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Outgassing Analysis of different Copper Materials for Ultra-High Vacuum by Thermal Desorption Spectroscopy

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Abstract

An extensive outgassing study has been performed for oxygen free electronic copper (Cu-OFE) with different surface treatments (electropolishing, passivation and SUBU) and for electroformed copper. Other materials like stainless steel or Molybdenum Carbide - Graphite composites have also been studied to complement the copper study. All these materials are used or will be used in different parts of the CERN accelerators complex for the vacuum chambers or in components that operate in ultra-high vacuum conditions.

Thermal desorption spectroscopy (TDS) is the method used to analyse the outgassing of these materials. The study was mainly focused on the outgassing of hydrogen and water. To complement the outgassing results obtained from the TDS, other analysis methods have been applied: X-ray photoelectron spectroscopy to analyse the surface and its oxidation states and optical microscope and scanning electron microscope to analyse the microstructure of the samples.

For the Cu-OFE it has been observed how the outgassing does not change between the electropolishing and the passivation treatments, but for the SUBU treatment around 10 times more outgassing of water is detected. This water is coming from the dissociation of the components that form the SUBU bath that are trapped in pinholes present at the surface. In general, for the Cu-OFE, it has been found that the hydrogen dissolved in the bulk of the copper can produce the reduction of the oxide layer when it diffuses through the surface oxide. The diffusion of hydrogen in copper happens at lower temperatures than the dissociation of the copper oxide.

For the electroformed copper it has been possible to establish a relation between the electroforming parameters, the amount of outgassing, the outgassing temperature and the microstructure of the copper. One of these relations is that the concentration of trapped hydrogen increases with the thickness. Also a correlation has been observed between the transient curves and the TDS outgassing results in terms of how the hydrogen is trapped in the copper.

Zusammenfassung

Für sauerstofffreies elektronisches Kupfer (Cu-OFE) mit verschiedenen Oberflächenbehandlungen (Elektropolieren, Passivierung und SUBU) und für Elektroplattieren Kupfer wurde eine umfangreiche Ausgasungsstudie durchgeführt. Andere Materialien wie Edelstahl oder Molybdänkarbid-Graphit Verbundwerkstoffe wurden ebenfalls untersucht, um die Kupferstudie zu ergänzen. Alle diese Materialien werden in verschiedenen Teilen des CERN-Beschleuniger-Komplexes für die Vakuumkammern oder in Komponenten verwendet, die in Ultrahochvakuumbedingungen arbeiten.

Die thermische Desorptionsspektroskopie (TDS) ist die Methode, die verwendet wird, um die Ausgasung dieser Materialien zu analysieren. Die Studie konzentrierte sich hauptsächlich auf die Ausgasung von Wasserstoff und Wasser. Zur Ergänzung der TDS erzeugten Ausgasungsergebnisse wurden weitere Analysemethoden angewendet: Röntgenphotoelektronenspektroskopie um die Oberfläche und ihre Oxidationsstufen zu analysieren und das optische Mikroskop und das Rasterelektronenmikroskop um die Mikrostruktur der Proben zu analysieren.

Für das Cu-OFE wurde beobachtet, wie sich die Ausgasung zwischen dem Elektropolieren und den Passivieren nicht ändert, aber für die SUBU-Behandlung wird etwa 10-mal mehr ausgegastetes Wasser festgestellt. Dieses Wasser kommt aus der Dissoziation der Komponenten, die im SUBU-Bad sind, die in kleinen Löchern gefangen sind, die auf der Oberfläche sind. Es wurde gefunden, dass der Wasserstoff, der im massiger Körper des Kupfers eingeschlossen ist, die Reduktion der Oxidschicht erzeugen kann, wenn er durch das Oxid diffundiert. Die Wasserstoff Diffusion in Kupfer erfolgt bei niedrigeren Temperaturen als die Dissoziation des Kupferoxids.

Für Elektroplattieren Kupfer war es möglich, eine Beziehung zwischen den Elektroplattierenparametern, dem Ausmaß der Ausgasung, der Ausgasungstemperatur und der Mikrostruktur des Kupfers herzustellen. Eine dieser Beziehungen ist, dass die Konzentration des gefangenen Wasserstoffs mit der Dicke zunimmt. Auch eine Korrelation zwischen den Vorübergehenden Kurven und den TDS-Ausgasungsergebnissen wurde beobachtet, wie der Wasserstoff in dem Kupfer eingefangen wird.

Résumé

Une vaste étude sur le dégazage de cuivre sans oxygène (Cu-OFE) avec différents traitements de surface (électropolissage, passivation et SUBU) et de cuivre électroformé a été effectuée. D'autres matériaux comme l'acier inoxydable ou le Carbure de molybdène - Graphite composite ont également été étudiés pour compléter l'étude sur le cuivre. Tous ces matériaux sont utilisés ou seront utilisés dans différentes parties du complexe d'accélérateurs du CERN, pour les chambres à vide ou dans des composants qui fonctionnent dans des conditions d'Ultra-vide.

La spectroscopie pour désorption thermique (TDS) est la méthode utilisée pour analyser le dégazage de ces matériaux. L'étude était centrée principalement sur le dégazage d'hydrogène et d'eau. Pour compléter les résultats de dégazage obtenus à partir de la TDS, d'autres méthodes d'analyse ont été appliquées: la spectrométrie photoélectronique X pour analyser la surface et ses états d'oxydation et le microscope optique et le microscope électronique à balayage pour analyser la microstructure des échantillons.

Pour le Cu-OFE, on a observé comment le dégazage ne change pas entre les traitements d'électropolissage et de passivation, mais pour le traitement de SUBU, on détecte environ 10 fois plus de dégazage d'eau. Cette eau provient de la dissociation des composants qui forment le bain de SUBU qui sont piégés dans des petits trous présents sur la surface. En général, pour le Cu-OFE on a constaté que l'hydrogène dissous dans le cuivre peut produire la réduction de la couche d'oxyde lorsqu'il diffuse à travers l'oxyde de surface. La diffusion de l'hydrogène dans le cuivre se produit à des températures plus basses que la dissociation de l'oxyde de cuivre.

Pour le cuivre électroformé, il a été possible d'établir des relations entre les paramètres d'électroformage, la quantité dégazé, la température de dégazage et la microstructure du cuivre. L'une de ces relations est que la concentration d'hydrogène piégé dans le cuivre augmente avec l'épaisseur. Une autre corrélation a également été observée entre les courbes transitoires et les résultats de dégazage par TDS de la façon comment l'hydrogène est piégé dans le cuivre.

Contents

Acknowledgement	iii
Abstract	v
Contents	xi
List of figures	xii
List of tables	xvi
List of abbreviations	xix
1 Motivation	1
2 Introduction	3
2.1 CERN and particle accelerators	3
2.2 Vacuum in particle accelerators	4
2.3 Reverse NEG coated vacuum chambers	5
2.4 Cu-OFE and its surface treatments	6
2.5 Thermal Desorption Spectroscopy	6
2.5.1 Diffusion coefficient and activation energy of diffusion of hydrogen by TDS	8
3 Outline	13
4 Experimental	15
4.1 TDS System commissioning	15
4.1.1 TDS System	15
4.1.2 Temperature control and calibration	17
4.1.3 RGA calibration	20
4.2 Preparation of samples	24
4.2.1 Surface treatments for Cu-OFE	24

4.2.2	Thermal treatments	25
4.2.3	Samples cutting	26
4.2.4	Electroformed copper	27
4.3	TDS analysis of copper	30
4.4	XPS analysis of copper	31
5	TDS results and discussion for copper	33
5.1	Cu-OFE	33
5.1.1	Surface treatment comparison	33
5.1.2	2nd water outgassing peak	35
5.1.3	Role of hydrogen diffusion on the oxide layer reduction	37
5.1.4	SUBU treatment	43
5.2	Electroformed copper	47
5.2.1	Outgassing of electroformed copper in the industrial baths	47
5.2.2	Comparison with Cu-OFE	51
5.2.3	TDS results of high current density copper pulse plating	54
5.3	Diffusion coefficient and activation energy of hydrogen	59
6	TDS analysis of other materials	63
6.1	LHC Beamscreen	63
6.1.1	Motivation	63
6.1.2	Results and discussion	64
6.2	MoGr Collimator	69
6.2.1	Motivation	69
6.2.2	Results and discussion	70
6.3	Glidcop	73
6.3.1	Motivation	73
6.3.2	Results and discussion	74
7	Conclusions and outlooks	77
	References	79

List of Figures

2.1	Production process of the Reverse NEG coated vacuum chamber, [1]	5
2.2	TPD system experimental set up scheme: 1. UHV chamber, 2. Heater and 3. Mass spectrometer	7
2.3	Parts of a QMS, [2]	8
2.4	Schematic representation of an exothermic and endothermic metal in terms of dissolution energy, [3]	9
4.1	TDS system: 1.Turbo-molecular pumps, 2.Pressure Gauge, 3.RGA, 4.Gas injection system, 5.Data acquisition system, 6.Sample Manipulation, 7.Main Chamber, 8.Pre-chamber, 9.Cooling system, 10.Primary pump, 11.Temperature and Pressure reading	15
4.2	Safety valves between the primary pump and the turbo molecular pump	16
4.3	Regulating flow valve and the flange that connects the cleaning line with the pre-chamber	17
4.4	TDS results for the Ar , $m/Z=40$, of a Cu-OFE and a LHC beamscreen samples with Ar implanted on the Cu surface	18
4.5	Sample during measurement	19
4.6	TDS results for the outgassing of water, $m/z = 18$, of three electroformed copper samples 1.5 A dm^{-2} AC-plated 1.1 mm thick	20
4.7	SEM voltage calibration	20
4.8	Gas injection system	21
4.9	RGA calibration with N_2	23
4.10	Samples for the TDS system	26
4.11	Aluminium pieces used as substrate for the copper plating	27
4.12	Cu-coated Al by DMS	28
4.13	Substrate ready to be electroplated	28
4.14	Electroforming set up at the bath in the building 118	29
4.15	Electroforming set up at the beaker	30

5.1	TDS results for the outgassing of hydrogen, $m/z = 2$, (a) and water, $m/z = 18$, (b) for the different surface treatments	33
5.2	TDS results for the outgassing of hydrogen, $m/z = 2$, (a) and water, $m/z = 18$, (b) for Cu-OFE with different thicknesses	34
5.3	TDS results for the outgassing of water, $m/z = 18$, for different samples Cu-OFE electropolished coming from the same batch	35
5.4	XPS results for the different oxidised samples with and without thermal treatment. Cu2p (a) and CuLMM (b). Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)	36
5.5	TDS results for the outgassing of hydrogen, $m/z = 2$, (a) and water, $m/z = 18$, (b) for the different oxidised samples with and without thermal treatment	37
5.6	Evolution of the XPS by increasing the temperature. Cu2p for the Passivation sample (a), CuLMM for the Passivation sample (b), Cu2p for the ThT + Passivation sample (c) and CuLMM for the ThT + Passivation sample (d). Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)	39
5.7	Evolution of the XPS by increasing the temperature. Cu2p for the Degreasing sample (a), CuLMM for the Degreasing sample (b), Cu2p for the ThT sample (c) and CuLMM for the ThT sample (d). Analysis done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)	40
5.8	Evolution of the O1s peak in function of the temperature	41
5.9	Evolution of the XPS on time by holding the temperature at 150 °C. CuLMM for the Degreasing sample (a) and CuLMM for the ThT sample (b). Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)	41
5.10	Ellingham diagram for Cu_2O , H_2O and CO_2	42
5.11	XPS results for the different surfaces treatments. Cu2p (a) and CuLMM (b). Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)	43
5.12	XPS results for the different surfaces treatments for C1s. Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)	44
5.13	TDS results for the outgassing of water, $m/z = 18$, for a Cu-OFE samples with SUBU treatment after removing the surface	44
5.14	Scanning electron microscope images of the surface of Cu-OFE SUBU treated (a) and electropolished (b). Images taken by Busom Descarrega, J. (CERN-EN-MME-MM)	45
5.15	Scanning electron microscope images of cross section of Cu-OFE SUBU treated cut with focused ion beam. Image taken by Lunt, A. (CERN-EN-MME-MM) . .	46
5.16	TDS results for the outgassing of water, $m/z = 18$, for a Cu-OFE samples with SUBU treatment cleaned 15 min in ultrasounds before the test	46

5.17	TDS results for the outgassing of H_2 , H_2O , O_2 and CO_2 for 1 mm 2 A dm ⁻² DC plated sample (a) and for 1 mm 2 A dm ⁻² AC plated sample (b)	47
5.18	From the TDS tests: $[H_2]$ DC plating (a), $[H_2]$ AC plating (b), $[O_2]$ DC plating (c), $[O_2]$ AC plating (d), $[H_2O]$ DC plating (e), $[H_2O]$ AC plating (f)	49
5.19	Schematization of a cross section of an electroformed copper in terms of hydrogen, oxygen and water content	50
5.20	Comparison of TDS results for the outgassing of H_2 for DC and AC plated samples 0.6 mm thick with 2 A dm ⁻² of current density	50
5.21	Optical microscope images after etching the cross section of DC and AC plated copper. Images taken by Busom Descarrega, J. (CERN-EN-MME-MM)	51
5.22	TDS results of outgassing of hydrogen (a) and water (b) for Cu-OFE, Bright 2 A dm ⁻² DC plated, Matt 2 A dm ⁻² AC plated and 70 A dm ⁻² 80 ms pulse ON AC plated	53
5.23	Transient curves for the matt bath (a) and TDS results of outgassing of hydrogen, $m/z = 2$, from the samples done in the beaker with the matt bath (b). The curve in b for the 70 A dm ⁻² 80 ms pulse ON was interrupted and restarted	55
5.24	Transient curves for the D-Xylose bath (a) and TDS results of outgassing of hydrogen, $m/z = 2$, from the samples done in the beaker with the D-Xylose bath (b)	56
5.25	Optical microscope images after etching the cross section of samples from the matt bath. 40 A dm ⁻² 20 ms pulse ON (a) and 40 A dm ⁻² 80 ms pulse ON (b)	57
5.26	Optical microscope images after etching the cross section of samples from the D-Xylose bath. 40 A dm ⁻² 20 ms pulse ON (a) and 40 A dm ⁻² 80 ms pulse ON (b)	57
5.27	Linear regression to obtain the diffusion coefficient and energy of diffusion from TDS with different heating rates	59
5.28	Linear regression to obtain the diffusion coefficient at different temperatures for Cu-OFE (a). Arrhenius plot comparing the different methods with the literature for Cu-OFE (b)	60
5.29	Linear regression to obtain the diffusion coefficient at different temperatures for SS-316LN (a). Arrhenius plot comparing the different methods with the literature for SS-316LN (b)	60
6.1	TDS results for the outgassing of hydrogen, $m/z = 2$, for C thin film coating by DMS over a quartz substrate	64
6.2	TDS results for the two types of the LHC beamscreen. 1 mm SS + 75 μ m Cu (a) and 0.6 mm SS + 75 μ m Cu (b)	65
6.3	TDS results for the outgassing of hydrogen, $m/z = 2$, for two LHC beamscreen sample one of them with the Cu layer mechanically removed	65

6.4	TDS results for the outgassing of hydrogen of the LHC beamscreen 1 mm SS + 75 μ m <i>Cu</i> . Comparison of two samples: one with the SS normal oxidised and the other with the oxide mechanically removed (a). Comparison of two samples: one with the <i>Cu</i> facing the RGA and the other facing the heater (b)	66
6.5	Hydrogen content evolution after each bake-out cycle	68
6.6	Outgassing acceptance test done in Building 113 at CERN, TB6: Normalised RGA SEM 1400V after bake out as a function of pumping time after bake out. Test done by Accettura, C. (CERN-EN-MME-EDS)	69
6.7	TDS results for the outgassing of hydrogen of MoGr samples for $m/z = 2, 18, 28, 41, 43, 44$ and 57. 1 mm thick sample (a) and 2 mm thick sample (b)	70
6.8	TDS results for the outgassing of hydrogen of MoGr sample for $m/z = 2, 18, 28, 41, 43, 44$ and 57. Sample exposed 1 week at air after a first TDS measurement (a) and Vacuum fired sample 2 h at 950 $^{\circ}$ C (b)	71
6.9	Images from scanning electron microscope. Magnification 1500 (a) and magnification 7000 (b). Images taken by Busom Descarrega, J. (CERN-EN-MME-MM)	72
6.10	TDS results for the outgassing of hydrogen of vacuum fired 2 h at 950 $^{\circ}$ C + CO_2 blasted MoGr sample for $m/z = 2, 18, 28, 41, 43, 44$ and 57	72
6.11	Bubbles on the coated Glidcop after brazing	73
6.12	TDS results for the outgassing of Glidcop and the surface treatments done for the brazing on a Cu-OFE. Hydrogen, $m/z = 2$, outgassing (a) and water, $m/z = 18$, outgassing (b)	74

List of Tables

4.1	Capillary calibration with the Permeation system for N_2	22
4.2	RGA Calibration	24
5.1	Hydrogen concentration taking into account $m/z = 2$ and $m/z = 18$. Values obtained by integration of the flow rate from 150 °C to 500 °C	37
5.2	Difference in outgassing of the Cu-OFE and electroformed copper after activation cycles	52
5.3	Concentration of H_2 in samples done in the beaker with the matt bath	54
5.4	Concentration of H_2 in samples done in the beaker with the D-Xylose bath	56
5.5	Horizontal grain size from the matt and D-Xylose samples done with 40 A dm ⁻² of current density	58
5.6	Diffusion coefficient and activation energy of diffusion for Cu-OFE	61
5.7	Diffusion coefficient and activation energy of diffusion for SS-316LN	61
6.1	Reduction of the total hydrogen outgassing, $m/z = 2$, of the bake-out samples respect to the not baked one	68
6.2	Atomic concentration of hydrogen and water and the increase respect to the Cu-OFE used as reference for the Glidcop and the surface treatments done for the brazing. * In these cases the outgassing coming from the Cu-OFE has been subtracted and then normalised with the thickness of the coating.	75

List of abbreviations

AC	Alternating Current
B.E.	Binding Energy
C	Conductance
C	Constant in a equation
c	Concentration
c_0	Initial concentration
c_s	Concentration on the surface
c_w	Concentration on the surface at a given time
Cu-OFE	Oxygen-Free Electronic Copper, C10100
Cu-OFS	Silver-Bearing Oxygen-Free Copper, C10400
D	Diffusion coefficient
D_0	Diffusion pre-exponential factor
DC	Direct Current
DMS	DC Magnetron Sputtering
E_d	Activation energy for diffusion
FCC	Future Circular Collider
HIE-Isolde	High Intensity and Energy - ISOLDE
HL-LHC	High Luminosity LHC
k_B	Boltzmann constant
K.E.	Kinetic Energy
ISOLDE	Isotope mass Separator On-Line facility
L	Thickness of the sample
LHC	Large Hadron Collider
m	Mass
MoGr	Molybdenum Carbide - Graphite
MRS	Mechanically Removed Surface
NEG	Non-Evaporable Getter
p	Pressure

PID	Proportional-Integral-Derivative controller
q	Outgassing rate
Q	Gas flow
QMS	Quadrupole Mass Spectrometer
QS	Quarter Wave Resonators Series
RF	Radio Frequency
RGA	Residual Gas Analyser
RSF	Relative Sensitivity Factors
RT	Room Temperature
S	Pumping speed
SEM	Secondary Electron Multiplier
SEY	Secondary Electron Yield
SPS	Super Proton Synchrotron
SS	Stainless Steel
SUBU	Chemical polishing
T	Temperature
t	Time
$T_{control}$	Control Temperature, temperature of the heater
TDS	Thermal Desorption Spectroscopy
t_H	Time when the maximum temperature is reached
ThT	Thermal Treatment under Vacuum
T_{MAX}	Temperature where the outgassing is maximal
$T_{measurement}$	Measurement Temperature, temperature of the sample
TPD	Thermal Programmed Desorption
UHV	Ultra-High Vacuum
XPS	X-ray photo-electron spectroscopy
x	Distance from the surface
Z	Number of elementary charges
β	Heating rate

1 Motivation

Two types of copper needed a deeper characterisation in their applications in the ultra-high vacuum (UHV) conditions in particle accelerators, as the Large Hadron Collider (LHC) at CERN. This two types of copper are the oxygen-free electronic copper (Cu-OFE) and the electroformed copper.

On one hand, Cu-OFE is used as a base material in different vacuum chambers and components of the LHC. This components are superconductor RF cavities coated with Niobium [4] or the long strait sections coated with Ti-Zr-V non-evaporable getter (NEG) thin films [5] [6] among others. The appropriate surface treatment of the substrate before any coating is applied is the key for success. An inadequate treatment could lead to a deterioration of the functional properties of the coating or its delamination.

On the other hand, electroformed copper is meant to be used also as base material for vacuum chambers coated with Ti-Zr-V non-evaporable getter thin films. The development of a new process to produce the vacuum chambers required a characterisation of the electroformed copper. The idea is to study the effect of different electroplating parameters in the functional performance of the NEG thin films. More specifically how the outgassing of the bulk materials affects the whole performance of this new type of vacuum chambers.

The acquisition of a new system for thermal desorption spectroscopy (TDS) from Hiden Analytical [7] [8] by the section, which allows to analyse the outgassing of different materials in UHV from room temperature up to 940 °C, opened the possibility to better characterise the different surface treatments, thin-film coatings and electroplating processes done at the section. The old TDS system owned by the section did not allow to obtain results at temperatures lower than the bake-out temperature. The reason was that to change the sample the system was needed to be vented. Then bake-out was needed in order to reach again UHV conditions to perform the test. This operation was limiting the system to do a maximum of one test per week. The new system allows to transfer the samples without losing the UHV in the test chamber. With this improvement up to three test per day can be done. Another improvement that brings the

new TDS system is the possibility to analyse very different kinds of materials. The old system could only analyse materials with sufficient electrical resistance, such as stainless steel.

2 Introduction

2.1 CERN and particle accelerators

CERN, the European Organization for Nuclear Research, is the world's largest physics laboratory. The aim of its research is to get a better understanding of the fundamental structure of the universe by studying the components of the matter and the forces that hold them together. The tool to accomplish this goal is the world's largest particle accelerator complex with its experiments. The accelerators boost beams of particles to high energies before they collide with each other or with stationary targets. And the experiments observe and record the results of these collisions. At the Large Hadron Collider, several tens of millions of particles collide almost at the speed of light every second creating new particles that are studied at the different experiments. [9]

To accelerate particles four main components are needed. First off all, particles, which can be accelerated, are charged particles such as electrons, positrons, protons or other ions. Second, an electric field is necessary to accelerate the particles; this electric field is generated by radio frequency (RF) cavities in the case of linear accelerators and synchrotrons. Third, magnets are necessary to bend, focus or guide the particles. In the case of the LHC the magnets are made of super conductor coils in order to be able to create strong magnetic field up to 8.3 T. And last but not least is a vacuum chamber where the particles circulate without colliding with undesired particles, which would produce losses and background noise in the experiments. Other components might also be needed at particles accelerators such as collimator systems, dumping areas, cooling systems or beam measurement instrumentation to be able to monitor possible instabilities, resonances or deviation of the beam of particles and correct them with the different kind of magnets. [10] [11]

2.2 Vacuum in particle accelerators

The CERN accelerator complex contains a total of 104 km of pipes under vacuum. Of these 104 km, 50 km pipes with a total volume of 15 000 m³ with pressures from 10⁻⁶ to 10⁻⁹ mbar. The other 54 km correspond to the LHC pipes that need to reach a pressure of the order of 10⁻¹⁰ to 10⁻¹¹ mbar.

In the case of the LHC 48 km of arc sections are in cryogenic conditions. The magnets are kept at 1.9 K to be able to use the superconducting properties of the coils that form them. And the beamscreen, which is the part of the vacuum pipe that is in line of sight of the beam is at around 15 - 20 K. In this sections the UHV conditions are maintained by the cryogenic pumping. A cryogenic pump is a vacuum pump where due to the extremely low temperatures the gases condense and adhere on the walls of the pump by adsorption. In this case the cryogenic pump are the walls of the pipe itself.

In the LHC there are also 6 km of straight sections that are kept at room temperature. These sections are the parts where beam-control systems and the collision points with the respective experiments are located. In this sections the cryogenic pump does not work. Therefore other pumping systems need to be used. In this straight sections a Non-Evaporable Getter (NEG) coating covers the walls of the vacuum chamber [12]. The NEG coating is a thin film of titanium-zirconium-vanadium alloy in the inner surface of the pipes produced by DC magnetron sputtering (DMS). This getter absorbs all the residual gases except methane and the noble gases when is activated by heating up the pipe. These residual gases are removed by ion pumps [13]. Only the collimators and some instruments are not NEG coated, therefore, it is necessary to bake-out these parts to remove mainly the adsorbed water.

In general, all the parts that work in UHV conditions (the measurement equipment, beam instrumentation, collimators systems, beamscreen, valves and even the vacuum chamber itself) need to be tested before being introduced in any accelerator. Different tests are performed to understand the behaviour of this components and be able to avoid or predict any degradation of the vacuum. The thermal desorption spectroscopy is one of these tests. The TDS analyses specifically the materials that conform these components well before their construction. From a TDS test it can be obtained which gases or elements are adsorbed or dissolved inside a material, in which quantity and at which temperature they are released.

2.3 Reverse NEG coated vacuum chambers

For the future of the particle accelerators technology there is the goal to go towards higher energy and intensity beams. To go to this higher energy without increasing the cost and accelerators' size a possible solution is to put the magnets closer to the beam. Therefore, beam pipes with smaller diameter will be needed. This is important for electron or lepton accelerators. It is very important for the focussing with quadrupoles for instance or wigglers and undulator pipes in radiation factories. The Future Circular Collider of hadrons machine (FCC) now under study at CERN has indeed a smaller diameter than LHC, but still in a size that could be manageable for sputtering. The smaller diameter pipes are difficult to coat with the present NEG technology. This difficulty comes from the way that the NEG coatings are produced, DC magnetron sputtering. DMS as other physical vapour deposition techniques has some limitation for properly coating complex shapes or the inner side of pipes with small cross sections. The present limit of cross section is about 8 to 10 mm for the NEG coatings. A new procedure of coating is under study in the TE-VSC group at CERN to enable the coating of such small diameter pipes. A scheme of this new proposed method can be seen at the Fig.2.1.

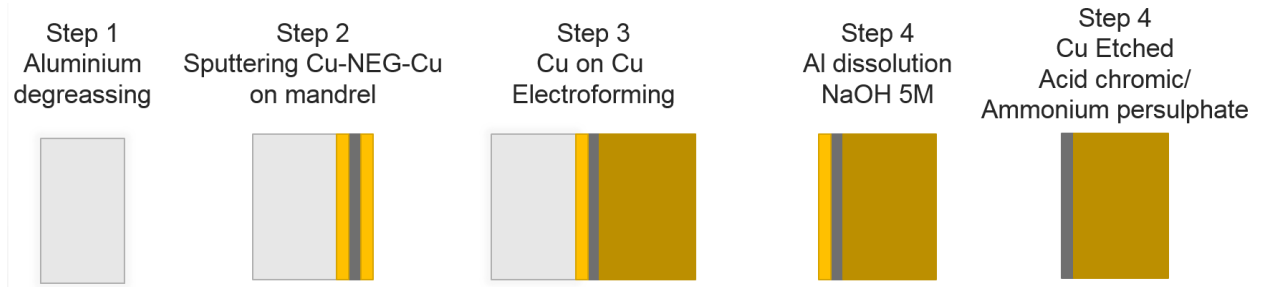


Figure 2.1. Production process of the Reverse NEG coated vacuum chamber, [1]

This procedure starts with an aluminium mandrel that is used as substrate of the NEG thin film coating by DMS. Once the coating is done, the vacuum chamber is created by copper electroforming. Finally the aluminium mandrel is chemically removed by etching it with $NaOH$ and what remains is the vacuum pipe made of electroformed copper with a NEG thin film coating in the inner part. [1]

The reverse NEG coated vacuum chambers is a completely new procedure. Therefore several parts of the process are currently under study, as well as the performance of the vacuum chamber once is finished. This study is made with pumping speed measurements to verify the integrity of the coating after the removal of the Al mandrel. The measurements performed so far indicate that the performance is reduced compared to the NEG produced with the stan-

standard method. This limitation might come from the outgassing properties of the substrate, the electroformed copper. Therefore, this material must be characterised by TDS.

2.4 Cu-OFE and its surface treatments

Electroformed copper is not the main type of copper used at CERN. Usually the components made of copper that are used at different parts of the accelerators and the experiments, are made of oxygen-free electronic Copper C10100 (Cu-OFE) [14]. Silver copper C10400 (Cu-OFS) gaskets are used between flanges that connect vacuum chamber and pipes. The same alloy is used as vacuum chamber in some parts of the straight sections of the LHC with a NEG coating. At the LHC beamscreen a co-laminated copper on stainless steel is used due to its high conductivity. [15] In the new QS cavities for the HIE-Isolde upgrade and in the RF cavities of the LHC, Cu-OFE is used as a substrate for a *Nb* superconducting coating. [16] [17] In all cases copper is not used directly as received, surface treatments are always applied after mechanical manufacturing. For all the copper used under UHV conditions a process of degreasing and passivation is applied. [18] In addition, in the case of the QS cavities a SUBU chemical polishing is done. [19] In the copper substrate for the LHC RF cavities an electropolishing treatment followed by a SUBU treatment is done. [20]

The study of the effect of these surface treatments on the copper outgassing were never done in a systematic way. The old TDS system was rather complex and heavy to operate so that for instance statistics were difficult to do. An enhanced outgassing of copper due to inappropriate surface treatments could degrade its vacuum performance, deteriorate the functional properties of applied coatings and reduce their adhesion to the substrate.

2.5 Thermal Desorption Spectroscopy

Thermal desorption spectroscopy or temperature programmed desorption is an important method employed in vacuum technologies, surface science and catalysis. Lots of different analysis can be carried with a TPD system from qualitative analysis, such as distinction of desorbed gases in a material or identification of degassing peaks at defined temperatures, to quantitative analysis, such as calculation of degassing rates, concentration of degassed species or determination of kinetic and thermodynamic quantities of decomposition reactions or desorption processes with different experimental approaches: [21], [22], [23], [24], [25], [3], [26], [27].

A TPD experimental setup consist mainly in 3 parts: An UHV system, a heater and a mass spectrometer. (Fig.2.2).

The UHV system consists of a vacuum chamber and a pumping system. The pumping system allows to maintain the UHV conditions. It is made of a turbomolecular pump backed by a primary rotary vane pump. The UHV conditions maintained with a very high pumping speed are necessary to reduce a possible reaction of the gases in the system with the sample and to reduce the amount of re-adsorption of gases coming from the sample. The UHV conditions allows also to detect very small desorption rates. If the vacuum was not good enough, the background signal of the spectra would be too high to identify these flows. With these conditions the pressure of the chamber can be considered proportional to the desorption rate of the sample.

The pressure of the vacuum is measured by an ionisation gauge. This kind of gauge consist of a filament that emits electrons and a grid cage with an electrical potential. The electrons emitted from the filament ionise the particles from the residual gas that are accelerated into the grid cage and they are collected by a target electrode. The detected ion current is an indirect measure of the gas density and for constant temperature, of the pressure. [2]



Figure 2.2. TPD system experimental set up scheme: 1. UHV chamber, 2. Heater and 3. Mass spectrometer

The heater usually is an electrical resistance that transfers the heat to the sample. By increasing the temperature of the sample it is possible to force the outgassing by increasing the diffusion coefficient of the gasses inside the bulk material or by reaching the temperatures at which recombination and desorption reactions from the sample can happen. To have a spectrum which associates a temperature with a time the heater needs to be able to control the

temperature of the sample at different heating rates, $\beta = dT/dt = \text{const.}$ With such a process, activation energies of the diffusion, recombination or desorption can be obtained. The heater also should allow to do analysis at a constant temperature, $\beta = 0$, to be able to simulate thermal treatments or to obtain, for example, diffusion coefficients.

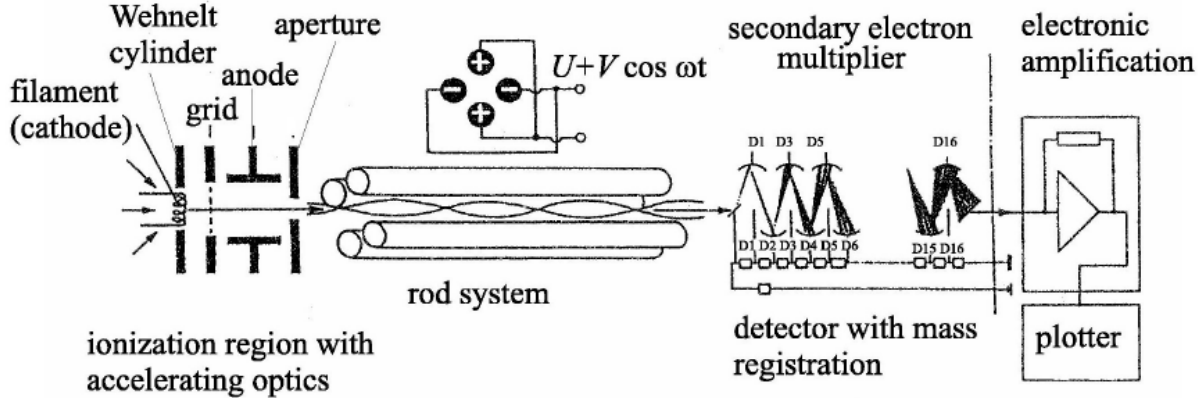


Figure 2.3. Parts of a QMS, [2]

Finally, the mass spectrometer or more specifically a quadrupole mass spectrometer, QMS, is the tool to identify the gasses and follow their quantity in the vacuum chamber. After a calibration the signal obtained from the QMS can be correlated to an outgassing rate. At the Fig.2.3 it can be seen that the parts forming a QMS are mainly three: ion production and acceleration, ions selection and signal amplification and recording. The operation is as follows, first the molecules are ionised at the filament and accelerated. Then the quadrupole analyser that consist of four cylindrical rods, creates an oscillatory electric field. This field only enables a stable trajectory for the ions that satisfy a defined mass/charge condition, m/Z , for which is defined. Finally the ions reach the secondary electron multiplier, SEM, that amplifies the signal.

2.5.1 Diffusion coefficient and activation energy of diffusion of hydrogen by TDS

The elements, dissolved into the bulk of materials during the production processing or by air exposure, can diffuse in vacuum after reaching the surface where they are released. In metals some atoms have enough mobility to reach the surface where they recombine to form multi-atomic molecules. Two mechanisms are used in order to model the flux (q) of the outgassing process of the dissolved atoms: diffusion limited outgassing (2.1) and recombination limited

outgassing (2.2), this last equation is only valid for atoms forming diatomic molecules.

$$q(t) \propto -\frac{\partial c}{\partial x} \quad (2.1)$$

$$q(t) \propto c_s^2 \quad (2.2)$$

Depending on the energy gain when a molecule is cracked and dissolved in the bulk of the metal, the controlling mechanism is one or the other (Fig.2.4). For exothermic metals, where the recombination and desorption energy is higher than the dissolution energy, the recombination is the controlling mechanism. Examples of exothermic metals are *Nb*, *Ti*, *Pd* and *Zr*. For the case of endothermic metals, the recombination and desorption energy are lower than the dissolution energy. Therefore, the desorption barrier can be considered as transparent and diffusion becomes the controlling mechanism. In cases of low gradient of concentration the recombination rate becomes again the limiting factor. In the family of the endothermic metals we can find, for example, *Fe*, *Ni*, *Cu*, *Mo* and stainless steel (SS). So, for *Cu*, as endothermic metal, it is possible to obtain the hydrogen diffusion coefficient and diffusion energy by TDS through some mathematical approximations, if we assume that the outgassing is only limited by diffusion and no other elements influence it, like the different ways that the hydrogen may be trapped in *Cu*.

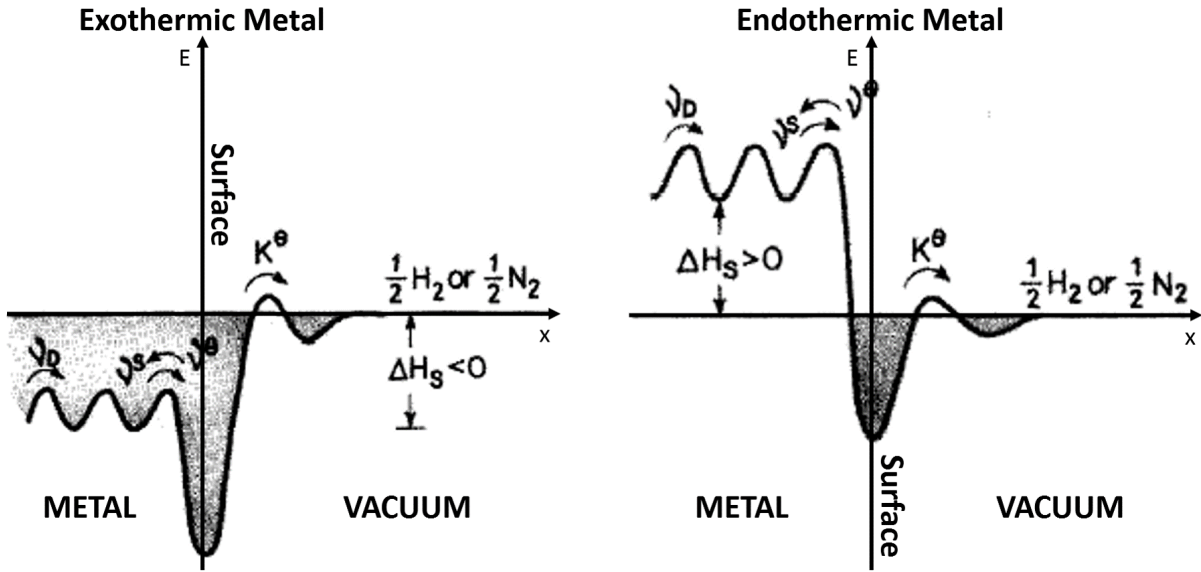


Figure 2.4. Schematic representation of an exothermic and endothermic metal in terms of dissolution energy, [3]

With the Fick's equations and with the assumption that for copper the outgassing is limited by diffusion, it can be considered that the outgassing rate is equal to the flux of molecules arriving at the surface from the bulk (eq.2.3).

$$q(t) = -D \frac{\partial c(x, t)}{\partial x} \quad (2.3)$$

For a thin sample (one dimension smaller than the other two) the Fick's equation can be solved by using the Slab approximation 2.4, where c_0 is the initial concentration, c_w is the concentration on the surface at a given time (for a diffusion limited outgassing can be considered $c_w = 0$) and L is the thickness of the sample.

$$q(t) = \frac{4(c_0 - c_w)D}{L} \exp \left[-\pi^2 \frac{Dt}{L^2} \right] \quad (2.4)$$

The diffusion mechanism is not only a time dependant process but is also temperature dependant. This dependency can be explained with an Arrhenius equation 2.5.

$$D(T) = D_0 \exp \left(-\frac{E_d}{k_B T} \right) \quad (2.5)$$

Taking into account the Slab approximation and the temperature dependency the outgassing rate for an arbitrary thermal cycle can be expressed as 2.6, where t_H is the time when the maximum temperature is reached.

$$q = \frac{4(c_0 - c_w)D}{L} \exp \left[-\pi^2 \frac{\int_0^{t_H} D(T) dt}{L^2} \right] \quad (2.6)$$

For a linear heating rate, as the one used in the TDS tests, this approach can be reformulated in such a way that the diffusion pre-exponential factor and the diffusion energy can be easily calculated by using several measurements at different heating rates (eq.2.10). T_{MAX} is the temperature when the degassing reaches the maximum rate for a specific heating rate, β . [3]

$$\frac{dq(t)}{dt} = 0 \rightarrow \frac{dD(t)}{dt} - D(t)^2 \left(\frac{\pi}{L} \right)^2 = 0 \quad (2.7)$$

$$T = T_0 + \beta t \rightarrow D(t) = D_0 \exp \left(-\frac{E_d}{k_B (T_0 + \beta t)} \right) \quad (2.8)$$

$$\frac{dD(t)}{dt} = \frac{E_d \beta D_0}{k_B T^2} \exp \left(-\frac{E_d}{k_B T} \right) \quad (2.9)$$

$$\frac{\beta}{T_{MAX}^2} = \frac{k_B D_0 \pi^2}{E_d L^2} \exp\left(-\frac{E_d}{k_B T_{MAX}}\right) \quad (2.10)$$

This method to obtain the diffusion coefficient and the energy of diffusion is also complemented in this study with another method. The diffusion coefficient for one temperature can be guessed from the Slab approximation directly. The idea is to fit the approximation 2.4 as a function of time by the least square method with the results of a TDS test. This TDS test must be done by fixing a temperature and let outgas the hydrogen.

$$RGA_{Signal}(t) \propto q(t) \rightarrow RGA_{Signal}(t) \propto D \exp\left[-\frac{\pi^2}{L^2} Dt\right] \quad (2.11)$$

$$\log(RGA_{Signal}(t)) = \log(D) - \frac{\pi^2}{L^2} Dt + C \quad (2.12)$$

The diffusion coefficient at the fixed temperature can be obtained from the slope of outgassing if its represented in a logarithmic plot (eq.2.12).

3 Outline

The goals of the present work are:

- To study the effect of the different surface treatments done at CERN on Cu-OFE on the outgassing under Ultra-High Vacuum conditions: passivation, electropolishing and SUBU.
- To understand and explain the outgassing of water and hydrogen of the Cu-OFE.
- To study how different electroforming parameters (type of current, current density and thickness) affect the outgassing of the Electroformed copper.
- To compare the outgassing behaviour of Cu-OFE and Electroformed copper.

4 Experimental

4.1 TDS System commissioning

4.1.1 TDS System

To be able to perform the TDS analysis of the copper materials the system from Hiden Analytical [7] [8] (Fig.4.1) needed to be commissioned as it was a new acquisition. To be able to analyse the outgassing quantitatively, the RGA needed to be calibrated for the sensitivity to different gases. Finally the results obtained through the calibration needed to be verified by comparison with known or established results.

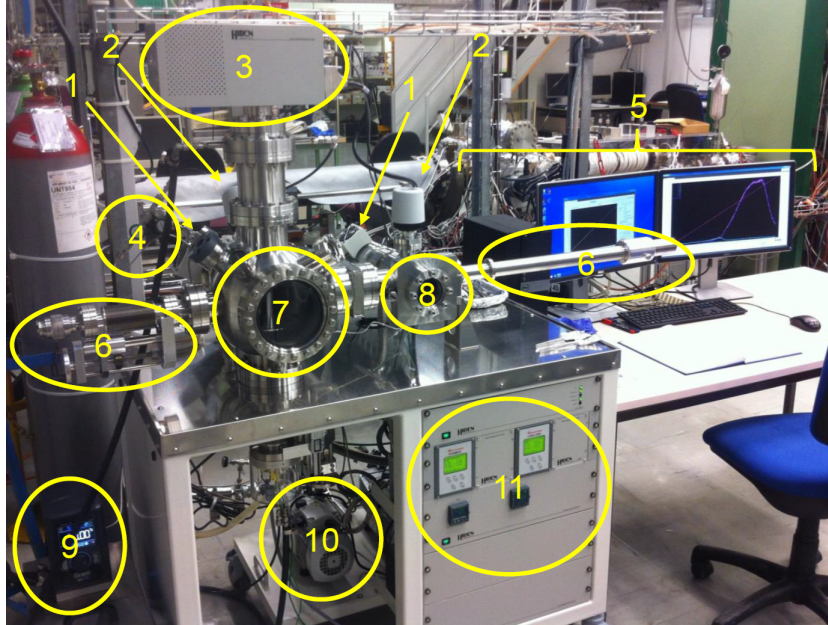


Figure 4.1. TDS system: 1.Turbo-molecular pumps, 2.Pressure Gauge, 3.RGA, 4.Gas injection system, 5.Data acquisition system, 6.Sample Manipulation, 7.Main Chamber, 8.Pre-chamber, 9.Cooling system, 10.Primary pump, 11.Temperature and Pressure reading

The big advantage that brings this system is the fact that no bake-out is needed to be per-

formed when a new sample is placed to be measured. This is possible due to the use of a pre-chamber (Fig.4.1.8) that brings the sample from the atmospheric pressure to a pressure around 10^{-7} mbar. When this pressure is reached the sample can be transferred to the main chamber (Fig.4.1.7) where the test is performed without any contamination of the UHV of the main chamber (10^{-9} mbar).

Even though the system was a new purchase, some upgrades were needed. These upgrades were done to protect the system. Safety valves (manual and automatic) were installed between the primary pump and the turbo molecular pumps (Fig.4.2). The automatic valve was installed only between the pumps of the main chamber. This valve closes in case of an electrical shut-down. The reason of putting this automatic valve there is to avoid that atmospheric air goes to the main chamber. If such case a bake-out of the system would be necessary and would take more than one day. Therefore at least one day of measurements is lost. The other reason of putting this safety valve is to avoid that the oil from the primary pump reaches the main chamber producing then a contamination.

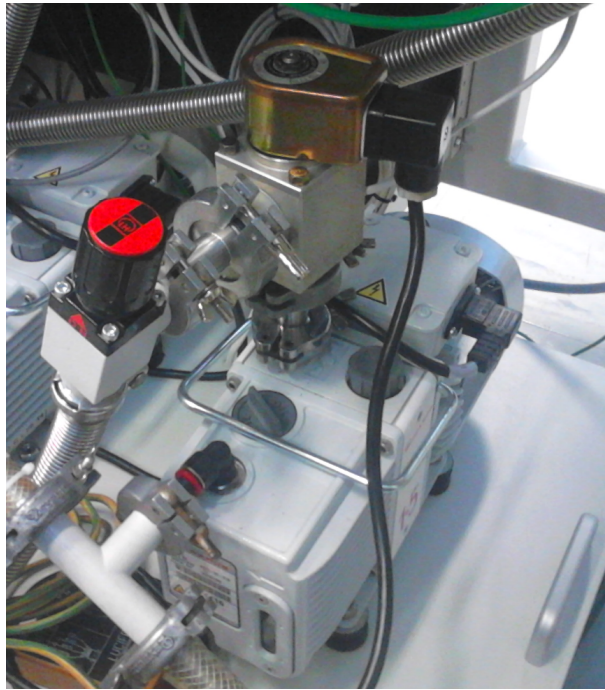


Figure 4.2. Safety valves between the primary pump and the turbo molecular pump

The other upgrades were done at the gas injection system. Regulating flow valves between the high gas pressure side toward the gas bottles and the vacuum side pumped by the turbo molecular pumps were installed replacing the ON-OFF valves which were originally installed. These valve were creating a peak of pressure when they were opened. This increment of pressure could damage the RGA, the turbo molecular pumps or the gauges. The other upgrade in the

gas injection system was done at the purging line. The purging line was initially connected directly to the high pressure side of the turbo molecular pump of the pre-chamber. To get a cleaner flow a new configuration that can purge the line from a side at lower pressure was installed. This new configuration consists of a flange between the pre-chamber and the turbo molecular pump (Fig.4.3). With this flange the line can be purged and pumped through the low pressure side of the turbo pump.

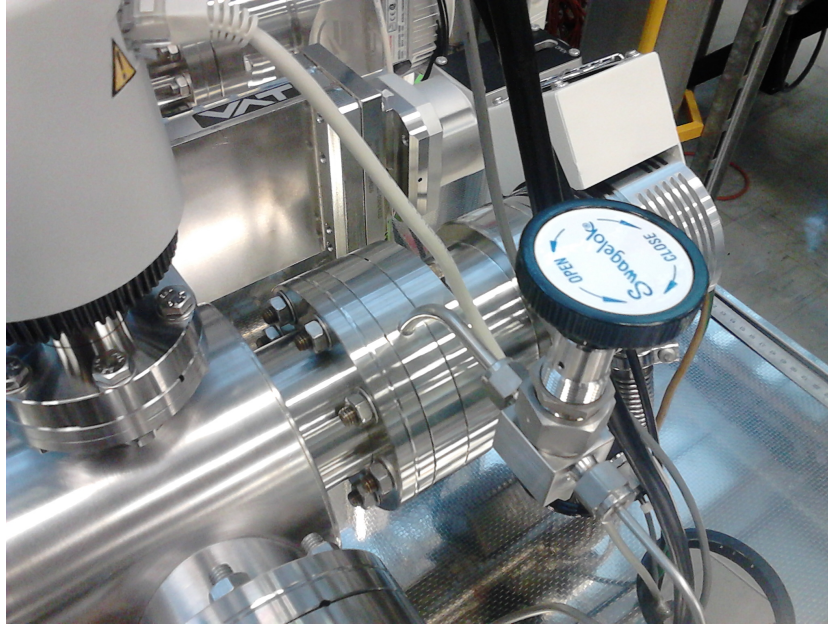


Figure 4.3. Regulating flow valve and the flange that connects the cleaning line with the pre-chamber

The last upgrade was to connect the data acquisition system to the CERN network. To acquire the data directly with a CERN computer allows to have access to the data from all the other CERN computers and to have periodic back-ups of all the data.

4.1.2 Temperature control and calibration

The temperature measurement limits of the system are from 25 °C up to 940 °C. The low limit is due to the cooling system that is water at 20 °C and the upper limit is set by software with a safety margin for the system. Even though the upper limit is never reached for the copper samples because at 940 °C the evaporation is high enough to cause possible damage at the system. The upper limit for copper measurement that it is used in this system is 700 °C. The Cu vapour pressure is 10^{-8} mbar at 990 K (717 °C) and 10^{-7} mbar at 1050 K (777 °C) [28]. It can be considered that for 10^{-8} mbar pressure, one mono-layer is deposited in 100 s and this is considered safe enough for the system.

The heating system has been tested for a heating rate up to $40\text{ }^{\circ}\text{C min}^{-1}$. The standard measurements have been performed with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. This choice is done because at this rate a sufficiently high signal is obtained, so it is not meaningful to go slower and by going faster there is always the risk that the temperature of the sample does not follow well the heating rate.

The sample temperature ($T_{\text{measurement}}$) is not measured directly on the sample but is get it from a calibration that was given by Hiden Analytical 4.1. A thermocouple is situated at the heater giving the T_{control} in the TPDsoft (the software that controls the system). With this thermocouple and PID controller the heater follows the set temperature.

$$T_{\text{Measurement}} = 0.94 T_{\text{Control}} \quad [^{\circ}\text{C}] \quad (4.1)$$

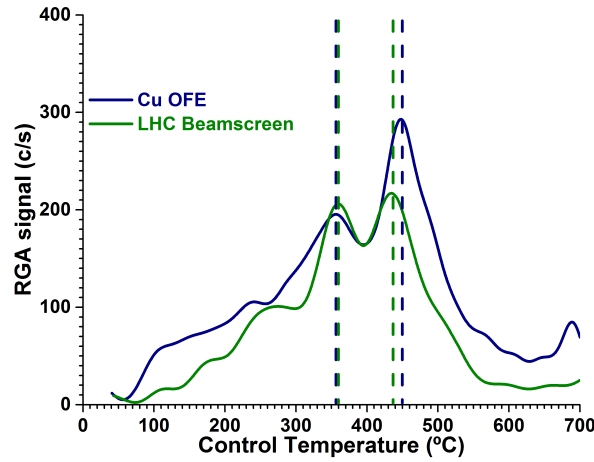


Figure 4.4. TDS results for the Ar , $m/Z=40$, of a Cu-OFE and a LHC beamscreen samples with Ar implanted on the Cu surface

A verification of the dependence of this calibration on the sample material was done to know if it was applicable in materials that have different thermal conductivity. The chosen materials were Cu-OFE and a piece of the LHC beamscreen. The LHC beamscreen was chosen because is made of stainless steel with copper co-laminated on one face [29]. The idea was to implant argon by an ion gun on the surface of the copper and check if there was a shift of the outgassing Ar peak in function of the material in contact with the heater. The Cu-OFE has a higher thermal conductivity than the SS. Therefore, if the calibration of the $T_{\text{measurement}}$ depends on the sample thermal conductivity it will be expected that the Cu-OFE with Ar implanted shows the outgassing peaks of the Ar at lower temperatures than the ones showed by the LHC beamscreen with Ar implanted in the Cu face.

Both samples were 1 mm thick. The LHC beamscreen has 1 mm SS with 75 μm of co-laminated *Cu*. They were also completely outgassed before doing the *Ar* implantation to reduce side effects. The implantation was done at the XPS system in the laboratory 101/R-013. The parameters of the ion gun were: 15 μA of a emission current, 3 keV of the energy for the *Ar*⁺, 5.3×10^{-6} mbar of *Ar* at the gun and a pressure of 1.8×10^{-8} mbar at the sample. The implantation was done for 30 min. At the Fig.4.4 it can be seen that 2 peaks of *Ar* were detected in both samples. The two peaks are very close to each other even if for one the heat is transferred by conduction through *Cu* and the other through SS. So, if tests are performed on materials with different thermal conductivity, at least for thickness up to 1 mm, there is no need to change the temperature calibration.

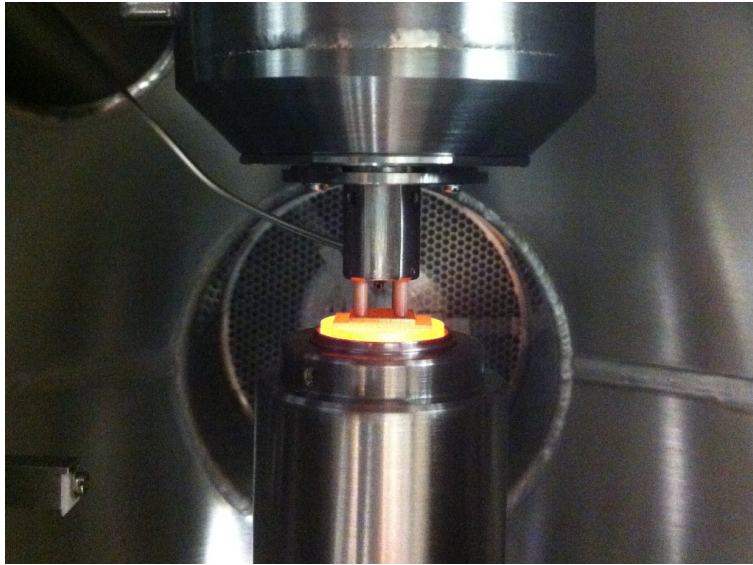


Figure 4.5. Sample during measurement

One important parameter regarding a good temperature control is the sample positioning. The four fingers from the RGA's head must touch and push the sample against the heater, as shown in the Fig.4.5. It is important to push always in the same pressure, otherwise the temperature of the sample does not increase following the fitting 4.1. A measurement has been done with a sample not touching the RGA fingers. With this measurement it has been observed a difference of temperatures of more than 300 °C. In Fig.4.6 it can be seen the water outgassing of two samples positioned in standard way and the outgassing of the sample not pushed with the RGA fingers. The samples positioned equally present the water outgassing peaks in the same temperatures, a 1st peak around 100 °C and a 2nd peak around 300 °C. But for the incorrect positioned sample the 1st peak of water is not observed until 400 °C. To avoid this problem a

standard positioning of the sample with respect to the RGA fingers has been established. The sample is always pushed up 0.6 mm more after it gets in contact (visually) with the RGA fingers. The reproducibility of the temperature value when the position of the sample is correctly done is better than 15 °C between identical samples.

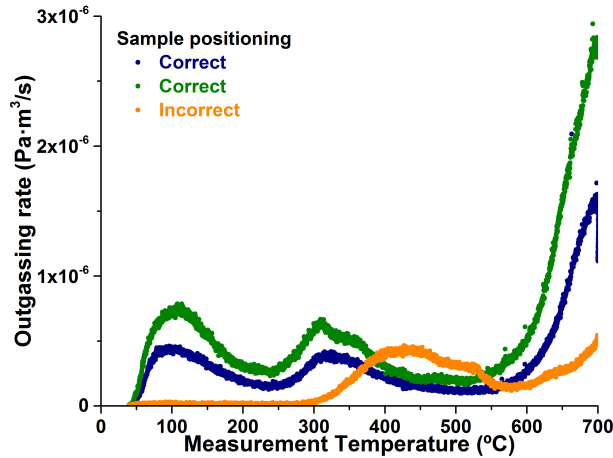


Figure 4.6. TDS results for the outgassing of water, $m/z = 18$, of three electroformed copper samples 1.5 A dm^{-2} AC-plated 1.1 mm thick

4.1.3 RGA calibration

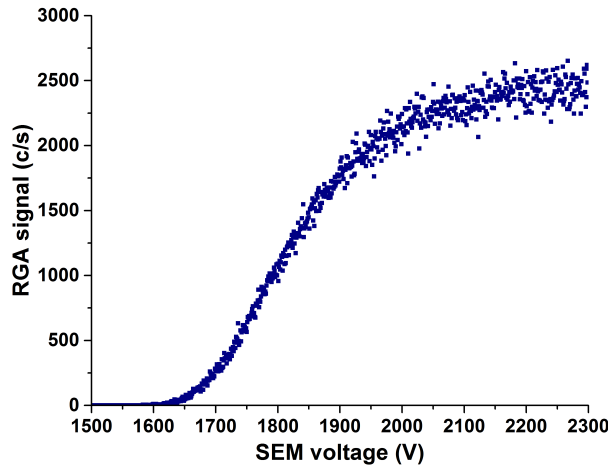


Figure 4.7. SEM voltage calibration

A quantitative analysis is required for this study. That is the reason why the RGA needs to be calibrated. To obtain the same results for different tests two parameters of the RGA need to be fixed. These parameters are the emission current and the secondary electron multiplier

(SEM) voltage before doing the calibration. If these parameters are changed the calibration will need to be corrected. The emission current is set at 20 μA . This value is chosen because is the one recommended by the TDS system constructor, Hidden Analytical. The SEM voltage is chosen by testing the signal of the RGA for the mass 18 (Fig.4.7). The RGA signal is given by counts per second (c/s). To reduce as much as possible the scattering of the signal the voltage needs to be in the plateau of the curve signal-voltage. If the voltage signal is too high the RGA can age faster. With this two limitations a voltage of 2100 V has been chosen as the one to be used for all the tests.

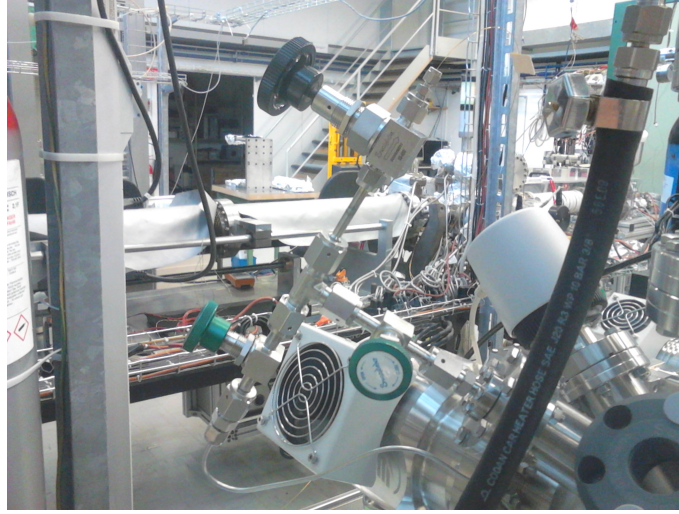


Figure 4.8. Gas injection system

The calibration is made by measuring which signal is given by the RGA when a known gas flow is injected to the vacuum chamber where the test is performed. A controlled gas injection is possible through a gas injection system (Fig.4.1.4) (Fig.4.8) connected to the main vacuum chamber. This gas injection system consists of a capillary of 10 m of length and 50 μm of diameter connected at one extreme to a gas bottle of the gas that needs to be calibrated and at the other extreme to a regulating valve toward the main chamber of the TDS system. The capillary produces a pressure drop from 1 or 2 bar coming from the gas bottle to 10^{-7} mbar.

To calculate the flow that comes out of the capillary its conductance has been approximated by a laminar flow [30].

$$C_{laminar} = \frac{\pi d^4}{256\eta l} (p_{bottle} - p_{chamber}) \quad (4.2)$$

$$Q_{laminar} = C_{laminar} (p_{bottle} - p_{chamber}) \quad (4.3)$$

Where l is the capillary length, d the capillary diameter, η the viscosity of the gas and p_{bottle} and $p_{chamber}$ are the pressures in the both extremes of the capillary, the pressure from the bottle and the pressure of the main chamber. The gas used for do the calibration has been nitrogen which viscosity is $\eta = 1.77 \times 10^{-5}$ Pa s [31] at room temperature.

The value of the flow obtained by eq.4.3 was verified by using the Permeation system at the same laboratory (101/1-001). This system has the turbo molecular pump with known pumping speed, so, the real flow of the capillary could be measured with the input pressure from the bottle (p_{bottle}), the pressure before the turbo molecular pump (p_{gauge}) and the known pumping speed ($S_{pump} = 31 \text{ L s}^{-1}$).

$$Q_{capillary} = S_{pump} p_{gauge} \quad (4.4)$$

Comparing the value given by eq.4.4 and the one given by eq.4.3 it was seen that a correction factor ($f_{correction}$) was needed to be introduced to correct the flow calculated in the laminar approximation to obtain the real conductance of the capillary (eq.4.5).

Table 4.1. Capillary calibration with the Permeation system for N_2

p_{bottle} (bar)	p_{gauge} (mbar)	S_{pump} (L s ⁻¹)	$Q_{capillary}$ (Pam ³ /s)	$Q_{lmainar}$ (Pam ³ /s)	$f_{correction}$
1.2	4.4×10^{-6}	31	1.4×10^{-5}	6.2×10^{-6}	1.80
1.5	5.6×10^{-6}	31	1.7×10^{-5}	9.7×10^{-6}	
1.9	7.2×10^{-6}	31	2.2×10^{-5}	1.6×10^{-5}	

$$\begin{aligned}
C_{capillary} &= f_{correction} \frac{\pi d^4}{256 \eta l} (p_{bottle} - p_{chamber}) \\
&= 1.80 \frac{\pi d^4}{256 \eta l} (p_{bottle} - p_{chamber})
\end{aligned} \quad (4.5)$$

Once the real flow of the capillary is known the RGA calibration can be performed. The calibration is done with N_2 and then extrapolated to other gases through the relative sensitivity factors (RSF) of the mass spectrometer. The RSF is the factor obtained by taking into account the ionisation probabilities, the fragmentation of the ions and the transmission of this ions through the quadrupole. The values are normalised to the value for N_2 [32]. For the calibration three different flows were introduced by the gas injection system and the RGA signals were recorded. Assuming a linear behaviour of the RGA signal with pressure, a linear regression is

done to be able to extrapolate to all the range of signals that are possible to obtain when a test is performed (Fig.4.9).

With the linear regression and the RSF of the gases to be studied it is possible to build the calibration (Tab.4.2). It is important to mention that the calibration was done in pressures around 10^{-6} mbar and extrapolated down to 10^{-9} mbar.

The extrapolation to other gases has been verified by introducing them through the gas injection system. Four gases were possible to use to do this verification: a mixture of 5 % H_2 and 95 % N_2 , a second mixture of 10 % CH_4 and 90 % Ar , and pure Kr . The differences between the calibration factor obtained with the extrapolation from the N_2 and the factor obtained with the gas mixtures injected are not very significant, even though the calculated flow has a larger uncertainty because the capillary was not calibrated in a system with known pumping speed for these mixtures. Therefore, it was decided to use the extrapolated value for all the cases. Only in the case of the Kr it was decided to not use the extrapolation and use the direct calibration (from the capillary flow calibration and then calibration of the RGA). The difference between the two values was too big and also the direct calibration was done with a pure gas, not with a mixture, so, it is a more reliable result.

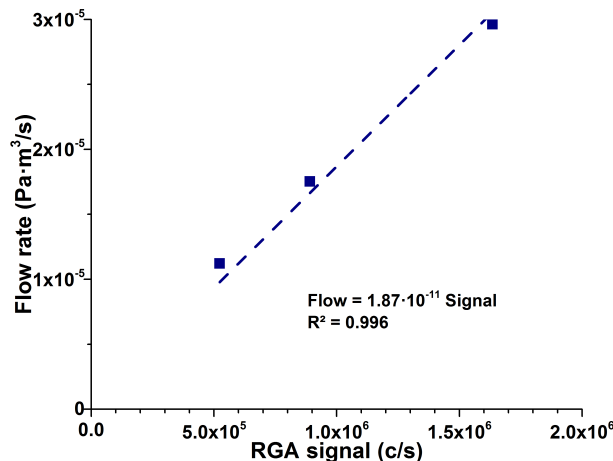


Figure 4.9. RGA calibration with N_2

A remark needs to be done about the ageing of the RGA. While doing the RGA calibration and the verifications with the different gases, it has been observed an ageing effect on the RGA due to operate it too much time under higher pressures (4.0×10^{-7} - 1.7×10^{-6} mbar). So, for future calibrations, it is important to switch off the RGA while the injection system is not in a steady state and only switch on when the measurements for the calibration are taken. The

Table 4.2. RGA Calibration

Gases	m/z	RSF	Calibration factor	Calibration factor	Relative difference
			N_2 Extrapolation (Pam ³ s ⁻¹ count ⁻¹)	Direct calibration (Pam ³ s ⁻¹ count ⁻¹)	
H_2	2	0.84	2.2×10^{-11}	1.4×10^{-11}	65
N_2	28	1	1.9×10^{-11}	1.9×10^{-11}	0
CH_4	15	0.75	2.5×10^{-11}	1.4×10^{-11}	79
H_2O	18	0.95	2.0×10^{-11}	-	-
CO	28	0.98	1.9×10^{-11}	-	-
O_2	32	0.86	2.2×10^{-11}	-	-
Ar	40	1.27	1.5×10^{-11}	2.1×10^{-11}	30
CO_2	44	1.17	1.6×10^{-11}	-	-
Kr	84	0.61	2.7×10^{-10}	4.5×10^{-11}	500

idea is to reduce as much as possible the ageing effect.

4.2 Preparation of samples

4.2.1 Surface treatments for Cu-OFE

The different surface treatments studied are done at the surface treatment workshops 102/R-023 and 118/R-001.

Degreasing

The degreasing has been done for 15 min under ultrasonic agitation in a bath with the detergent NGL Cleaning Technology 17.40 spec. ALU III [18].

Bath parameters:

- Concentration: 10 - 20 g l⁻¹.
- Temperature: 45 - 55 °C

Passivation

The passivation treatment has been done for 30 s in the chromic acid bath.

Bath parameters:

- Concentration: Chromic acid $70 - 80 \text{ g l}^{-1}$ + sulphuric acid 3 ml l^{-1} .
- Temperature: Room temperature.
- Etching rate: $1 \mu\text{m min}^{-1}$.

Electropolishing

$60 \mu\text{m}$ of the copper surface layer were removed by electropolishing.

Bath parameters:

- Composition: 55% in volume of phosphoric acid + 45% in volume of Ethanol.
- Etching rate: $1 \mu\text{m min}^{-1}$.

SUBU

The chemical polishing SUBU has been applied for 20 min to remove $10 \mu\text{m}$.

Bath parameters:

- Composition: Sulfamic acid 5 g l^{-1} + ammonium citrate 1 g l^{-1} + 5% in volume of hydrogen peroxide + 5% in volume of n-butanol.
- Temperature: $70 - 75^\circ\text{C}$
- Etching rate: $0.5 \mu\text{m min}^{-1}$.

4.2.2 Thermal treatments

Two different thermal treatments were done to the Cu-OFE samples in order to prove some of the hypothesis made in the study.

Thermal treatment under vacuum

The thermal treatment under vacuum (ThT) is done in the vacuum firing oven at the building 153/R-004. The fired samples are previously degreased. The conditions of the firing are 2 h at 600°C in a pressure of 10^{-7} mbar.

The aim of this treatment is to remove the hydrogen from the bulk of the copper. The samples

obtained after this treatment can be directly tested or other surface or thermal treatments can be performed.

Air oxidation

The air oxidation is done over degassed and ThT samples with a fan dryer at the atmosphere. The aim of this treatment is to get a fully oxidised layer on the copper. The use of completely degassed sample allows a clean oxidation of the copper surface without the influence of the H from the bulk. Therefore, not controlled variables could be effecting the oxidation and difficult a proper the interpretation of further results.

4.2.3 Samples cutting

The TDS system has a requirement in terms of the size of the samples. The samples need to be 10 mm x 10 mm (Fig.4.10). The thickness of the sample is limited to 6 mm but to have a uniform increase of temperature of the whole sample the thickness cannot be increased too much. In this study the maximum thickness analysed has been 3 mm without observing any temperature shift of the outgassing peaks.

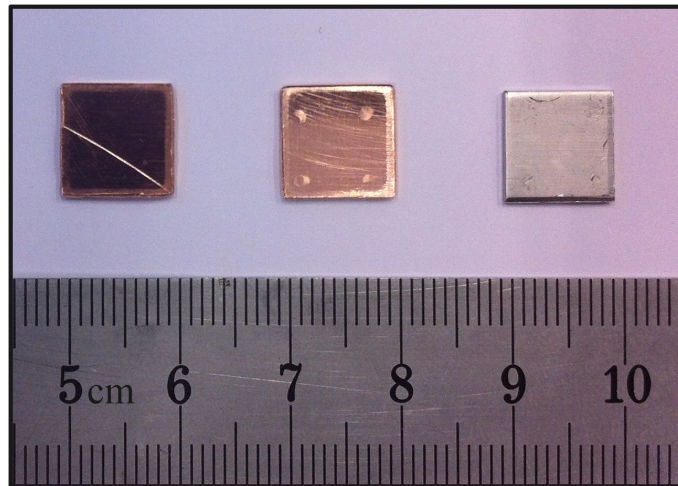


Figure 4.10. Samples for the TDS system

For the different copper materials studied all the samples are cut by using the hydraulic punch press of the main workshop at the building 100/R-002 with the punch of 10 mm by 10 mm. The punch is properly degassed to avoid the introduction of any pollution when the sample is cut.

4.2.4 Electroformed copper

Substrates preparation

For the measurement of the electroformed copper by TDS a substrate with the suitable size of 10 mm x 10 mm is necessary. In this case the substrate material selected is the aluminium. Aluminium plates of 150 mm x 150 mm x 0.5 mm are cut in smaller pieces of 50 mm x 50 mm (Fig.4.11).

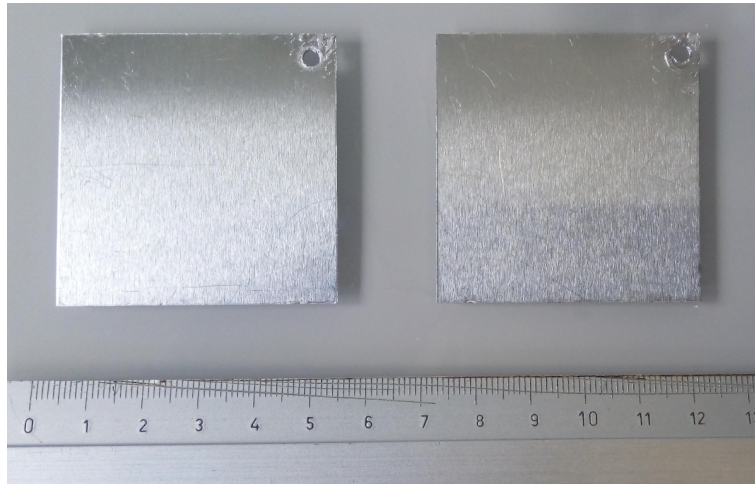


Figure 4.11. Aluminium pieces used as substrate for the copper plating

Before the electroplating a first layer of copper is coated over the aluminium substrate by DC magnetron sputtering (Fig.4.12). This first copper layer helps the initiation of the plating.

Once the substrates are coated they are hanged to a Cu-OFE strip that will be used to allow a good current conduction between the power supply and the aluminium substrate. The part of the strip that is submerged into the electroplating bath is covered with a heat-shrinkable plastic to avoid a plating over the strip. The bare side of the aluminium substrate is masked with Abdecklack Nr.1 from ERNE surface SA to reduce the plating surface to only the Cu-coated face of the substrate (Fig.4.13). The masking is done twice and let dry before the substrate can be put into the electroplating bath.

Electrochemical baths

Three baths are used to produce the electroformed copper samples. Two industrial baths are the ones used for the production of electroplated pieces used for the CERN accelerators and

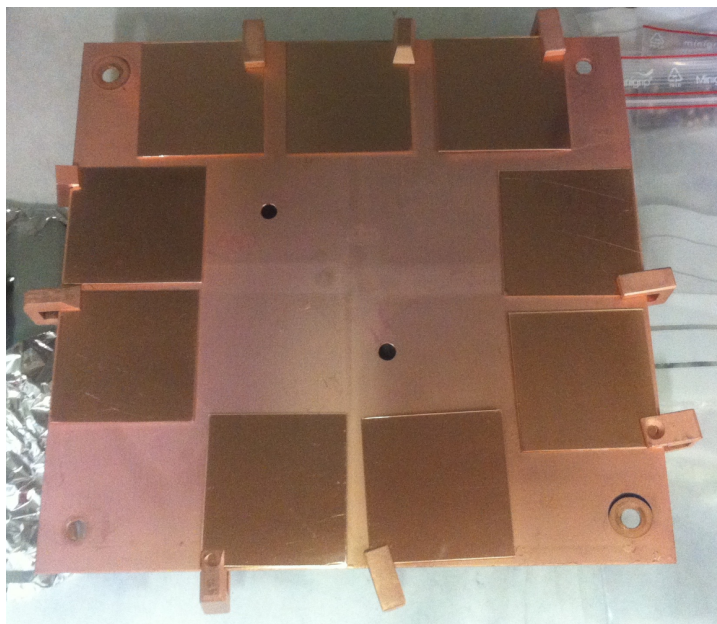


Figure 4.12. Cu-coated Al by DMS

experiments. These two baths present different compositions: The bath in the building 102 has 30 g l^{-1} of Cu and 95 ml/l of H_2SO_4 and it is used to produce the AC plated copper (7 ms ON, 8 ms OFF). The bath in the building 118 has 40 g l^{-1} of Cu , 101 ml/l of H_2SO_4 and 7.5 ml/l of brightener COPPER GLEAMTMHGX Electrolytic Copper from Dow Chemical and it is used to produce the DC plated copper.

The third bath is only a 10l beaker to produce reproducible samples in a very controlled conditions. With this bath 2 different compositions has been used. One with the same composition of the bath at the building 102 (this bath will be called matt bath) and the other with the initial bath composition of the bath at the building 102 plus 33 ml/l of D-Xylose (this



Figure 4.13. Substrate ready to be electroplated

bath will be called D-Xylose bath). The bath with D-Xylose is introduced after knowing two studies that claim a reduction of the hydrogen and oxygen content at the copper plated using this substance in the plating bath. [33] [34]

Electroplating and sample finishing

Before electroplating the substrates need to be degreased in the degreasing bath for 15 min to have a clean surface and then submerged in a 20 % in volume H_2SO_4 solution for 30 s to activate the surface. After it, the substrates can be dipped in the plating bath. The substrate is connected to the cathode of the power supply and the copper source to the anode. The power supply is set with the desired plating parameters (pulse type and current intensity) and switched on for the plating. In the figure Fig.4.14 and Fig.4.15 are shown the plating set up for the bath at the building 118 and the set up for the beaker bath, respectively.

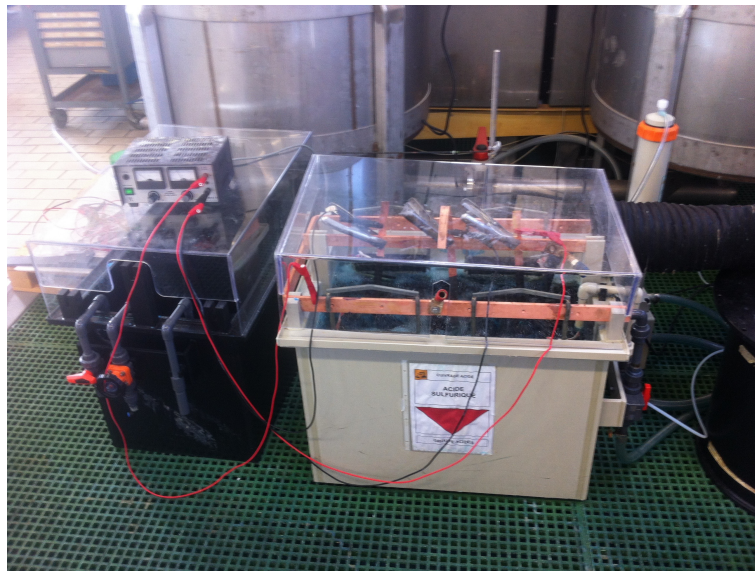


Figure 4.14. Electroforming set up at the bath in the building 118

When the plating is done the substrate with the electroformed copper is removed from the bath and is passivated in the passivation bath for 30 s. Then the water is removed with alcohol and filtered air and the sample is let dry for 10 min at the oven at 60 °C.

After drying, the electroformed copper is separated from the *Al* substrate by peeling it off. The electroformed copper is then cut in samples of 10 mm by 10 mm with the hydraulic punch press of the main workshop. Due to the grease of the machine the samples are degreased in the degreasing bath for 15 min to get a clean sample ready to be used for the test at the TDS system.

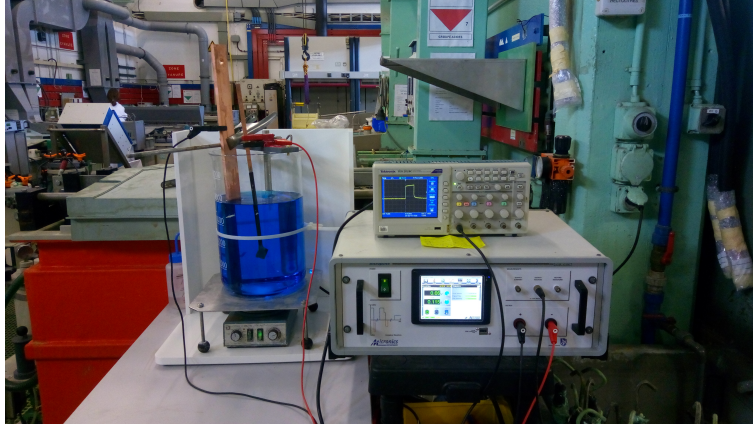


Figure 4.15. Electroforming set up at the beaker

4.3 TDS analysis of copper

The parameters for a standard TDS measurement has been set to obtain comparable results for all the samples tested. The conditions that are need to be set for all the measurements are the heating rate, the temperature range of measurement and the gasses that will be followed.

- Heating rate: $\beta = 10 \text{ K min}^{-1}$.
- Temperature rage: from $T_{min} = 40^\circ\text{C}$ to $T_{max} = 750^\circ\text{C}$ for the heater control. At the sample these temperatures are translated to $T_{min} = 38^\circ\text{C}$ to $T_{max} = 700^\circ\text{C}$.
- Gasses followed by default:
 - Hydrogen, H_2 , ($m/z = 2$).
 - Nitrogen, N_2 , ($m/z = 14$). N_2 is followed through the mass 14 (second ionisation) because the mass 28 (first ionisation) overlaps with CO .
 - Methane, CH_4 , ($m/z = 15$). The mass 15 is preferred to the mass 16 because it is less influenced by CO , CO_2 or O_2 .
 - Water, H_2O , ($m/z = 18$).
 - Carbon monoxide, CO , ($m/z = 28$).
 - Oxygen, O_2 , ($m/z = 32$).
 - Argon, Ar , ($m/z = 40$).
 - Carbon dioxide, CO_2 , ($m/z = 44$).
 - $m/z = 41$, $m/z = 43$ and $m/z = 57$ are the masses followed as witness of possible hydrocarbon contamination of the sample or the system.

4.4 XPS analysis of copper

All the XPS analysis have been performed at the XPS system in the laboratory 101/R-013 at CERN. The same samples 10 mm by 10 mm that are prepared for the TDS system are the ones used for the XPS analysis. The spectra are recorded from 0 eV to 1100 eV of binding energy (B.E.). Four regions of the spectra are deeply studied and quantified.

- 280-290 eV of B.E. corresponding to the carbon, $C1s$.
- 330-345 eV of B.E (910-925 eV of K.E.). corresponding to the copper Auger lines of copper, $CuLMM$.
- 528-538 eV of B.E. corresponding to the oxygen, $O1s$.
- 930-970 eV of B.E. corresponding to the copper, $Cu2p$.

The carbon is followed because is one of the main pollutants of the surfaces when is exposed at the atmosphere. Following the CERN criteria for UHV applications the relative composition of carbon at the surface should not be higher that 44 %. [35]

For the copper not only the XPS lines are considered, but also the main Cu LMM Auger line. From the combination of Cu level lines and Auger lines it is possible to have a proper explanation of the oxidation state of the oxide-layer. With the XPS spectra we mainly can identify 2 peaks: at 932.5 eV of B.E. there is a peak coming from the metallic copper, Cu , and the copper(I) oxide, Cu_2O ; [36] [37] [38] a second peak at 934.4 eV of B.E corresponds to the copper hydroxide, $Cu(OH)_2$. [39] So, the Cu_2O cannot be distinguished from the metallic copper, but the Auger spectra enable to distinguish them. At 334.9 eV of B.E there is the peak of the metallic copper, [36] the Cu_2O peak appears at 336.4 eV of B.E [37] [38] and the $Cu(OH)_2$ peak appears at 337.4 eV of B.E. The Cu_2O and $Cu(OH)_2$ peaks are difficult to separate at Auger spectra because of the broadness of the peak.

5 TDS results and discussion for copper

5.1 Cu-OFE

5.1.1 Surface treatment comparison

The three surface treatments mentioned before: passivation, electropolishing and SUBU, are studied independently. In addition a combination of electropolishing plus SUBU in a same sample is also considered, since it is applied for superconducting cavities substrates at CERN. The results of the TDS measurements shows that for all the samples the main gasses observed are water and hydrogen. A clear result appears for the outgassing of hydrogen, Fig.5.1(a). The amount and temperature of hydrogen outgassing does not depend on the surface treatment. The atomic hydrogen concentration (from $m/z = 2$) is in the range of 8 - 10 ppm for all the tested samples.

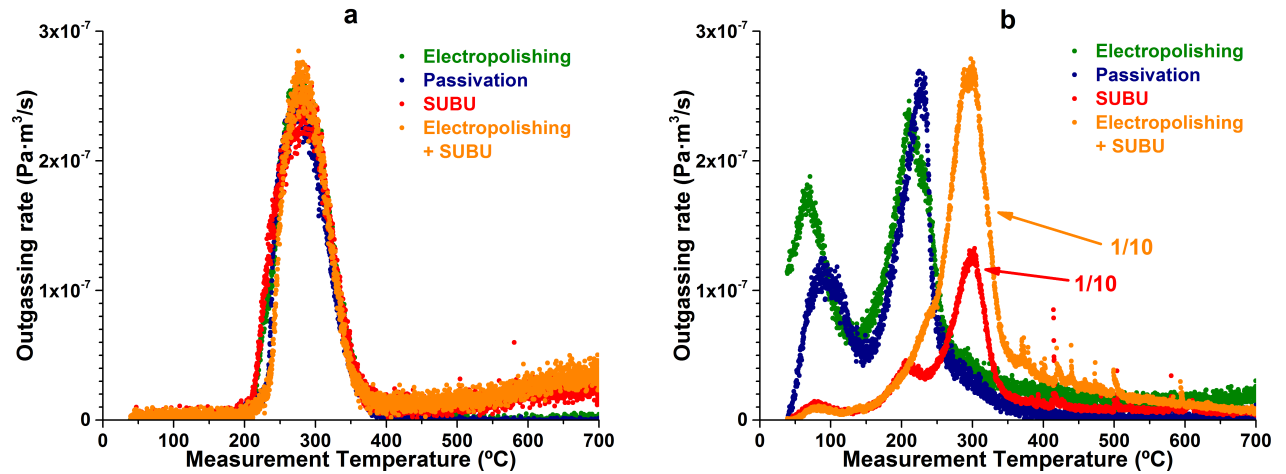


Figure 5.1. TDS results for the outgassing of hydrogen, $m/z = 2$, (a) and water, $m/z = 18$, (b) for the different surface treatments

A further study was carried on to try to completely verify this observation. The samples at Fig.5.1 were 1 mm thick. The idea was to measure 1, 2, 3 mm thick samples and see how the hydrogen content was scaling with the increase of thickness. These samples were cut from a bulk Cu-OFE whereas the 1 mm thick samples are from a laminated sheet (all from CERN stores). The samples were degreased and passivated with chromic acid before the TDS measurement. These samples showed such a low content of hydrogen that it was at the limit of detection (Fig.5.2(a)). Even though the content of hydrogen is low it is possible to conclude that the H is proportional to the bulk volume, but that different bulks contain different amounts of H . In the water spectra (Fig.5.2(b)) in these samples show how the 2nd peak of water is lower than one observed in the water spectrum of the Passivation sample in Fig.5.1(b).

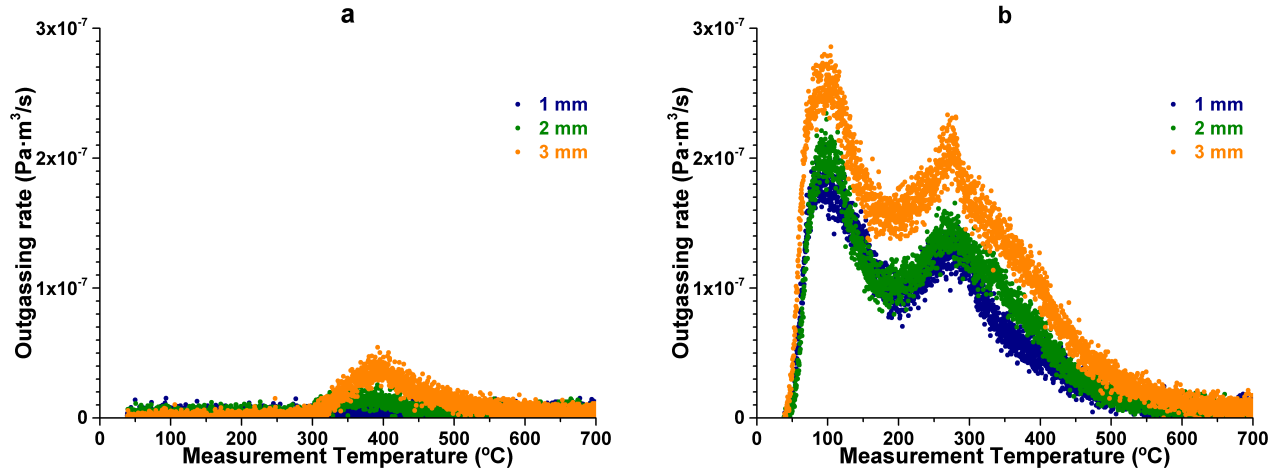


Figure 5.2. TDS results for the outgassing of hydrogen, $m/z = 2$, (a) and water, $m/z = 18$, (b) for Cu-OFE with different thicknesses

At the Fig.5.1(b) it can be observed that water outgassing presents a big difference between the SUBU and the other treatments. The main difference is that the SUBU treated samples, with and without electropolishing, have a peak which is around 10 times higher than the peaks observed for the samples with passivation and the electropolishing treatments (at the Fig.5.1(b) the outgassing rate of the SUBU and Electropolishing + SUBU has been divided by 10). The other observation is the appearance of a clear 2nd peak of water for the Electropolishing, Passivation and SUBU samples. The 1st peak of water definitely comes from the adsorbed water at the surface of the samples. Analysing all the samples tested at the TDS system, it has been seen that this 1st peak of water changes a lot in function of the roughness of the samples and the humidity at which has been exposed the sample during the storage at air. In Fig.5.3 it can be seen for different samples of Cu-OFE electropolished coming from the same batch that the 1st peak of water changes for each sample, but the 2nd peak remains very similar for all of them.

So, two questions appear. One concerning the source of the 2nd peak of water and the other concerning the source of this huge peak observed at the SUBU treated samples.

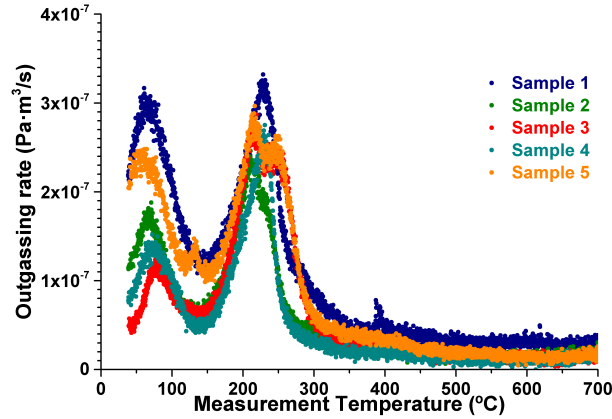


Figure 5.3. TDS results for the outgassing of water, $m/z = 18$, for different samples Cu-OFE electropolished coming from the same batch

5.1.2 2nd water outgassing peak

To try to answer the question of the source of the 2nd peak of water, two hypotheses are made:

- There is H_2O retained in the oxide layer.
- The peak of H_2O is due to the oxidation of hydrogen passing through the oxide layer.

A series of tests are proposed to be able to verify one of the hypotheses:

- Cu-OFE samples with different oxide thickness. A different oxide thickness should also influence the resulting amount of water. If the 2nd peak of water comes from the retained water in the oxide layer, a thicker oxide layer should retain more water and therefore this peak should increase for a more oxidised sample. This result would confirm the 1st hypothesis.
- Cu-OFE samples containing hydrogen and samples without hydrogen. To remove the hydrogen the samples are thermal treated under vacuum (ThT). If the 2nd water peak is produced by the oxidation of hydrogen a sample without hydrogen should not exhibit such a peak. This result would confirm the 2nd hypothesis.

We tried to obtain 3 different oxide thicknesses: first by passivation with the chromic acid (Passivation and ThT + Passivation samples); second by spontaneous reaction of the copper with the oxygen of the atmosphere (Degreasing and ThT samples); and third thermal oxidation of the copper at air with the dryer (ThT + Air Oxidation sample). The oxidation of the samples has been studied by XPS (Fig.5.4). The Passivation and ThT + Passivation samples present similar oxides and a higher peak of *Cu* (relative to the oxide peak) in the Auger spectra than for the Degreasing and ThT samples. From the XPS it can be extracted that the thinnest oxide layer is formed on the passivated samples. The ThT + Air Oxidation sample was not tested at the XPS but it was visibly (red coloured) more oxidised than the other ones. So, three different oxide thicknesses were obtained.

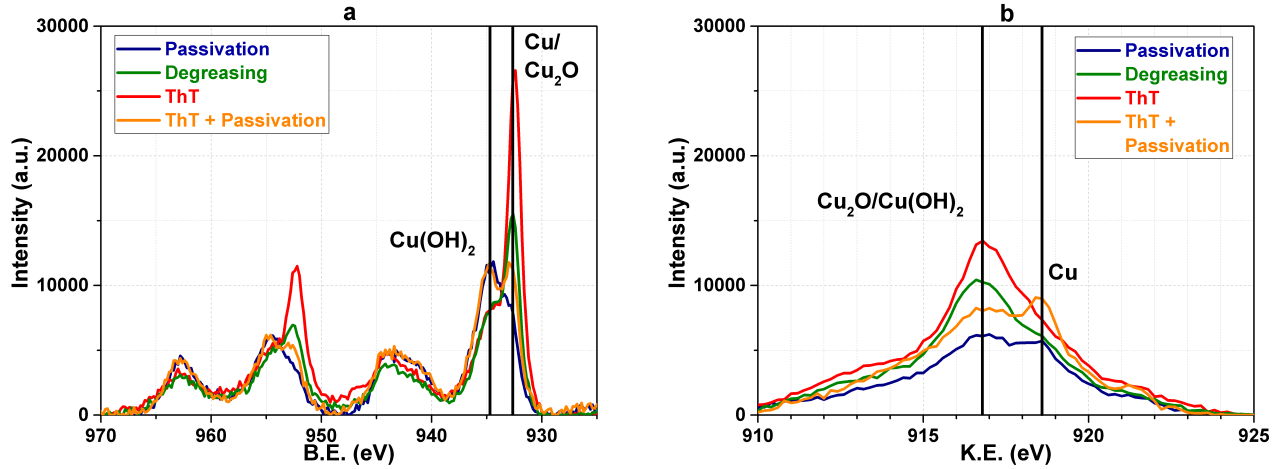


Figure 5.4. XPS results for the different oxidised samples with and without thermal treatment. Cu₂p (a) and CuLMM (b). Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)

With the TDS results obtained for the hydrogen outgassing (Fig.5.5(a)), it can be seen how the samples with the ThT do not present any hydrogen, as it was expected. The Degreasing sample has a smaller hydrogen peak than the Passivation sample and also a peak which is delayed in temperature. For the TDS results of the water (Fig.5.5(b)) in all ThT samples the 2nd peak of H_2O is much smaller than the one of the samples without the ThT. For the samples without ThT the Degreasing sample presents a higher 2nd peak of H_2O than the one of the Passivation sample.

The results coming from the TDS tests show:

- Almost no 2nd outgassing peak of water for the thermal treated samples which do not contain hydrogen. No difference is observed for different levels of oxidation of these samples.

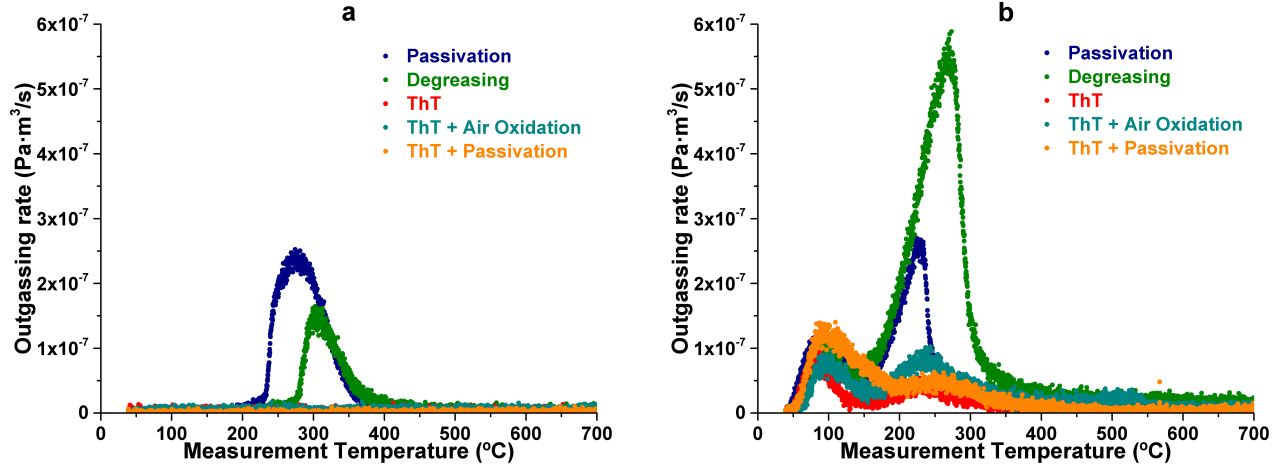


Figure 5.5. TDS results for the outgassing of hydrogen, $m/z = 2$, (a) and water, $m/z = 18$, (b) for the different oxidised samples with and without thermal treatment

- For the samples containing hydrogen: The more oxidised samples present an increase in the 2nd peak of water and a reduction of hydrogen peak (Tab.5.1).

These bring to validate the second hypothesis that has been presented. So, the 2nd peak of water is due to the oxidation of the hydrogen passing through the oxide layer.

Table 5.1. Hydrogen concentration taking into account $m/z = 2$ and $m/z = 18$. Values obtained by integration of the flow rate from 150 °C to 500 °C

Samples	$[H_2]$	$[H_2O]$	$[H]$
	$m/z = 2$	$m/z = 18$	$2[H_2] + 2[H_2O]$
	(<i>at.ppm</i>)	(<i>at.ppm</i>)	(<i>at.ppm</i>)
Passivated	3.7	4.1	16
Degreasing	2.0	10	24
ThT	0.18	1.0	2.4
ThT+Oxidation	0.31	2.5	5.6
ThT+Passivation	0.05	1.8	3.7

5.1.3 Role of hydrogen diffusion on the oxide layer reduction

After confirming that the 2nd outgassing peak of water in the TDS results is caused by the oxidation of hydrogen passing through the oxide layer a new hypothesis has been made:

- The hydrogen diffusion and reaction decreases the temperature of reduction of the copper oxide layer.

A lot of research has been done on the reduction of the copper oxide layer under vacuum. Copper has an importance in the technological point of view for the corrosion and heterogeneous catalysis. Copper catalysts are used, for example, in methanol synthesis, in the recombination of carbon dioxide and in electronic applications. Another emergent application of copper catalysts is the use in the generation of hydrogen from partial oxidation of hydrocarbons. [40] [41] Some of these studies prove that the carbon on the surface of the copper acts as a reducing agent of the oxide layer. The reduction of the copper oxide layer in an hydrogen atmosphere has also been studied. [42] But no studies have been found about the reduction effect of the hydrogen contained in the copper bulk.

Two XPS tests are proposed to try to verify the hypothesis:

- One test will be done by increasing the temperature of the sample while recording the spectra at some selected temperatures. The heating rate used is around 0.5 K/min and while the measurement is done the temperature is kept constant, the time for each measurement is around 10 min. The idea is to identify the temperature where the oxide starts to reduce. If the hypothesis is correct, for the sample containing hydrogen, the reduction should start at the same temperature when the hydrogen starts to diffuse. For the samples without hydrogen the reduction should happen at a higher temperature. The temperature where the hydrogen starts to diffuse is around 150 °C, this temperature is considered as the temperature where the 2nd peak of water starts to appear in the TDS measurement (Fig.5.5(b)).
- The second test will be done in a fixed temperature to observe the evolution of the oxide during time. The temperature selected for this measurement is the temperature where the hydrogen starts to diffuse, 150 °C. If the hypothesis is correct the oxide should get reduced for the samples with hydrogen. For the samples without hydrogen the oxide layer should not present any change during the time.

The first test by increasing the temperature is done for the passivated samples, one with thermal treatment and another without (Fig.5.6). As already seen before the oxidation is similar for both samples at room temperature (RT). At 200 °C it is observed for both samples that the $Cu(OH)_2$ is reduced, probably to Cu_2O (Fig.5.6(a), Fig.5.6(c)). The Auger spectra shows a reduction of the Cu_2O for the Passivation (Fig.5.6(b)) but much less for the ThT + Passivation sample (Fig.5.6(d)). Finally at 250 °C both samples are completely reduced.

This test gives a first prove for the verification of the hypothesis. The sample containing hydrogen (Passivation sample) gets reduced at lower temperatures.

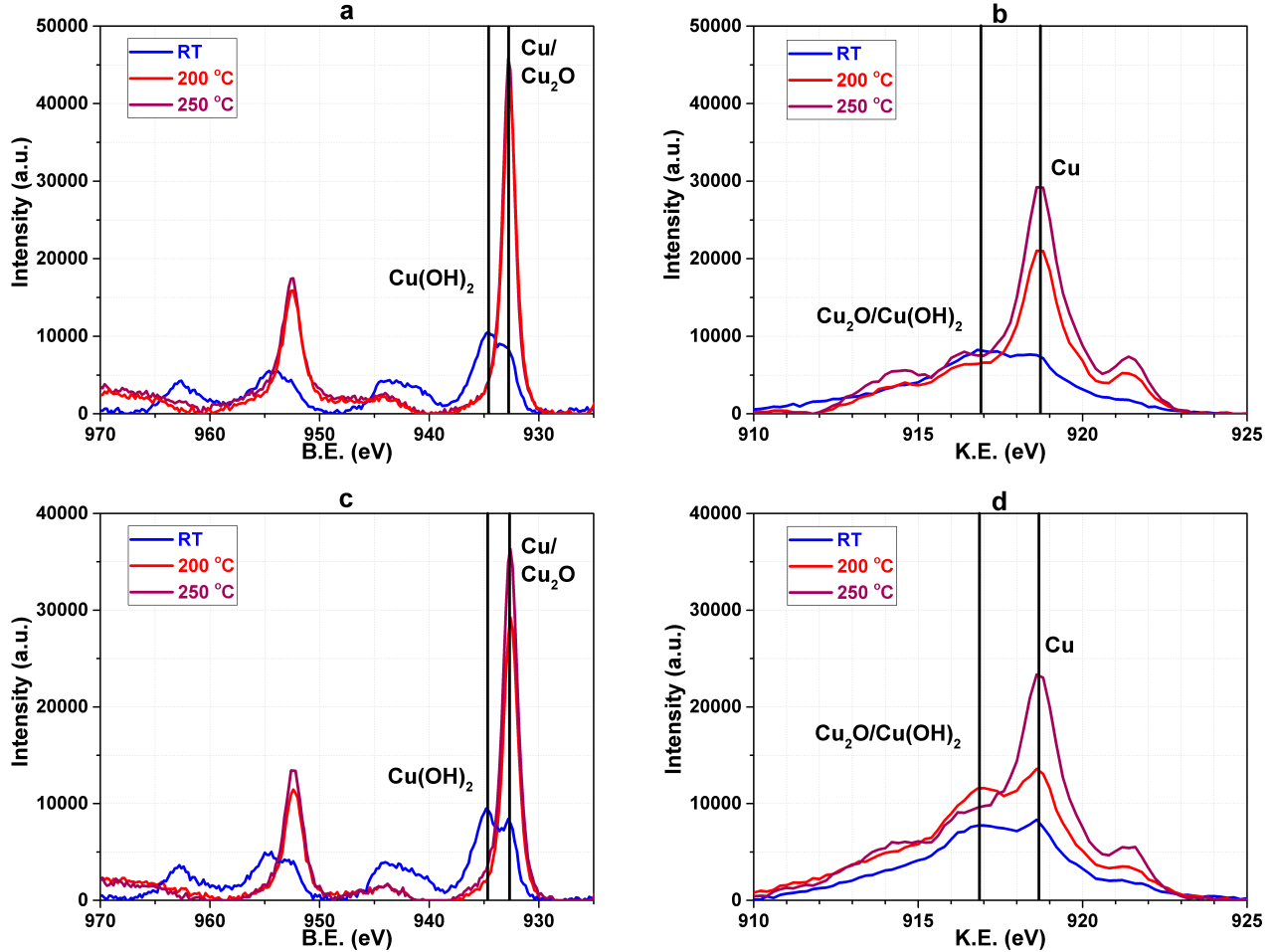


Figure 5.6. Evolution of the XPS by increasing the temperature. Cu2p for the Passivation sample (a), CuLMM for the Passivation sample (b), Cu2p for the ThT + Passivation sample (c) and CuLMM for the ThT + Passivation sample (d). Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)

A more detailed test is done for a Degreased sample and ThT sample. These two samples present a thicker oxide layer than the passivated ones. So, the oxide layer should be more difficult to reduce. The results of this second test can be seen at the Fig.5.7. At room temperature both samples present a similar oxidation. At 120 °C the $\text{Cu}(\text{OH})_2$ is already reduced for both samples (Fig.5.7(a) and Fig.5.7(c)). The $\text{Cu}(\text{OH})_2$ gets reduced at very low temperature. Therefore, it was not possible to detect this temperature with the XPS system. The Auger spectra shows a reduction of the Cu_2O of the Degreasing sample at 160 °C. This reduction con-

tinues since until 220 °C (Fig.5.7(b)). The start of the reduction at 160 °C is a good indicator for the verification of the hypothesis because from the TDS the start of reduction was foreseen to be at 150 °C. For the case of the ThT sample (the sample without hydrogen in the bulk) the Cu_2O starts to reduce at 160 °C (Fig.5.7(d)). All the results of this last test also go in the way of proving the hypothesis.

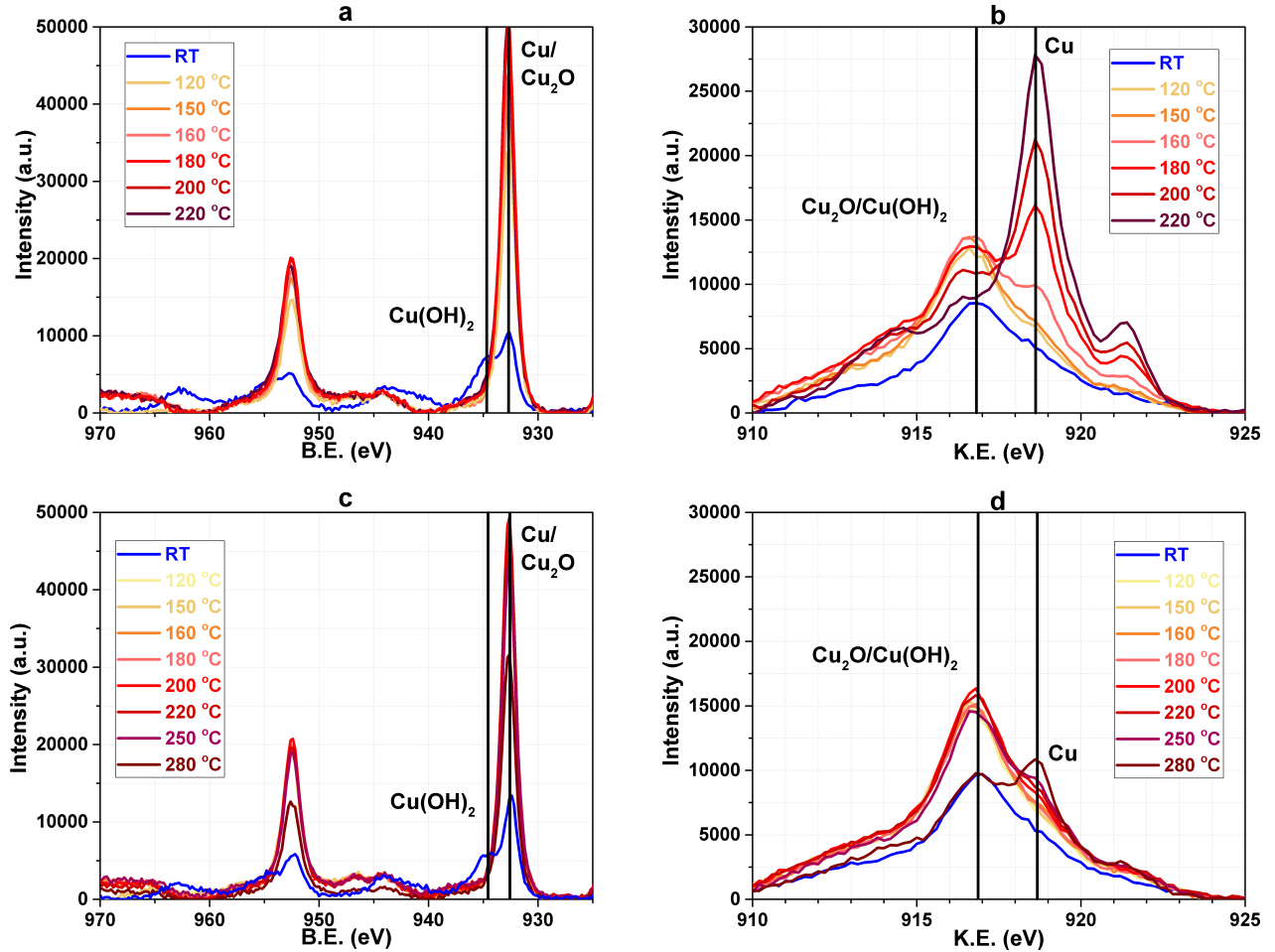


Figure 5.7. Evolution of the XPS by increasing the temperature. Cu2p for the Degreasing sample (a), CuLMM for the Degreasing sample (b), Cu2p for the ThT sample (c) and CuLMM for the ThT sample (d). Analysis done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)

If we look at the $O1s$ peak in function of the temperature for this last test we can observe how the evolution of the peak is different for the samples different samples. The sample with H in the bulk (Degreasing) present a faster reduction of the area of the peak than the sample without H (ThT) (Fig.5.8). In this case even at 120 °C one can see a considerable reduction of oxygen peak. At the Auger lines this change becomes more significant after 150 °C. Even

though the temperature is slightly different in both cases the reduction of the oxide is faster for the sample with H .

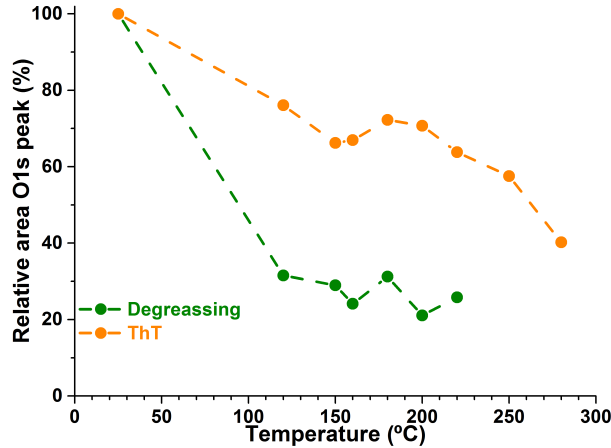


Figure 5.8. Evolution of the O1s peak in function of the temperature

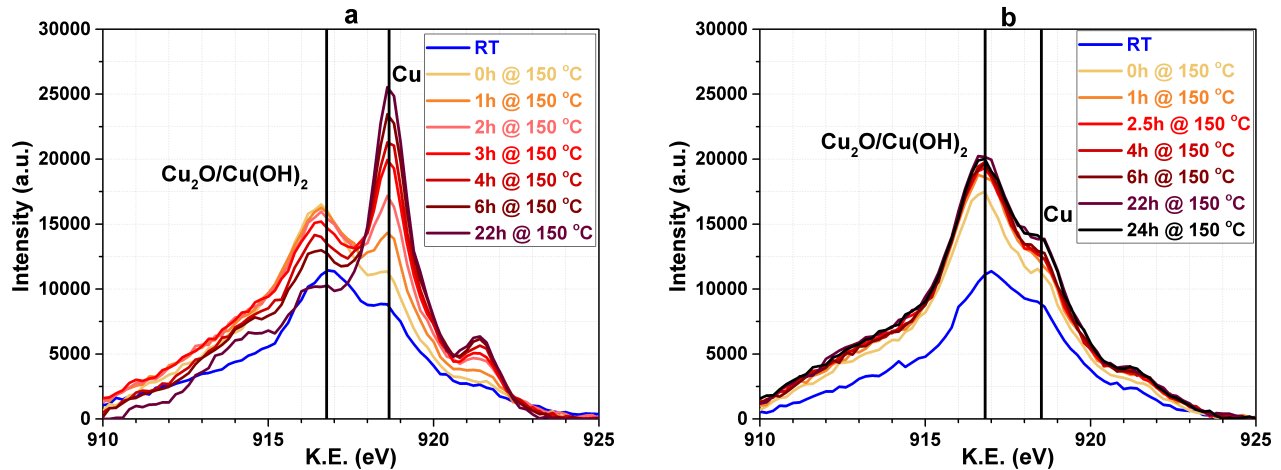


Figure 5.9. Evolution of the XPS on time by holding the temperature at 150 °C. CuLMM for the Degreassing sample (a) and CuLMM for the ThT sample (b). Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)

For the last test the samples are heated up to 150 °C. This temperature is kept for 24 h. In this case the analysed samples are also a Degreassing sample and a ThT sample. For the sample with hydrogen in the bulk (Degreassing sample) it is observed how the copper is getting reduced as the time is advancing (Fig.5.9(a)). From 6 h to 22 h the spectra does not show more changes. Probably the hydrogen is all diffused. For the sample without hydrogen (ThT sample) a small change is observed when the spectra is recorded at room temperature and at 150 °C but no

further changes are observed for the rest of the 24 h of measurements.

The results of the tests show:

- The hydrogen starts to diffuse out of the copper in UHV conditions at 150 °C.
- The oxide-layer can be completely reduced at 150 °C if there is sufficient hydrogen inside the copper.
- If there is no hydrogen inside the copper the reduction will start at higher temperatures. This temperature is 250 °C for a passivated copper and even higher than 280 °C for copper with a thicker oxide layer.

A part from the experimental data if one look at the thermodynamics of the hydrogen reaction with the copper oxide, it can be seen that this reaction is favoured among others. A simple way to check the thermodynamics of this reaction is with an Ellingham diagram. An Ellingham diagram is a graphic representation of the thermodynamic driving force for a reaction to occur at different temperatures. From a Ellingham diagram it can be extracted the pressure of O_2 below which the oxide can be decomposed. At 150 °C the O_2 pressure is above 10^{-34} mbar the Cu_2O does not decompose. [43] This pressure is way below any real pressure. Therefore at this temperature the decomposition of the oxide is not favoured. Another information that can be extracted from a Ellingham diagram is a comparison of different reducing agents. If we compare the reduction of the Cu_2O with hydrogen and carbon we can see that at 150 °C the reduction of the Cu_2O is favoured for hydrogen forming water. This trend is true until 600 °C when then the standard free energy gets higher for a reduction with carbon (Fig.5.10).

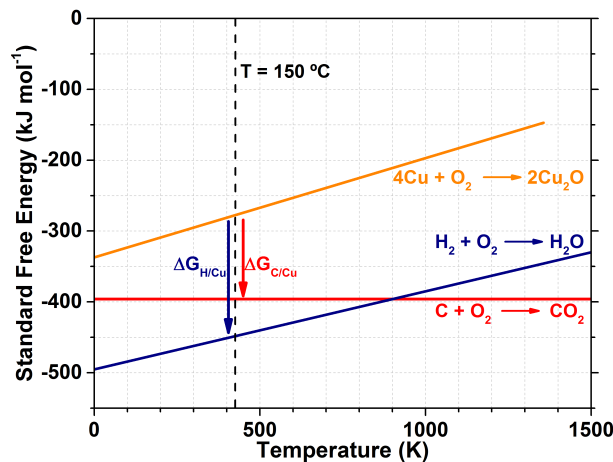


Figure 5.10. Ellingham diagram for Cu_2O , H_2O and CO_2

With the data from the Ellingham diagram it can be said that from the thermodynamic point of view the reaction described in the hypothesis can be accomplished. And all the experimental results bring to verify the hypothesis. The hydrogen diffusion decreases the temperature of reduction of the copper oxide layer.

5.1.4 SUBU treatment

As commented before, the Cu-OFE with the SUBU treatment has different outgassing than the other studied surface treatments. In the SUBU treated samples a large peak of water together with other gases was observed at 300 °C. To try to see if there was a difference in the oxidation or some contamination on the surface a XPS analysis was performed on a Passivation sample, on a Electropolishing sample and on a SUBU sample. As it can be seen at the Fig.5.11 the results of the XPS analysis, the SUBU sample does not present any different kind of oxide. From the strong water outgassing at the TDS, it was expected to find a higher peak for the $\text{Cu}(\text{OH})_2$ at the XPS but the XPS results show that the sample with a higher content of $\text{Cu}(\text{OH})_2$ is the Passivation sample.

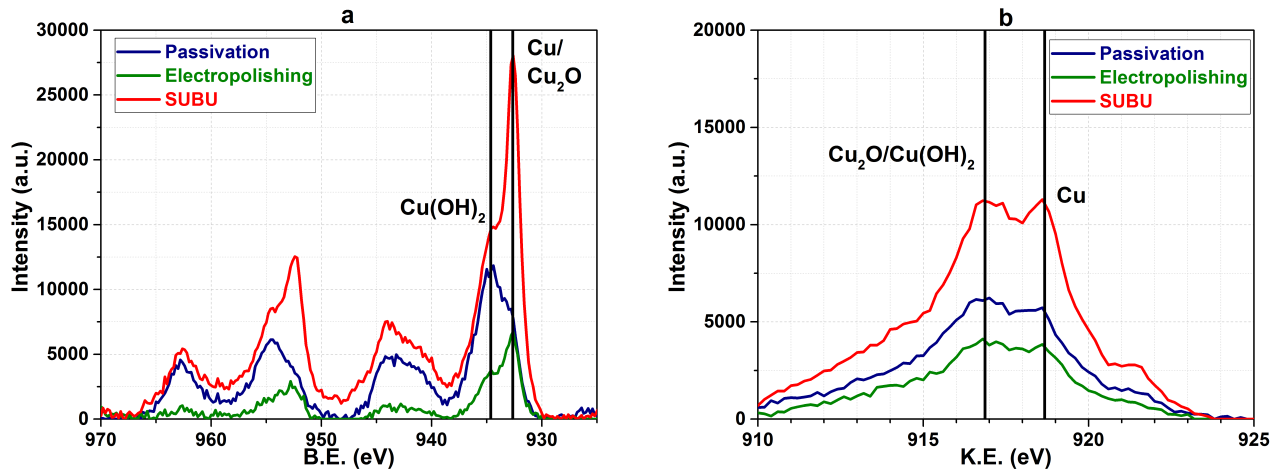


Figure 5.11. XPS results for the different surfaces treatments. Cu2p (a) and CuLMM (b). Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)

In terms of carbon at the surface, the SUBU sample also presents the cleanest surface compared to the Electropolishing sample and Passivation sample (Fig.5.12). Even if the SUBU treatment only affects the surface the XPS that only analyse the sample surface can not detect the origin of the contamination found with the TDS tests.

In order to see how deep this contamination is located, it was thought to remove the first layers of the surface of a sample. The first method used to remove these layers was by sputtering the surface with an ion gun. The ion gun used was the one from the XPS system (101/R-013). As the sputtering was done in the XPS it was possible to follow the oxide state of the surface. It was decided to remove the surface until the point where the oxygen was not detected. After sputtering both sides of the sample, it was tested in the TDS system. The TDS results of this sample show how the contamination is not removed (Fig.5.13).

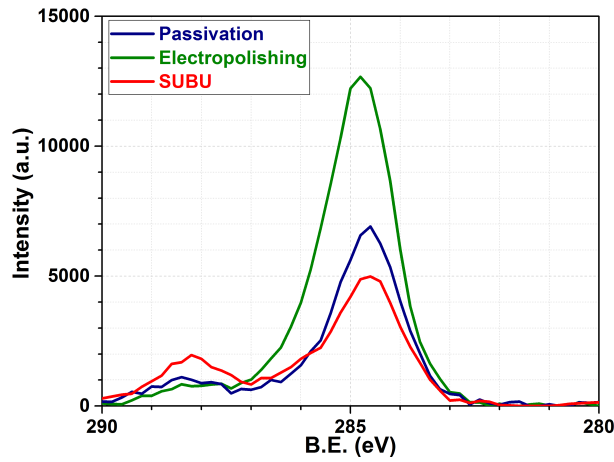


Figure 5.12. XPS results for the different surfaces treatments for C1s. Analyses done by Garcia-Tabares, E. (CERN-TE-VSC-SCC)

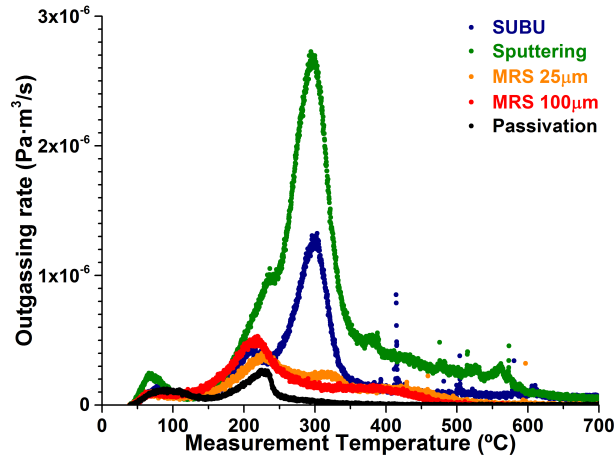


Figure 5.13. TDS results for the outgassing of water, $m/z = 18$, for a Cu-OFE samples with SUBU treatment after removing the surface

Now the idea was to go deeper in surface to see when the contamination is removed. A mechanically removal of the surface was done at two other samples. This procedure was done with

a file. At one sample around 25 μm were removed from each side and for the second sample 100 μm . In the case of the sample with 25 μm removed, a small outgassing peak of water is still appearing at 300 °C. For the sample with 100 μm removed the TDS results shows how the contamination is completely gone.

This results were compared with a scanning electron microscope images of the surface of the copper (Fig.5.14). The microscope study shows that the surface of the Cu-OFE after the SUBU treatment presents pinholes. On the other hand, for the Cu-OFE after electropolishing no pinholes were not detected. With the images taken (Fig.5.15) of a cross section of a SUBU sample it can be seen how the pinholes reach a depth of 0.2 μm . These pinholes on the surface of the SUBU sample could explain where the water contamination is set and the reason why in the other surface treatments it is not present.

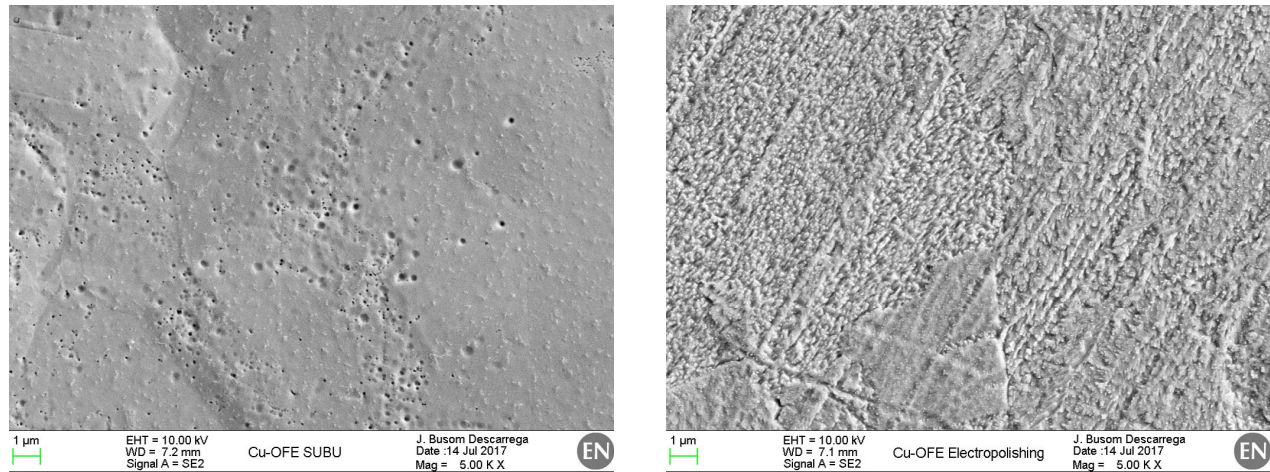


Figure 5.14. Scanning electron microscope images of the surface of Cu-OFE SUBU treated (a) and electropolished (b). Images taken by Busom Descarrega, J. (CERN-EN-MME-MM)

The existence of these defects in the surface of the SUBU samples made us think on the way the SUBU samples are rinsed. The SUBU sample usually are only rinsed with water from the acids and other substances that form the bath. This water rinsing might not be able to remove all substances if some of them are trapped in the pinholes of the surface. The hypothesis is that the huge peak of water might be related with the some of these trapped substances.

To try to get the answer a SUBU sample has been further cleaned in an ultrasounds bath with ethanol for 15 min. After it a TDS test has been performed.

The TDS results show a reduction around 70 % of the peak at 300 °C (Fig.5.16). This reduction confirms the hypothesis that this peak was coming from the substances of the SUBU

bath. More probably the water peak comes from the dissociation of carboxylic acid groups that are contained in the sulfamic acid and the ammonium citrate.

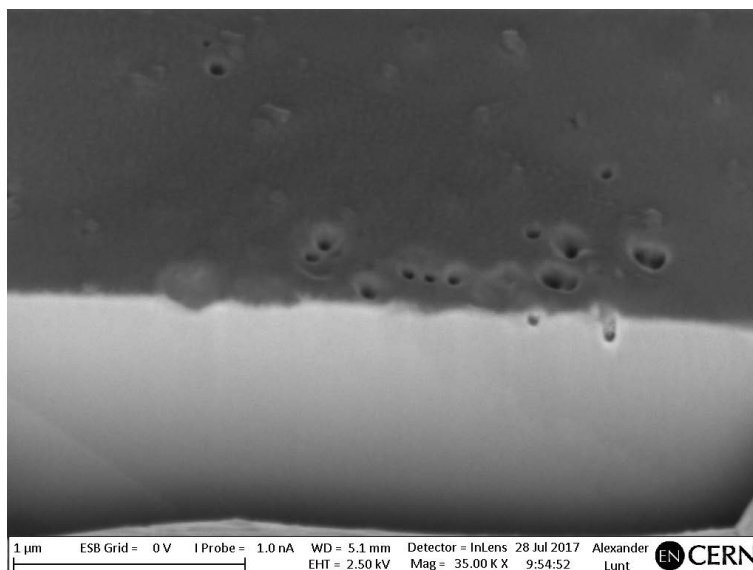


Figure 5.15. Scanning electron microscope images of cross section of Cu-OFE SUBU treated cut with focused ion beam. Image taken by Lunt, A. (CERN-EN-MME-MM)

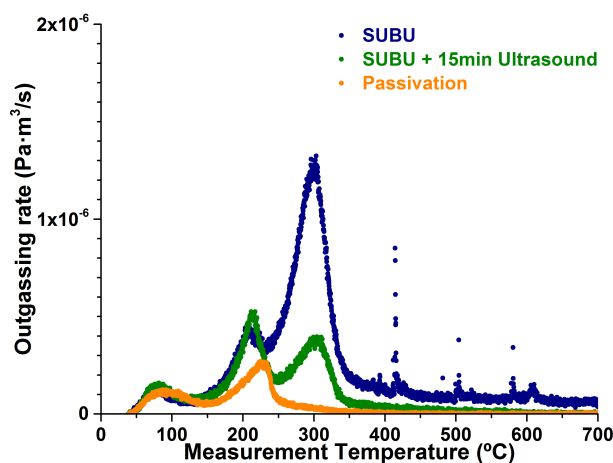


Figure 5.16. TDS results for the outgassing of water, $m/z = 18$, for a Cu-OFE samples with SUBU treatment cleaned 15 min in ultrasounds before the test

5.2 Electroformed copper

5.2.1 Outgassing of electroformed copper in the industrial baths

In order to understand how outgassing of the electroformed copper used in the reverse NEG coated vacuum chambers, different series of tests have been performed. First of all it has been compared the outgassing of water, hydrogen and oxygen in different platings done in the two industrial baths used in the workshop. The effect of the current density, the thickness of the plating, the composition of bath (see in section 4.2.4) and the type of pulse was investigated.

A first overview of how the outgassing changes from an AC to a DC electroformed copper can be seen on the TDS spectra of two samples (Fig.5.17). The most remarkable difference can be seen in for water outgassing. The AC plated (Fig.5.17(b)), where three peaks of water can be detected, present a larger quantity of water than the DC (Fig.5.17(a)), where only the two outgassing peaks of water are identified. This effect has been present in almost all AC plated samples and in some of them the water was coming out in form of multiple spikes. Also the amount of hydrogen is higher for the AC plated sample.

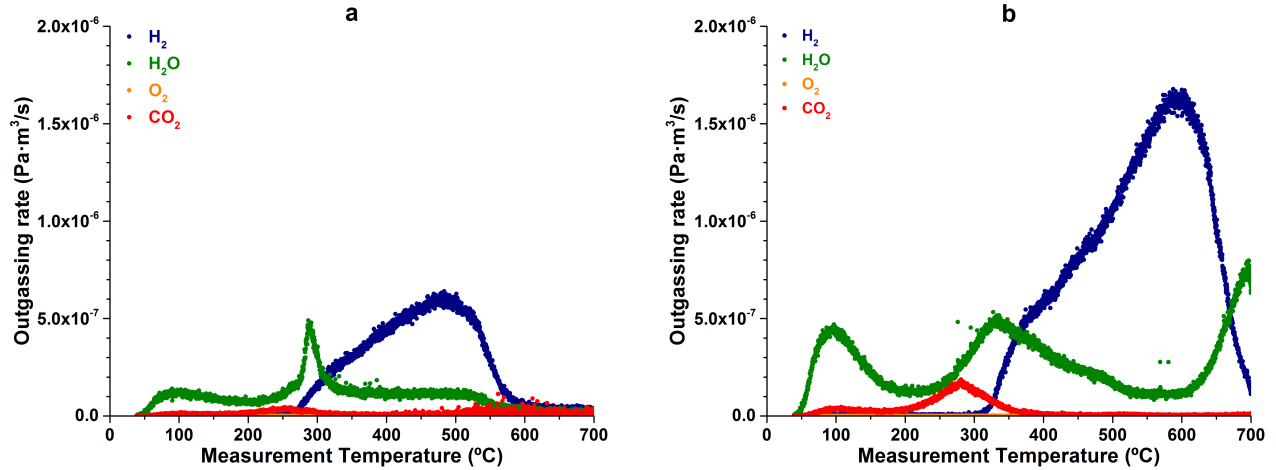


Figure 5.17. TDS results for the outgassing of H_2 , H_2O , O_2 and CO_2 for 1 mm 2 A dm^{-2} DC plated sample (a) and for 1 mm 2 A dm^{-2} AC plated sample (b)

In Fig.5.18 the results of these tests are presented in terms of the concentration of the gas in the sample in function of the thickness of the sample. To obtain the concentration the total outgassing of the gas has been divided by the mass of the sample. The samples produced with the same current density have been group to have a better visualisation of the different tendencies. Different samples for each current and thickness have been tested in order to have

more reliable results.

In the case of the H_2 for the all samples (Fig.5.18(a) and Fig.5.18(b)) a similar tendency is found. This tendency is an increment of the concentration of hydrogen in the samples while the thickness increases. Therefore, more hydrogen is incorporated as the sample grows.

In terms of O_2 content the most important aspect is the difference of content between the DC plating samples (Fig.5.18(c)) and the AC plating (Fig.5.18(d)) (the scale is logarithmic). The DC plated sample outgas a high amount of O_2 . The origin of this oxygen is related to the use of brightener in the composition of the bath. The behaviour of the O_2 is different from the one of hydrogen, since its concentration is constant when the thickness increases. This behaviour means that there is a uniform concentration of the oxygen all along the bulk. Therefore, from the TDS results there is apparently no relation between O_2 and H_2 in terms of trapping H .

The H_2O has a different behaviour from the O_2 and the H_2 . In both groups of samples, DC plated (Fig.5.18(e)) and AC plated (Fig.5.18(f)), the concentration gets reduced with the thickness. In fact the total outgassing of the samples is almost constant. That it means that the outgassing of H_2O is not coming from the bulk but from the surface. The reproducibility of the results of water was more difficult than for H_2 or O_2 because the outgassing is very dependent on the roughness of the surface of the sample. Therefore, if the plating was not done properly (obtaining of very rough surfaces due to problems with the air agitation or the stability of the sample holder) the outgassing of water was increasing up to a point that the TDS measurement was not possible to be finished. This effect was mostly seen on the AC plated sample, because in this bath there is no brightener. The brightener acts as a leveller that reduce the roughness and therefore less water on the surface can be detected and also is more difficult to produce voids during the plating.

A schematic view of the results obtained with the TDS measurements can be seen at the Fig.5.19. The water in the surface, the hydrogen in the bulk with an increase of concentration as the copper grows and a homogeneous concentration of oxygen also in the bulk. The oxide layer in the surface is not represented but it also has an effect in the outgassing of these three molecules.

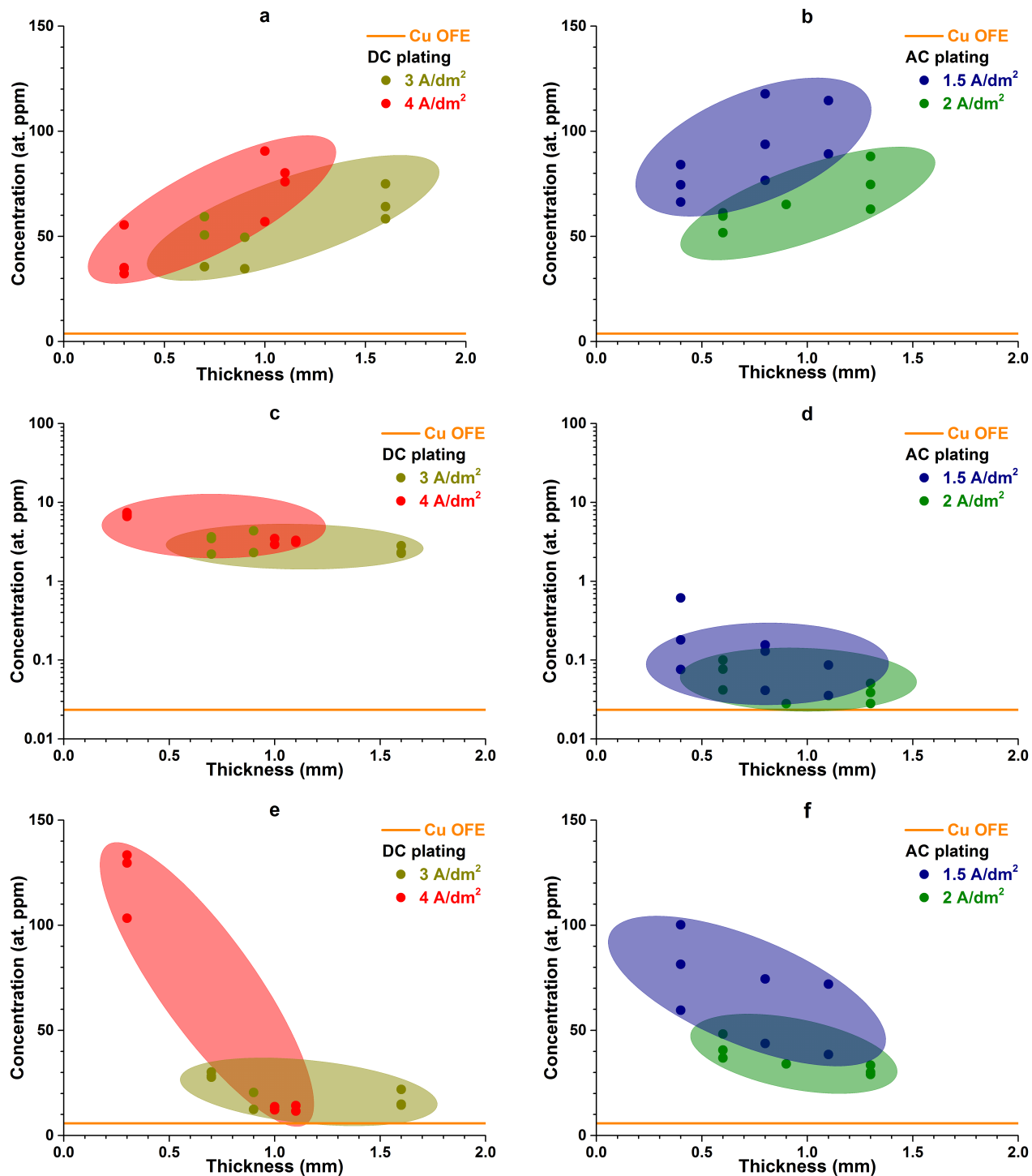


Figure 5.18. From the TDS tests: $[H_2]$ DC plating (a), $[H_2]$ AC plating (b), $[O_2]$ DC plating (c), $[O_2]$ AC plating (d), $[H_2O]$ DC plating (e), $[H_2O]$ AC plating (f)

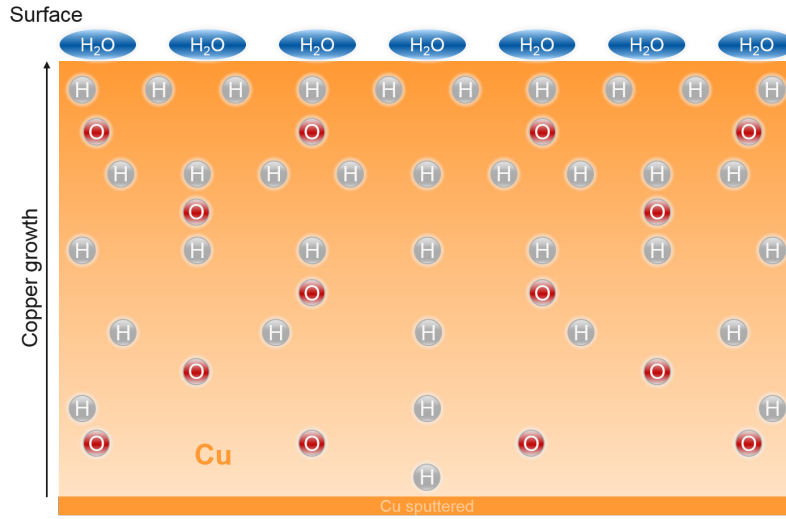


Figure 5.19. Schematization of a cross section of an electroformed copper in terms of hydrogen, oxygen and water content

Some more differences are found between the DC and AC plated samples apart from the outgassing quantity. Looking at the hydrogen outgassing spectra (Fig.5.20) a difference is observed in the peak position. For the DC samples the maximum of the outgassing peak is around 450 °C and for the AC sample the peak is around 550 °C.

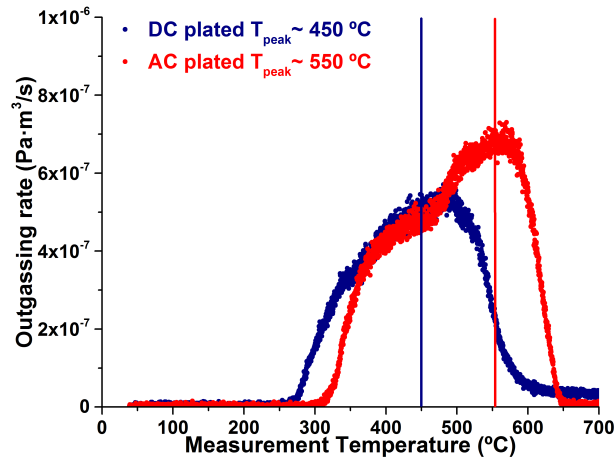


Figure 5.20. Comparison of TDS results for the outgassing of H_2 for DC and AC plated samples 0.6 mm thick with 2 A dm^{-2} of current density

As can be seen at the Fig.5.21 the grain size of the AC plated ($14 \mu\text{m}$) is bigger than the DC plated ($37 \mu\text{m}$). The AC plated also presents a columnar growth and the DC plated presents a homogeneous growth. In the AC plated it can also be seen how the grain size evolves from

very small, coming from the sputtered *Cu* layer, to the bigger grains seen closer to the surface. These differences in the grain size between the tow sample could be a possible explanation of the differences observed in the outgassing temperature of the hydrogen. Bigger grains imply fewer grain boundaries and therefore fewer pathways for diffusion meaning a slower diffusion that it is reflected in the TDS as later outgassing peak. In diffusion two terms can define the positioning of the outgassing peak, the activation energy of diffusion (E_d) and the diffusion coefficient (D_0). The E_d should be identical if the hydrogen is bound to the copper in the same way but the D_0 could be the changing factor.

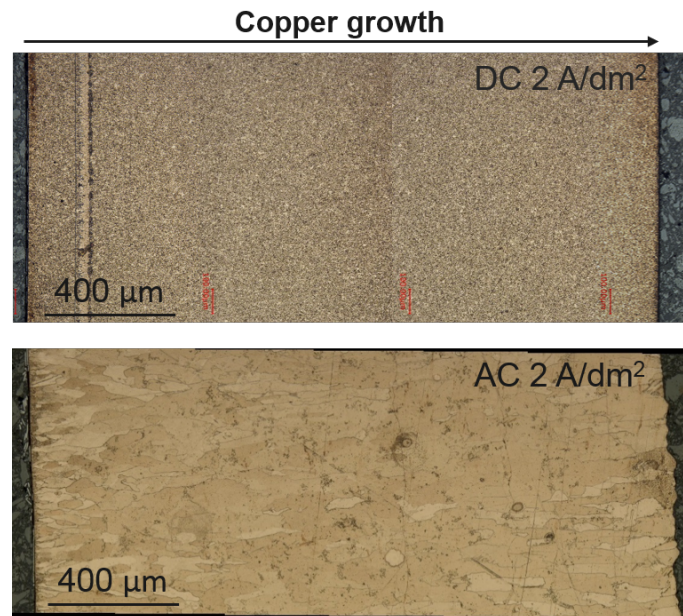


Figure 5.21. Optical microscope images after etching the cross section of DC and AC plated copper. Images taken by Busom Descarrega, J. (CERN-EN-MME-MM)

5.2.2 Comparison with Cu-OFE

For the study of reverse NEG coating it is important to see how is the outgassing of the electroformed copper compares with the Cu-OFE used as substrate of the standard NEG coating procedure. From the results presented at the Fig.5.18 it is possible to see that the amounts of hydrogen, water and oxygen are higher for the electroformed copper samples than Cu-OFE. This information is not sufficient to explain the different performance of the NEG on electroformed copper. A very important information is to know how much of these gasses can be transferred to the NEG coating during the activation process. For these reason two simulations of activation cycles have been performed at the TDS system. One simulation is done by keeping

the sample 24 h at 230 °C in the main chamber of the TDS system before doing the standard TDS measurement. The other simulation is done by keeping the sample 2 h at 350 °C.

In Tab.5.2 the results of these tests can be seen. For the Cu-OFE almost all the hydrogen and the water are outgassed in the two activations, but for the electroformed coppers only a small fraction is outgassed. These differences are due to the position of the outgassing peaks. The outgassing peak of H_2 in the Cu-OFE is around 300 °C much lower temperature than the peak of the DC and AC electroformed copper that have the peak around 450 °C and 550 °C, respectively. Even though in the case of electroformed copper samples only a small fraction is outgassed, this fraction is already higher than the total quantity of hydrogen and water outgassed from the Cu-OFE. Therefore, this higher quantity could be a problem for a faster saturation of the NEG coating.

Table 5.2. Difference in outgassing of the Cu-OFE and electroformed copper after activation cycles

Samples thickness 1 mm	Concentration in at. ppm					
	As received	After 24 h at 230 °C		After 2 h at 350 °C		
	H_2	H_2O	ΔH_2	ΔH_2O	ΔH_2	ΔH_2O
Cu-OFE	3.8	4.2	3.3	2.7	3.6	3.2
2 A dm ⁻² DC plated	23	11	0	0	10	6.6
2 A dm ⁻² AC plated	65	28	5.9	7.6	17	8.5

As already commented, different positions of the outgassing peaks of hydrogen has been found in the different types of copper. The Fig.5.22 presents four different types of copper (Cu-OFE, Bright 2 A dm⁻² DC plated done in the industrial bath in the building 118, Matt 2 A dm⁻² AC plated done in the industrial bath in the building 102 and 70 A dm⁻² 80 ms pulse ON AC plated done in the beaker with D-Xylose). The four samples present different outgassing peaks for the hydrogen and water. In the case of the hydrogen:

- Cu-OFE: Single peak from 230 °C to 370 °C.
- 2 A dm⁻² DC Bright: Single peak from 270 °C to 600 °C.
- 2 A dm⁻² AC Matt: Two peaks superposed from 310 °C to 470 °C and from 470 °C to 650 °C.
- 40 A dm⁻² AC D-Xylose: Two peaks from 290 °C to 520 °C and from 520 °C to 700 °C.

At least four different peaks can be identified. The peak of copper OFE, the first peak of the three electroformed samples, the second peak of the 2 A dm^{-2} AC Matt sample and the second peak of the 40 A dm^{-2} AC D-Xylose sample. These different peaks might come from hydrogen trapped in different ways in the copper. As the quantity of hydrogen outgassed is much higher than equilibrium of hydrogen that can be dissolved in copper at room temperature [44]. Some studies are made about how the hydrogen is trapped in copper. Some claim that it is trapped in form of molecular hydrogen [45], [46] and other in vacancies [47], [48]. If the hydrogen was trapped in form of molecular hydrogen the energy of dissociation would be too high to allow the detection in the TDS. But some similarities with our study can be found in studies the explanation of the vacancies. They claim that the peaks appearing in the range of 270°C - 340°C is coming from single atoms H trapped in single vacancies, called Vac-H cluster. Another range of outgassing is 430°C - 440°C where the H is trapped in pairs of vacancies. The first range could fit with the peak observed in the Cu-OFE and the second range could fit with the first peak observed in the electroformed copper. For the peaks we detected at higher temperature no explanations could be found.

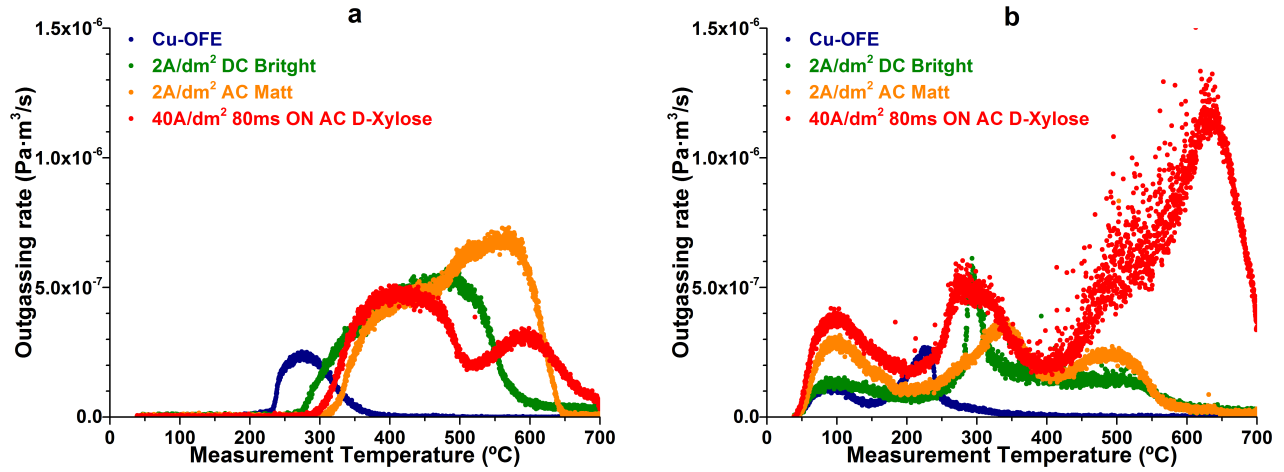


Figure 5.22. TDS results of outgassing of hydrogen (a) and water (b) for Cu-OFE, Bright 2 A dm^{-2} DC plated, Matt 2 A dm^{-2} AC plated and 70 A dm^{-2} 80 ms pulse ON AC plated

Different outgassing peaks are also found for water:

- Cu-OFE: Two peaks from 50°C to 150°C and 150°C to 250°C
- 2 A dm^{-2} DC Bright: Two peaks from 50°C to 200°C and 200°C to 350°C and a plateau from 350°C to 570°C .
- 2 A dm^{-2} AC Matt: Three peaks superposed from 50°C to 200°C , from 200°C to 400°C and 400°C to 570°C .

- 40 A dm⁻² AC D-Xylose: three peaks from 50 °C to 200 °C, from 200 °C to 400 °C and 400 °C to 700 °C.

The first peak that appears in all the samples comes from the water adsorbed at the surface as already explained. The second peak of water in the Cu-OFE sample (section 5.1.2) is coming from the oxidation of hydrogen when goes through the oxide layer. The second peak in the electroformed samples might also be coming from the oxidation of the hydrogen, as it is also appearing before the first peak of hydrogen, but it has not been studied. The third peaks observed in the AC samples and the plateau in the DC sample are completely unknown.

5.2.3 TDS results of high current density copper pulse plating

It has been tried to do a correlation between the outgassing of hydrogen detected with the TDS system and the transient curves from a copper electroplating in controlled conditions in the laboratory in a 10 L beaker. In a potential-time transient curve, for example the 60 A dm⁻² in Fig.5.23(a), the different behaviours of a plating are illustrated [49]. In this case we can observe:

- From 0 to 10 ms: Double layer loading. The ions go to the cathode and anode.
- From 10 ms to 40 ms: Faraday range. Only the copper (Cu^{+2}) is plated.
- From 40 ms to 70 ms: Diffusion limited range. Not all copper (Cu^{+2}) can be plated because hydrogen is starting to be produced.
- From 70 ms to 90 ms: Hydrogen plateau. No more copper is being plated.
- From 90 ms to 100 ms: Double layer discharge. The ions can move freely again.

In an AC plating the pulse and the current density can be tuned to avoid entering in the diffusion range and the hydrogen plateau. The objective is to remain only in the Faraday range because then the plating is performed in the best conditions.

Table 5.3. Concentration of H_2 in samples done in the beaker with the matt bath

Current density (A dm ⁻²)	Time pulse ON	
	20 ms	80 ms
40	65 at. ppm	100 at. ppm
70	100 at. ppm	73 at. ppm

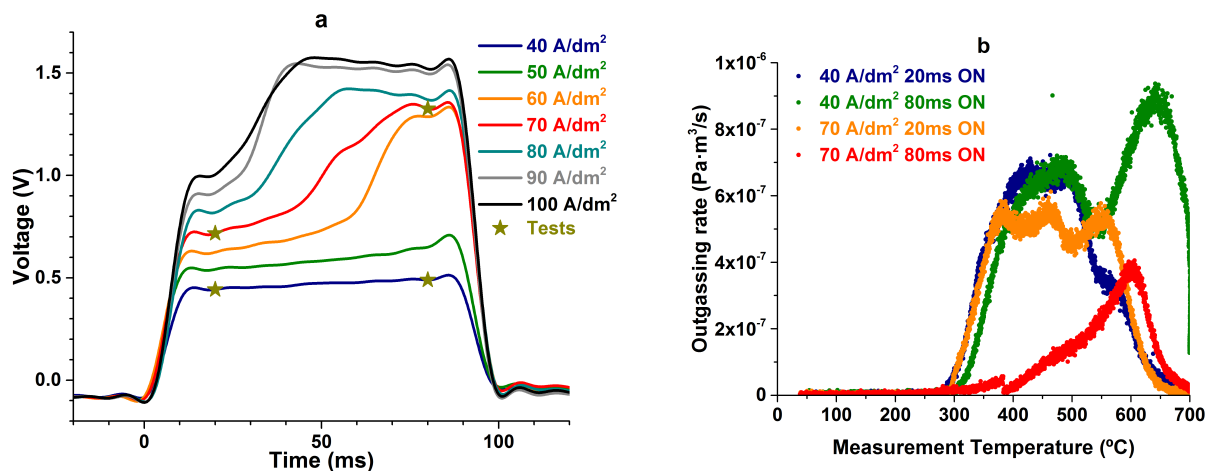


Figure 5.23. Transient curves for the matt bath (a) and TDS results of outgassing of hydrogen, $m/z = 2$, from the samples done in the beaker with the matt bath (b). The curve in b for the 70 A dm^{-2} 80 ms pulse ON was interrupted and restarted

To see how the hydrogen content is changed platings are done with different pulse conditions. Four different points have been chosen in the transient curves to do samples and test them in the TDS system. In the Fig.5.23(a) and Fig.5.24(a) the four points tested are shown.

For the matt bath 3 samples (40 A dm^{-2} 20 ms pulse ON, 40 A dm^{-2} 80 ms pulse ON and 70 A dm^{-2} 20 ms pulse ON) are entirely in the Faraday range (Fig.5.23(a)), but on the TDS results (Fig.5.23(b)) we see a different behaviour of the outgassing peak for the sample 40 A dm^{-2} 80 ms pulse ON. A second peak of hydrogen around 600°C is appearing. So probably at the 80 ms the pulse is already at the diffusion range and extra hydrogen is formed, the concentration increases (Tab.5.3). For the fourth sample done at the matt bath the pulse clearly reaches the hydrogen plateau. The analysis of this sample by TDS was stopped around 350°C due to a huge water outgassing. So the measurement was restarted and some information from the sample was lost, but it is still possible to see the second peak of hydrogen. Probably the fact that the pulse reaches the hydrogen plateau produces a very rough surface. Different samples were produced in the same conditions but always the same kind of problem was found.

Also for the D-Xylose bath 3 samples were plated with the pulse in Faraday range (40 A dm^{-2} 20 ms pulse ON, 40 A dm^{-2} 80 ms pulse ON and 70 A dm^{-2} 20 ms pulse ON). In this case also the TDS results (Fig.5.24(b)) show different behaviours of the hydrogen outgassing. For the samples 40 A dm^{-2} 80 ms pulse ON and 70 A dm^{-2} 20 ms pulse ON also the second peak of hydrogen is observed as seen for two samples done in the matt bath. Therefore, probably for this point the pulse reaches also the diffusion range. For the 70 A dm^{-2} 80 ms pulse ON sample,

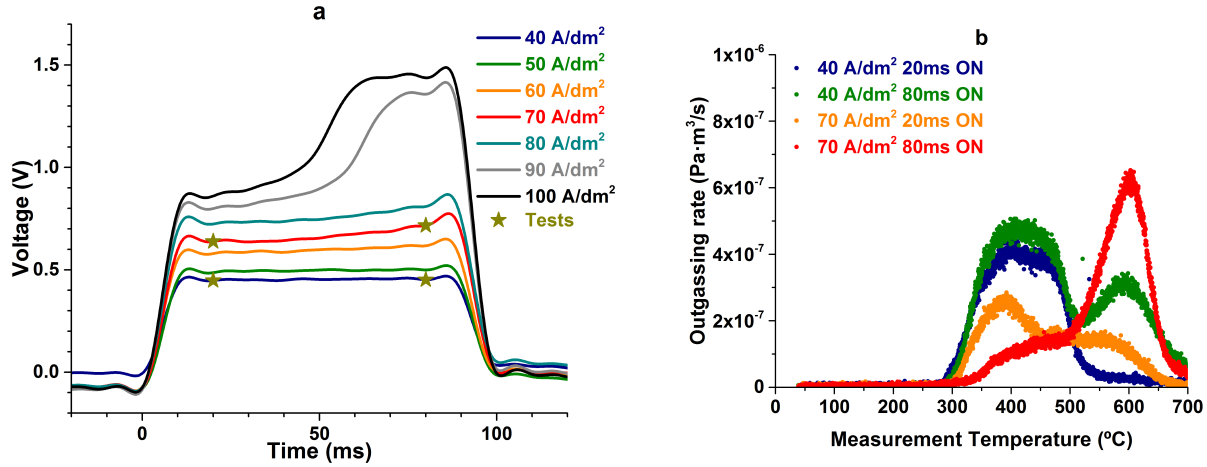


Figure 5.24. Transient curves for the D-Xylose bath (a) and TDS results of outgassing of hydrogen, $m/z = 2$, from the samples done in the beaker with the D-Xylose bath (b)

Table 5.4. Concentration of H_2 in samples done in the beaker with the D-Xylose bath

Current density (A dm ⁻²)	Time pulse ON	
	20 ms	80 ms
40	43 at. ppm	51 at. ppm
70	36 at. ppm	53 at. ppm

that reaches clearly the diffusion range, the second peak of hydrogen is clearly the dominant one. For these four samples the concentration of hydrogen does not change too much between them (Tab.5.4).

It can be concluded from this study that the type of pulse affects the temperature of the hydrogen degassing peak more than the total quantity of hydrogen.

By comparing the samples from the D-Xylose bath and the samples from the matt bath it can be seen that the quantity of hydrogen is much lower for the samples from the D-Xylose bath. So, the results match with the previous studies done with D-Xylose in the plating bath: [33] and [34]. The next step would be to introduce the D-Xylose in one of the industrial baths, to test it at lower current density and to see if this tendency can be kept.

For these sample also a microstucture study has been performed. In this study only the samples done with 40 A dm⁻² of current density have been analysed. Therefore only the effect of the pulse time and the bath type is analysed. In both types of bath a same tendency in terms of

grain growth is observed. The 20 ms pulse ON samples (Fig.5.25(a) and Fig.5.26(a)) present finer grains than the 80 ms pulse ON samples (Tab.5.5) (Fig.5.25(b) and Fig.5.26(b)). Comparing the two baths, the samples from the D-Xylose bath (Fig.5.26) present a more isotropic structure than the samples from matt bath (Fig.5.25) even though the columnar growth still present. The D-Xylose samples present also less voids than the matt samples.



Figure 5.25. Optical microscope images after etching the cross section of samples from the matt bath. 40 A dm⁻² 20 ms pulse ON (a) and 40 A dm⁻² 80 ms pulse ON (b)

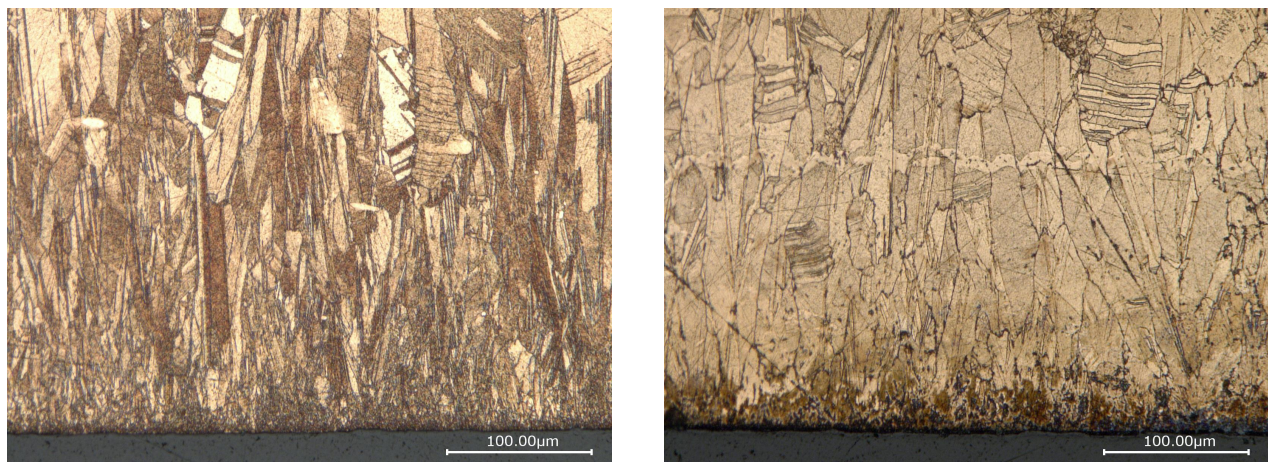


Figure 5.26. Optical microscope images after etching the cross section of samples from the D-Xylose bath. 40 A dm⁻² 20 ms pulse ON (a) and 40 A dm⁻² 80 ms pulse ON (b)

Table 5.5. Horizontal grain size from the matt and D-Xylose samples done with 40 A dm^{-2} of current density

Samples	20 ms pulse ON	80 ms pulse ON
Matt	$23 \mu\text{m}$	$46 \mu\text{m}$
D-Xylose	$20 \mu\text{m}$	$34 \mu\text{m}$

5.3 Diffusion coefficient and activation energy of hydrogen

Two methods have been used to calculate the diffusion coefficient and energy of diffusion of hydrogen in Cu-OFE and in SS-316LN, with the assumption that the outgassing of hydrogen in copper is limited by diffusion. The values of diffusion coefficient of hydrogen and energy of diffusion in copper and stainless steel can be found in literature:

- Cu-OFS: $E_d = 0.39$ eV, $D_0 = 8.34 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ [26]
- SS-316LN: $E_d = 0.50$ eV, $D_0 = 1.58 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ [50] [26]

The idea is to find a method that can be applied to obtain the diffusion coefficient and energy of diffusion for other elements and in other materials. Therefore, it is necessary to compare the values obtained from the two methods used with ones found in the literature.

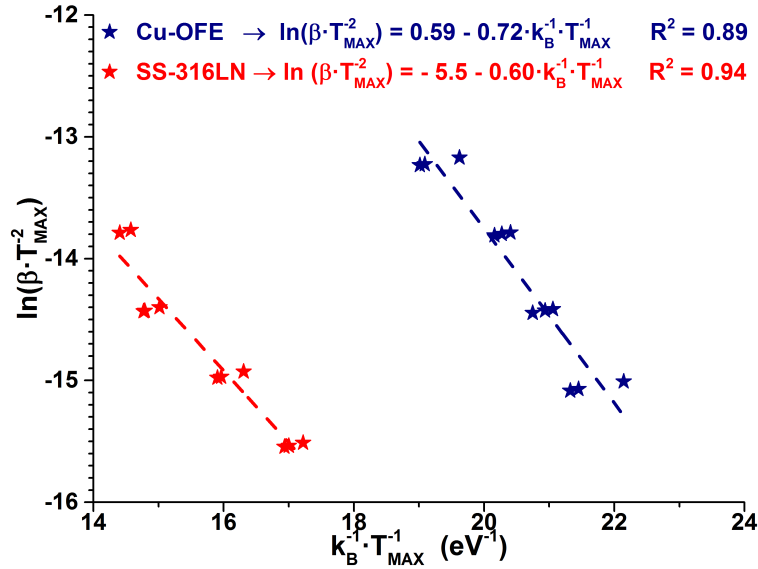


Figure 5.27. Linear regression to obtain the diffusion coefficient and energy of diffusion from TDS with different heating rates

The first method used exploits equation (2.10). Four different heating rates ($\beta = 5, 10, 20$ and 40 K min^{-1}) have been used. For each heating rate three samples have been tested. To be able to do the regression a plot of $\ln(\frac{\beta}{T_{MAX}^2})$ in the y axis and $\frac{1}{k_B T_{MAX}}$ in the x axis (Fig.5.27) allows to obtain the diffusion coefficient (D_0) and activation energy of diffusion (Tab.5.6 and Tab.5.7).

The second method used exploits equation (2.12) and the method described in the section 2.5.1. With this method it is possible to obtain the diffusion coefficient at a single temperature. For this reason tests at different temperatures have been performed. For the Cu-OFE the tested temperatures are: 200, 225, 250 and 300 °C (Fig.5.28(a)). For the SS-316LN the temperatures are: 350, 400 and 450.0 °C (Fig.5.29(a)). With the different values with an Arrhenius like plot (Fig.5.28(b) and Fig.5.29(b)) one can obtain the diffusion coefficient and the activation energy of diffusion (Tab.5.6 and Tab.5.7).

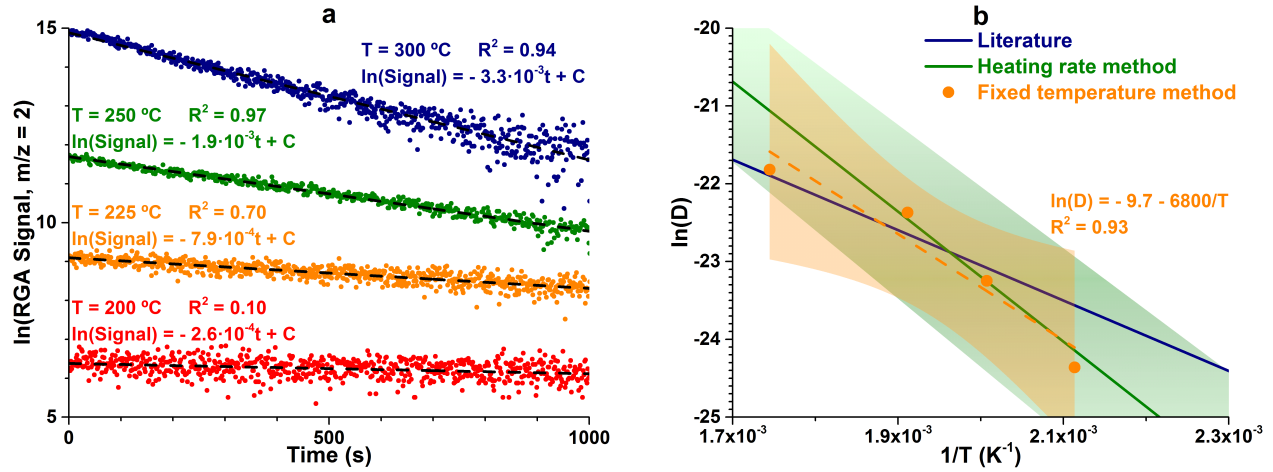


Figure 5.28. Linear regression to obtain the diffusion coefficient at different temperatures for Cu-OFE (a). Arrhenius plot comparing the different methods with the literature for Cu-OFE (b)

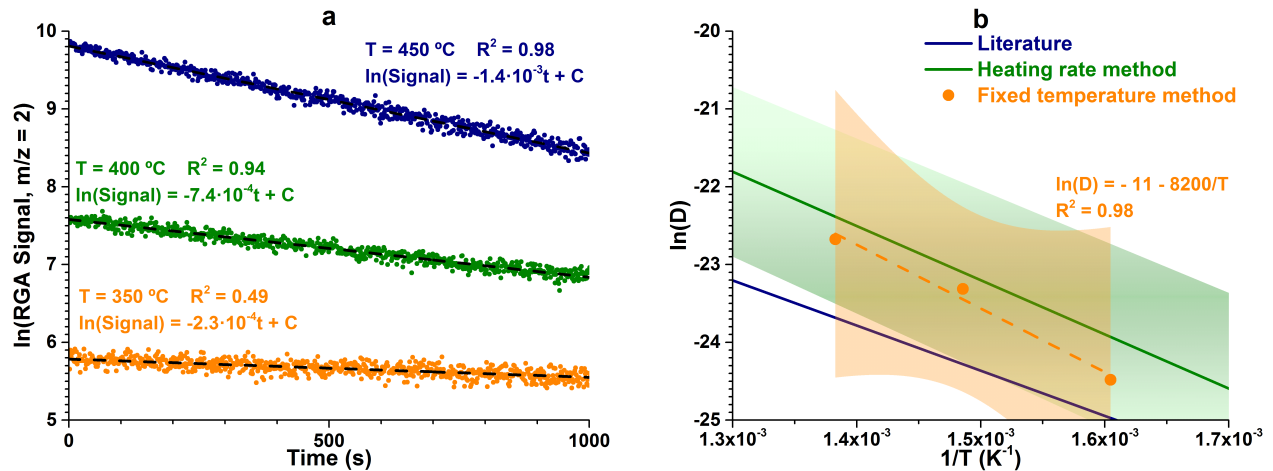


Figure 5.29. Linear regression to obtain the diffusion coefficient at different temperatures for SS-316LN (a). Arrhenius plot comparing the different methods with the literature for SS-316LN (b)

The values obtained with the TDS for the diffusion coefficient and energy of diffusion differ quite a lot from the literature. Between them, they are closer. Even though for the regions where the outgassing peak appears in the TDS, the values of the diffusion coefficient for a specific temperature from the different methods and the literature get close to each other as we can see in the Fig.5.28(b) for the Cu-OFE. In this case for the 2 methods between 160 °C and 315 °C the values can match with the literature values in a confidence interval of 95 %. In the case of the SS-316LN, in the Fig.5.29(b), the 2 methods are valid up to 440 °C in the confidence interval of 95 %.

Table 5.6. Diffusion coefficient and activation energy of diffusion for Cu-OFE

Source	E_d (eV)	D_0 (m ² s ⁻¹)
Literature	0.39	8.3×10^{-7}
Heating rate method	0.72 ± 0.08	$(3 \times 10^{-4}, 7 \times 10^{-3})$
Fixed temperature method	0.6 ± 0.1	$(5 \times 10^{-6}, 9 \times 10^{-4})$

Table 5.7. Diffusion coefficient and activation energy of diffusion for SS-316LN

Source	E_d (eV)	D_0 (m ² s ⁻¹)
Literature	0.50	1.6×10^{-7}
Heating rate method	0.59 ± 0.06	$(1 \times 10^{-6}, 7 \times 10^{-6})$
Fixed temperature method	0.71 ± 0.09	$(3 \times 10^{-6}, 6 \times 10^{-5})$

As conclusion it is possible to say that the diffusion coefficient and the energy of diffusion obtained are wrong, but they can be used to calculate the diffusion coefficient for a specific temperature in the range of temperatures where the outgassing peak appears. Out of this range the diffusion coefficients for a specific temperature differs too much from the ones from literature.

There are possible explanation for this differences between the values obtained with the TDS and the literature. The first one could be a non-linearity of RGA signal. This one is very unlikely because the RGA signal change fits with the pressure read at the gauge. The other explanation could come from the temperature calibration. The calibration used is the one presented at the equation (4.1). It is a linear calibration. A verification of the calibration factor has been done. If we assume that the temperature is wrongly calibrated then may be another calibration factor would bring D_0 and E_d values closer to the literature. By changing

the calibration factor for 0.8 and 1 instead of 0.94 it has been seen that only the D_0 is significantly changed. The E_d is not strongly affected. Therefore, if the temperature calibration is not correct the problem might be that the calibration is not linear.

6 TDS analysis of other materials

Apart from copper other materials used at CERN have been studied with the TDS system. These materials are part or will be part of the vacuum chambers and components inside the vacuum pipes of the LHC or other CERN accelerators and experiments. The aim of these studies is to identify problems that could come from the outgassing of these materials.

6.1 LHC Beamscreen

6.1.1 Motivation

At LHC the superconducting magnet cold bores are shielded by a beamscreen. The beamscreen has several functions in the case of the dipoles. The primary function is to intercept the synchrotron radiation and the image current generated by the proton beam at a temperature which is higher than the cold bores, about 20 K instead of 1.9 K. The second function is to enable cryopumping of H_2 by the cold bore without particle induced desorption. The inner surface of the beamscreen is covered with a high electrical conductivity copper layer to minimise the power dissipated by the beam image current and the impedance seen by the beam. [15]

An upgrade of the SPS magnets is in progress with the aim to reduce the electron cloud formed around the protons' beam. This electron cloud is formed by the secondary emitted electrons. At the SPS a thin film of amorphous carbon is sputtered on the walls of the vacuum pipes. The effect of applying this carbon coating is the reduction of the secondary electron yield (SEY) rate. The same technology is developed to be used now in some of the LHC magnets close to the interaction region (triplets) in the context of the HL-LHC project. In the case of the LHC this coating is applied on the beamscreen. [51]

While analysing the SEY of carbon coated prototypes of beamscreen, it has been observed a higher SEY than the one expected. Already when developing for the SPS it was discovered that the SEY of carbon increases with the content of H_2 in the sputtering gas. The H is incorporated in the coating in some way that it is not precisely known and also the mechanism

which increases the SEY is not clear. At present CERN does not have a technique to measure the content of H in carbon coatings. Different carbon thin films were tested by TDS to try to measure the H content of the coating. However, the H was starting to outgas at very high temperatures, without having the possibility to quantify (Fig.6.1). During the development of the carbon coatings for the beamscreen of LHC it was known in advance that the copper or the steel of the beamscreen might contain some H, due to the production technique. However, it was neither known how much and it was nor at which time it could come out and perturb the coating. This is the reason of the TDS measurements on the beamscreen.

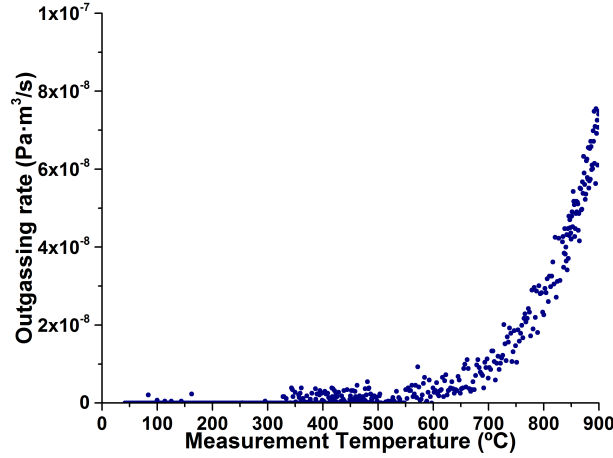


Figure 6.1. TDS results for the outgassing of hydrogen, $m/z = 2$, for C thin film coating by DMS over a quartz substrate

6.1.2 Results and discussion

Two different types of beamscreen were provided for this study. These two types of beamscreen are formed by:

- 1 mm SS + 75 μm Cu
- 0.6 mm SS + 75 μm Cu

A first TDS measurement is done in order to identify which are the main outgassed molecules. In Fig.6.2 it can be clearly seen that indeed the hydrogen is the main one. The H_2 presents an outgassing 10 times higher (340 at ppm) than the second and third most abundant species, which are H_2O and CO_2 . The other thing that can be seen from these results is that the hydrogen might come from the bulk of the stainless steel as the difference found between the two sample scales with the thickness of the steel part. Compared to SS-316LN and Cu-OFE the hydrogen content detected in the beamscreen is also much higher. For SS-316LN is around

50 at ppm and for Cu-OFE is around 10 at ppm.

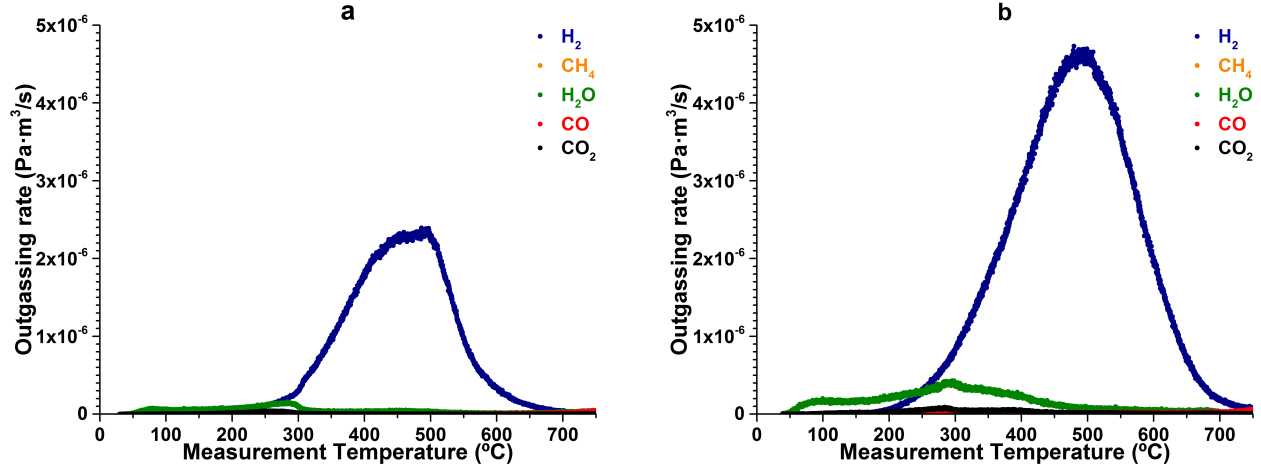


Figure 6.2. TDS results for the two types of the LHC beamscreen. 1 mm SS + 75 μ m *Cu* (a) and 0.6 mm SS + 75 μ m *Cu* (b)

To truly confirm if the hydrogen was coming from the SS, the *Cu* was removed mechanically with a file from one of the samples. The TDS results of this sample shows that the amount of hydrogen is the same with and without the copper. This confirms that the hydrogen is coming from the SS. (Fig. 6.3) Unexpectedly the sample without copper outgasses the hydrogen at lower temperatures. Two hypotheses were done in order to explain this shift of the peak.

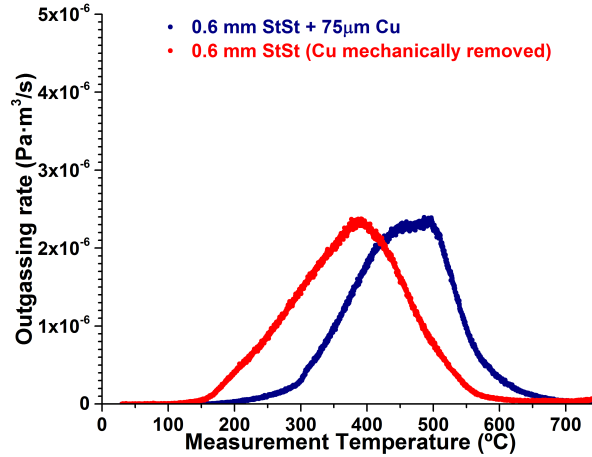


Figure 6.3. TDS results for the outgassing of hydrogen, $m/z = 2$, for two LHC beamscreen sample one of them with the Cu layer mechanically removed

- The oxide layer over the stainless steel retards the outgassing of the hydrogen acting as a barrier. The face, on which the *Cu* was removed, was exposed a very short time to air.

- The RGA is not detecting the bottom face in the same way is detecting the one facing it directly. Therefore, the hydrogen has to diffuse through the *Cu* before being detected. The samples with SS + *Cu* have been always placed with the Cu facing up. In the case of the one without the *Cu*, the SS was facing directly the RGA.

In order to verify or deny these hypotheses two tests are done. One by removing the oxide of the SS mechanically, in order to have the same type of surface of the sample with the *Cu* removed. And an other test by placing the sample with the *Cu* facing the heater instead of the RGA.

The results in the Fig.6.4(a) show that the hydrogen outgassing between the two sample is not shifted for the sample where the oxide has been removed. Therefore, the first hypothesis is denied. A similar result is also obtained for the second test Fig.6.4(b). The way that the sample is faced does not cause any significant difference in the results. So, also the second hypothesis is denied.

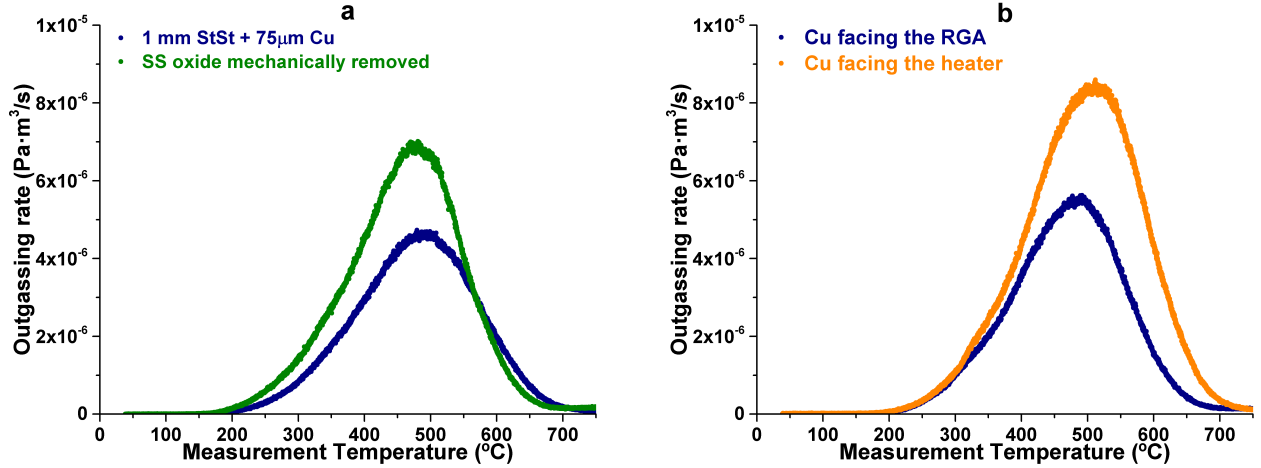


Figure 6.4. TDS results for the outgassing of hydrogen of the LHC beamscreen 1 mm SS + 75 μm *Cu*. Comparison of two samples: one with the SS normal oxidised and the other with the oxide mechanically removed (a). Comparison of two samples: one with the *Cu* facing the RGA and the other facing the heater (b)

No further tests were done to find an explanation of the shift of the peaks of the sample with the removed *Cu* (Fig.6.3). So, it is left for future studies. The main goal of this study was to see if during the coating the hydrogen could be outgassed and react with the carbon of the coating to produce hydrocarbons.

Now it is known that hydrogen is present. But it is important to see if this hydrogen is actually outgassed during the coating or not. The temperature reached by the beamscreen during coating is not known, what it is known is the temperature reached during the bake-out before the coating. So the idea is to see if it is possible to outgas the hydrogen from the beamscreen with the bake-out. If the hydrogen is completely outgassed during the bake-out then the hydrogen from the beamscreen would not be the problem causing the increase of the SEY.

The beamscreen is warmed during the bake out through a capillary tube welded at the top side where hot air or hot nitrogen can flow. The temperature at one end reaches 180 °C but at the other end the temperature is only of 100 °C. For this reason two bake-out cycles are done, one flowing the air in one direction and the second in the other direction. With this method the lowest temperature seen by the beamscreen is 130 °C in the middle point of the beamscreen length.

At the TPD system this bake-out cycle has been simulated with different samples. The idea is to keep the samples 24 h at a constant temperature at 130 °C and 180 °C. In the case of 130 °C the temperature is also kept for 48 h, to simulate the two consecutive cycles. After staying at these temperatures the samples are cooled down to room temperature and without extracting the sample from the main chamber of the TPD system the outgassing test is then performed. The results of the outgassing are then compared to a sample tested without any initial thermal treatment, like that it is possible to see if the concentration of hydrogen in the beamscreen has changed respect to the initial quantity.

The results, Tab.6.1, show that no reduction on the hydrogen outgassing occurs during the 24 h at 130 °C bake-out. A small outgassing reduction is observed when the sample is kept 48 h at 130 °C. For the bake-out simulation at 180 °C a bigger reduction of hydrogen happens. At the Fig.6.5 it can be seen how the evolution of the hydrogen content in the beamsecreen is before and after the bake-out cycles. As a conclusion of these study it can be said that the hydrogen is still present in a high amount. Therefore if the beamscreen reaches temperatures higher than 180 °C the hydrogen will outgas with the possibility of reacting with the sputtered *C*.

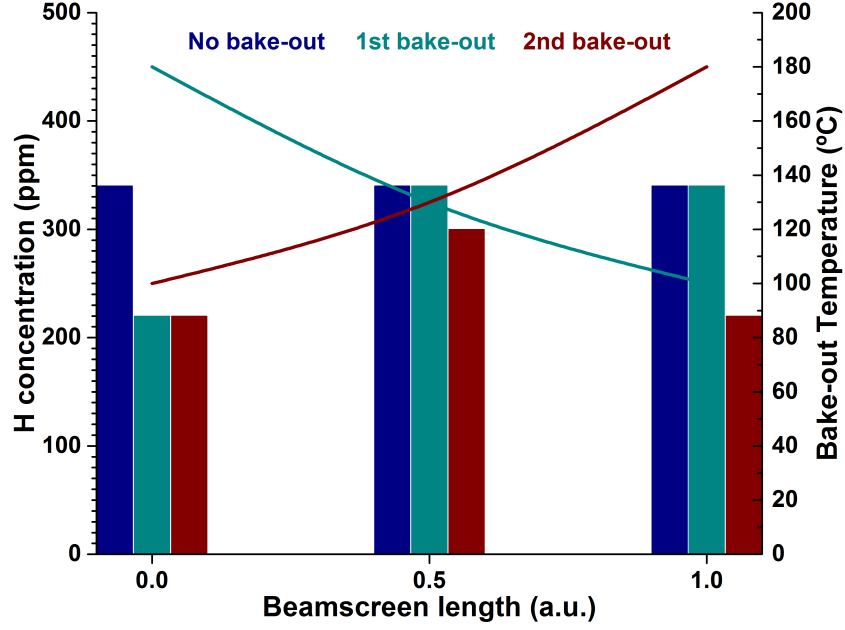


Figure 6.5. Hydrogen content evolution after each bake-out cycle

Table 6.1. Reduction of the total hydrogen outgassing, $m/z = 2$, of the bake-out samples respect to the not baked one

Bake-out	$[H]$ (at. ppm)	reduction (%)
No	340	-
24 h at 130 °C	340	0
48 h at 130 °C	300	12
24 h at 180 °C	220	35

6.2 MoGr Collimator

6.2.1 Motivation

New types of collimator are under study to be implemented in upgrade that will undergo the LHC collimation system for the HL-LHC. A program has been launched to develop novel materials with high shock resistance and high thermal conductivity. The materials investigated with more promising properties are Copper-Diamond and Molybdenum Carbide - Graphite (MoGr) composites. [52]

While doing vacuum acceptance tests for the MoGr (Fig.6.6) outgassing rates higher than the acceptance limits for the masses 14, 28 and 40 have been observed. The masses 14 and 28 are related with N_2 and the mass 40 with Ar . Therefore, these results brought the idea that air was still being outgassed from the MoGr sample even though the sample has been vacuum fired. These outgassing excesses could cause problems in the vacuum of the LHC if they are not reduced. In order to identify the origin of this excessive outgassing different test were performed with the TPD system.

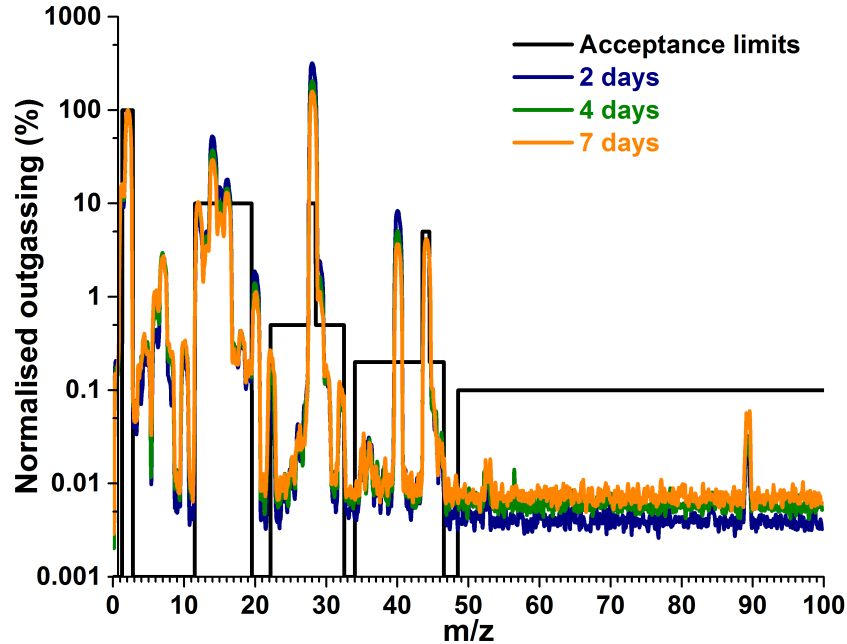


Figure 6.6. Outgassing acceptance test done in Building 113 at CERN, TB6: Normalised RGA SEM 1400V after bake out as a function of pumping time after bake out. Test done by Accettura, C. (CERN-EN-MME-EDS)

6.2.2 Results and discussion

All the tests on the MoGr samples as received, without vacuum firing, were done by analysing the whole mass spectra from $m/z = 1$ to $m/z = 100$. The heating rate used was the standard one, $\beta = 10 \text{ K min}^{-1}$.

A first series of tests were done on samples of 1 mm and 2 mm thickness (Fig.6.7). In these tests huge amounts of hydrocarbons were detected (a peak around 400°C for $m/z = 28, 41, 43$ and 57) but neither nitrogen nor argon were detected. The amount of outgassing in terms of hydrocarbons is higher for the 2 mm thick sample than for the 1 mm thick. This difference indicates that these hydrocarbons might come from the bulk. The hydrocarbons were not expected because the samples were treated clean and the fabrication process of the material was done under vacuum. The process that followed the samples was tracked and finally the problem was found. The material supplier confirmed a problem with a vacuum pump during the sintering process. The oil of the pump was the source of the hydrocarbons detected in the TPD system.

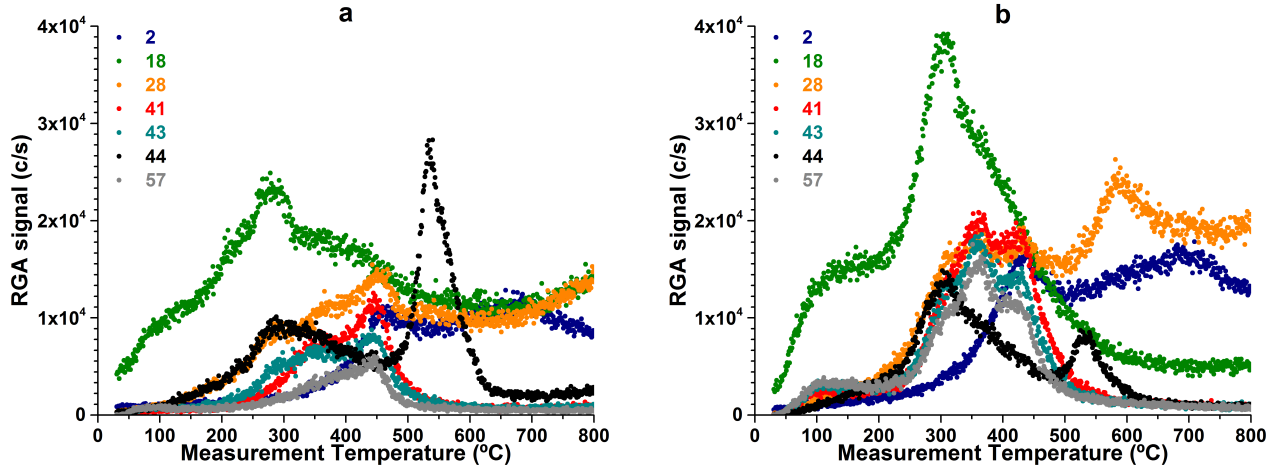


Figure 6.7. TDS results for the outgassing of hydrogen of MoGr samples for $m/z = 2, 18, 28, 41, 43, 44$ and 57 . 1 mm thick sample (a) and 2 mm thick sample (b)

The samples used for doing the outgassing acceptance test were vacuum fired 2 h at 950°C and exposed to air. It was thought that maybe this air exposure was the responsible of the detection of N_2 and Ar . For this reason a 2 mm thick sample after a TDS test was exposed to air for 1 week and then tested (Fig.6.8(a)). For this sample again N_2 and Ar were not detected. A proper vacuum fired sample was also tested in the TDS obtaining almost the same results as the sample that was exposed 1 week at air (Fig.6.8(b)). At least it was possible to see that

in both samples the hydrocarbons detected before were removed by a vacuum firing.

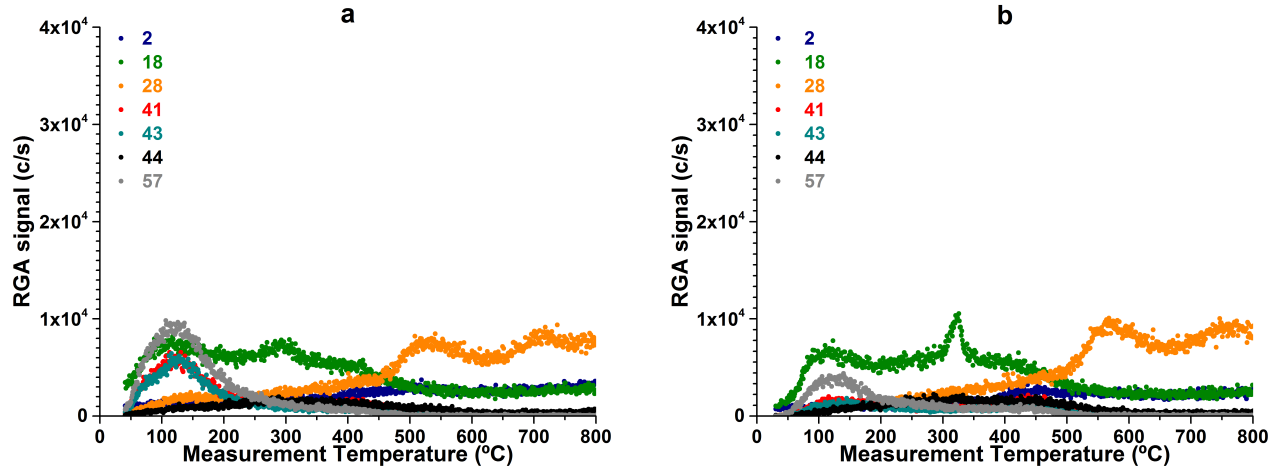


Figure 6.8. TDS results for the outgassing of hydrogen of MoGr sample for $m/z = 2, 18, 28, 41, 43, 44$ and 57 . Sample exposed 1 week at air after a first TDS measurement (a) and Vacuum fired sample 2 h at $950\text{ }^{\circ}\text{C}$ (b)

At the same time of this study the structure of the MoGr was being studied by the microscopy section of CERN (EN-MME-MM).

Some images were taken of a cross section of the material by a scanning electron microscope (Fig.6.9). In these images big voids can be seen close to the surface. The presence of free air in these voids could explain why N_2 and Ar were not detected with the TPD system. If there are no chemical bonds between the molecules and the material, there is no activation energy for the molecules to move freely. In a TDS this energy is reflected by the appearance of an outgassing peak at a specific temperature. This kind of peaks appear because the outgassing often depends exponentially of the temperature. In the other hand, the mobility of free molecules depends on the square root of the temperature. This dependency comes from the relation between the velocity of the molecules (mobility) and the kinetic energy (temperature). Therefore, for free molecules there is not a specific temperature where the outgassing increases drastically forming the peaks observed for chemically bond molecules.

To conclude this study on the MoGr a last outgassing test was performed in the TPD system. The sample analysed was a MoGr sample 2 mm thick that has been vacuum fired 2 h at $950\text{ }^{\circ}\text{C}$ and it was treated with CO_2 blasting. The CO_2 blasting it is used on the MoGr because it has been seen that the adhesion of coatings done by sputtering increases with respect to the

samples that have not suffered this process. With the TDS test (Fig.6.10) it has been seen that the CO_2 blasting increases a lot the outgassing in all the different gasses but mainly for the CO and the CO_2 .

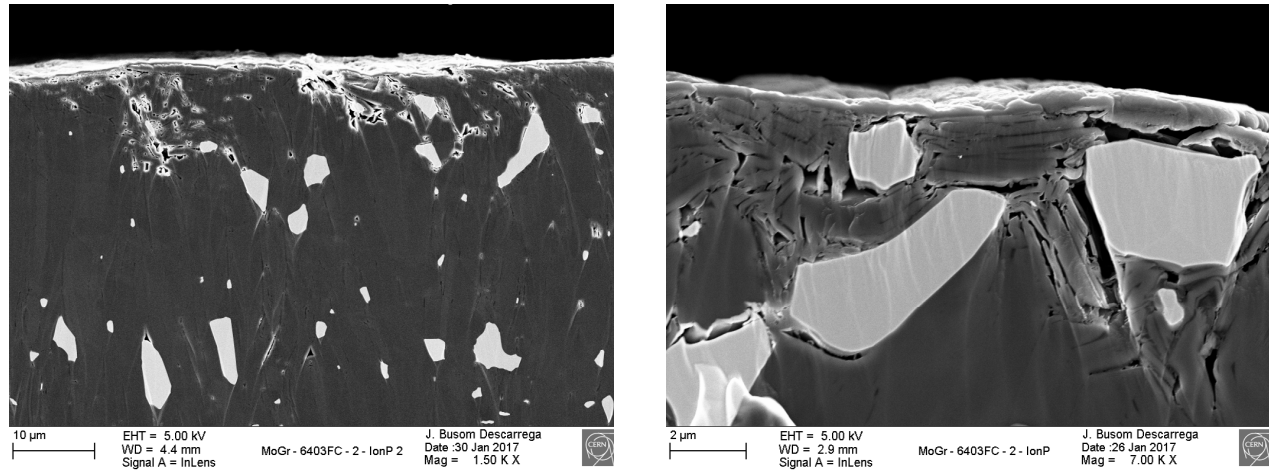


Figure 6.9. Images from scanning electron microscope. Magnification 1500 (a) and magnification 7000 (b). Images taken by Busom Descarrega, J. (CERN-EN-MME-MM)

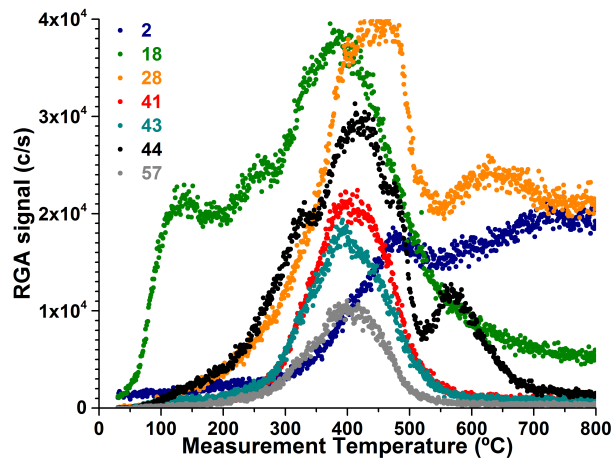


Figure 6.10. TDS results for the outgassing of hydrogen of vacuum fired 2 h at 950 °C + CO_2 blasted MoGr sample for $m/z = 2, 18, 28, 41, 43, 44$ and 57

6.3 Glidcop

6.3.1 Motivation

In the development of new collimator systems for the LHC, one of the materials under study is Glidcop. Glidcop is a registered trademark from Höganäs AB. [53]. It is a material from the family of copper-based metal matrix composites mixed with aluminium oxide particles.

Glidcop used in the collimator system undergoes a brazing cycle. To perform a brazing on a Glidcop a series of surface treatments are done. First of all an electrolytic degreasing is done to the Glidcop surface. Then 20 μm of copper are electroplated in a cyanide bath and finally 10 μm of nickel are electroplated over the plated copper. During the brazing process, bubbles have appeared between the *Ni* and the *Cu* layer (Fig.6.11).

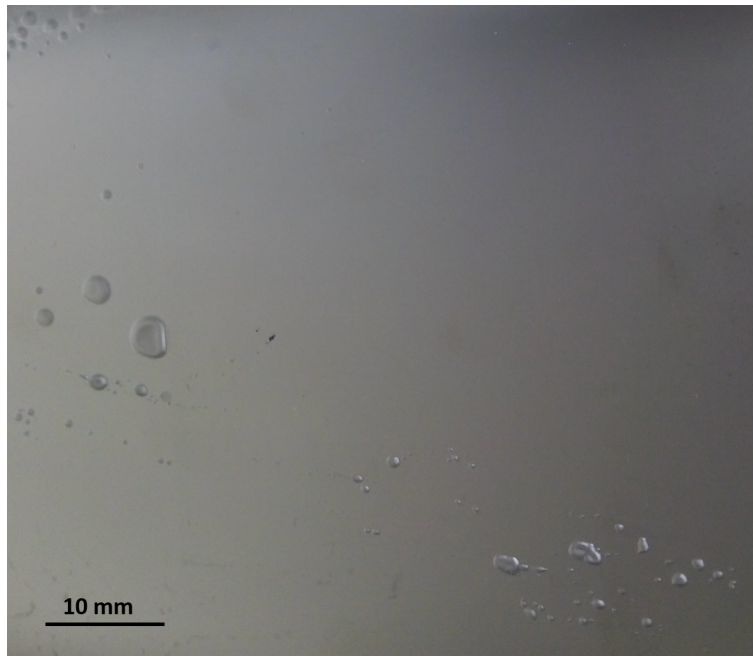


Figure 6.11. Bubbles on the coated Glidcop after brazing

To search for the origin of these bubbles a series of test on the TPD system have been proposed:

- 1 mm Glidcop sample. To know the effect of the bulk material.
- 1 mm Cu-OFE + Degreasing + Passivation. It is used as a reference sample.
- 1 mm Cu-OFE + Electrolytic degreasing + Passivation. To see the effect of the electrolytic degreasing

- 1 mm Cu-OFE + 20 μm cyanide *Cu* plating. To see the effect of the cyanide *Cu* plating.
- 1 mm Cu-OFE + 20 μm cyanide *Cu* plating + 10 μm *Ni* plating. To see how all the surface treatments work together.

The idea is to compare the different TDS results to identify if the bubbles are coming from the outgassing of the Glidcop, one of the surface treatments or a combination of some of them.

6.3.2 Results and discussion

The results of these series of experiments are shown in the Fig.6.12 and in the Tab.6.2. The first observation done on the Glidcop sample is that the hydrogen outgassing peak appears in a higher temperature (400 °C) than in the Cu-OFE (300 °C). There is also an increase of the outgassing of hydrogen and water. From the test on electrolytic degreasing sample no changes are observed respect to the reference sample. Therefore, the contribution of this process in the appearance of bubbles could be discarded, at least on a Cu-OFE. It will be interesting to analyse a Glidcop sample after this process.

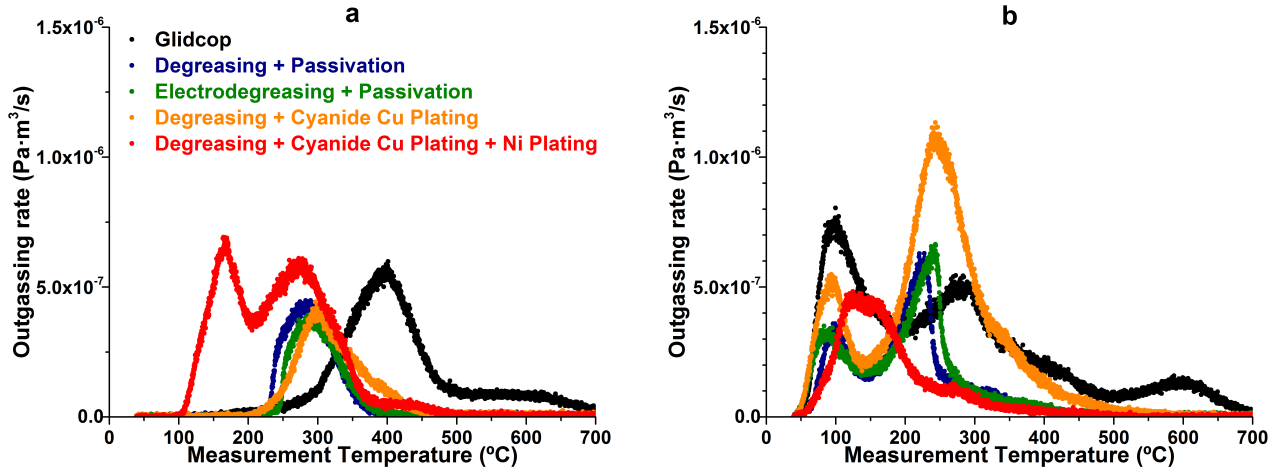


Figure 6.12. TDS results for the outgassing of Glidcop and the surface treatments done for the brazing on a Cu-OFE. Hydrogen, $m/z = 2$, outgassing (a) and water, $m/z = 18$, outgassing (b)

The coatings show more interesting results. The cyanide *Cu* plating itself has a water concentration more 60 at ppm higher than the Cu-OFE. This amount of water is coming mostly from the 2nd peak of water, see orange line in the Fig.6.12(b). This peak as explained before is related with the hydrogen from the bulk after its oxidation in the surface. It is important to remark that this 2nd peak of water detected in Cu-OFE + Cyanide *Cu* plating sample

is not detected in the Cu-OFE + Cyanide *Cu* plating + *Ni* plating sample (red line in the Fig.6.12(b)). It looks like the water is trapped in under the *Ni* plating. If we look at the Fig.6.12(a), it can be seen how the hydrogen from the *Ni* plating and the Cu-OFE is diffusing easily through the *Ni* but the water does not. Therefore, the bubbles observed on the Glidcop could come from water trapped between the nickel and the copper.

After this study a solution to avoid the formation of bubbles has been proposed. As this 2nd peak of water is coming from the hydrogen trapped in the copper, the Glidcop, after the cyanide *Cu* plating, should be thermal treated in vacuum to remove all the hydrogen from the bulk. After it the *Ni* plating can be done. If all the hydrogen is removed, then this 2nd peak of water will not be able to form when the brazing is done. No water will be formed between the *Cu* and the *Ni* forming the bubbles. To verify this hypothesis a similar study using Glidcop as base material should be done together with tests with the real pieces.

Table 6.2. Atomic concentration of hydrogen and water and the increase respect to the Cu-OFE used as reference for the Glidcop and the surface treatments done for the brazing. * In these cases the outgassing coming from the Cu-OFE has been subtracted and then normalised with the thickness of the coating.

Concentration (at. ppm)	H_2	H_2O	$H_2 / H_{2(Cu-OFE)}$	$H_2O / H_{2O(Cu-OFE)}$
Glidcop	15	31	2.2	2.6
Cu-OFE + Degreasing + Passivation	6.9	12	1.0	1.0
Cu-OFE + Electrodegreasing + Passivation	6.5	15	0.94	1.3
Cu-OFE + Cyanide <i>Cu</i> plating	7.4	28	1.1	2.3
Cyanide <i>Cu</i> plating *	18	770	2.6	64
Cu-OFE + Cyanide <i>Cu</i> plating + <i>Ni</i> plating	21	11	3.0	0.92
Ni plating *	590	520	86	43

7 Conclusions and outlooks

The whole outgassing study has been quite broad in terms of analysed materials and different methods used to complement the TDS tests. Some general conclusions can be extracted and also some outlooks can be proposed.

For the TDS system some important remarks should be done. To have reproducible measurements the most important thing is to place always the sample at the same distance from the RGA fingers to keep a good thermal contact between the heater and the sample. The other important point is to realise always the measurements with the same heating rates, if not the position and the intensity of the peaks might change not allowing the comparison of the measurements. In terms of control temperature as an outlook it would be good to redo a calibration of the sample temperature in function of the temperature of the heater, where the thermocouple is attached. For all the measurements done in this study the calibration used has been the one given by the system manufacturer. An attempt has been performed with pure iron to try to observe the ferrite-austenite transition in terms of hydrogen outgassing or the Curie temperature where there is a change of the emissivity, but in both cases nothing was observed.

For the Cu-OFE, the 2nd peak of water, $m/z = 18$, found in the TDS measurements is coming from the hydrogen from the bulk that reacts with the oxide layer. Also the reduction of the oxide layer favoured by the diffusion of the hydrogen from the bulk must be taken into account when coating on copper substrates is performed. This reduction can already happen at 150 °C depending on the quantity of hydrogen dissolved in the bulk. More studies should be done to better understand the behaviour of the oxide layer for different hydrogen contents in the bulk. It has been tried to load a copper sample with hydrogen by putting it in an oven at 1000 °C at 10 mbar of H_2 , but no hydrogen was introduced, since the sample remained in equilibrium and no hydrogen outgassing was seen in the TDS system. Therefore, other methods to load a copper sample with hydrogen should be searched.

The different surface treatments applied to Cu-OFE (passivation, electropolishing and SUBU) showed how the outgassing is not changed in terms of hydrogen, as it is coming from the bulk.

Only for the water it has been observed 10 times stronger outgassing for the SUBU treated samples. This water is coming from the dissociation of the acids that form the SUBU bath if they are not removed properly from the surface. The pinholes present at the surface and the fact that the surfaces are only rinsed with water after the treatment allow these molecules to get retained at the surface. So, what it is proposed for the pieces in which a SUBU is applied, to finish the treatment with rinsing in ultrasonic agitation.

The possibility to establish a relation between the electroforming parameters, the outgassing and the microstructure on the electroformed copper has opened a possibility to optimise the process. The same analysis method can be applied to *Ni* plating. But also in the electroformed copper more investigation can be done to understand the origin of the different peaks of water and hydrogen observed in the TDS measurements.

The values obtained through the TDS system for the diffusion coefficient and the activation energy of diffusion are different from the ones that can be found in the literature. The values only can be considered valid for the temperature where the outgassing peak appears. Different explanations can be found in literature of the trapping of hydrogen in copper but none of them can explain properly the values obtained from the TDS.

In general only the water and hydrogen, $m/z = 18$ and $m/z = 2$ are the gasses that have been studied for the TDS measurements. Other gases such as carbon dioxide or carbon monoxide that are also outgassed should be analysed more carefully. Also it can be interesting to try to find a relation, if it exists, with the microstructure of the different materials with the outgassing, in some cases it has already been done, but it has not been analysed deeply.

References

- [1] L. Lain, *Production of ultra-high-vacuum chambers with integrated getter thin-film coatings by electroforming*. Geneva, Switzerland: CERN - Université de Franch-Comté, June 2016.
- [2] S. L. M. Schroeder and M. Gottfried, “Temperature-Programmed Desorption (TPD) thermal Desorption Spectroscopy (TDS),” *Advanced Physical Chemistry Laboratory, FU Berlin*, vol. V18, 2002.
- [3] P. Chiggiato, “Outgassing,” in *CERN Accelerator School 2006*, (Platja d’Aro, Spain), May 2006.
- [4] N. Jecklin, S. Calatroni, B. Delaup, L. Ferreira, I. Mondino, A. Sublet, M. Therasse, and W. Venturini Desolaro, “Niobium coatings for the HIE-ISOLDE QWR superconducting accelerating cavities,” in *Cavity preparation and production*, (Paris, France), CERN, September 2013.
- [5] P. Chiggiato and P. Costa Pinto, “Ti-Zr-V non-evaporable getter films: from development to large scale production for the Large Hadron Collider,” *Thin Solid Films*, vol. 2, no. 512, pp. 382–388, 2006.
- [6] C. Benvenuti, P. Chiggiato, P. Costa Pinto, A. Escudeiro Santana, T. Hedley, A. Mongelluzzo, V. Ruzinov, and I. Wevers, “Vacuum properties of tiZrV non-evaporable getter films,” *Vacuum*, vol. 1-2, no. 60, pp. 57–65, 2001.
- [7] Hiden-Analytical, “Mass spectrometers for catalysis & thermal analysis applications,” Tech. Rep. Technical data sheet 184/3, Hiden Analytical Ltd., 420 Europa Boulevard Warrington WA5 7UN England, 2016.
- [8] Hiden-Analytical, “Mass spectrometers for thin films, plasma & surface engineering,” Tech. Rep. Technical data sheet 184/3, Hiden Analytical Ltd., 420 Europa Boulevard Warrington WA5 7UN England, 2016.
- [9] “About CERN,” Jan 2012. <http://cds.cern.ch/record/1997225>.

- [10] S. Baird, *Accelerators for Pedestrians*. Geneva, Switzerland: CERN - A&B Department, February 2007.
- [11] R. Steerenberg, *Accelerators Explained for everybody - without Maths*. Geneva, Switzerland: CERN, April 2016.
- [12] C. Benvenuti, “Pumping device by non-vaporisable getter and method for using this getter,” Dec. 24 1997. WO Patent App. PCT/EP1997/003,180.
- [13] “A vacuum as empty as interstellar space,” Aug 2012. <http://cds.cern.ch/record/1997379>.
- [14] S. Sgobba, “Materials for high vacuum technology, an overview,” tech. rep., CERN, 2006.
- [15] B. Angerth, F. Bertinelli, J. Brunet, R. Calder, F. Caspers, O. Gröbner, *et al.*, “The lhc beam screen-specification and design,” *Proc. of EPAC94*, p. 208, 1994.
- [16] S. Calatroni, A. Miyazaki, G. Rosaz, A. Sublet, W. Venturini Delsolaro, R. Vaglio, and V. Palmieri, “Performance analysis of superconducting rf cavities for the cern rare isotope accelerator,” *Phys. Rev. Accel. Beams*, vol. 19, p. 092002, Sep 2016.
- [17] A. Sublet, L. Alberty, K. Artoos, S. Calatroni, O. Capatina, M. Fraser, N. Jecklin, Y. Kadi, P. Maesen, G. Rosaz, K. Schirm, M. Taborelli, M. Therasse, W. Venturini Delsolaro, and P. Zhang, “Status of HIE-ISOLDE SC Linac Upgrade,” 2015.
- [18] M. Malabaila, “Cleaning procedure for copper parts,” Tech. Rep. EDMS-1084640, CERN, Geneva, Switzerland, 2014.
- [19] M. Malabaila, “Procdure pour le polissage chimique SUBU des cavits HIE-ISOLDE QS en cuivre,” Tech. Rep. EDMS-1440237, CERN, Geneva, Switzerland, 2014.
- [20] F. Fesquet, “Procdure d’électropolissage des tubes cut-off et des brides des cavits LHC (prototype),” Tech. Rep. EDMS-1801304, CERN, Geneva, Switzerland, 2017.
- [21] P. Redhead, “Thermal desorption of gases,” *Vacuum*, vol. 12, no. 4, pp. 203 – 211, 1962.
- [22] D. A. King, “Thermal desorption from metal surfaces: A review,” *Surface Science*, vol. 47, no. 1, pp. 384 – 402, 1975.
- [23] J. Falconer and R. Madix, “Flash desorption activation energies: DCOOH decomposition and CO desorption from Ni (110),” *Surface Science*, vol. 48, no. 2, pp. 393 – 405, 1975.
- [24] A. de Jong and J. Niemantsverdriet, “Thermal desorption analysis: Comparative test of ten commonly applied procedures,” *Surface Science*, vol. 233, no. 3, pp. 355 – 365, 1990.

- [25] W. Ranke, “Thermal analysis-TDS,” in *Modern methods in heterogeneous catalysis research: Theory and experiment*, 2002.
- [26] P. Chiggiato, “Outgassing and its reduction,” in *CNRS-Orsay 09-2009*, (Orsay, France), Septemeber 2009.
- [27] D. Rosenthal, “TDS,” in *Modern methods in heterogeneous catalysis research*, 2011.
- [28] C. Alcock, V. P. Itkin, and M. K. Horrigan, “Vapor pressure of the metallic elements,” *Canadian Metallurgical Quarterly*, vol. 23, p. 309, 1984.
- [29] A. Vidal, “Technical specification supply of special austenitic grade stainless steel strip and forged billets,” Tech. Rep. EDMS-1572427, CERN, 2016.
- [30] Pfeiffer-Vacuum, “Introduction to vacuum technology. Conductance,” 2016. <https://www.pfeiffer-vacuum.com>.
- [31] National Institute of Standards and Technology, “Thermophysical properties of nitrogen,” 2016. <https://www.nist.gov/>.
- [32] Hiden-Analytical, “Relative sensitivity,” Tech. Rep. Technical Informtation TI-20013, Hiden Analytical Ltd., 420 Europa Boulevard Warrington WA5 7UN England, 2016.
- [33] G. Malone, W. Hudson, B. Babcock, and R. Edwards, “Improved electroformed structural copper and copper alloys,” 1998.
- [34] J. W. Dini and D. D. Snyder, *Electrodeposition of Copper*, pp. 33–78. John Wiley & Sons, Inc., 2010.
- [35] M. Taborrelli, “Cleaning and surface properties,” 2007.
- [36] D. Briggs, “Handbook of X-ray Photoelectron Spectroscopy,” *Surface and Interface Analysis*, vol. 3, no. 4, 1981.
- [37] S. Chawla, B. Rickett, N. Sankarraman, and J. Payer, “An X-ray photo-electron spectroscopic investigation of the air-formed film on copper,” *Corrosion Science*, vol. 33, no. 10, pp. 1617–1631, 1992.
- [38] S. Poulston, P. M. Parlett, P. Stone, and M. Bowker, “Surface Oxidation and Reduction of CuO and Cu₂O Studied Using XPS and XAES,” *Surface and Interface Analysis*, vol. 24, no. 12, pp. 811–820, 1996.
- [39] N. McIntyre and M. Cook, “X-ray photoelectron studies on some oxides and hydroxides of cobalt, nickel, and copper,” *Analytical chemistry*, vol. 47, no. 13, pp. 2208–2213, 1975.

- [40] S. Lee, N. Mettlach, N. Nguyen, Y. Sun, and J. White, “Copper oxide reduction through vacuum annealing,” *Applied Surface Science*, vol. 206, no. 14, pp. 102 – 109, 2003.
- [41] M. Bagge-Hansen, R. A. Outlaw, K. Seo, C. E. Reece, J. Spradlin, and D. M. Manos, “Thermal-vacuum stability of the surface oxide complex on cu,” *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 29, no. 5, p. 053001, 2011.
- [42] P. D. Kirsch and J. G. Ekerdt, “Chemical and thermal reduction of thin films of copper (ii) oxide and copper (i) oxide,” *Journal of Applied Physics*, vol. 90, no. 8, pp. 4256–4264, 2001.
- [43] University of Cambridge, “The interactive Ellingham diagram,” 2015. https://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/interactive.php.
- [44] W. R. Wampler, T. Schober, and B. Lengeler, “Precipitation and trapping of hydrogen in copper,” *Philosophical Magazine*, vol. 34, no. 1, pp. 129–141, 1976.
- [45] S. Nakahara and Y. Okinaka, “The hydrogen effect in copper,” *Materials Science and Engineering: A*, vol. 101, pp. 227 – 230, 1988.
- [46] J. E. Graebner and Y. Okinaka, “Molecular hydrogen in electroless copper deposits,” *Journal of Applied Physics*, vol. 60, no. 1, pp. 36–39, 1986.
- [47] Y. Fukai, “Formation of superabundant vacancies in mh alloys and some of its consequences: a review,” *Journal of Alloys and Compounds*, vol. 356, pp. 263 – 269, 2003. Proceedings of the Eighth International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications (MH2002).
- [48] Y. Fukai, M. Mizutani, S. Yokota, M. Kanazawa, Y. Miura, and T. Watanabe, “Superabundant vacancyhydrogen clusters in electrodeposited ni and cu,” *Journal of Alloys and Compounds*, vol. 356, pp. 270 – 273, 2003. Proceedings of the Eighth International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications (MH2002).
- [49] F. Lallemand, L. Ricq, E. Deschaseaux, L. De Vettor, and P. Berçot, “Electrodeposition of cobalt-iron alloys in pulsed current from electrolytes containing organic additives,” *Surface and Coatings Technology*, vol. 197, no. 1, pp. 10–17, 2005.
- [50] E. Herms, J. Olive, and M. Puiggali, “Hydrogen embrittlement of 316l type stainless steel,” *Materials Science and Engineering: A*, vol. 272, no. 2, pp. 279 – 283, 1999.
- [51] S. Pandolfi, “A new type of coating to chase the clouds away,” *CERN Bulletin*, vol. 10, no. 9, pp. 1–2, 2016.

- [52] A. Bertarelli, O. Sacristan De Frutos, L. Gentini, F. Carra, A. Dallochio, E. Quaranta, M. Guinchard, S. Redaelli, A. Rossi, M. Garlasche, *et al.*, “Novel materials for collimators at LHC and its upgrades,” tech. rep., CERN, 2014.
- [53] “Höganäs AB. GLIDCOP.” <https://www.hoganas.com/en/business-areas/glidcop/>. Accessed: 14-07-2017.