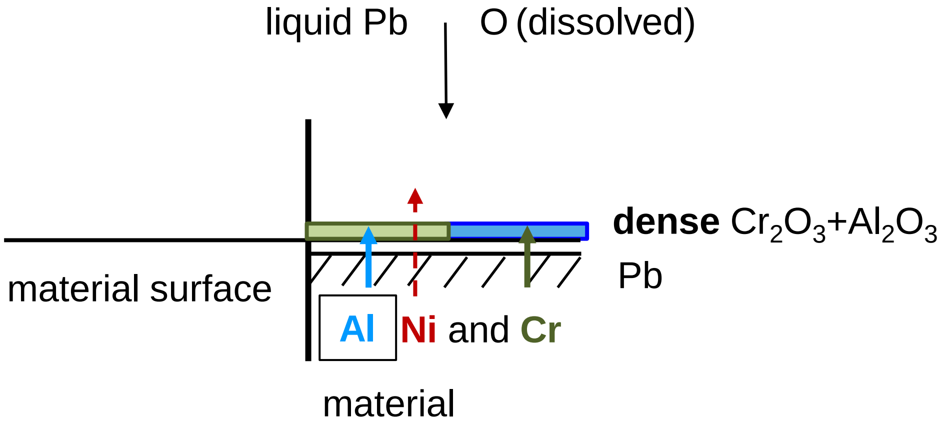
finish





Ni35Cr5Al





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

Funding by the EURATOM 7th Framework Programme within the cross-cutting project GETMAT (contract no.FP7-212175) is gratefully acknowledged.