



Thermal outgassing of hydrogen: models and methods for reduction.

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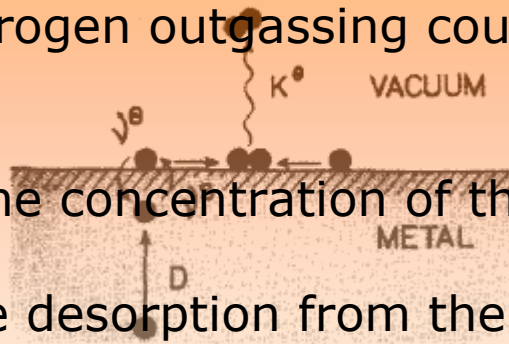
Thursday, May 18, 2006, CAS, Spain

1. Introduction
2. Decreasing the H concentration:
 - a. the thermodynamic frame
 - b. kinetics models: diffusion or recombination?
 - c. efficiency of bakeout
 - d. vacuum firing
3. Hindering H desorption from the surface
 - a. air bakeout
 - b. passive coatings
 - c. active coatings
4. Internal trapping

Hydrogen is released in the gas phase after migration in the metal lattice and recombination on the surface.

It follows that hydrogen outgassing could be reduced in essentially three ways:

1. decreasing the concentration of this gas in the solid,
2. hindering the desorption from the surface
3. reducing the mobility of atomic hydrogen in the lattice.



by adding internal H traps (internal pumping)

Heating of UHV components is applied:

- in-situ: bakeout of the vacuum system already assembled
- ex-situ: vacuum firing of the components or of the rough materials

The Significant temperature is limited by the materials:

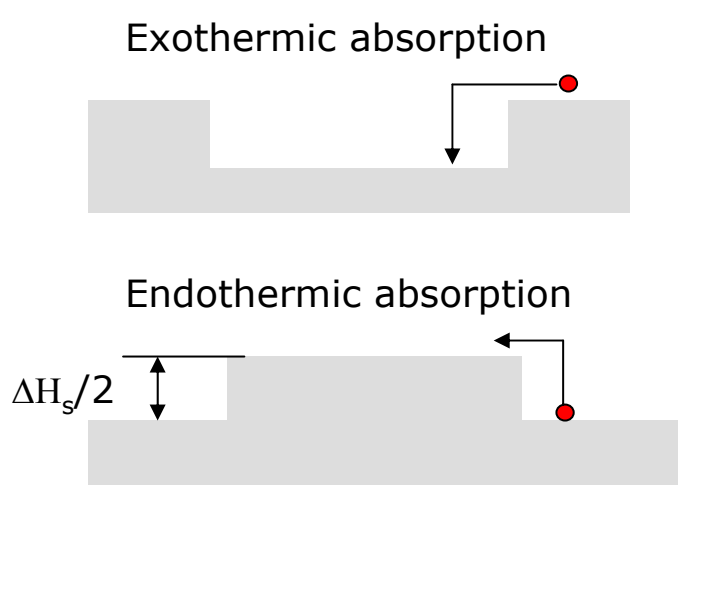
in general applied in a vacuum furnace at temperatures in the range

Al alloys → 200°C
Cu alloys → 250°C
450°C ÷ 1050°C

or by the kind of flange adopted:

Standard Conflat® ⇒ 400°C

H depletion is possible during the thermal treatment only if the H₂ pressure is lower than the dissociation pressure.

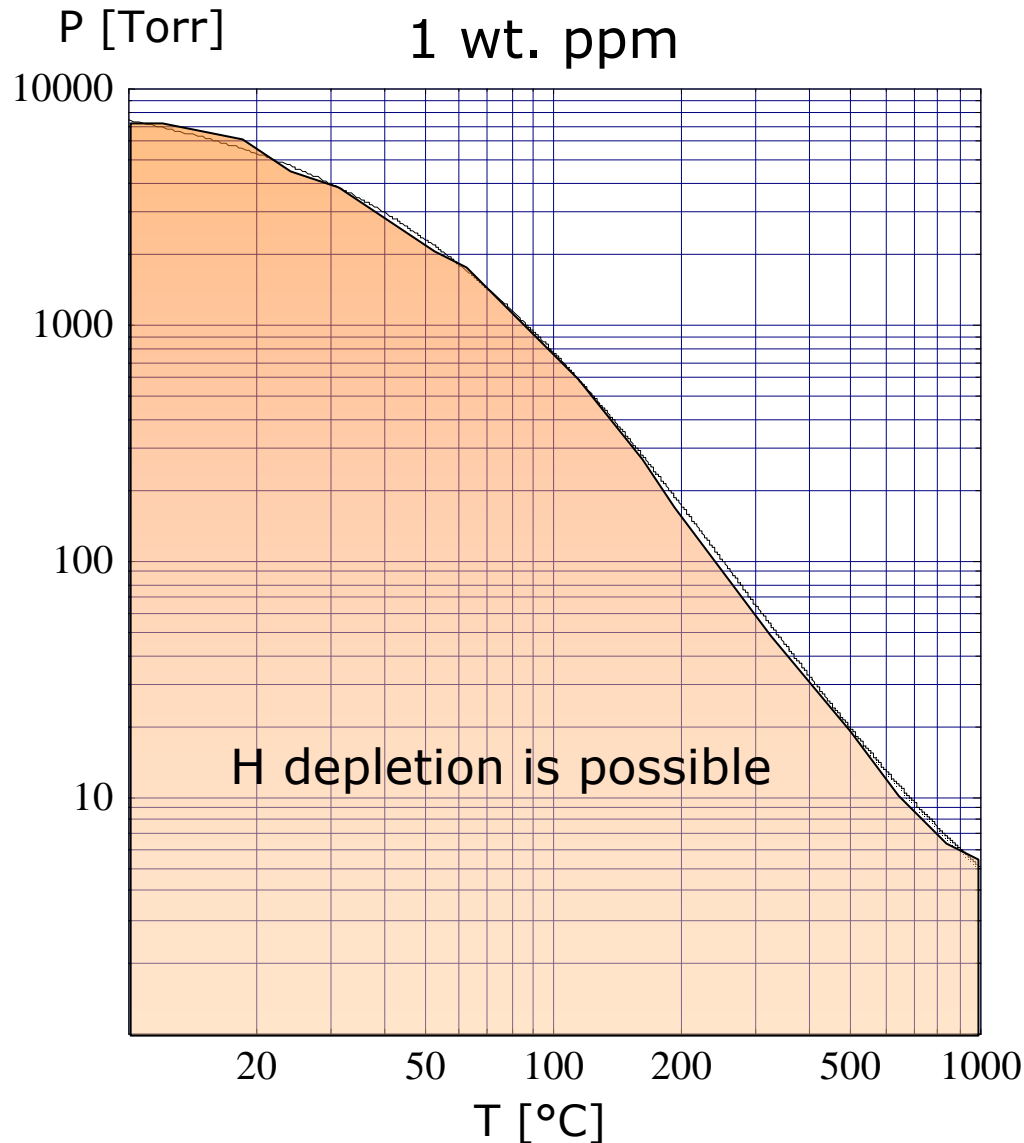


$$x_H = B \cdot e^{-\frac{\Delta H_s^0}{2k_B T}} \cdot \sqrt{P_{H_2}}$$

Sieverts' law

Most of the metals used for the construction of UHV vessels absorb H₂ endothermically ($\Delta H_s > 0$).

For these materials, for a constant applied pressure, increasing the temperature results in an increase of the equilibrium concentration of H in the solid.



Solubility of H₂ in stainless steel:

$$x_H[at.ppm] = 71.8 \cdot \sqrt{P[Torr]} \cdot e^{-\frac{0.114[eV]}{k_B \cdot T}}$$

The H content in standard austenitic stainless steels is about 1 ppm in weight (≈ 50 at. ppm).

H₂ pressures lower than 6 Torr are necessary to reduce the H content of as received stainless steels at 950°C.

Treatments at lower temperatures are much more efficient from a thermodynamic point of view.

But time...

The efficiency of the degassing treatment can be calculated once the limiting mechanism of the outgassing process is identified.

Two mechanisms could cause an obstruction to the degassing process:

1. diffusion in the metal $\rightarrow q(t) \propto -\frac{\partial c}{\partial x}$ ← Concentration gradient
2. recombination on the surface $\rightarrow q(t) \propto c_s^2$ ← Square of the concentration on the surface

After one bakeout at the temperature T_{bo} for a duration t_{bo} the outgassing rate is:

Diffusion model

$$q_n(t) = \frac{4 \cdot c_0 \cdot D(T_{RT})}{L} \exp\left(-\pi^2 \cdot \frac{n \cdot D(T_{bo}) \cdot t_{bo}}{L^2}\right)$$

supposing $F_0 > 5 \times 10^{-2}$.

It can be shown that after n identical bakeout:

$$q_n = A \cdot \exp(-B \cdot n)$$

where $A = \frac{4 \cdot c_0 \cdot D(T_{RT})}{L}$ $B = \pi^2 \cdot \frac{D(T_{bo}) \cdot t_{bo}}{L^2}$

→ Linearity in Log(q)-n plot

$$\frac{q_{n+1}(t)}{q_n(t)} = \exp\left(\pi^2 \cdot \frac{D(T_{bo}) \cdot t_{bo}}{L^2}\right)$$

→ **Each bakeout reduces the outgassing rate at room temperature by the same factor.**

Recombination model

$$q_1 = K[T_{RT}] \cdot \left(\frac{c_0}{1 + B \cdot c_0}\right)^2 \quad \text{where } B = \frac{K_R \cdot t_{bo}}{L}$$

$$q_n = K[T_{RT}] \cdot \left(\frac{c_0}{1 + n \cdot B \cdot c_0}\right)^2 \propto n^{-2}$$

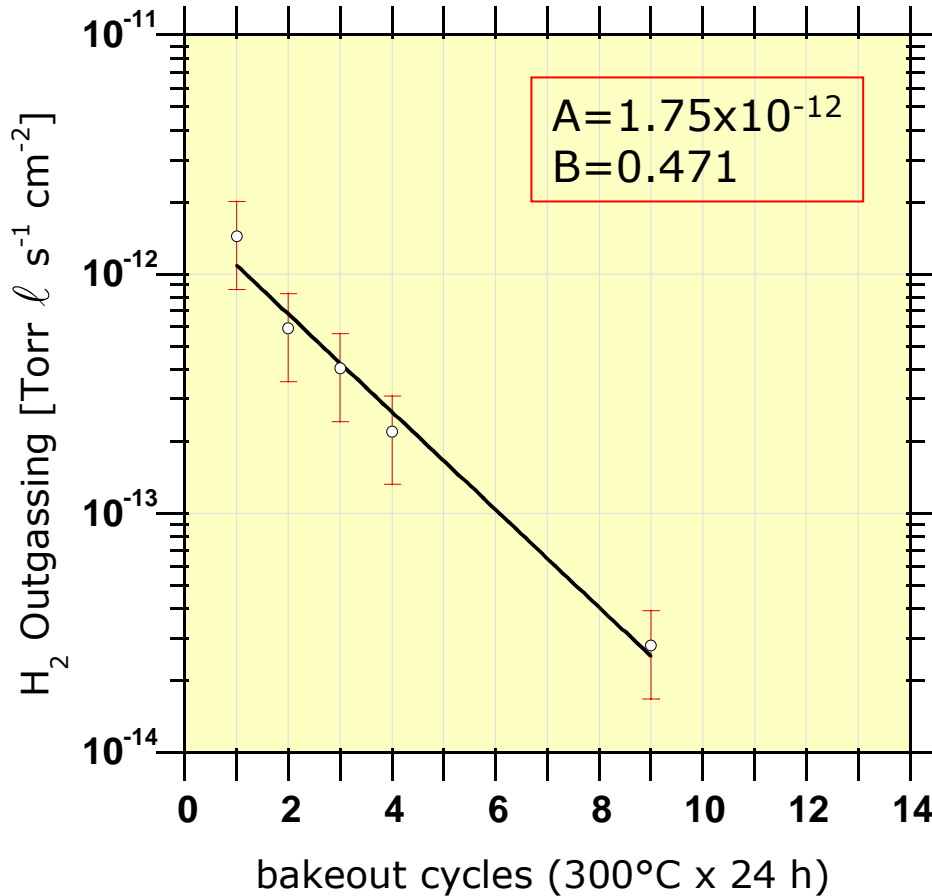
→ **Additional bakeout are less efficient.**

Experimental verification ⇨

Case study 1:

Stainless steel: CERN unpublished results (P.C.)

stainless steel sheets 2 mm thick
bakeout at 300°C for 20 h



Each bakeout reduces the outgassing rate by a factor of ≈ 1.6 .

From B:

$$D(300^\circ\text{C}) = 2.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$$

If the diffusion rate at room temperature reported in the literature is assumed, from the value of A:

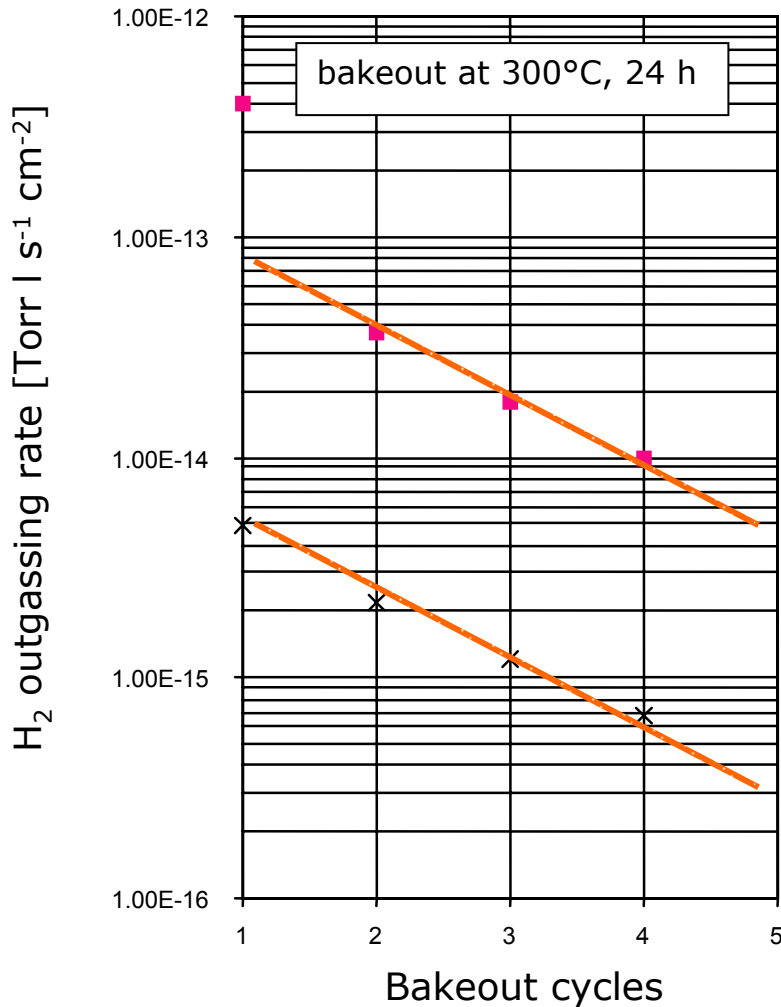
$$C_0 = 0.05 \text{ Torr l/cm}^3 = 0.75 \text{ wt. ppm}$$

This is a very reasonable quantity for austenitic stainless steels.

Case study 2:

316 LN Stainless steel: CERN
 AT-VAC int. note
 J-P Bojon, N. Hilleret, B. Versolatto

stainless steel sheets 1.5 mm thick



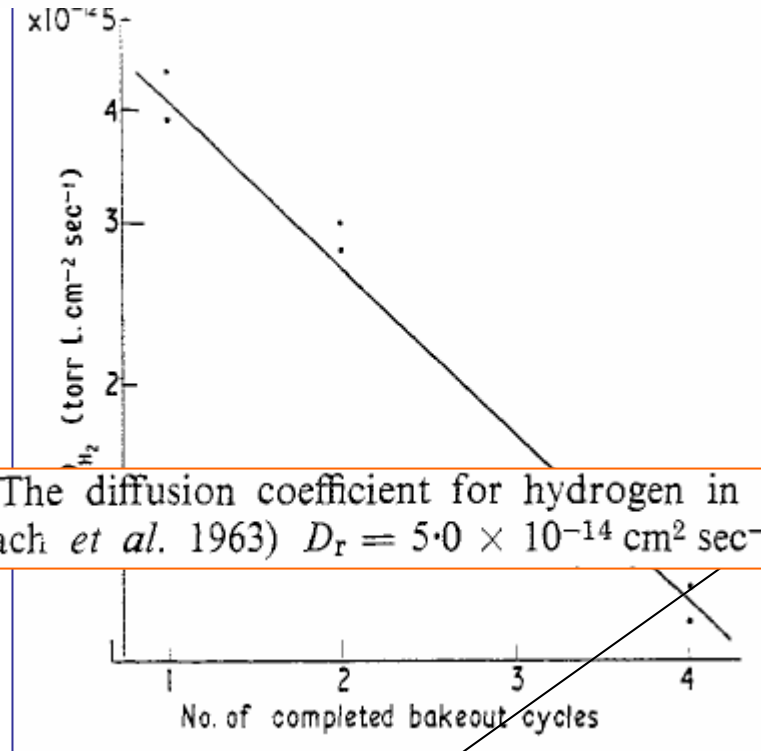
- As received
- × After vacuum firing

Each bakeout reduces the outgassing rate by a factor of ≈ 1.8

Case study 3:

R. CALDER and G. LEWIN: BRIT. J. APPL. PHYS., 1967, VOL. 18. PRINTED IN GREAT BRITAIN

stainless steel sample
2.0 mm thick
Bakeout @ 300°x25h



ESCHBACH, H. L.,
et al. 1963,
Vacuum, 13, 543-7.

$c_0 = 0.3 \text{ torr l. cm}^{-3}$. The diffusion coefficient for hydrogen in stainless steel at room temperature is (Eschbach *et al.* 1963) $D_r = 5.0 \times 10^{-14} \text{ cm}^2 \text{ sec}^{-1}$. The application of

“...a logarithmic decrease with successive bakeouts, behaviour to be expected from the analysis, though the slope is somewhat smaller than expected (-0.43 instead of -0.75 from equation. This could be attributed to a slightly different diffusion coefficient...”

The experimental results indicate that diffusion could be the rate limiting process for bakeout carried out at 300°C and for \approx mm thick sheets.

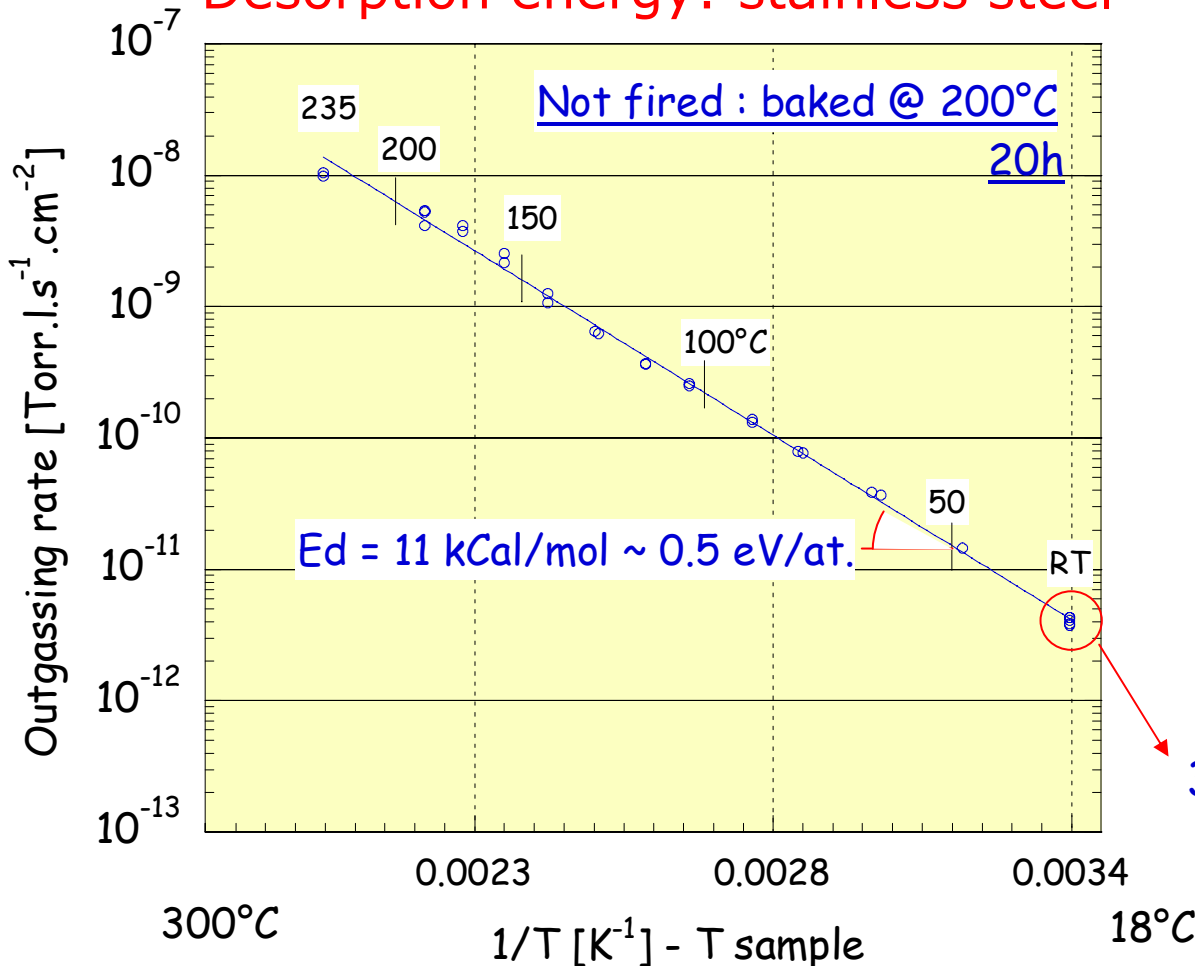
Other experimental results shows that, for samples of similar thickness, a unique energy is associated to the desorption process: the diffusion energy

Other experimental cases \Rightarrow

Case of study 4:

Stainless steel: CERN unpublished results
(Géraldine Chuste)

Desorption energy: stainless steel



Vacuum pipe dimensions

Length	200 cm
Diameter	3.4 cm
Thickness	2 mm

Literature:

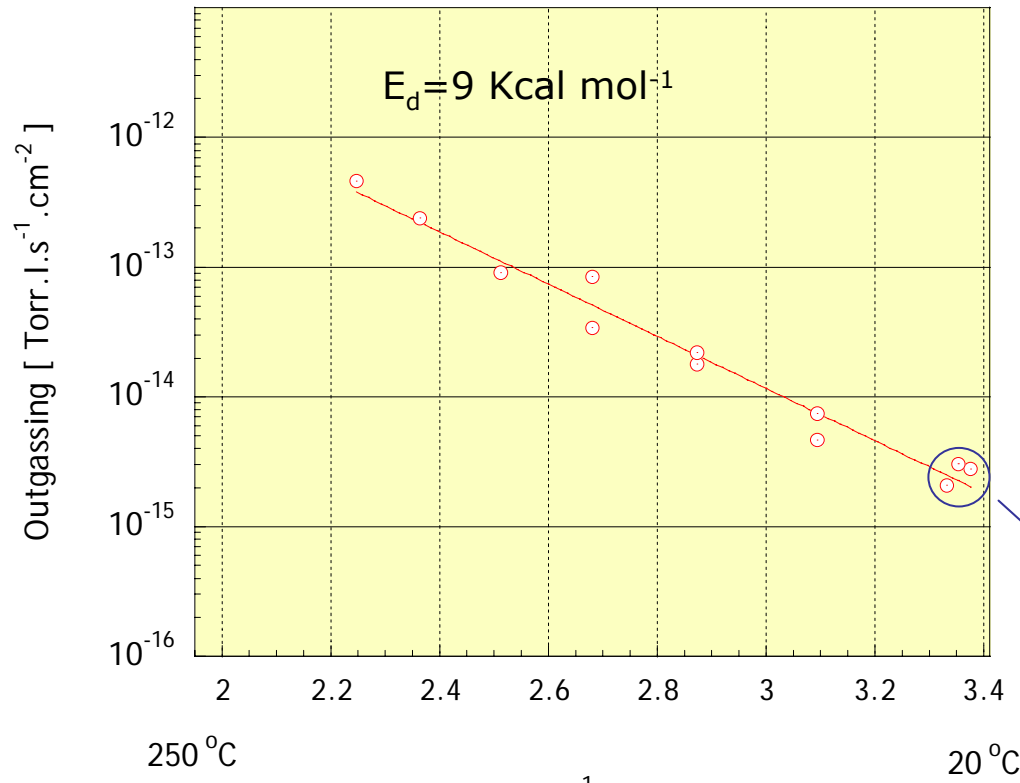
0.5 eV/ at. \approx diffusion energy of hydrogen in austenitic stainless steel

OK!

Case of study 5:

OFS copper bakes at 200°C for 20h:
CERN unpublished results (Géraldine Chuste)

Desorption energy: surface etched OFS copper



Vacuum pipe dimensions

Length	700 cm
Diameter	8 cm
Thickness	2 mm

Literature:

0.39 eV/ at. \approx diffusion energy of hydrogen in copper

OK!

$$D = 8.34 \cdot 10^{-3} \exp\left[-\frac{0.39}{k_B \cdot T}\right]$$

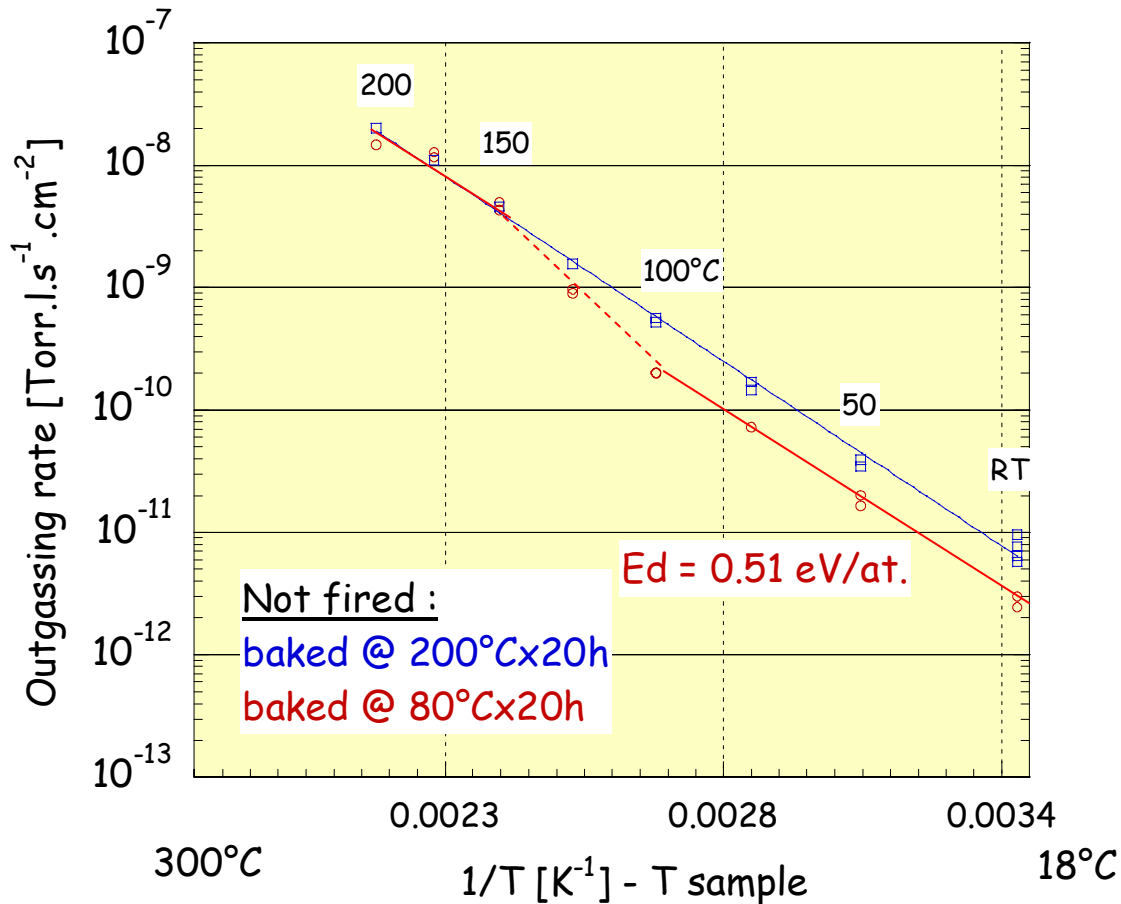
1000/T [K⁻¹] - T sample

$2 \cdot 10^{-15}$ Torr.l.s⁻¹.cm⁻²

Case of study 6:

Stainless steel: CERN unpublished results
(Géraldine Chuste)

Bakeout at low temperature (stainless steel)



RT-100°C:

The outgassing rate is 2 times lower when a bakeout at 80°C is applied

Between 100 and 150°C:

The outgassing rates after bakeout at 200°C and 80°C converge.

Hydrogen is blocked or converted to water.

$1 \text{ eV/at} = 23 \text{ kCal.mol}^{-1}$

Vacuum firing

Vacuum firing

➤ **$T < 500^{\circ}\text{C}$**

diffusion is too slow

➤ **500°C (600°C) $< T < 900^{\circ}\text{C}$** (depending on the steel grade)

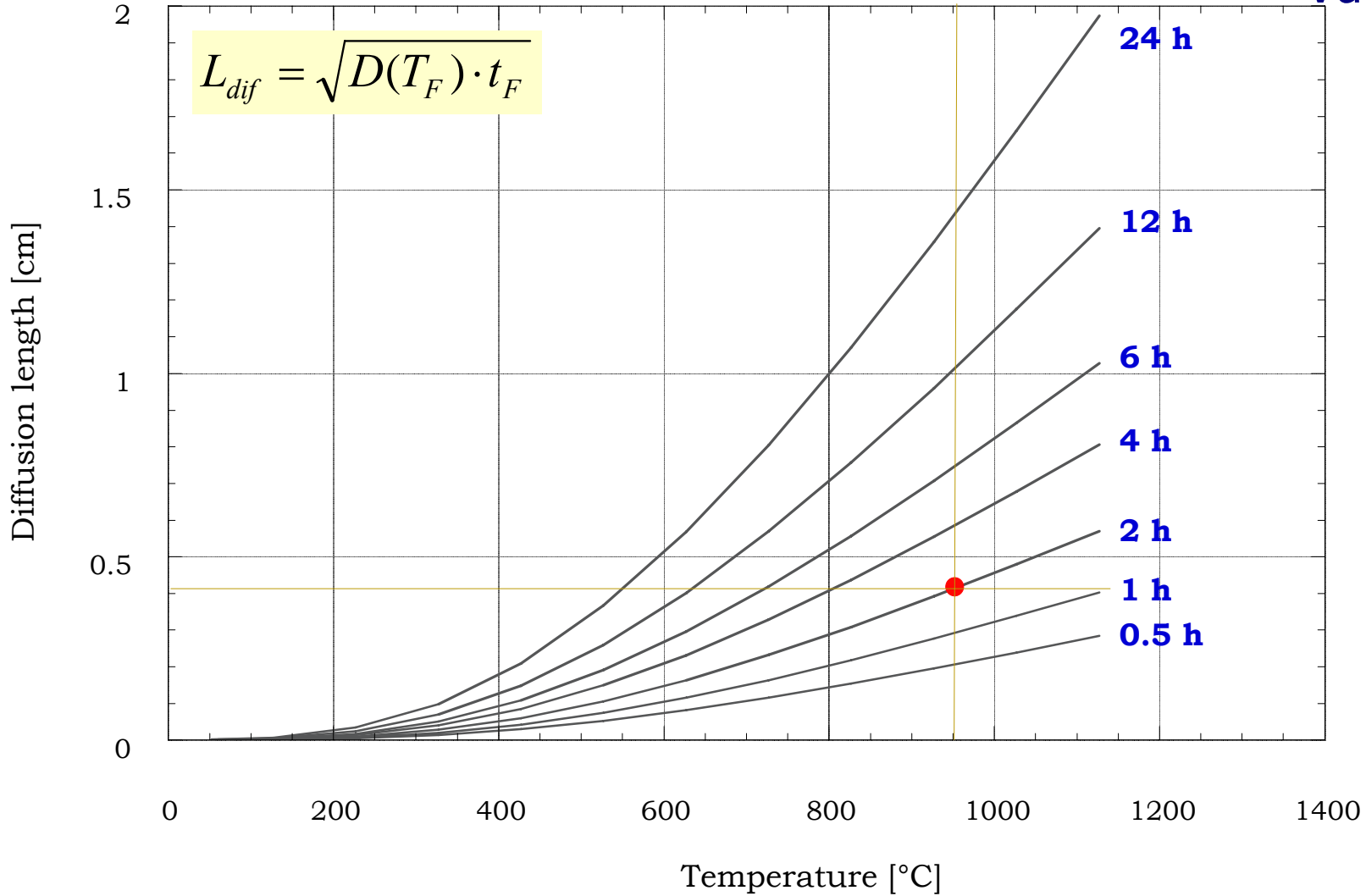
carbide and carbo-nitride precipitation

residual δ -ferrite transformation into σ - phase (very brittle)

➤ **$T > 1050^{\circ}\text{C}$**

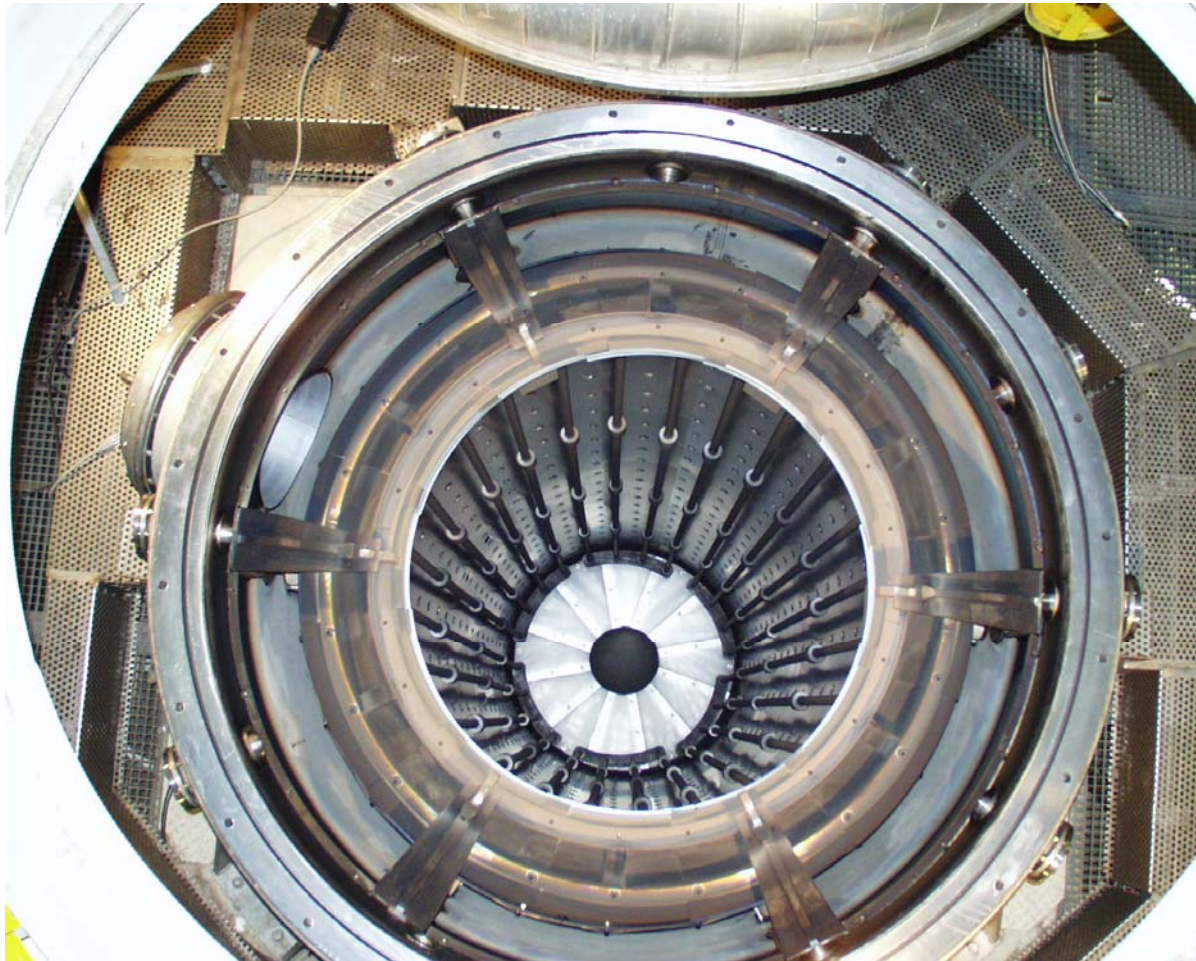
Solution annealing, abnormal grain growth, recrystallisation, excessive nitrogen loss

Vacuum firing



The CERN large furnace

Vacuum firing



Length:
6 m

Diameter:
1 m

Maximum charge weight:
1000 Kg

Ultimate pressure:
 8×10^{-8} Torr

Pressure at the end of the
treatment:
high 10^{-6} Torr range

Melting in electric Arc furnace (ARC) + AOD

Refinement: Electro-Slag Remelting (ESR):
Final ingot

Preliminary considerations:
production of austenitic stainless steels for UHV applications

Rolling — Thermo-Mechanical treatments — Forging

Thickness ≥ 5mm: Hot-rolling

Thickness < 5mm: Cold-rolling

Sheets (vacuum chambers)

Plates (for flanges)

Solution annealing (1050-1100°C) + water quenching

Acid pickling (HNO₃ solution)

Skin-passing (for very thin sheets)

Modification of Mechanical and Metallurgical properties after vacuum firing

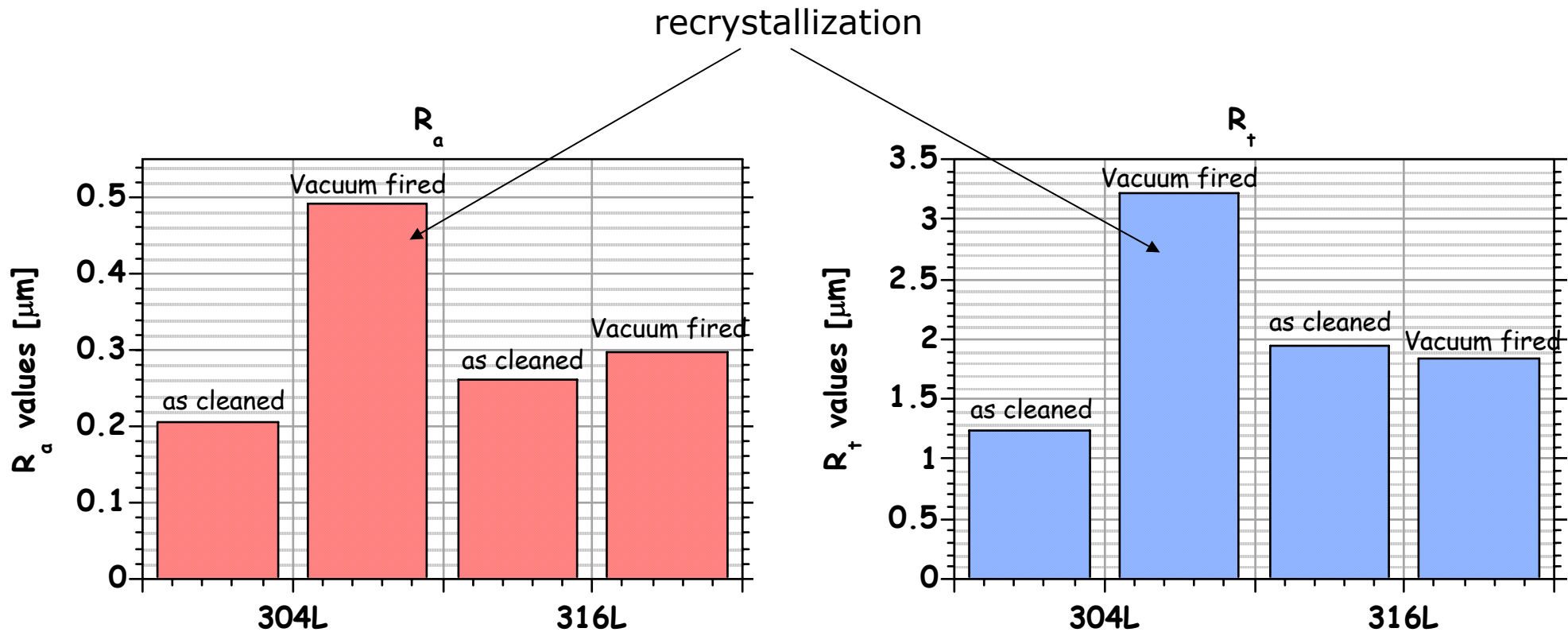
Hardness HB (ISO 6506)

	As received	Fired 950° C	Fired 1050° C
304L	150	128	126
316L	130	121	109
316LN	155	151	139

No additional precipitates have been detected after vacuum firing at 950° C

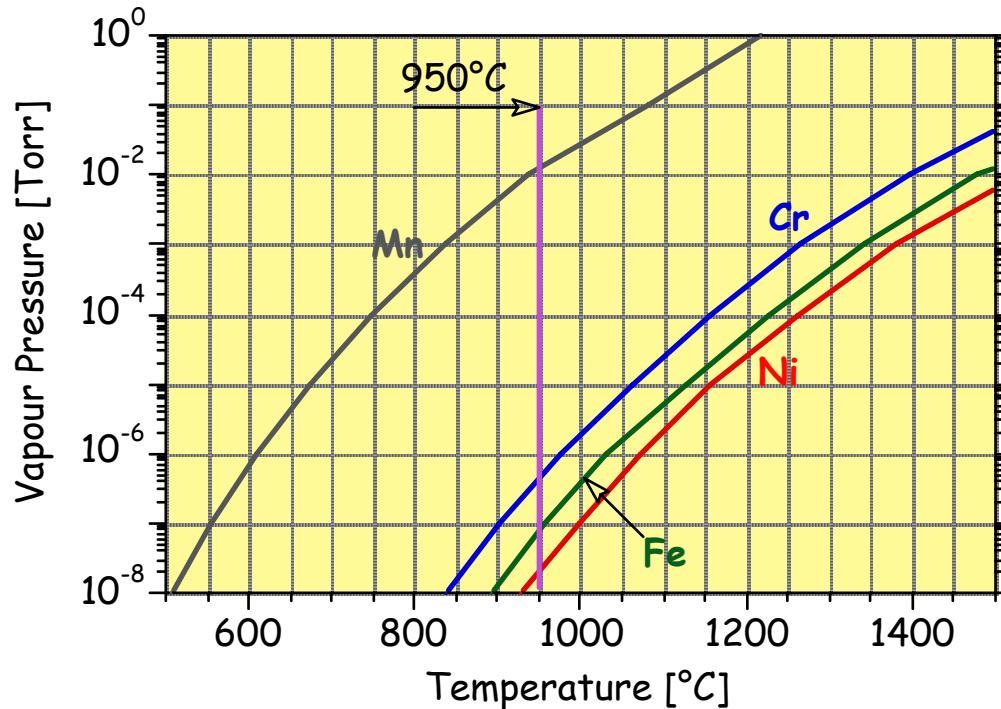
No significant variation of "rupture strength" and "stretch at break": less than 5%

Modification of the surface roughness induced by vacuum firing



Sublimation of metallic elements during vacuum firing

Vapor Pressure of the pure elements



Diffusion coefficients at 950°C in austenite:

[R.K. Wild, Corrosion Science, 14(1974)575]
[A.F. Smith, R. Hales, Metals Science
Journal, 9(1975)181]

$$D_{Cr} = 7 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$$

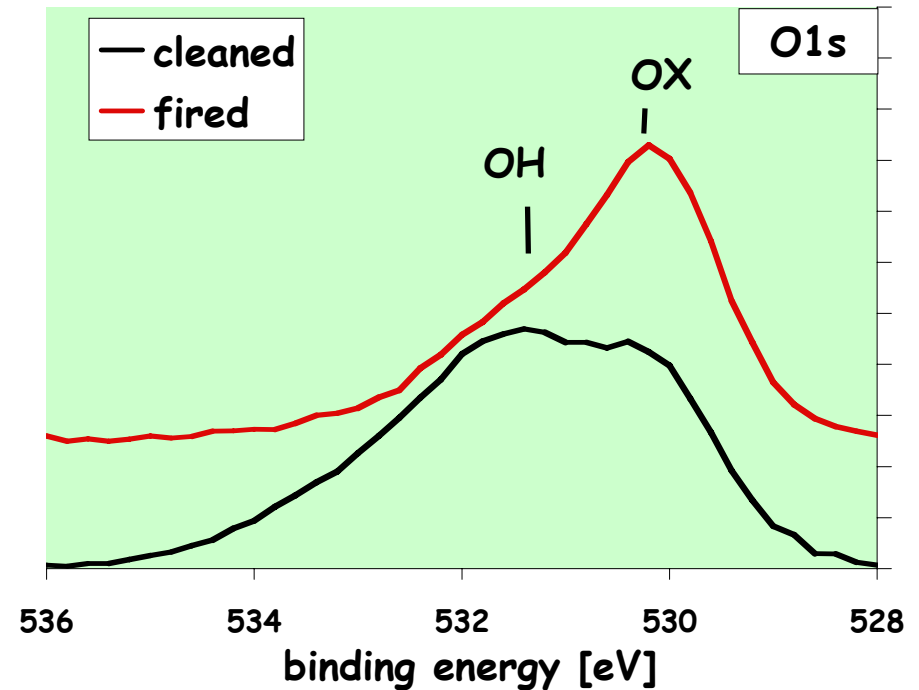
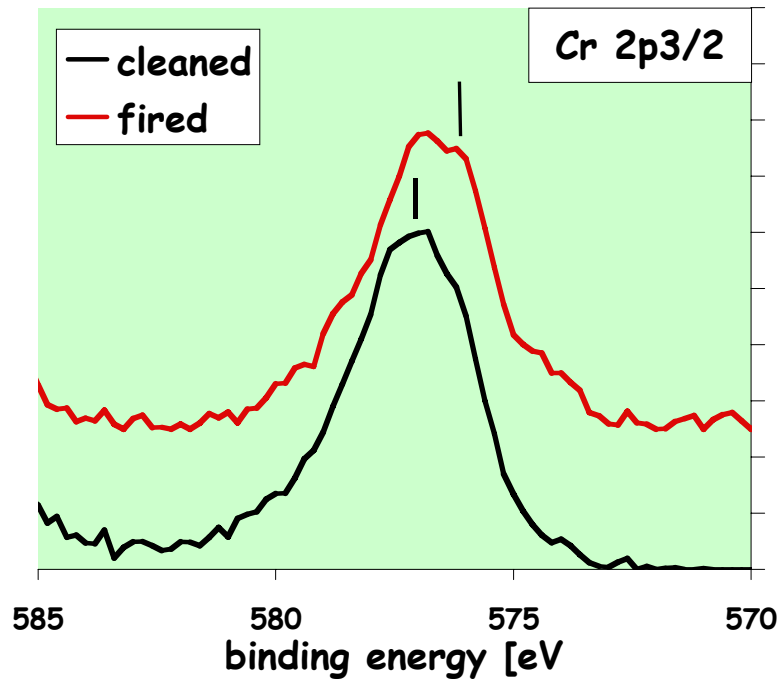
$$D_{Mn} = 6 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$$

$$D_{Fe} = 2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$$

$$D_{Ni} = 5 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$$

Because of the higher sublimation rate of Cr, the surface of stainless steels is expected to be **enriched with Fe** after firing .

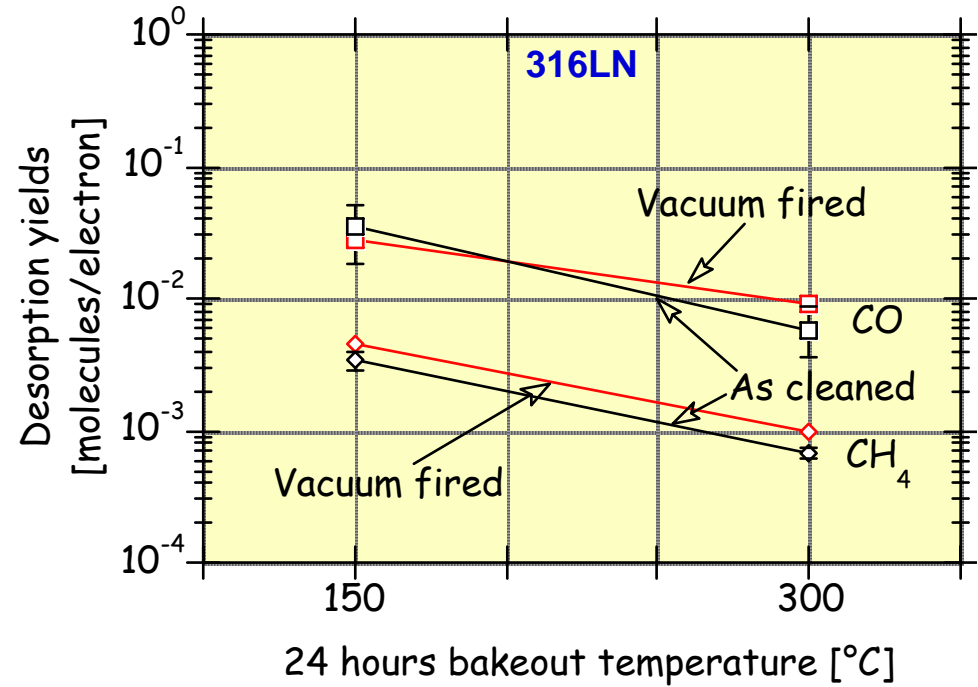
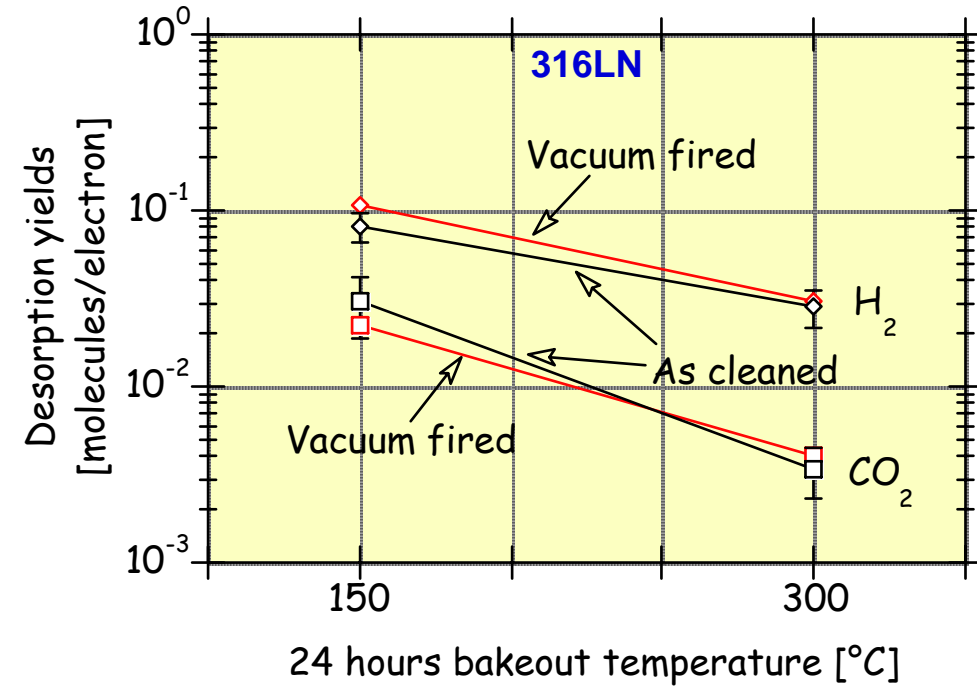
Surface composition after vacuum firing



- After vacuum firing the oxide layer is **strongly enriched with Fe**: Cr/Fe= 0.33 for 316L and 0.22 for 304L (0.75 for cleaned); oxide thickness as for cleaned.
- Cr2p^{2/3} and O1s lines indicate the presence of **less hydroxides** than on cleaned samples (Cr₂O₃ and Fe₂O₃)

J. Gavillet and M. Taborelli, unpublished results

Decreasing the concentration: Vacuum firing



The desorption yields of vacuum fired stainless steels are similar to those of cleaned samples \Rightarrow vacuum firing does not reduce electron stimulated desorption.

BN surface segregation

- At temperature higher than 700°C , boron segregates to the surface and, in N added stainless steels (316LN), can form h-BN. Heating temperatures higher than 1150°C are needed to dissolve the h-BN layer.
- BN does not form for B concentration lower than 9 ppm.
- When the concentration is equal or larger than 9 ppm BN forms only when B is free to move, namely not blocked in BN precipitates already existing in the steel bulk.
- The BN layer strongly reduces the surface wettability and may produce peel-off of thin film coatings.
- The BN layer can be effectively removed by electropolishing.

Vacuum firing

The outgassing rate after the vacuum firing treatment can be calculated in the frame of the diffusion limited model.

Two asymptotic values are identified.

- For **thin sheets** the initial gas content is fully emptied. In this case **the H_2 pressure in the furnace can't be neglected**: it defines the final concentration through the Sieverts' law.

$$c \left[\frac{\text{Torr l} (H_2)}{\text{cm}^3} \right] = 8.21 \cdot 10^{-2} \sqrt{P[\text{Torr}]} \cdot e^{-\frac{2650}{1.99 \cdot T[K]}}$$

An ultimate minimum concentration of about **6×10^{15} atoms H cm^{-3}** could be attained after the treatment when the pressure in the furnace is about 10^{-5} Torr.

- For **thick slab**, the model has to converge to the **semi-infinite solid** approximation. Actually, in this case the pressure in the furnace has a very limited influence

Vacuum firing

After firing the concentration in the solid is given by:

$$c(x, t) = c_w + (c_o - c_w) \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n-1} \cos \frac{(2n+1)\pi \cdot x}{L} e^{-(2n+1)^2 \pi^2 F_o(T_f, t_f)}$$

$F_o(T_f, t_f)$ is the Fourier number for the firing treatment

$$F_o(T_f, t_f) = \frac{D(T_f) \cdot t_f}{L^2}$$

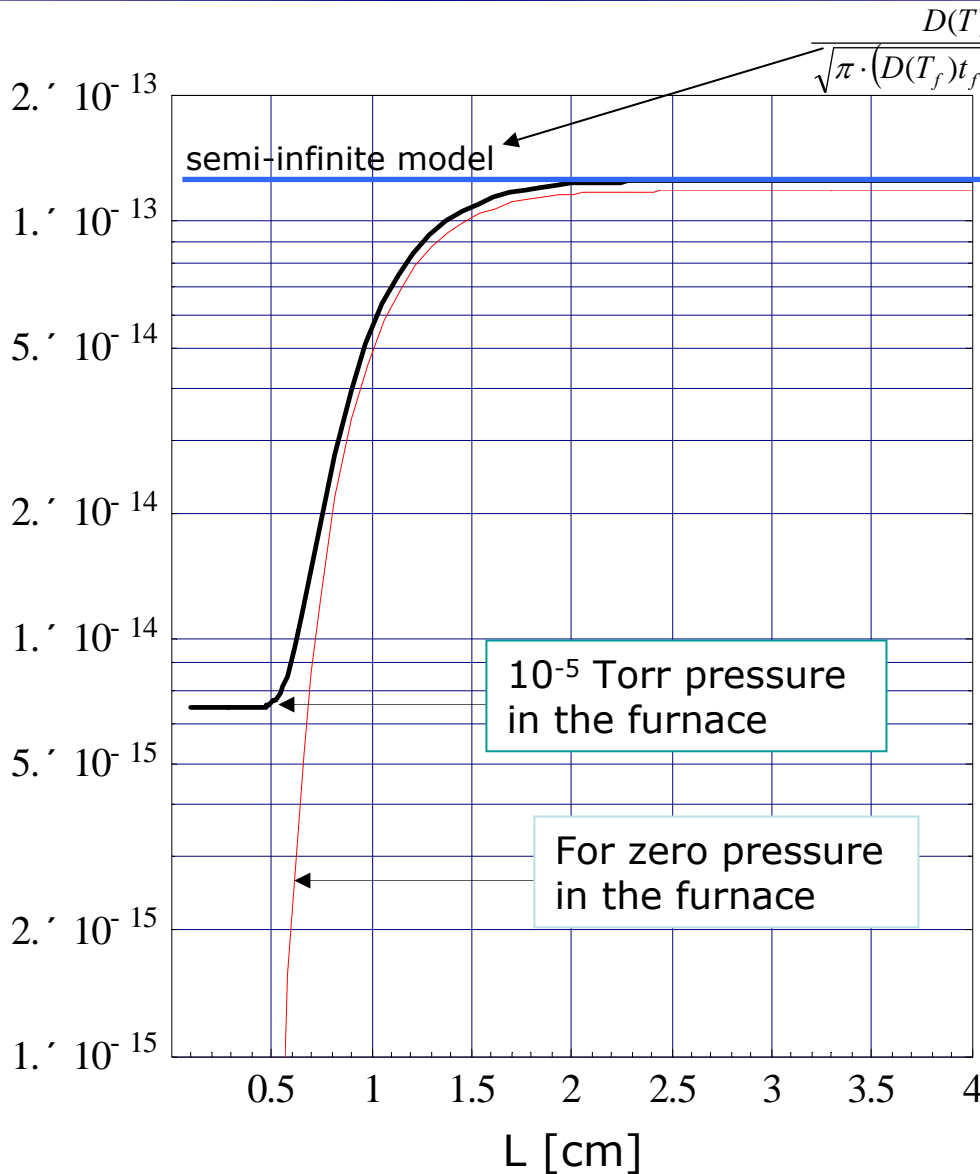
In the consecutive bakeout it evolves as the concentration in a plane sheet with uniform initial concentration c_w and close to zero surface concentration

In the consecutive bakeout the Fourier number is increased accordingly.

$$q(t) = \frac{4 \cdot c_w \cdot D(T)}{L} \sum_{n=0}^{\infty} e^{-(2n+1)^2 \pi^2 \cdot F_o(T_{bo}, t_{bo})} + \frac{4 \cdot (c_o - c_w) \cdot D(T)}{L} \sum_{n=0}^{\infty} e^{-(2n+1)^2 \pi^2 \cdot [F_o(T_f, t_f) + F_o(T_{bo}, t_{bo})]}$$

where T is the temperature of the measurement.

Vacuum firing



Calculation performed for 1 wt. ppm initial concentration and in-situ bakeout at 150° C for 24 h.

Values for diffusivity and solubility taken from P. Tison, Thesis Université Pierre et Marie Curie, Paris 6 CEA-R-5240(1) 1984



Outgassing rates in the 10^{-15} Torr ℓ s $^{-1}$ cm $^{-2}$ range are expected. For thick plates (flanges) the rate is 20 times larger

Case study of 1: CERN unpublished results (G eraldine Chuste)

Material:

316LN

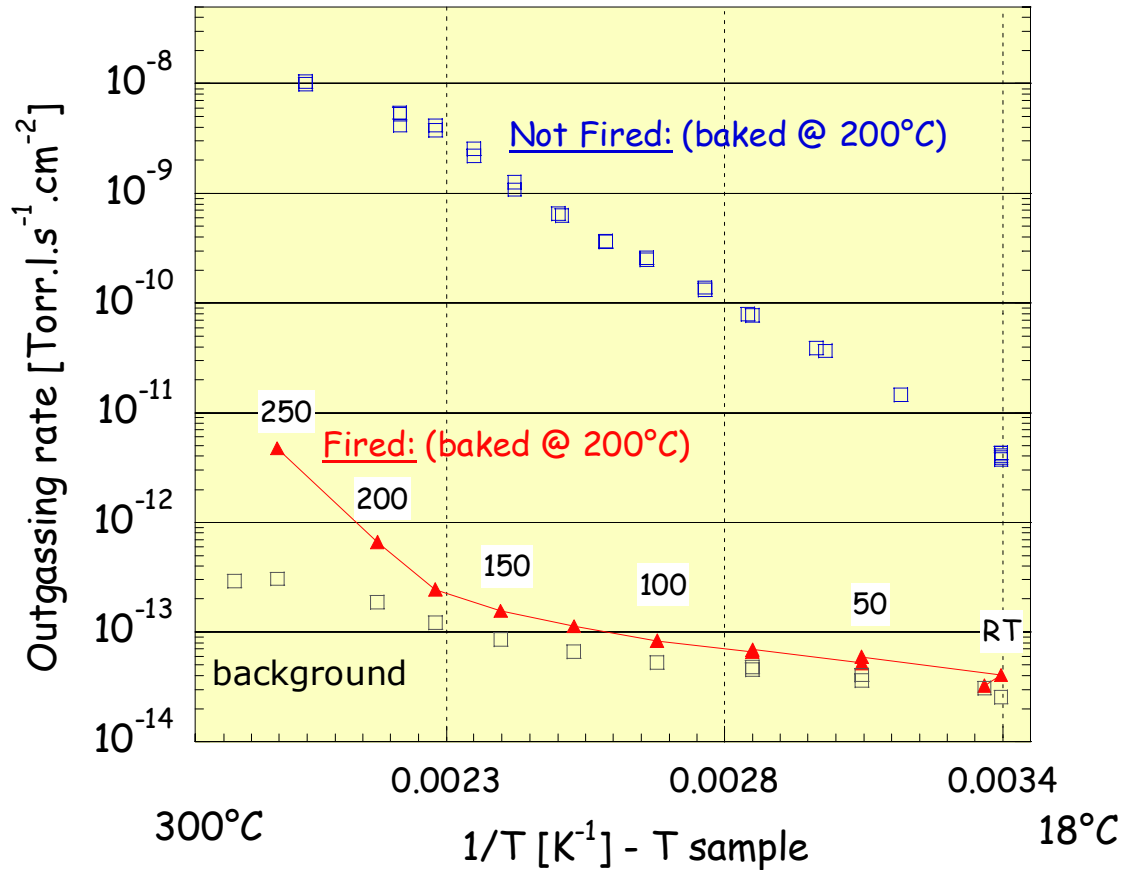
Wall thickness:

2 mm

Vacuum firing:

950  C x 2 h, 10^{-5} Torr H₂

For the fired chambers, the outgassing rate is limited by the background signal. The results were confirmed in a second system. On both systems, the upper limit at RT is 10^{-14} Torr.l.s⁻¹.cm⁻².



Case study of 2: R Calder and G. Lewin, Brit. J. Appl. Phys., 1967, Vol. 18, p 1459

In 1967, **R. Calder and G. Lewin** reported several data for vacuum fired stainless steels (firing: 1000° C for 3 h in 2×10^{-6} Torr residual H₂ pressure, in situ bakeout: 360° C for 25 h, dimensions: 1.1×10^3 cm² of 2 mm thick vacuum chamber + 10^4 cm² of 0.25 mm thick strip). Their main results, obtained by the throughput method, were:

1. the measured outgassing rates at room temperature of fired and in-situ baked stainless steels were **between 6.9×10^{-15} and 1.3×10^{-14} Torr l s⁻¹ cm⁻²**.
2. **the value of the outgassing rate does not increase by heating** the sample up to 100° C, and a small increase can be record only at 200° C (1.9×10^{-14} Torr l s⁻¹ cm⁻²). They explained this unexpected behavior by arguing that the untreated section of the system (1.4% of the total area) could be responsible for all the H₂ observed up to 100° C.

The implication of the results is that "*the specimen outgassing rate was very much less than 10^{-14} Torr l s⁻¹ cm⁻²*".

Calculations performed with the diffusion model show that the outgassing rate should be lower than 10^{-16} Torr l s⁻¹ cm⁻²

Case study of 3:

G. Grosse and G. Messer, Proc. of the 7th Int. Vac. Cong., Vienna, 1977, p. 223
 G. Grosse and G. Messer, Proc. of the 8th Int. Vac. Cong., Cannes, 1980, p. 399

G. Grosse and G. Messer measured the outgassing rate of several materials by accumulation and selective molecular beam methods. The detection limit of such a method was extremely low: $10^{-17} \text{ Torr l s}^{-1} \text{ cm}^{-2}$.

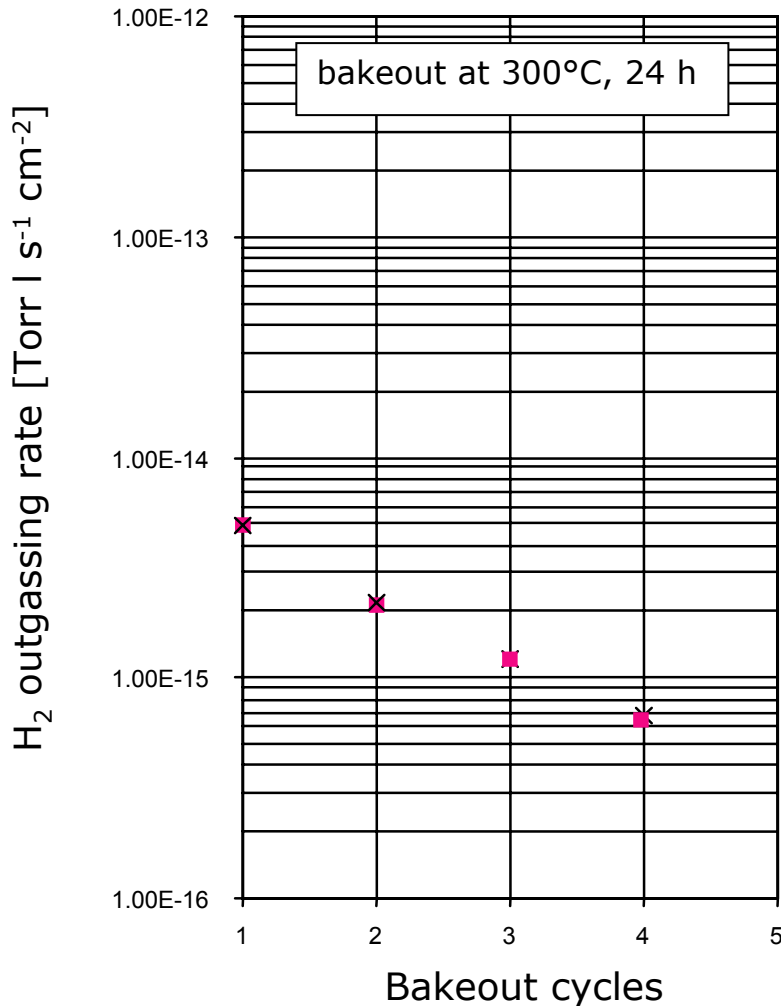
Stainless steel was heated at **550° C for 3 days** in an excellent vacuum of 10^{-8} Torr . The accumulated F_0 was very high (7.9) and the final in-situ bakeout was done at 280° C for 24 h. From the diffusion limited model:

$$q = \frac{4 \cdot (1.6 \cdot 10^{-6}) \cdot 1.9 \cdot 10^{-12}}{0.3^2} \exp\left(-\pi^2 \cdot \frac{2.6 \cdot 10^{-8} \cdot 3600 \cdot 24}{0.3}\right) \cong 3 \cdot 10^{-17} \frac{\text{Torr} \cdot \text{l}}{\text{s} \cdot \text{cm}^2} \cong 1000 \frac{H_2 \text{ molecules}}{\text{s cm}^2}$$

The lowest value reported by the authors is $9 \times 10^{-17} \text{ Torr l s}^{-1} \text{ cm}^{-2}$.

The implication of this result is that the diffusion limited model can provide estimation of the outgassing rate for concentration as low as 1 at. H ppb.

Case study of 4:



316 LN Stainless steel: CERN
AT-VAC int. note
J-P Bojon, N. Hilleret, B.
Versolatto

stainless steel sheets 1.5 mm thick

✕ After vacuum firing

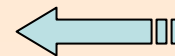
For mm thick vacuum chambers, the outgassing of H after vacuum firing can be reasonably described by a diffusion model only if the pressure of H during the treatment is taken into account

This approach consists in covering the surface with a thin layer of a material having either:

- very low hydrogen permeability (passive barriers) or
- high hydrogen solubility (active barriers).

The surface layer can be produced by:

- deposition techniques,
- segregation of elements contained in the alloy
- or oxidation.



Air bakeout

This method, originally proposed by **Petermann** (French Patent, No 1, 405, 264), consists in forming a thick oxide layer on the metal by heating in air.

D.G. Bills, J. Vac. Sci. Technol. **6**, 166 (1969):

“Such processing is reported to decrease the hydrogen diffusion rate [he means outgassing rate] by **10^3 times** if the oxidized surface is not subsequently baked above about 200° C”

Case of study 1:

V. Brisson et al., Vacuum 60(2001)9. and
M. Bernardini et al., J. Vac. Sci. Technol. A16(1998)188

After air bakeout at 450° C for 38 h and in-situ bakeout at 150° C for 7 days:

$$q \approx 10^{-15} \text{ Torr l s}^{-1} \text{ cm}^{-2}$$

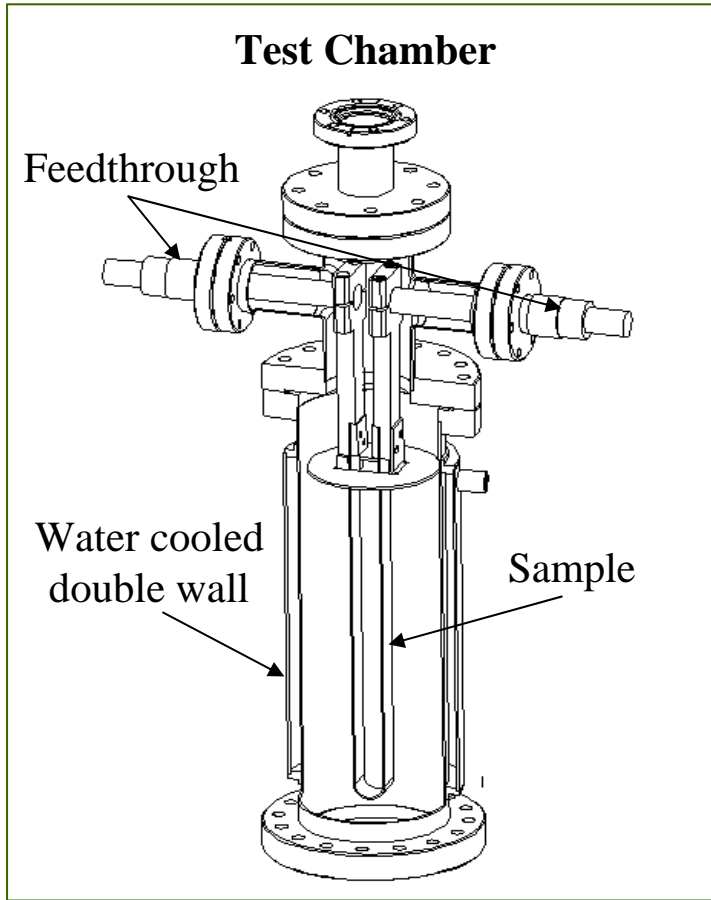
The result confirm the indication given by the Bills' paper in '69.

It would be worthwhile to understand whether the benefit of the treatment is due to hydrogen depletion or not.

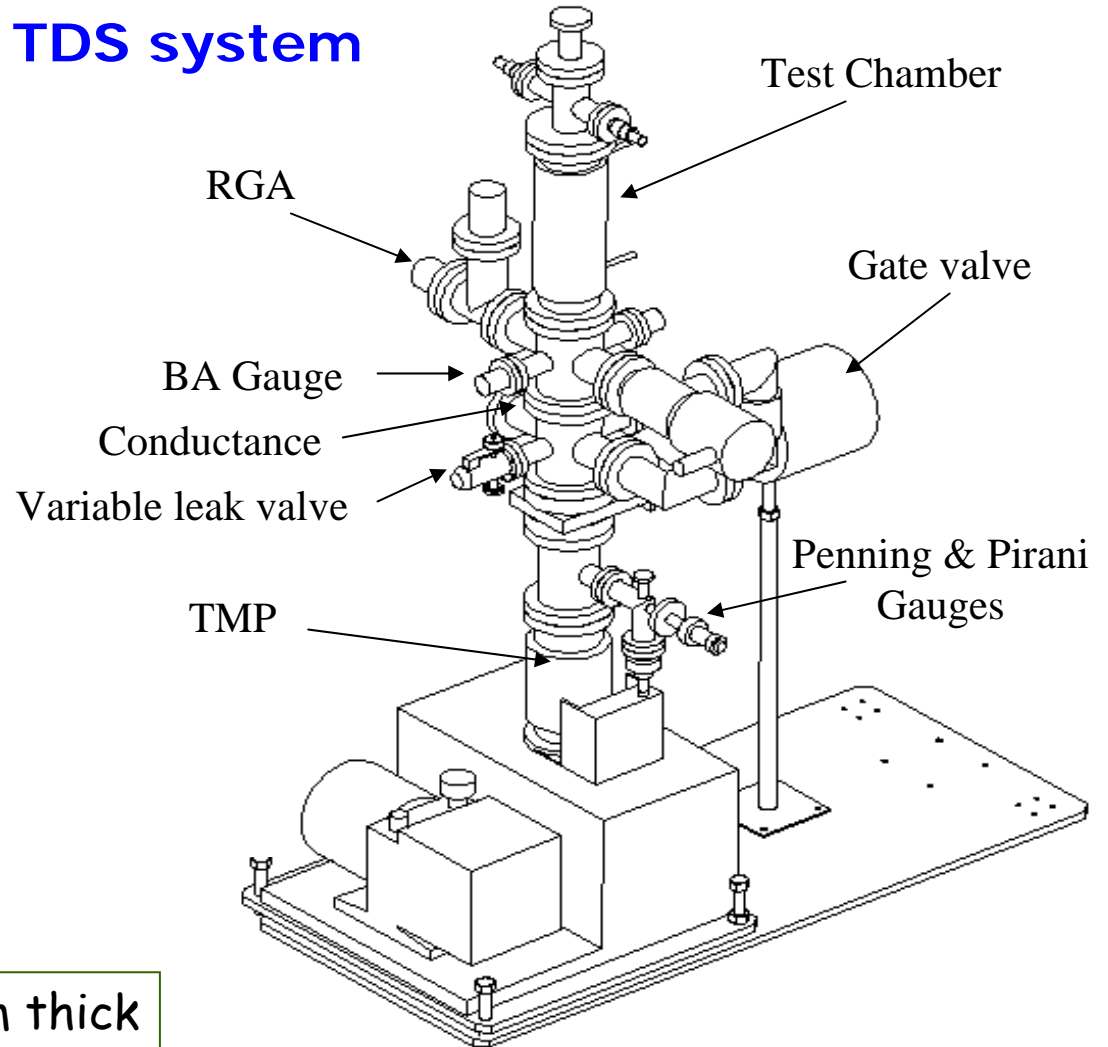
A dedicated experiment was performed at CERN by thermal desorption. The 1 mm thick 316 LN samples were air-baked at 450°C for 24 h and 100 h. The in-situ baking was at 200°C for 12 h. The heating ramp was 5 K/min.

Hindering the desorption from the surface

Passive barriers: air bakeout



TDS system

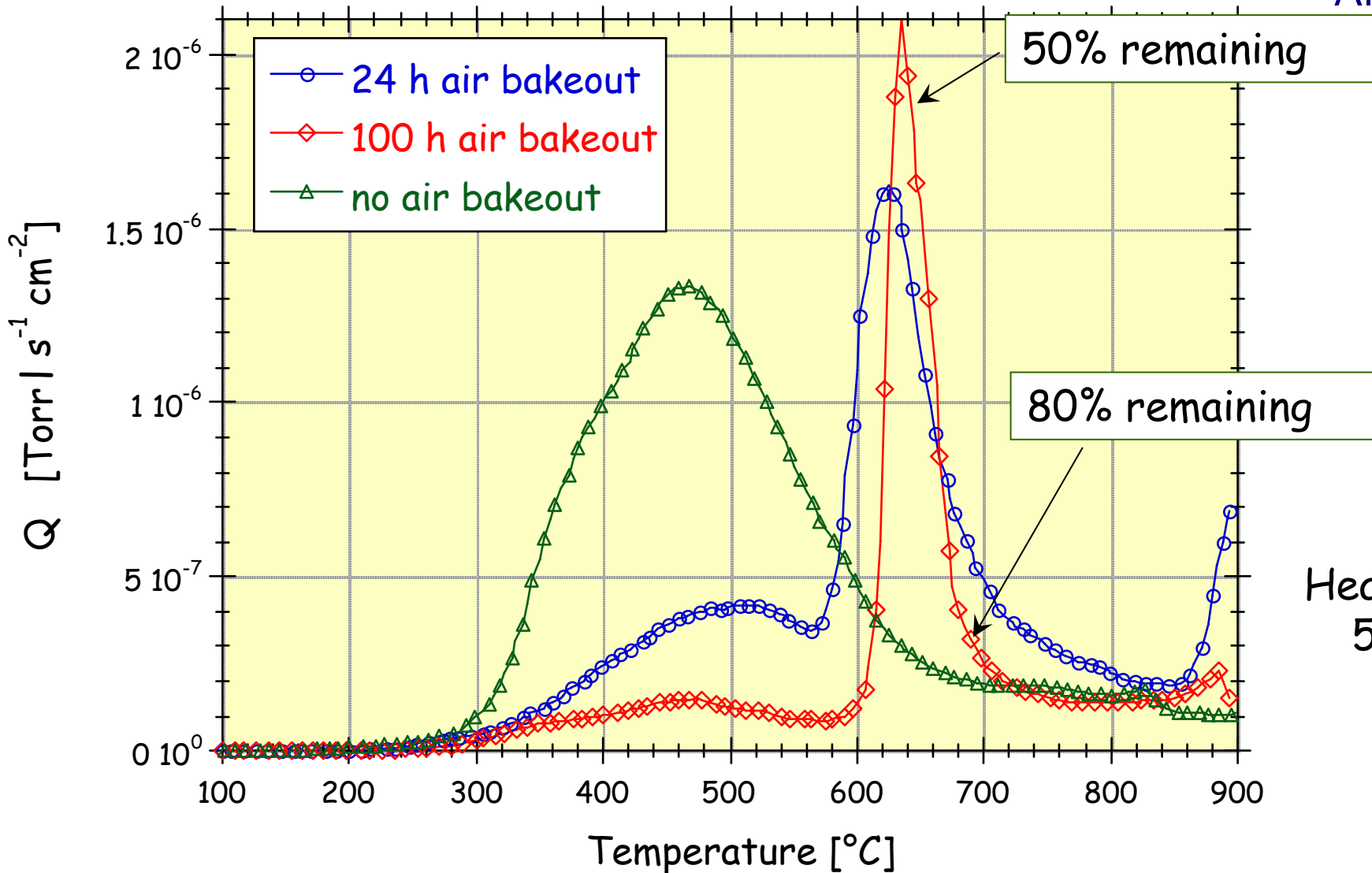


Sample: 60 cm long, 1 cm wide, 1 mm thick
 Thermocouple: 0.1 mm diameter S type

Hindering the desorption from the surface

Passive barriers: air bakeout

Air bakeout



Heating rate
5 K min⁻¹

The quantity of hydrogen extracted by TDS from air baked samples is of the same order of that from untreated stainless steels.

Consequence: air bakeout decreases the outgassing rate without depleting the residual hydrogen significantly.

However, the main hydrogen peak is shifted to higher temperatures (650°C).

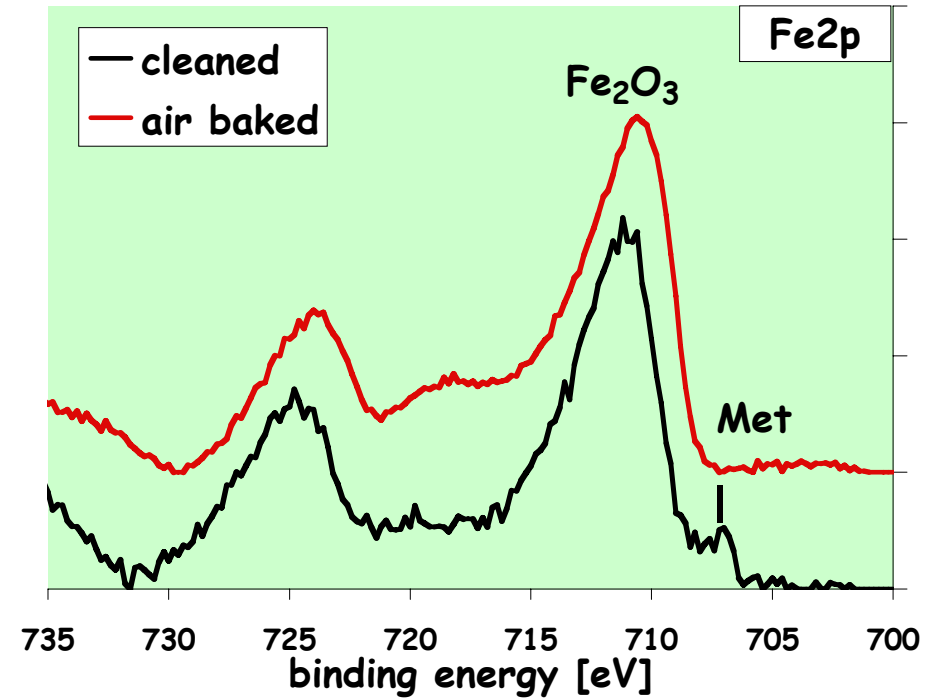
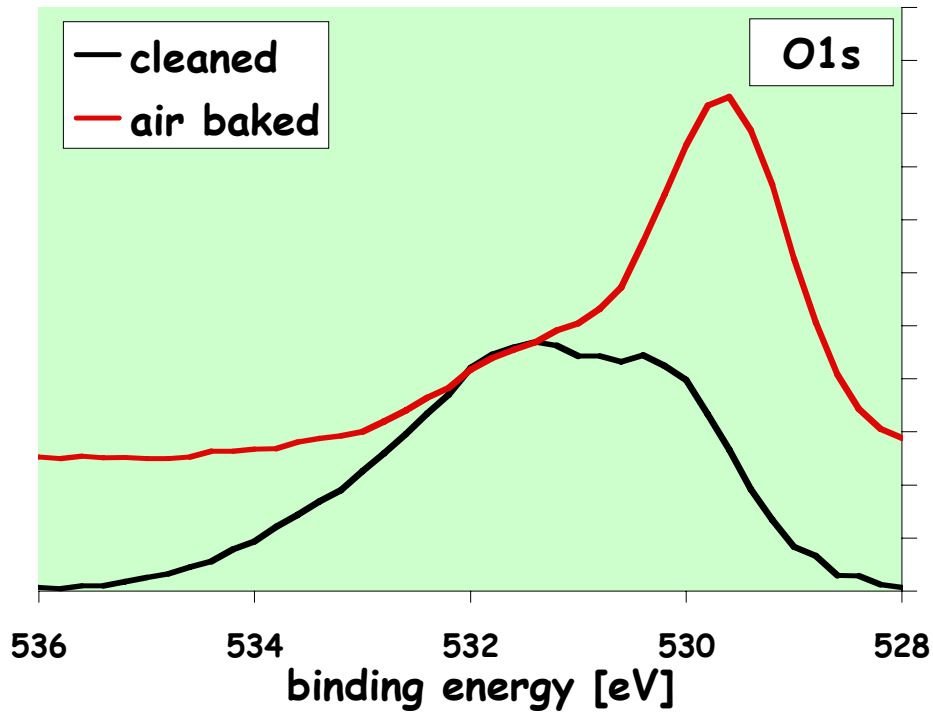
Consequence: hydrogen is blocked or trapped by the thick oxide layer.

How thick is the oxide?

Which is the nature of this oxide?



The oxide layer of air baked austenitic stainless steels

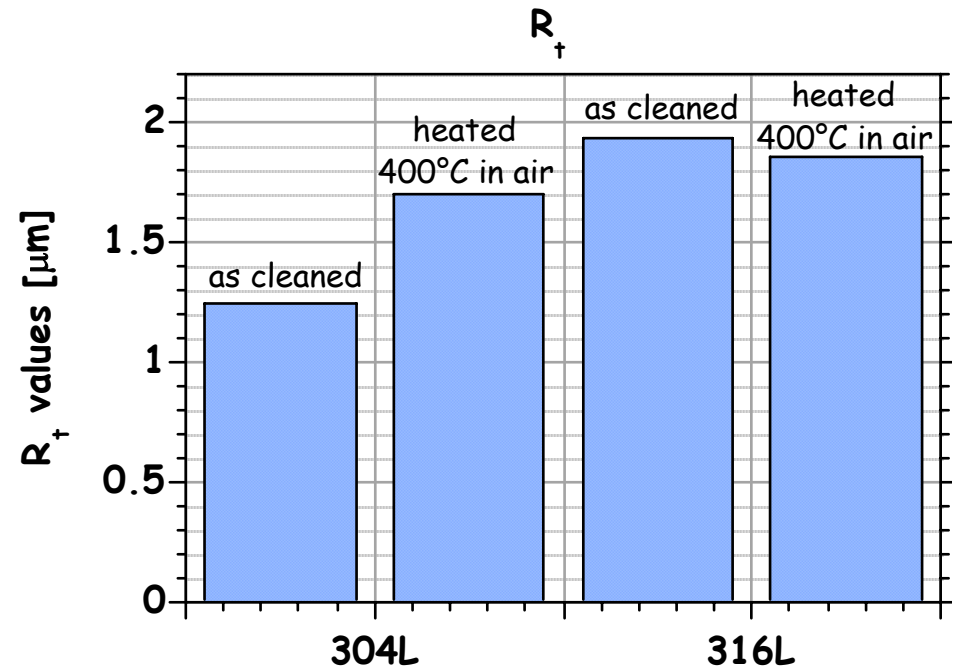
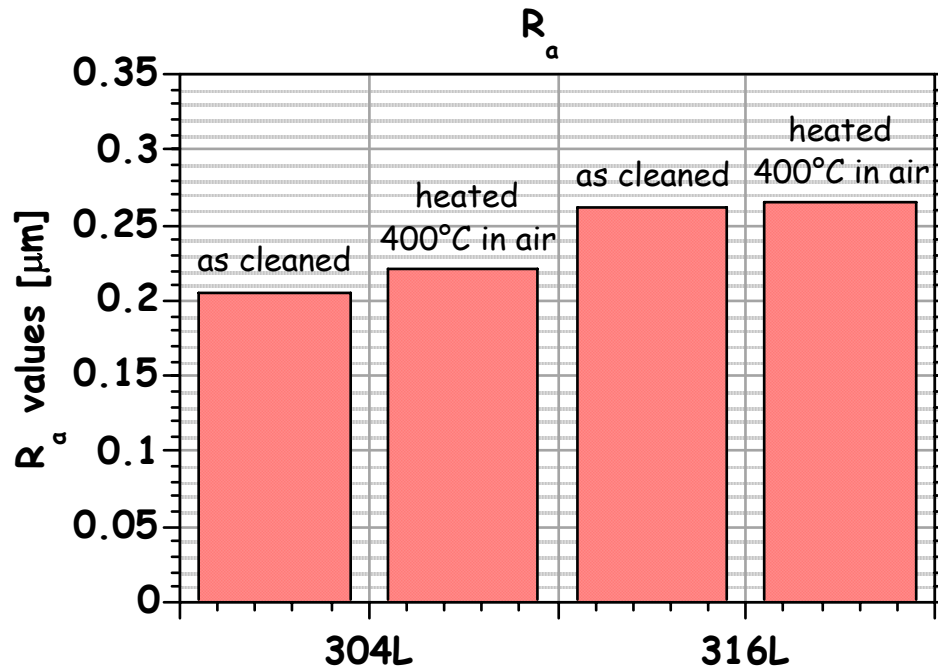


- Cr/Fe= 0.01 (0.75 for cleaned) → very high Fe concentration
- Oxide thickness 10 times larger than for as cleaned samples.

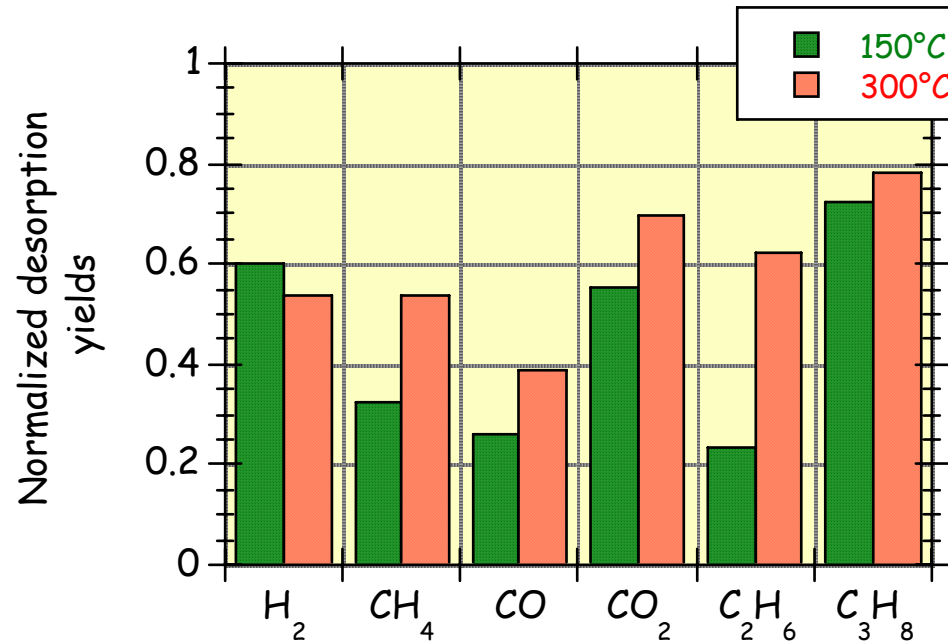
J. Gavillet and M. Taborelli, unpublished results

Hindering the desorption from the surface

Passive barriers: air bakeout

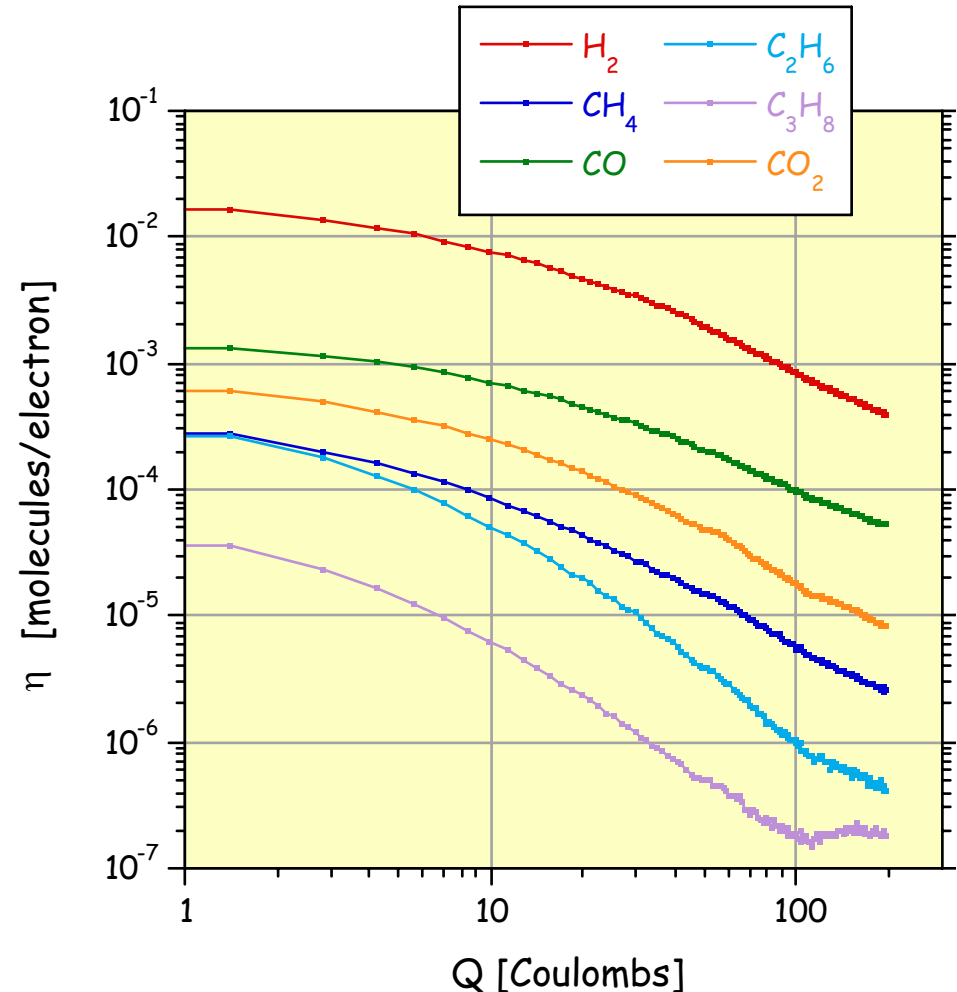
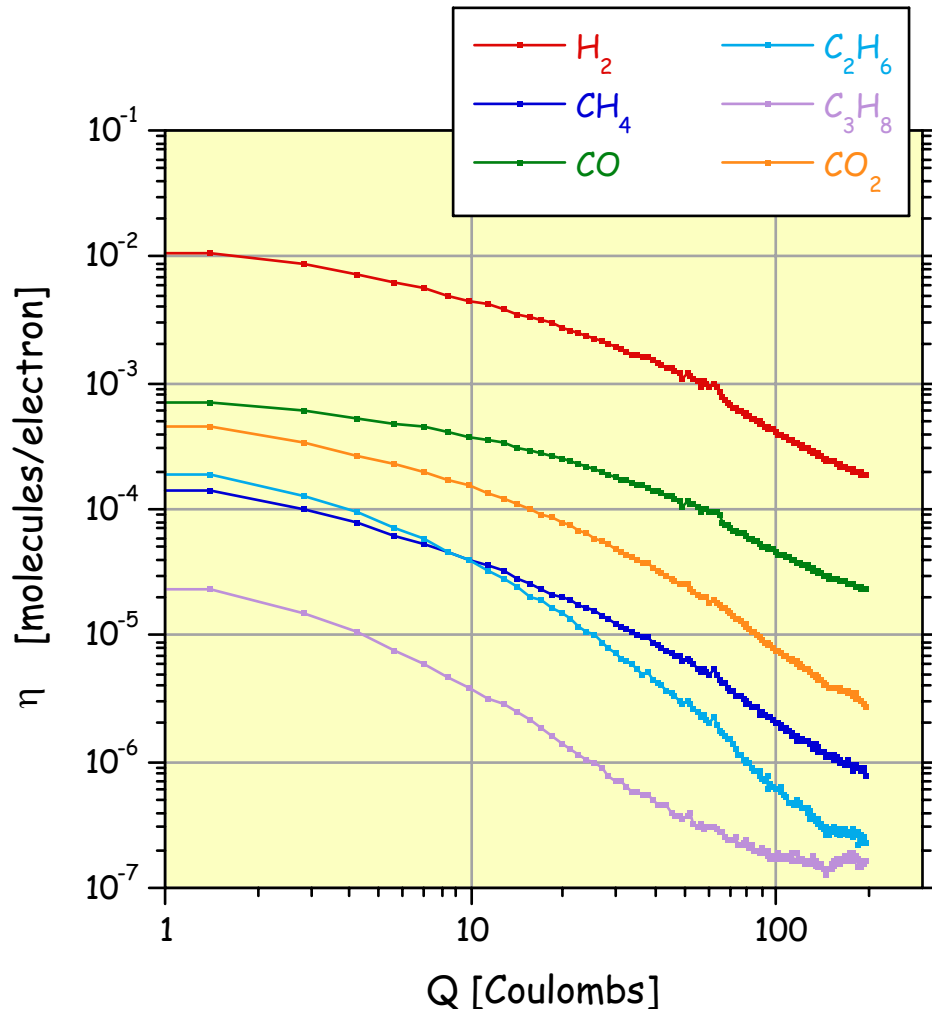


Electron induced desorption yields of an air baked sample (400°Cx24h) normalized to those of the cleaned samples:



Air baked at 400°C for 24h

As cleaned

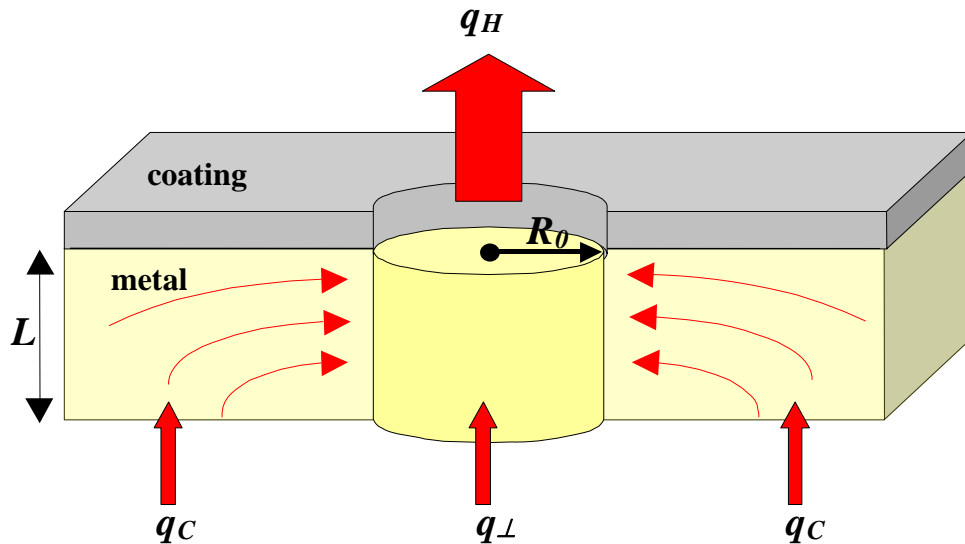


- A variety of compounds (Al_2O_3 , BN, TiN, ZrO_2 , etc...) deposited as a thin film should entirely block H_2 outgassing and permeation from the metallic substrate since their permeability is negligible for H.
- However, experimental results have shown that only a partial reduction of the flux is attained.
- This could be attributed to defects on the coating (**pinholes or scratches**) that cause discontinuity on the surface coverage.
- Pinholes are produced during the deposition process and they are presumably due to atmospheric dust particles.

Hindering the desorption from the surface Passive barriers by deposition

Normalised uncoated surface areas of the order of 10^{-4} are usually measured for sputter coated film (due to atmospheric dust). The diameters of the pinholes is of the order of some μm .

But the residual H_2 flux is much higher than 10^{-4} because lateral diffusion around the pinhole dominates.



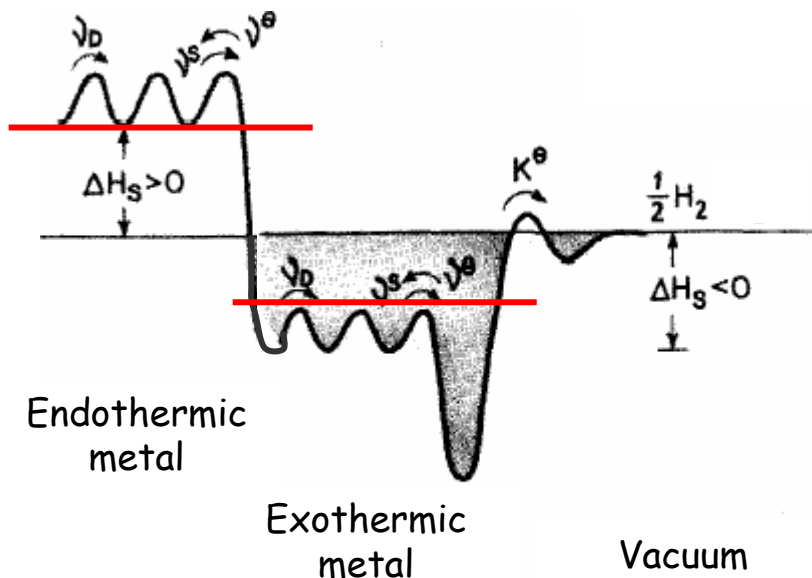
Barrier improvement factor:

$$BIF = \frac{\rho}{\rho_0} = \frac{\Theta \times \left(1 + 1.18 \frac{L}{R_0} \right)^*}{\Theta \times \left(1 + 1.18 \frac{L}{R_0} \right)}$$

Amplification factor

* After W.Prins and J.J.Hermans, J.Phys.Chem., 63 (1959) 716.

Active barriers absorb H exothermically. The solution enthalpy is negative. They should absorb the H atoms coming from the substrate. Possible candidates: transition metals of the first groups.



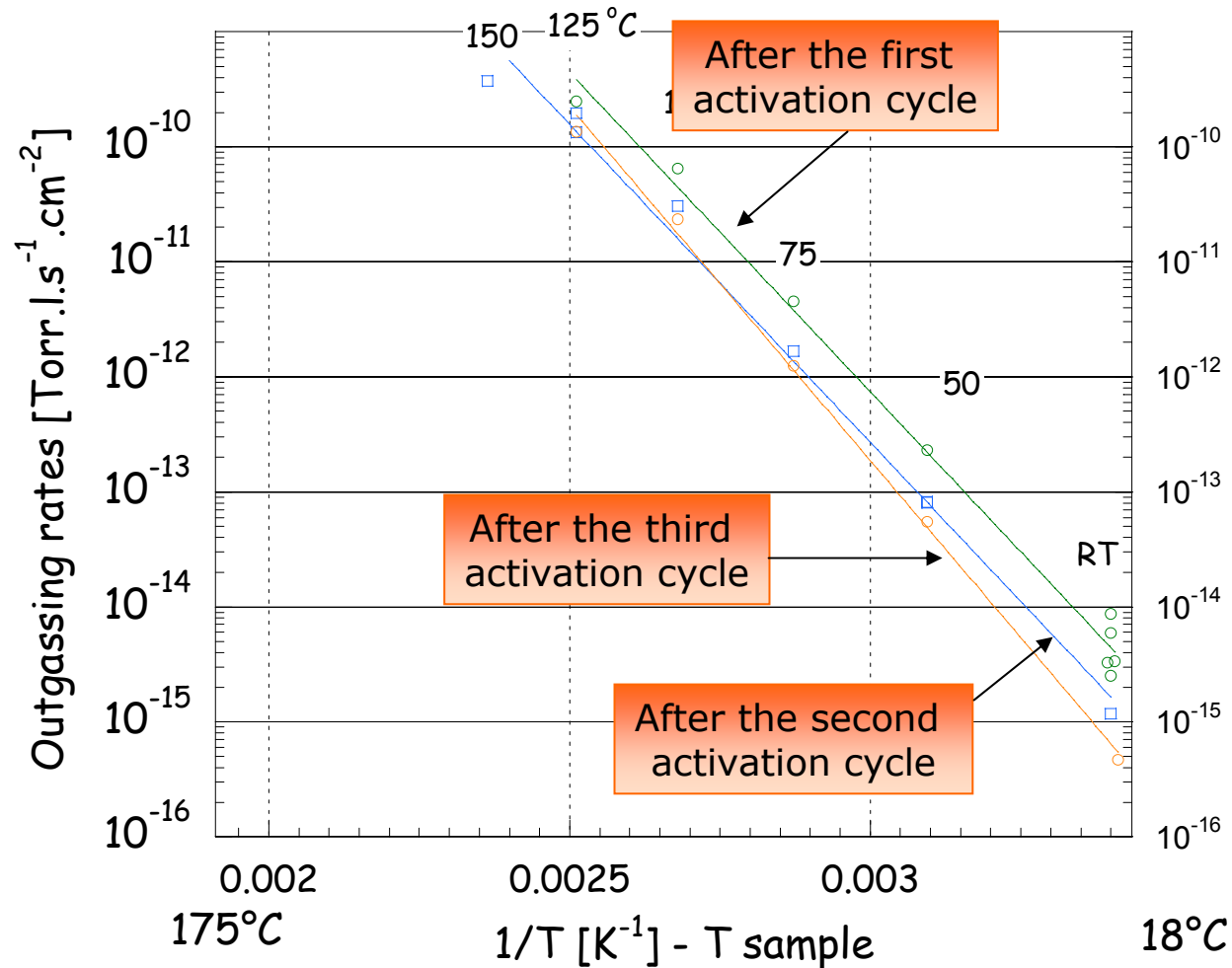
For the elements of the 4th group and their alloys, surface activation is also possible by dissolution of the native oxide (Non Evaporable Getters) .

The lowest activation temperature has been found for the Ti-Zr-V sputter-deposited alloys:

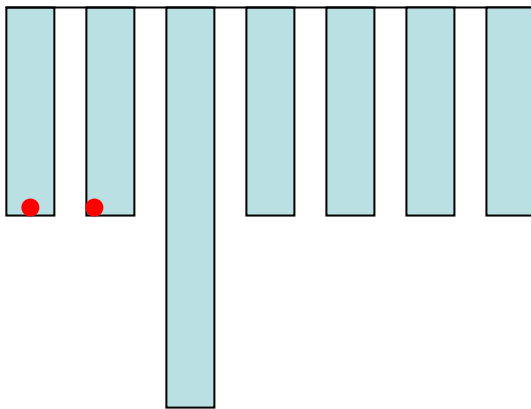
180°C for a 24 h heating

Efficiency of Ti-Zr-V as H barrier CERN unpublished results: (Géraldine Chuste)

OFS Copper



Trapping sites are generated in the metal with the purpose of blocking hydrogen migration to the surface, hence providing a sort of **internal pumping**. This technique, which is not applied intentionally at present, requires a modification of the material production process.



The trapping effect can be taken into account by introducing an effective diffusion coefficient D_{eff} .

The outgassing rate is then calculated with the usual diffusion equations.

Because $D_{\text{eff}} \ll D$, a much lower outgassing rate is expected.

c_L, c_{Trap} : H atoms in the regular interstitial site, trapping sites

1. H outgassing rates of the order of 10^{-15} Torr l s⁻¹ cm⁻² are obtained by vacuum thermal treatment for 1 ÷ 2 mm thick vacuum chambers made of copper or austenitic stainless steel.
2. In this respect stainless steel is worst than copper because its H diffusivity is very low and, as a consequence, it needs higher temperature for degassing.
3. Diffusion theory provides the mathematical tools to describe and predict outgassing rates for 1 ÷ 2 mm thick vacuum chambers. Recombination theory could be useful for thinner walls or for very low H content (*less than 10 at. ppb?*).
4. When vacuum firing is considered, the H pressure in the furnace is the crucial parameter for sheets thinner than 5 mm.
5. Air bakeout at 400°C for 24h reduced the H outgassing rate by at least two order of magnitude.

6. The efficiency of passive barriers is limited by the enhanced diffusion gradient around pinholes.
7. The potentiality of active barriers is obtained only after surface activation.
8. Internal pumping is for the future.