Determination of Cr diffusivity in pure Ni and Ni-20Cr alloy

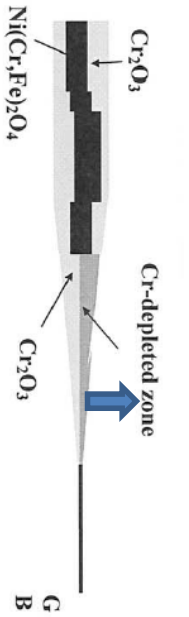
Thomas Gheno, Laure Martinelli, Clara Desgranges, François Jomard (CNRS)

Context: **WP4** environmental effect of cold-work on Stress Corrosion Cracking susceptibility

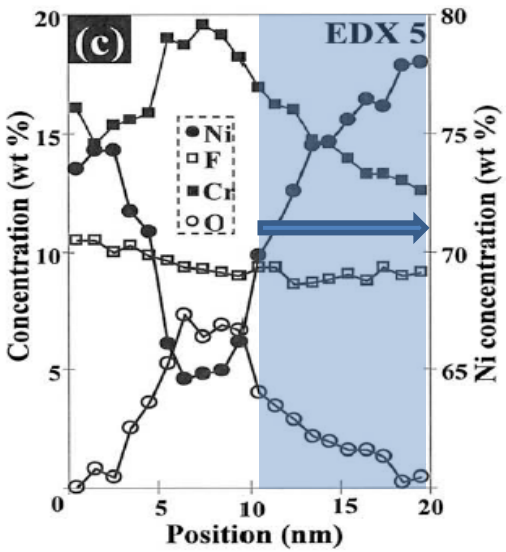
→ 4.2 Characterisation of cold work effects on microstructure

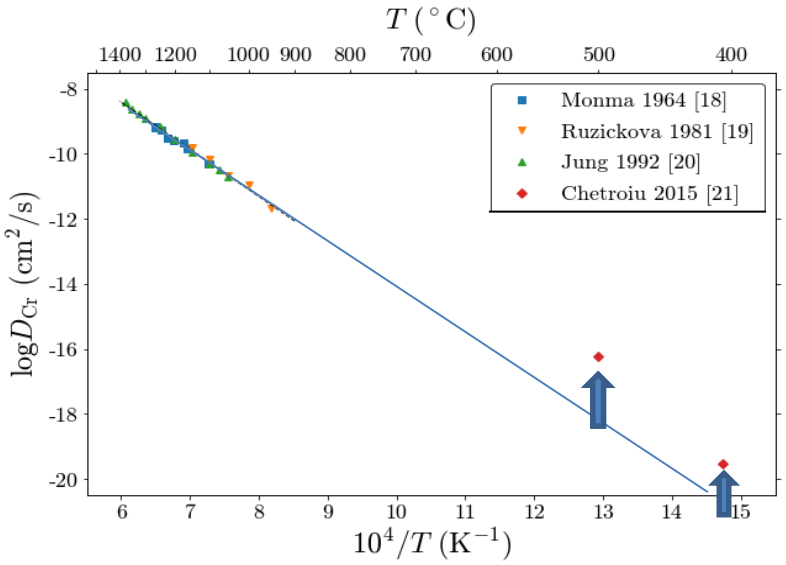
Objective is to understand the Cr depletion depth observed at low temperatures in oxidized cracks formed by stress corrosion cracking in PWR: extrapolation made from high temperature measurements of Cr diffusivity cannot explain it. However if diffusion coefficients are higher at low temperature (as data obtained by Chetriou *et al*), the Cr depletion depth could be explained

→ Need of Cr diffusion coefficient at low temperature



Sennour et al, JNM, 2009





Content

1. In volume
   - Cr in Ni
   - ^{54}Cr in Ni-20Cr
2. In grain boundaries (Cr in Ni)
   - Annealed samples, regimes B and C
   - Rolled samples

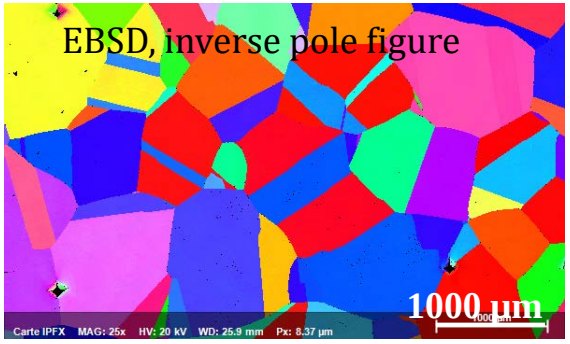
Method

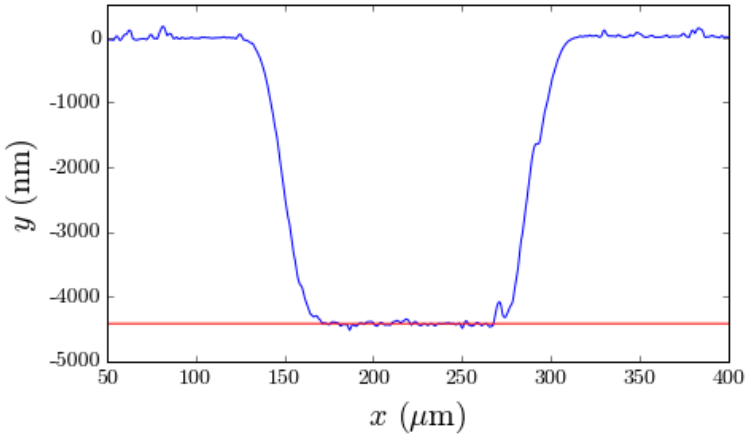
Experimental protocole:

- rolling-recristallization of the substrat (Ni/Ni-20Cr)
- Mechanical grinding until 1 µm
- Thin deposit (5 nm) of natural Cr (for diffusion in pure Ni)/^{54}Cr (for diffusion in Ni-20Cr) by sublimation
- Ageing in glass ampoule under vaccuum, with Zr chips
- Concentration profile measured by SIMS
- Abrasion depth is then measured by contact profilometric method

SIMS Analyses : ⦰ 8-60 µm
→ measure performed within one grain or for one single grain boundary

Ni rolled-recristallized



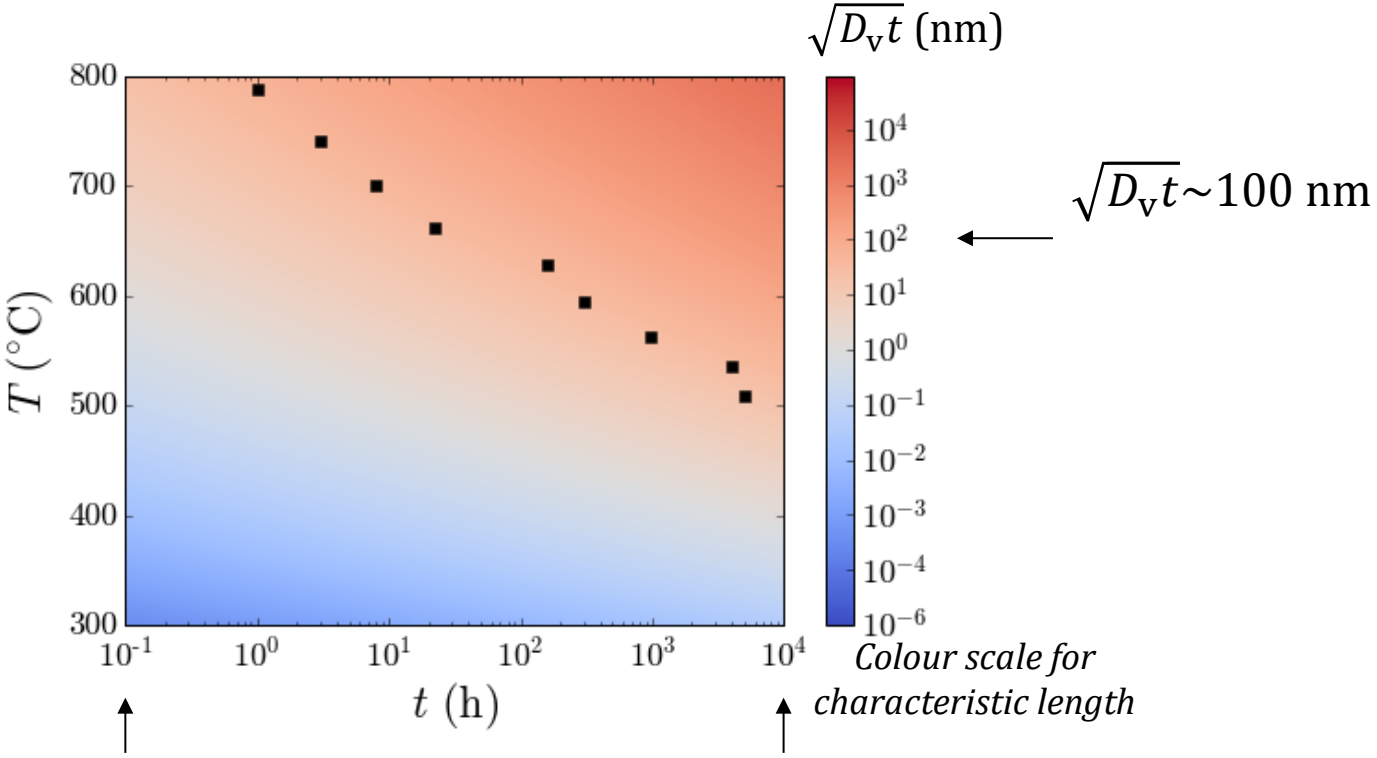


Depth profile of a SIMS crater

1. Volume diffusion:
temperature / time conditions for ageing

Conditions:

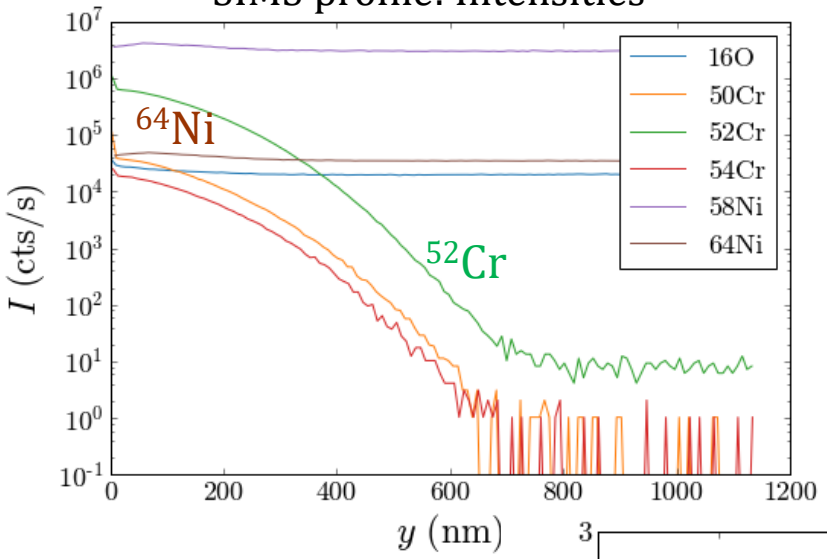
- Characteristic diffusion depth > 100 nm small enough for having SIMS flat floor crater and deep enough for having enough points for good fit
- Ageing time has to be much higher (10 times) than the incompressible heating/cooling time (5 min) and reasonable (one year at maximum)



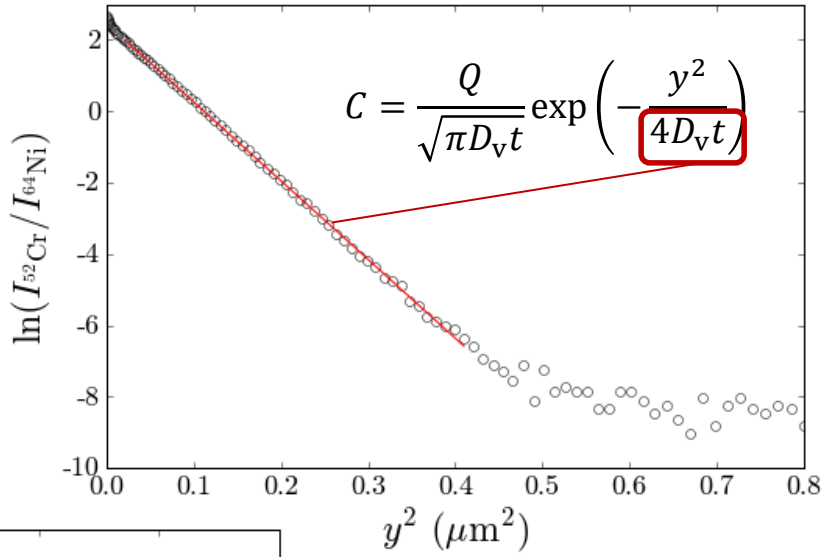
1. Volume diffusion: results treatments

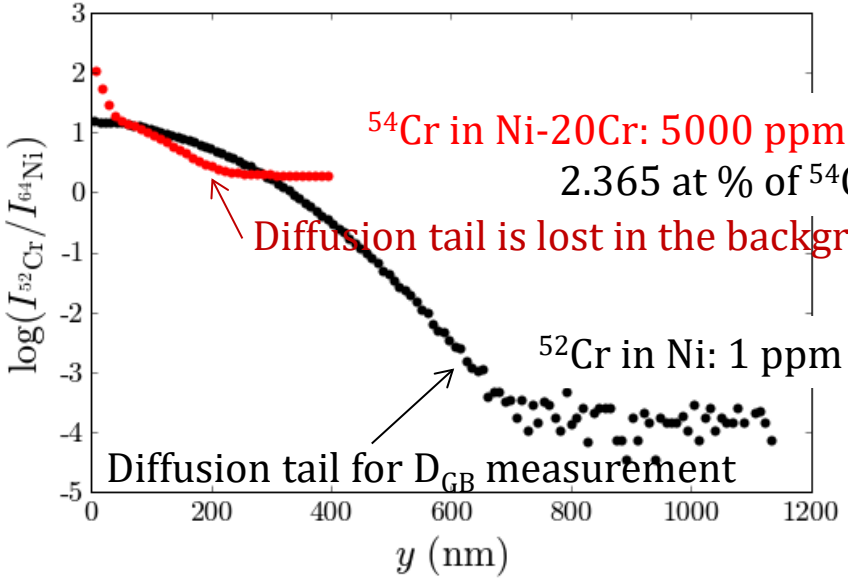
Cr in Ni 162 h at 627 °C

SIMS profile: Intensities



Fit performed for ^{52}Cr/ ^{64}Ni vs. y^2





^{54}Cr in Ni-20Cr: 5000 ppm of ^{54}Cr at the crater floor

2.365 at % of ^{54}Cr within natural Cr

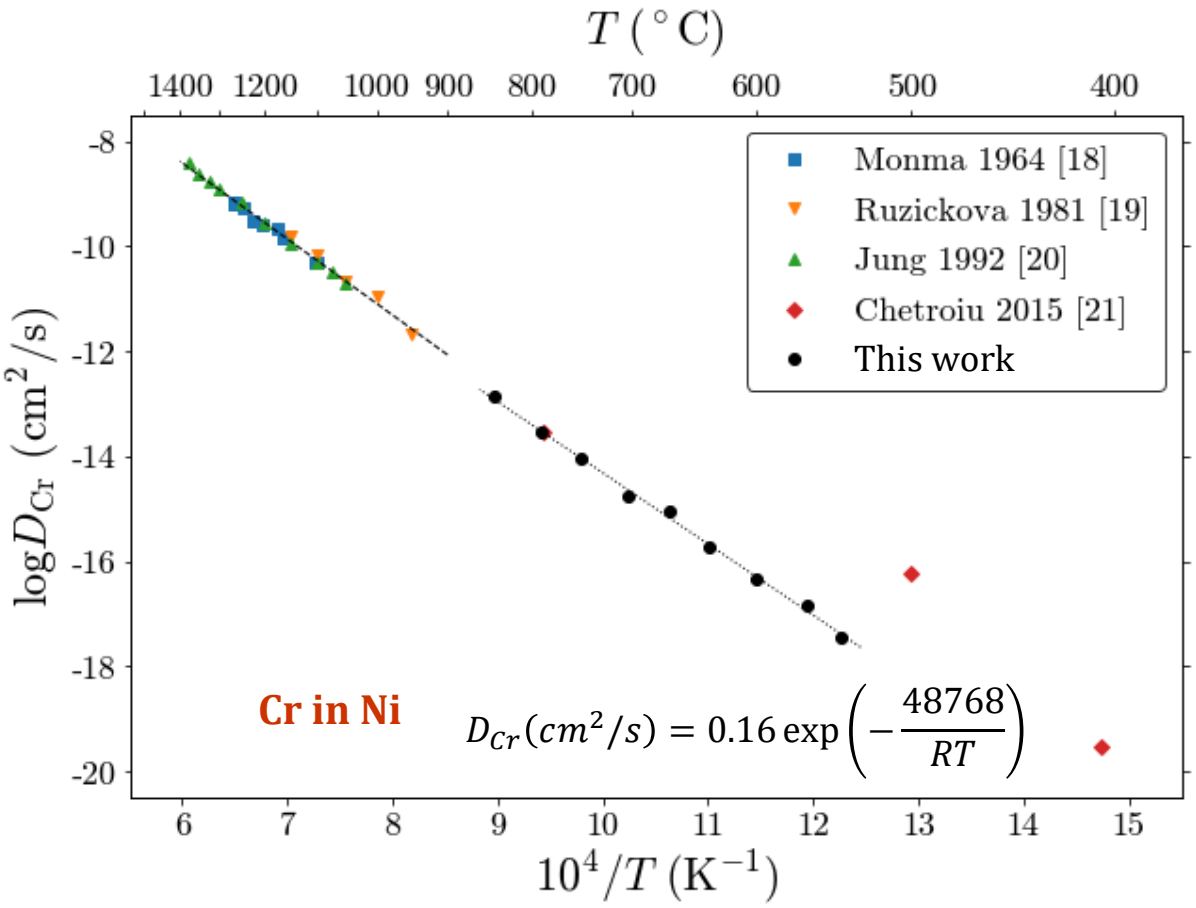
Diffusion tail is lost in the background

^{52}Cr in Ni: 1 ppm of ^{52}Cr at the crater floor

Substrat Ni vs. Ni-20Cr:

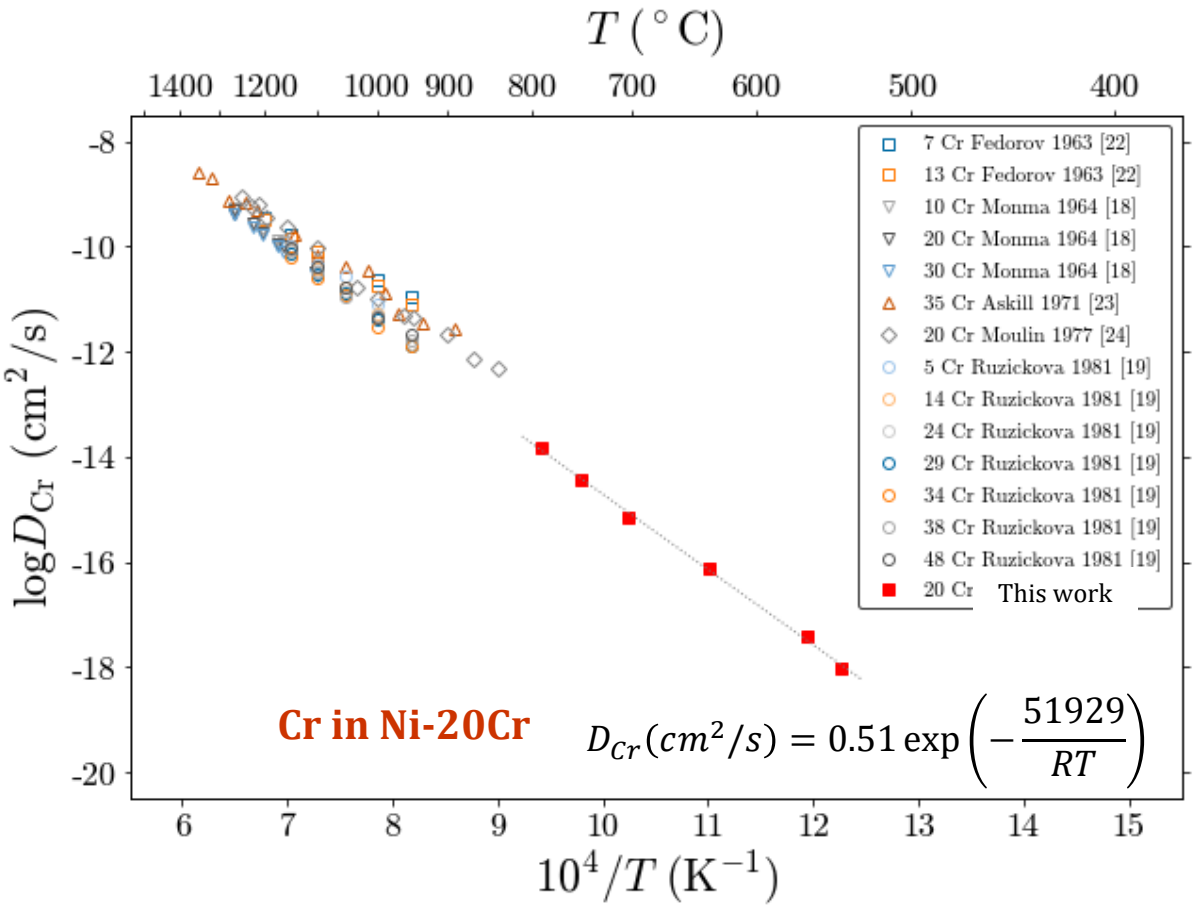
→ diffusion coefficient in GB cannot be measured in Ni-20Cr

1. Volume diffusion:
results for Cr in Ni



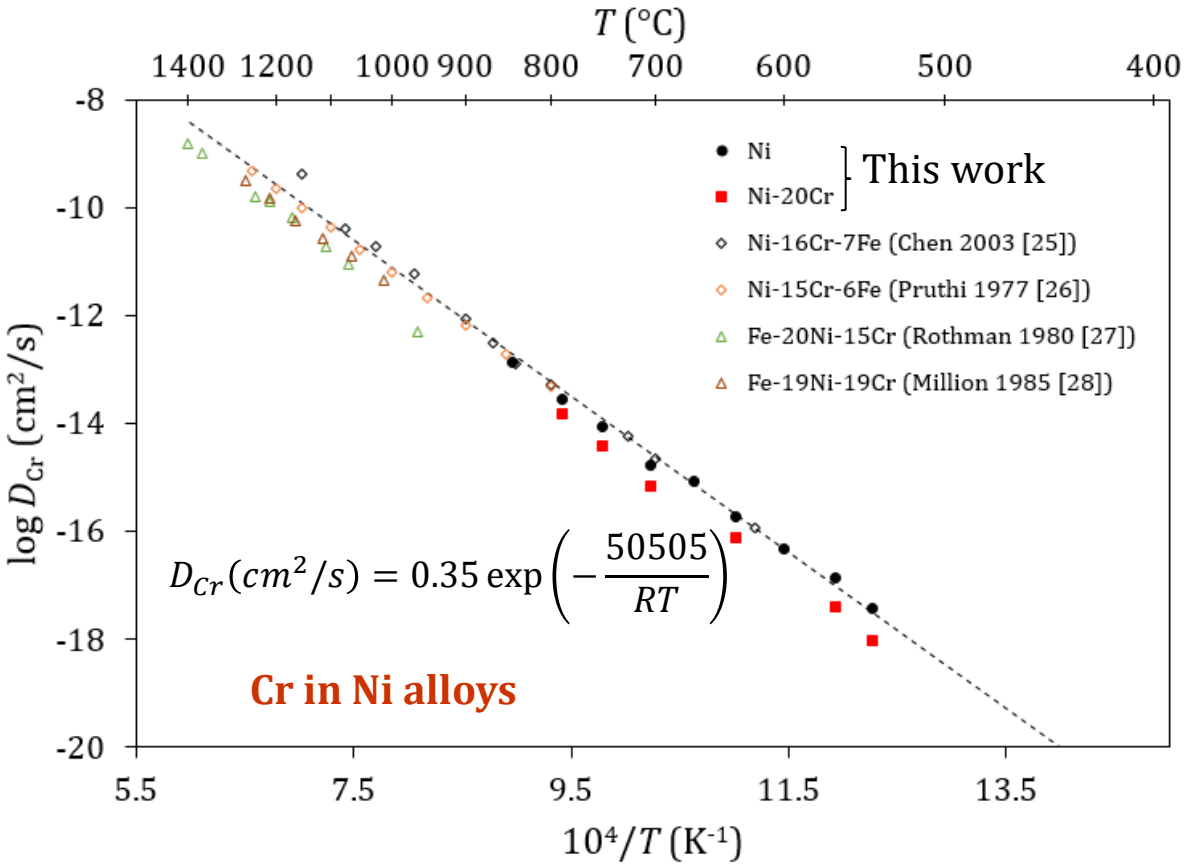
- Very good agreement with extrapolation at low temperatures of measurements made at high temperatures → no accelerated diffusion at low temperature
- These results cannot explain the higher Cr depletion depth observed during oxidation in PWR

1. Volume diffusion: results for Cr in Ni-20Cr



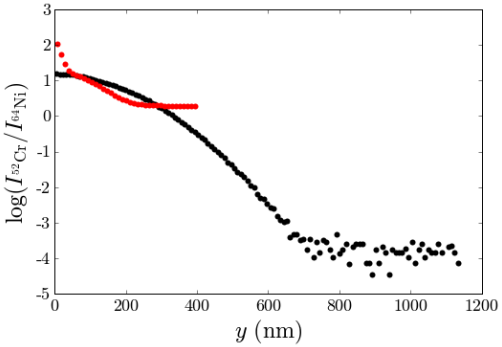
Very good agreement with extrapolation at low temperatures of measurements made at high temperatures

1. Volume diffusion:
all data for Cr in Ni alloys and pure Ni



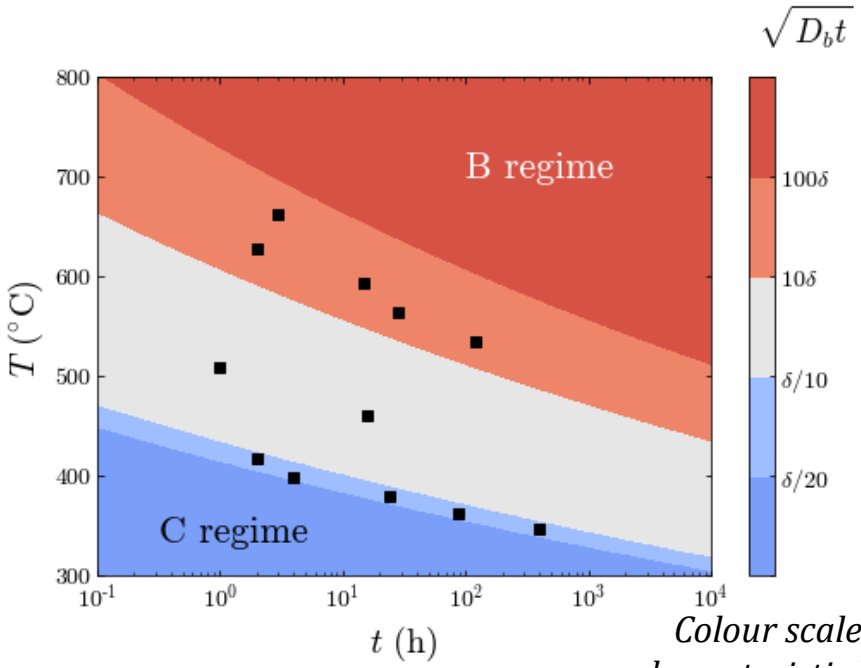
- Our results in agreement with data measured at high temperatures
- D_{Cr^*} is similar in Ni, Ni-Cr, Ni-Fe-Cr, Fe-Ni-Cr → model alloys are good candidates for measurement of Cr diffusivities in FCC Ni-Fe-Cr alloys

2. Grain boundary diffusion:
temperature / time conditions for ageing → **only Cr in Ni**

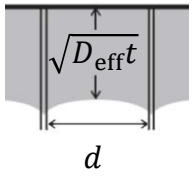
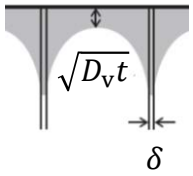
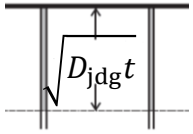


Conditions:

- For B regime $\delta < 10\sqrt{D_v t}$ and for C regime $\delta > 10\sqrt{D_v t}$
- Ageing time has to be much higher than the incompressible heating/cooling time (5 min)



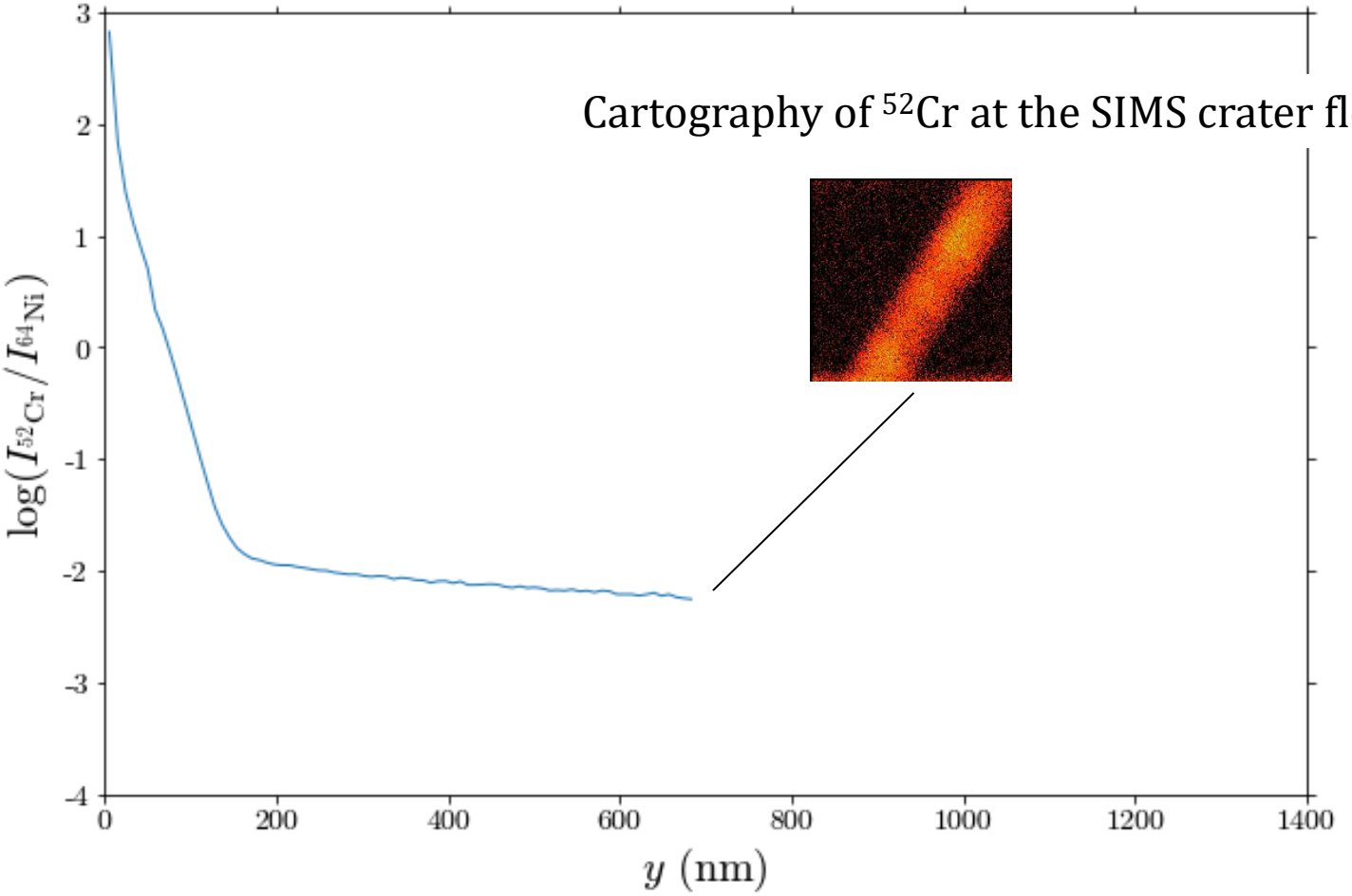
Colour scale for characteristic length

Regimes		Profiles shape
	$\sqrt{D_v t} \gg d$	
A		exp/erf law with weighted D
	$\delta \ll \sqrt{D_v t} \ll d$	
B		profile with diffusion tail
	$\delta \gg \sqrt{D_v t}$	
C		erf law with D_{GB}

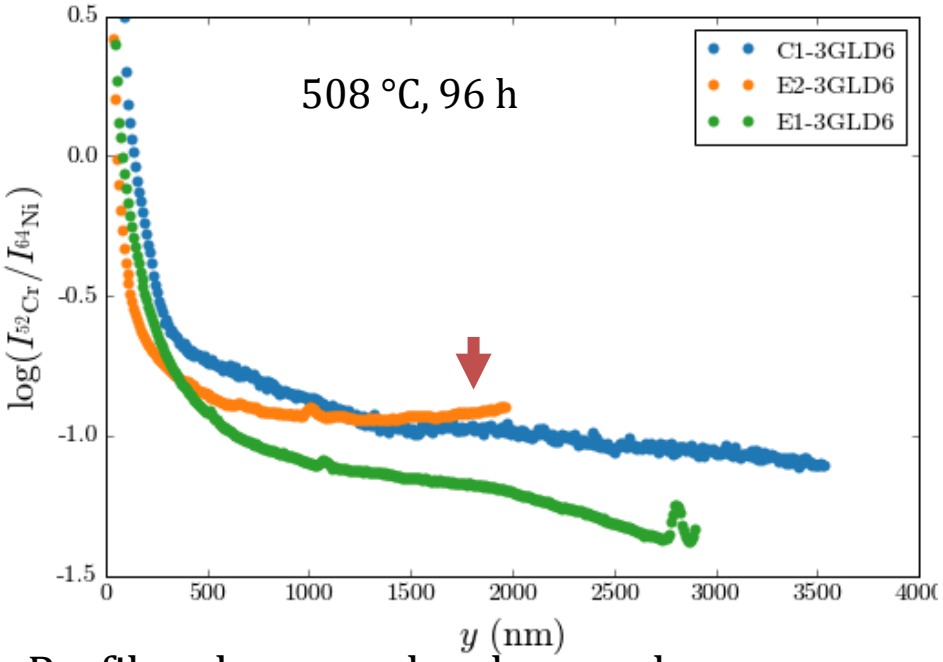
I. Kaur, Y. Mishin, W. Gust, Fundamentals of Grain and Interphase Boundary Diffusion, 1995
H. Mehrer, Diffusion in Solids, 2007

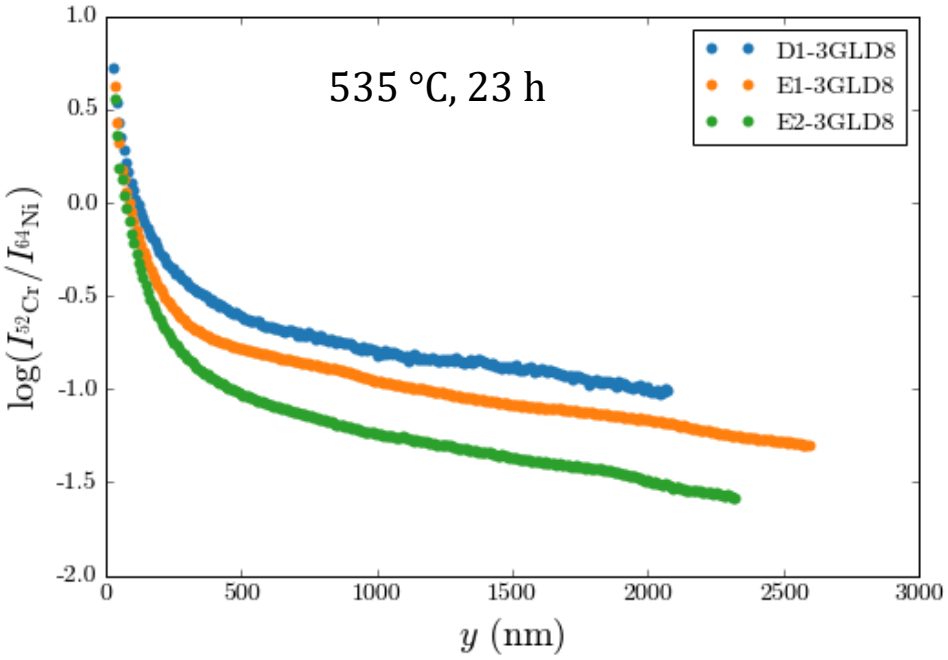
2. Grain boundary diffusion:
Regime B SIMS profiles

Ageing: 28 h at 563 °C



2. Grain boundary diffusion:
Regime B 90% rolled Ni



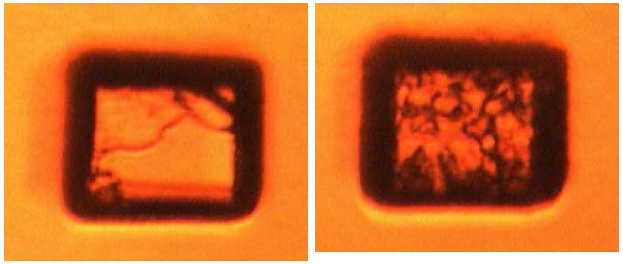


Profiles shape can be abnormal

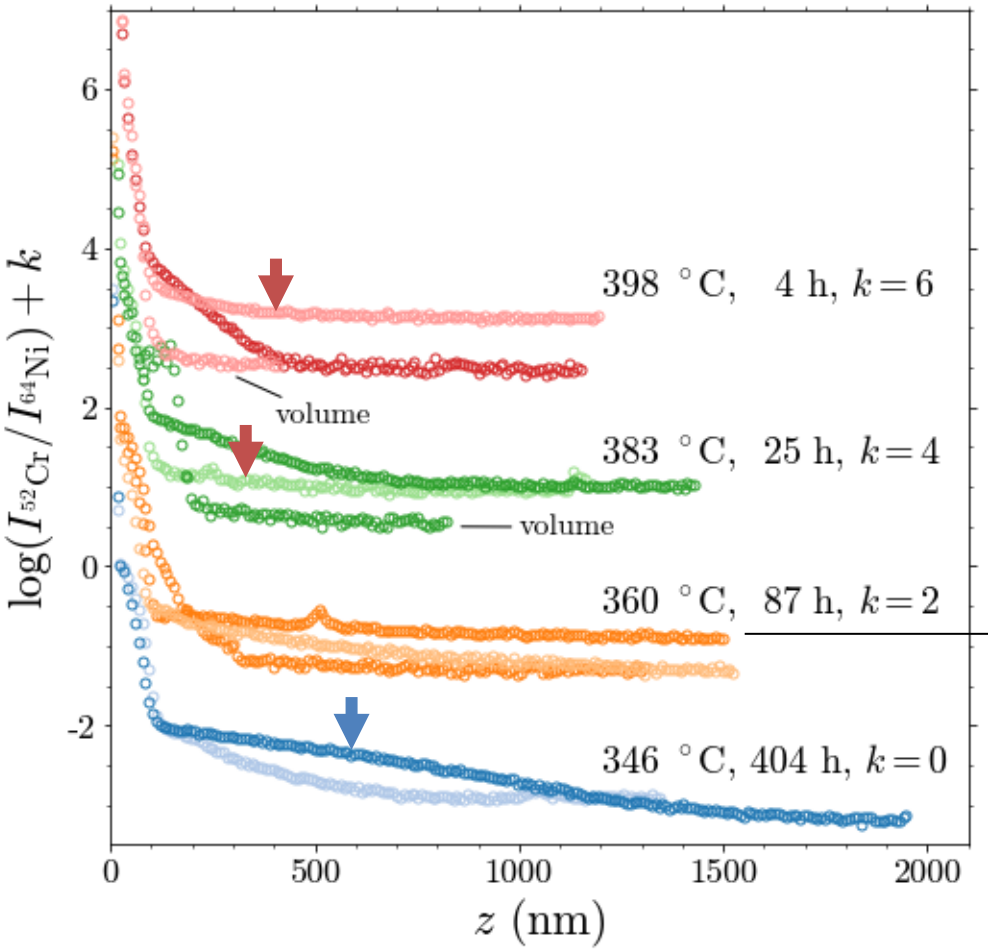
- Positive slope

During diffusion step→ fast recristallization

Optical image of the crater floor

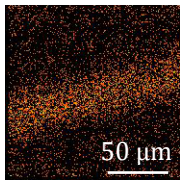


2. Grain boundary diffusion:
Regime C SIMS profiles



Profiles shape can be abnormal

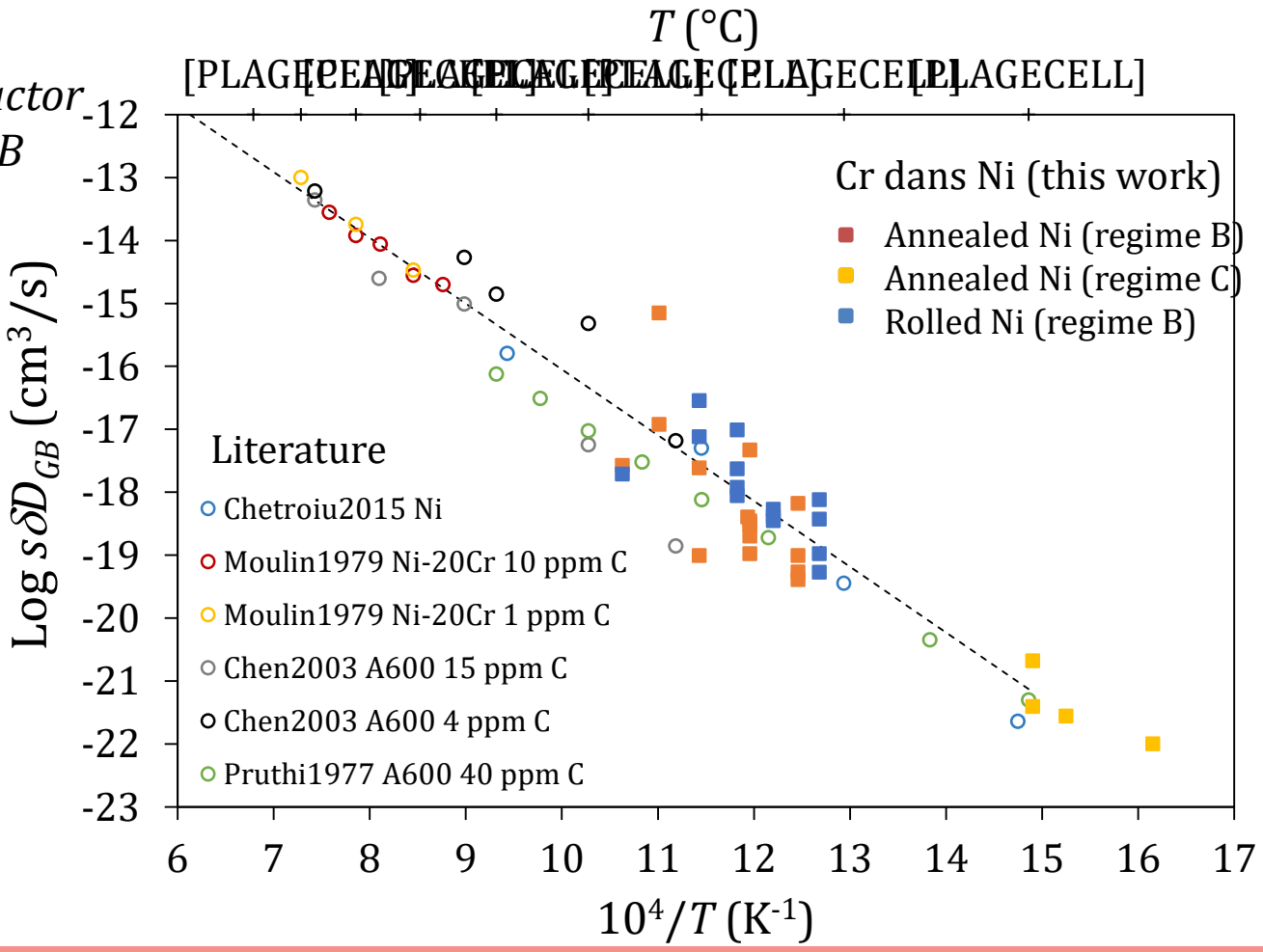
- Convex shape of profile
- Flat profile



Equilibrium segregation?

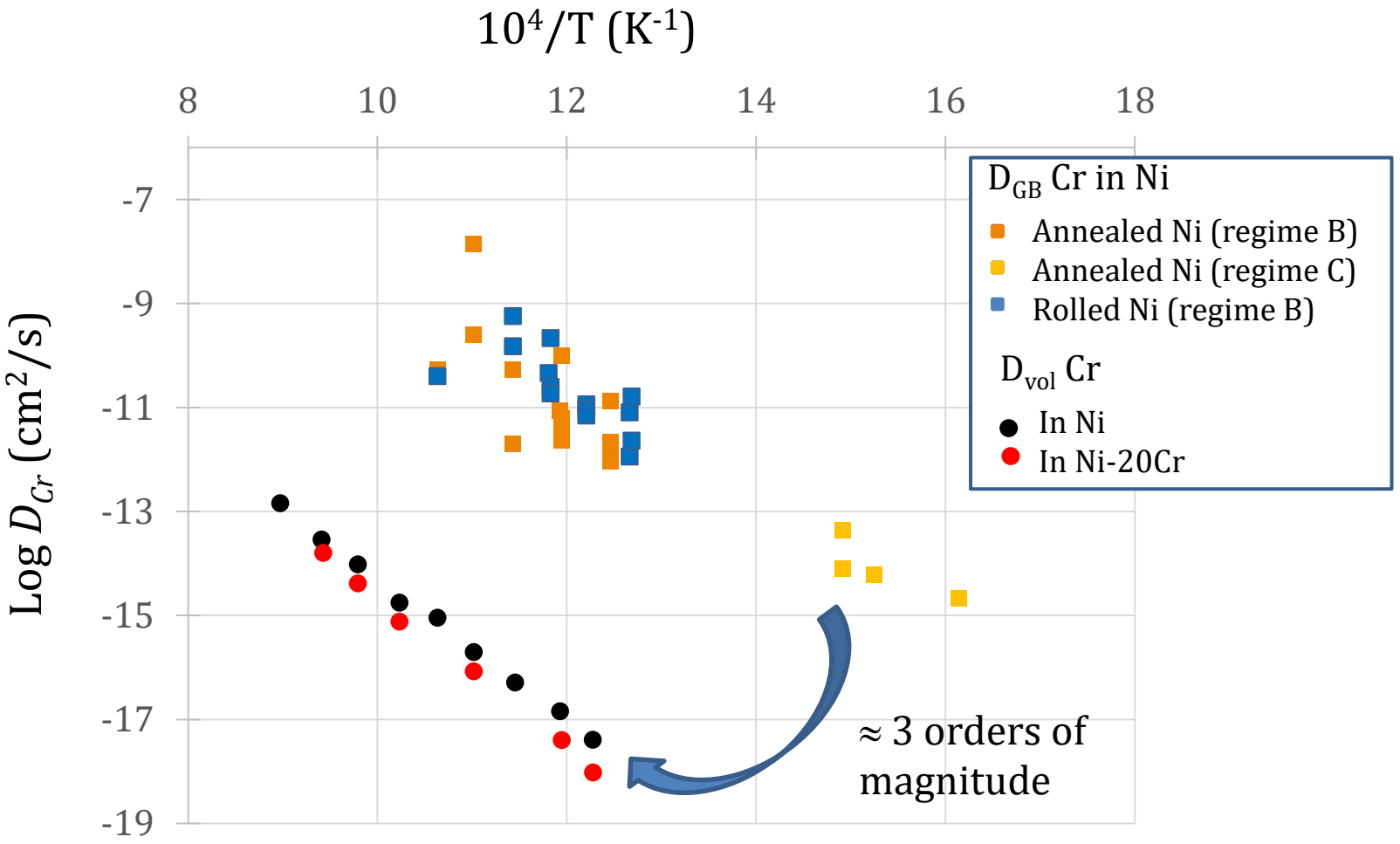
2. Grain boundary diffusion:
all results

s=segregation factor
δ=thickness of GB



- Intergranular Diffusivity very scattered → due to various GB misorientation? Statistics could be done
- Trend in agreement with data obtained at high temperature
- No effect of cold-work & recrystallization on Cr diffusion

3. Summary



3 orders of magnitudes between diffusion in grain boundaries and in volume → order of magnitudes frequently obtained

4. Conclusions and prospects

Tracer Diffusion

In volume

- $D_{Cr^*}^{Ni}$ measured until 542 °C (versus 950 °C before)
- Q constant between 1400 and 542 °C
- Lower temperatures: need a surface cleaning before Cr deposit, and SIMS profile for very small depth (SIMS until 50 nm, Tomographic Atom Probe for lower?)
- D_{Cr^*} is very similar for Ni, Ni-Cr, Ni-Fe-Cr, Fe-Ni-Cr

In grain boundaries

- Measurements of $D_{Cr^*}^{Ni}$ performed until 346 °C
- Very complicated
- $D_{Cr^*}^{Ni-20Cr}$ impossible due to high level (2.365 at %) of ^{54}Cr within natural Cr

- Obtained results in agreement with data measured at high temperatures→ no accelerated diffusion at low temperature
- Cr diffusion is not increased in rolled samples → no accelerated diffusion due to cold-work

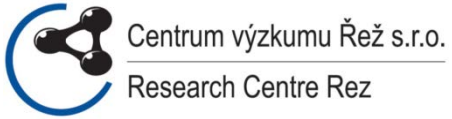
4. Conclusions and prospects

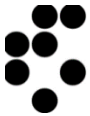
This study cannot explain the higher Cr depletion depth observed in oxidized cracks formed by stress corrosion cracking in PWR

- Is it due to combine effect of diffusion and stress?
  →Cr tracer diffusion coefficient could be measured under creep test (will be done in other project)

- Is it due to combine effect of diffusion and oxidation? Vacancies created in alloy by oxidation could accelerate the Cr diffusion
  → oxidation tests with sample of various microstructures are conducted in gas environments firstly and in PWR conditions secondly → in progress

The SOTERIA Consortium





Institut "Jožef Stefan", Ljubljana, Slovenija