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# Role of grain boundaries in the diffusion of deuterium in nickel base alloy 600 studied by thermal desorption mass spectroscopy

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## Context and objectives

The role grain boundaries (GBs) play in the diffusion of hydrogen in polycrystalline alloys has long been debated, with some researchers reporting a “short-circuit” [1-7], slowing [8,9] or even mixed effect depending on grain size and orientation [6,10,11] of GBs on the transport of hydrogen across a metal membrane.

This study aims to:

1. address the **role of GBs** in the diffusion of deuterium (<sup>2</sup>H) in a model alloy 600 with a grain size of tens of micrometers and
2. derive the diffusion coefficient of <sup>2</sup>H in this alloy through coupled experimental analysis and simulation.

## Choice of model and initial hypotheses

The system could be defined one of three ways: (i.) system where GBs are <sup>2</sup>H diffusion short circuits, (ii.) system where GBs act as potential trap sites or (iii.) **Fick's second law**. Systems (i.) and (ii.) require the determination of many temperature dependent parameters that may not readily be available in literature – therefore for simplicity (iii.) was initial used.

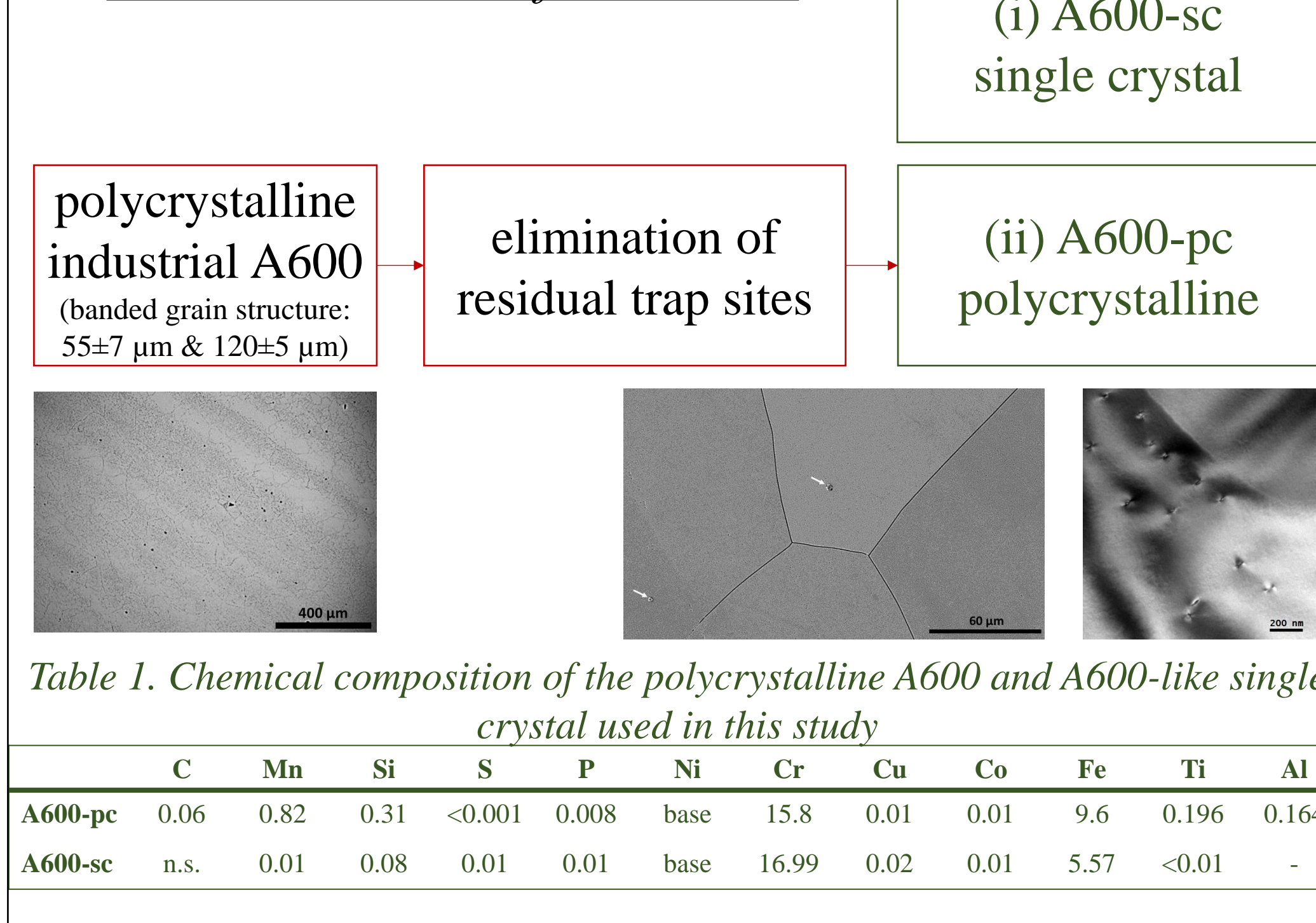
To use Fick's second law to describe the system, the following assumptions were made:

- a) the **diffusion coefficient (D) follows an Arrhenius relationship**,
- b) <sup>2</sup>H diffusion along GBs can be neglected compared to the <sup>2</sup>H flux from interstitial diffusion in the grain volume,
- c) the **sample is free of <sup>2</sup>H before cathodic charging**
- d) **constant imposed surface concentration** during cathodic charging

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

## Materials and method

### “Model material” fabrication



### Thermal desorption mass spectroscopy (TDS)

- (1) **Cathodic charging** of sample with deuterium (<sup>2</sup>H) at one face (opposite face and sides are protected with a resistant varnish)
- (2) **Transfer** from electrochemical cell to TDS system
- (3) **<sup>2</sup>H desorption flux (J<sub>H</sub>) monitoring** in function of t or T
  - a) “**traditional**” analysis – linear temperature ramp
  - b) “**hybrid**” analysis – extended (RT or HT) isothermal period followed by linear temperature ramp

Table 2. Experimental conditions for “traditional” and “hybrid” TDS analysis.

Analysis type	Charging	Transfer	Aging	T ramp (φ)
Traditional			-----	
Hybrid – RT	30 min / 298 K / 0.1 M NaO <sup>2</sup> H	15 ± 3 min / 294 ± 2 K	360 min / 294 ± 2 K	10 K.min <sup>-1</sup>
Hybrid – HT			360 min / 409 ± 1 K	

RT aging aims to enhance short circuit grain boundary diffusion [5] while at HT grain boundary dominated diffusion should be minimized [7]

### 1. Acquisition of experimental TDS spectra for A600-pc and A600-sc

- a) traditional
- b) hybrid – RT
- c) hybrid – HT

similar intensities, peak temperatures and spectral forms

### 2. Derive <sup>2</sup>H diffusion coefficient in polycrystalline A600 (d)

$$D \text{ (cm}^2 \cdot \text{s}^{-1}\text{)} = D_0 \cdot \exp \left[ \frac{-E_D}{RT} \right]$$

$$D_0 = (1.0 \pm 0.5) \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$$

$$E_D = (45 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$$

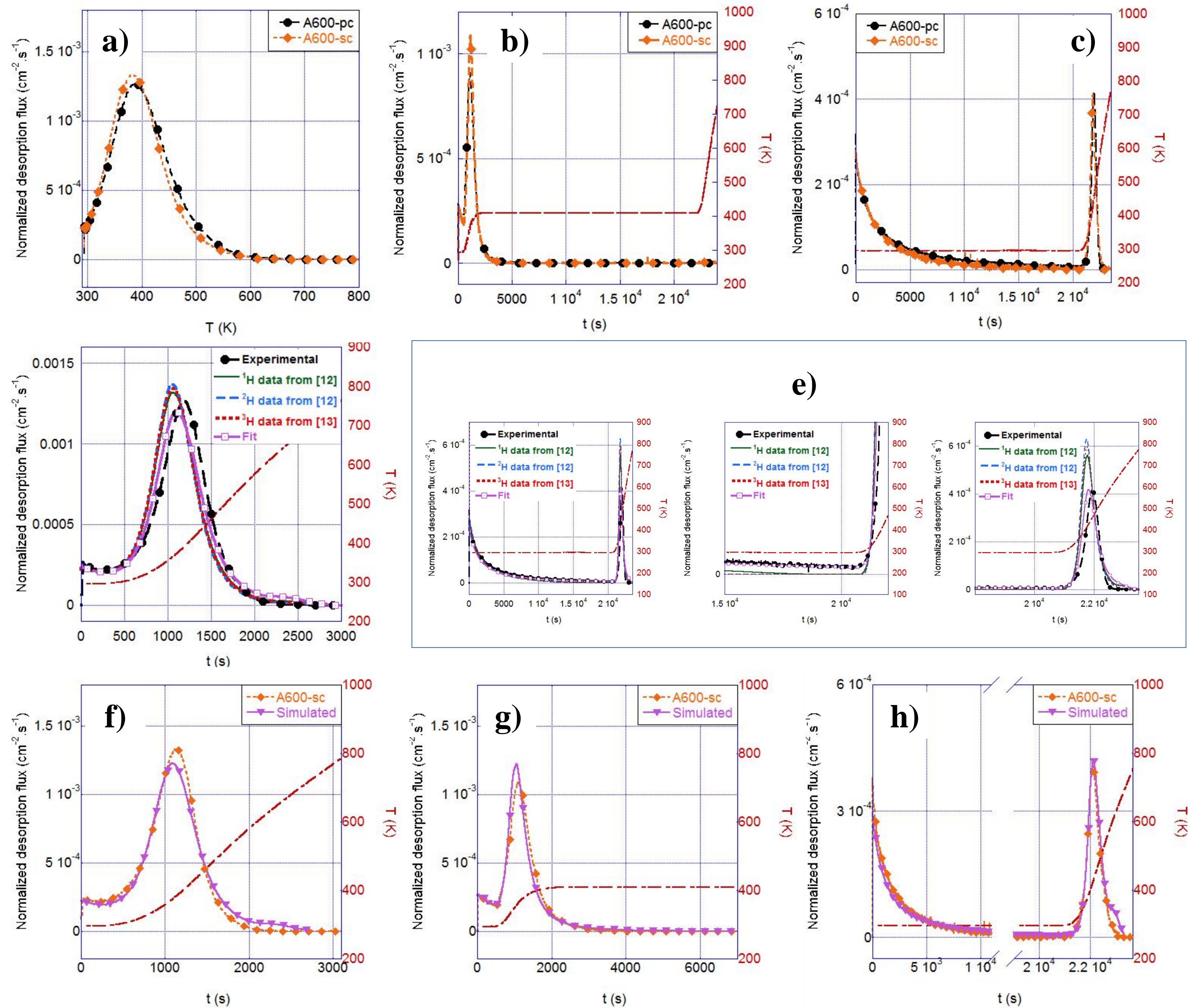
### 3. Validate derived diffusion coefficient by simulating aged spectra (e)

superior reproduction of normalized aged spectrum using derived diffusion coefficient as compared to literature diffusion coefficients [12,13]

### 4. Simulate A600-sc TDS spectra using the <sup>2</sup>H diffusion coefficient derived from A600-pc

- f) traditional
- g) hybrid – RT
- h) hybrid – HT

very good reproduction of normalized A600-sc spectra using A600-pc <sup>2</sup>H coefficient



## Conclusions

- clear similarities in peak temperature, peak intensity and peak form between normalized experimental polycrystalline and single crystal spectra were observed,
- **diffusion coefficient for <sup>2</sup>H in polycrystalline A600 was derived and validated** by fitting an experimental spectra [14, 15] and
- single crystal A600 TDS spectra were successfully simulated and well reproduced using the derived D from A600-pc.

Therefore it can be concluded that...

**grain boundaries do not play a significant role in the transport of <sup>2</sup>H in alloy 600 for the grain size and experimental conditions studied.**

## Perspectives

- continue this work using other industrial alloys (i.e. stainless steels) and grain sizes
- evaluate using other charging (T and t), aging (T and t) and TDS (φ) conditions
- improving numerical model and fitting routine

As in this alloy grain boundary interactions can be neglected more focus can be placed on studying the interactions between hydrogen and trap sites such as chromium carbides → this work will be presented in the oral presentation on Tuesday at 10:00 pm.