

UNIVERSITY OF HELSINKI

BEHAVIOR OF METAL SURFACES EXPOSED TO HIGH-FLUENCE HYDROGEN ION IRRADIATION IN VACUUM BREAKDOWN CONDITIONS

CATARINA FILIPA DA PALMA SERAFIM

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Behavior of Metal Surfaces Exposed to High-Fluence Hydrogen Ion Irradiation in Vacuum Breakdown Conditions

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DOCTORAL DISSERTATION

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This doctoral thesis is dedicated to Desidério, Assunção, and Rita.

Abstract

Radio Frequency Quadrupoles (RFQs) operating in linear accelerators often face significant challenges in terms of surface degradation. Concerns are focused upon vacuum arcs or vacuum breakdowns, phenomena triggered by the exposure of the surfaces to high accelerating fields. Additionally, surface degradation in the form of blistering, caused by beam losses under hydrogen ion beam operation, exposes also a concern, not only because it can affect accelerator operation by itself, but because it has not yet been clarified if the increase of roughness due to blisters could induce an increase of breakdown rate.

The work developed in this thesis, aims to address these phenomena by exploring what are the implications in terms of breakdown resistance when a material went through hydrogen ions irradiation. All the tests were sequentially done in different metals, in order to assess better alternative material candidates for future RFQ manufacturing, guaranteeing higher efficiency and durability. In this sense, seven materials were selected for the experiments: pure oxygen free copper, copper chromium zirconium, copper beryllium, stainless steel, titanium alloy, niobium and tantalum. Materials were selected based either on their higher mechanical strength compared to copper, or on their higher hydrogen diffusivity, in both cases aiming at reducing the surface blistering phenomenon. Irradiation was performed using low energy H^- beam, while a DC pulsed high voltage experimental system was used to study the high-voltage conditioning process and electrical breakdown statistics. Metallurgical properties of the materials were investigated using advanced microscopic techniques to observe and characterize the different surfaces and to compare results before and after irradiation and breakdown testing.

The author has identified the materials with the higher electric field handling capabilities and robustness to low-energy irradiation. Also, additional studies were specifically conducted in irradiated copper samples, where blistering growth has been identified to be dependent on crystal orientations. Furthermore, and contrarily to what it was anticipated, it has been concluded that blistering caused by irradiation have no detrimental effects in conditioning procedures. However, carbon contamination due to hydrocarbon cracking during the irradiation process, has been identified as a main concern for accelerating structures, with results showing a direct consequence on lower electric field performance with the presence

of carbon.

Taking in consideration the latest finding, studies involving oxygen plasma treatment, in order to remove carbon from contaminated surfaces, were conducted in CuBe₂, Cu-OFE and SS316LN. Treated materials were tested with high pulsing voltages and results compared with non-irradiated electrodes and irradiated without treatment. The study has identified plasma treatment, as a successful method to remove carbon from metal surfaces, allowing irradiated materials to achieve performances comparable with the electric field strength of pristine surfaces.

Tiivistelmä

Lineaarikiihdyttimissä radiotaajuuskvadrupolit (RFQ) kohtaavat usein merkittäviä haasteita pintojen heikkenemisen suhteen. Suurimmat huolenaiheet liittyvät tyhjiö- kaaripurkauksiin tai tyhjiön sähköisiin läpilyönteihin, jotka syntyvät pintojen altistuessa voimakkaalle kiihdytys-sähkökentille. Lisäksi vedyn ionisuihkun käytön aiheuttamat säteenmenetykset voivat johtaa pintavaurioihin rakkulam muodostumana, mikä herättää huolta paitsi kiihdyttimen toiminnan kannalta, myös siksi, että ei ole vielä selvitetty, lisääkö rakkuloiden aiheuttama pinnan karhentuminen hajoamisnopeutta. Tässä väitöskirjassa tutkitaan näitä ilmiöitä selvittämällä, kuinka vety-ionisäteilytys vaikuttaa materiaalien kestävyyskykyyn sähköisiä purkauksia vastaan. Kokeet suoritettiin eri metallien osalta järjestelmällisesti, jotta voitiin arvioida parempia vaihtoehtoisia materiaaleja tulevaisuuden RFQ-rakenteisiin, parantaen niiden tehokkuutta ja kestävyyskykyä. Tähän tarkoitukseen valittiin seitsemän materiaalia kokeiden suorittamiseksi: puhdas happivapaa kupari, kupari-kromi-zirkonium, kupari-beryllium, ruostumaton teräs, titaanilejееrinki, niobium ja tantaali. Materiaalit valittiin joko niiden parempien mekaanisten ominaisuuksien perusteella verrattuna kupariin tai niiden korkeamman vedyn diffuusiokykyyn takia. Molemmissa tapauksissa tavoitteena oli vähentää pinnan rakkulam muodostusta. Säteilytys suoritettiin matalaenergisellä H^- säteellä, ja korkeaajännitekäsitelyprosessi sekä sähköisten purkausten tilastollinen analyysi toteutettiin tasavirta (DC)-pulssitetulla korkeaajännitejärjestelmällä. Materiaalien metallurgisia ominaisuuksia tutkittiin kehittyneillä mikroskopiakentäillä, joiden avulla analysoitiin ja karakterisoitiin eri pintoja sekä verrattiin tuloksia ennen ja jälkeen säteilytyksen sekä kaaripurkaustestauksen. Tutkimuksessa tunnistettiin materiaalit, joilla on parhaat sähköisten kenttien sietokyky ja kestävyys matalaenergiselle säteilylle. Lisäksi suoritettiin lisätutkimuksia säteilytykselle kuparinäytteille, joissa havaittiin, että rakkulam muodostus riippuu kiteen orientaatiosta. Yllättäen havaittiin, että säteilyn aiheuttamalla rakkulam muodostuksella ei ole haitallisia vaikutuksia korkeaajännitekäsitelyyn. Sen sijaan hiilikontaminaatio, joka johtuu hiilivetyjen hajoamisesta säteilytyksen aikana, tunnistettiin merkittäväksi ongelmaksi kiihdytinrakenteille. Tulokset osoittivat, että hiilen esiintyminen johti sähköisen kentän suorituskykyyn heikkenemiseen. Näiden havaintojen perusteella tehtiin tutkimuksia hapettavan plasmakäsittelyn käytöstä hiilikontaminaation poistamiseksi. Kokeet suoritettiin CuBe₂, Cu-OFE ja SS316LN mate-

riaaleille. Käsiteltyjä materiaaleja testattiin korkeilla pulssijännitteillä, ja tuloksia verrattiin sekä käsittelemättömiin että säteilytettyihin mutta käsittelemättömiin näytteisiin. Tutkimus tunnisti plasmakäsittelyn tehokkaaksi menetelmäksi hiilen poistamiseen metallipinnoilta, mahdollistaen säteilytettyjen materiaalien sähköisen suorituskyvyn palauttamisen vastaamaan alkuperäisten pintojen suorituskkyä.

Common abbreviations

AISI		American Iron and Steel Institute
BCC		Body-Centered Cubic
BD		Breakdown
BSE		Backscattered Electrons
CERN		European Organization for Nuclear Research
CLIC		Compact Linear Collider
DC		Direct Current
EAM		Embedded Atom Model
EBSD		Electron Backscatter Diffraction
EDS		Energy Dispersive Spectroscopy
FCC		Face-Centered Cubic
FIB		Focused Ion Beam
HCP		Hexagonal Close Packed
LES		Large Electrode System
LHC		Large Hadron Collider
LINAC		Linear Accelerator
MD		Molecular dynamics
OPC		Oxygen Plasma Cleaning
Ra		Roughness
RF		Radio-Frequency
RFQ		Radio-Frequency Quadrupole
RPM		Revolutions Per Minute
SE		Secondary Electrons

SEM Scanning Electron Microscope

UNS Unified Number System

XPS X-ray Photoelectron Spectroscopy

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CHAPTER 1

Introduction

1.1 Structure of Dissertation

This dissertation is composed of 6 chapters with the following structure. The first chapter is dedicated to a literature review, where the fundamental problems that justify the bases of the experimental work are presented. Chapter 2 consists in presenting the purpose of the conducted research and present to the reader the summary of scientific publications that came from it. In chapter 3, the materials investigated, experimental apparatus and analysis methodologies are described. The results are discussed in chapters 4 and 5, followed by the summary and outlook in chapter 6. At last, the scientific publications can be found in the Annex of the manuscript.

1.2 Linear accelerators

Linear accelerators (LINACs) are structures dedicated to particle beam acceleration. LINACs involve the use of radio-frequency electric field in order to sequentially accelerate charged particles along a linear path. Linear accelerators have a substantial importance in today's industry and medicine. Cancer radiotherapy represents the largest market for electron LINACs while industrial applications come in second [1]. Currently, the total market size of linear accelerators, accounting for scientific research, medical and industrial applications exceeds the 4 billions USD, with expectations of reaching 7 to 8 % of growth until the end of the decade [2, 3].

At the time of the writing, LINAC4 is the current linear proton accelerator in work at the European Organization for Nuclear Research (CERN), Geneva. Figure 1.1 shows CERN's accelerator and experience complex. Here, LINAC4 represents the initial acceleration, before the beam of particles enters the following chain of circular accelerators until the Large Hadron Collider (LHC).

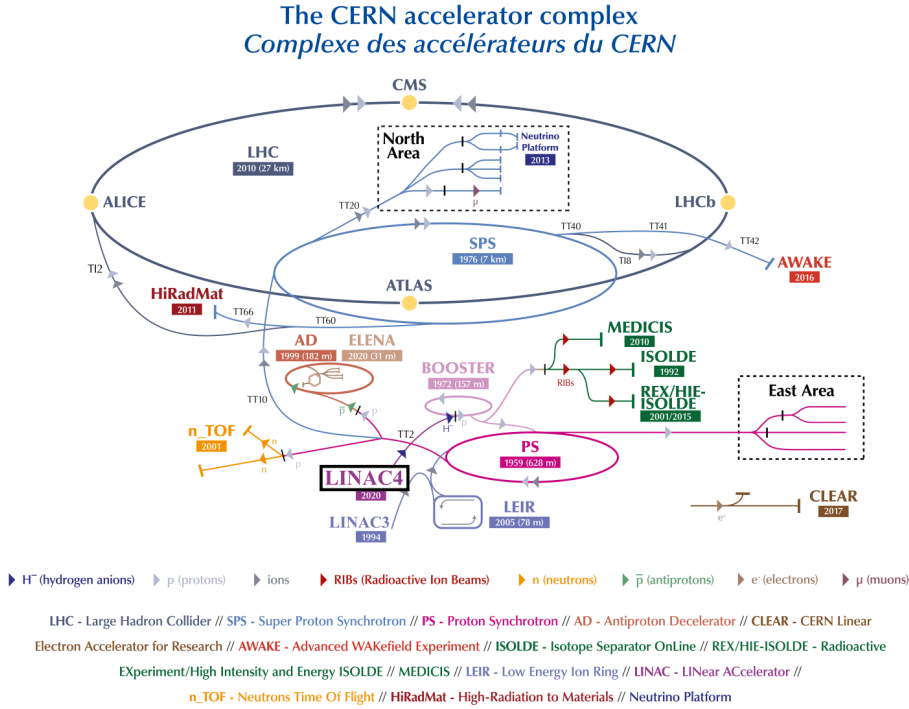


Figure 1.1: Schematic of CERN's accelerator complex. Adapted from [4].

One of the primary and most fundamental components of linear accelerating structures is the Radio-Frequency-Quadrupole (RFQ) which allows for high ions intensities in a very compact structure. The first stage of acceleration in the linear accelerator happens in the RFQ. At CERN, the current RFQ (L4 RFQ) is a three meter-long structure made of oxygen-free copper (Cu-OFE) which accelerates a 45 keV beam from the ion source to the energy of 3 MeV [5–7]. For these accelerating voltages, it has been reported in [8, 9] that the surface electric field in the inter vanes to be 34 MV/m, enough to cause vacuum arcing in their surfaces, as discussed below.

The structure is a four vane type brazed with high precision alignment [10]. These four electrodes or vanes, connected to the cylinder along their length, form the RF cavity responsible for the efficiency of beam bunching and acceleration, along with its focus and transmission. The importance of design and machinery of the four vanes is something that should be emphasized, as the geometrical precision of these components is responsible for efficient acceleration and preventing beam dispersion. More information regarding the mechanical design, brazing and assembly can be found in [10–12].

Due to the continuous and prolonged exposure to high power RF and particle

bombardment, these structures have a limited time-life, consequently leading to material degradation with the years of operation. At CERN, during the last LHC long shut-down, in-situ microscopic inspections were done inside the RFQ, previously installed in 2013 at LINAC4 [13]. Observation into the vanes showed surface damages, as seen in Figure 1.2, after only six years of operational work.

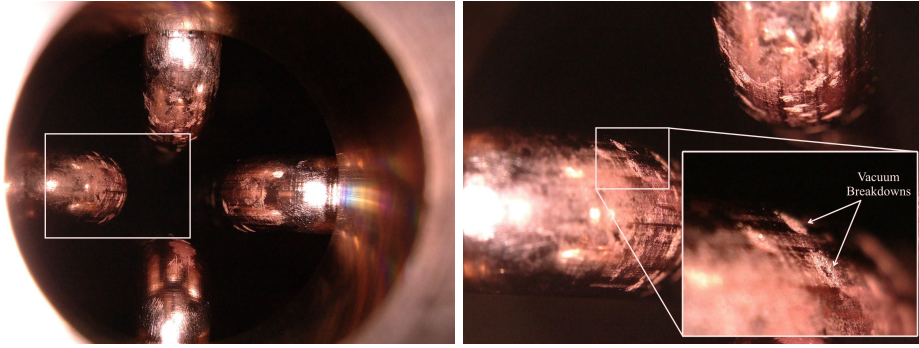


Figure 1.2: Endoscope optical images taken on the front of the LINAC4 RFQ interior vanes, at CERN.

The observed damages, were reported to be associated with the long exposure to high electric fields causing vacuum arcs or vacuum breakdowns. Due to the difficult access into the vanes, and limited in-situ magnification, evidences of hydrogen implantation was not conclusive. The concern regarding hydrogen implantation, comes from the fact that during RFQ operation, the structure is exposed to beam losses. Beam losses can induce blistering on materials, which in fact was observed, by scanning electrons microscopy (SEM) inspections, in the extracted copper collimators, located at the beam entrance of the RFQ.

It was speculated that damages as the ones observed increase the likelihood of further electrical discharges, causing a justified concern for the integrity of the RFQ accelerating structure. Such degradation can increase beam losses, which adversely affect both the stability and efficiency of the accelerator's performance. Moreover, changes in the material mechanical properties, such as an increase of surface roughening, enhanced electrical resistance or even cracking, are all consequent factors that can eventually lead to failure of the RFQ.

At the moment, RFQs are considered consumables - after degradation and consequential failure, the decommission of the RFQ is necessary, along with the fabrication and assembly of a new structure. The production of an entire RFQ structure is valued between 1 and 2 Million CHF [14, 15] with limited lifetime expectancy. By mitigating the current problems that exist today, in terms of material degradation, the usability of these machines could be massively extended.

1.3 Surface Damages - Vacuum Breakdowns

Vacuum breakdowns or vacuum arcs are an electric discharge in a small gap between two conductive electrodes under vacuum. Damages from breakdowns, as seen in Figure 1.2, are observed, in the local points of discharge, as melted material in the form of craters [16–19]. The phenomenon is well known and has been studied for decades - an extensive review of several publications can be found in [20, 21]. Also, a full review comprehending experimental, theoretical and simulation work regarding the behavior of high-field devices and the fundamental process of vacuum arcing, has been recently published [22].

When a high voltage is applied in a vacuum environment, if the electric field at the cathode surface reaches sufficient intensity, the emission of neutral atoms and electrons from the surface leads to the formation of a plasma. The local heating on the surface contributes to the thermal evaporation of neutrals to this plasma. In fact, according to [23] the thermal evaporation of neutral vapor was found to dominate over the surface sputtering.

With the subsequent ionization, the positive ions are accelerated in the direction of the electric field towards the cathode causing, along with local heating, a cascade, which leads to erosion of surface atoms and feeding the plasma. Consequently, the plasma expands until it reaches the surface of the anode. At this stage, the conductive plasma that has grown across the gap between the two electrodes acts as a conductive bridge between the anode and the cathode surfaces, allowing current flow between the two, resulting in a vacuum arc discharge.

Currently, it is believed that the emission of electrons from the cathode occurs due to field emitters or nanoprotusions present at the surface, which would enhance the electric field strength locally [24]. If so, these nanoprotusions would be the initial stage of the process for the formation of a vacuum arc. To date, no microscopic analysis has identified such features on the surface, mainly and presumably because they would only grow in the presence of an electric field as described in [25] and after a vacuum arc event the local region is melted and left with craters.

In the literature, there is a consensus that, like protrusions, other surface features, such as roughness, impurities or defects, grain boundaries, chemical effects such as the formation of an oxide, can also be or contribute to the cause of the phenomenon [26]. A study [27], simulating high electric fields at a metal surface containing a near-surface void, concludes that the tensile stress caused by the surface electric field induces plastic deformations above the void, which under stress, will develop in a self-reinforcing manner resulting in a protrusion at the surface. Additionally, it has been reported in [28] a dependence of breakdown strength according to the material crystal structure by associating dislocation mobility with the amount of slip planes in the different lattice types. Also, a model is described in [29] which attributes dislocations population in copper cathodes to cause electric breakdowns.

Although the process that triggers the formation of vacuum breakdowns remains uncertain, several publications agree that they are influenced by the type of material [30, 31]. Properties like work function, electric and thermal conductivity, mechanical strength and hardness [17] can play a major role in mitigating the probability of a breakdown to occur or endure the surface condition for a longer time.

Breakdown phenomena are not only a problem of current RFQs, as seen above, but becomes an even higher concern for the development of shorter linear accelerators, as smaller dimensions means a higher voltage and therefore higher surface electric fields that can give rise to higher breakdown rates. This problem is described in [32–35] on the Compact Linear Collider (CLIC), where accelerating gradients in the order of 100 MV/m are reached. Also, vacuum arcs affect not only particle accelerators but also high-voltage equipment used, per example, in power distribution and vacuum interrupters [36–38].

While the origin of breakdown initiation is not yet understood, significant material damage can be mitigated by using a material that is less prone to such events. Additionally, conditioning processes, i.e. systematic exposure of the material to a controlled accelerating field, can be applied to enable the surface to adapt to the required operational conditions.

1.4 Hydrogen in metals

The alignment of hydrogen benefits with the urgency of transitioning to a low-carbon economy, as discussed in the Paris Agreement adopted in 2015 [39], has made the study of hydrogen in metals a topic of research with great scientific investment. While being an element with significant industrial and environmental prospects [40], the use of hydrogen pairs with multiple challenges when it comes to its interaction with metals. Hydrogen implantation research not only benefits the operation of RFQs but also advances the field of material science, which in today's economy, diverges across multiple sectors, such as energy storage, nuclear fusion and refining industry [41–44]. The primary challenge associated with hydrogen implantation comes from the degradation of the metal mechanical properties by inducing degradation, corrosion, blistering and cracking [45, 46]. Atomic hydrogen implantation tends to form defects in the lattice, such as dislocations and vacancies. Additionally, and according to [47], the presence of vacancies and vacancy clusters, dislocations or even impurities will become probable trap sites for incoming hydrogen, causing agglomeration of H and consequent growth of H bubbles. Furthermore, the continuous growth of H bubbles within the lattice may reach the surface in the form of blisters.

Surfaces with continuous exposure to hydrogen, as is the case of the RFQ internal vanes, can lead to blistering as a consequence of supersaturation of hydrogen within the target's material structure [48]. This phenomenon has been reported

not only in particle accelerators and fusion power plants, where high fluences and different energies of H are used, but also in hydrogen environments like with the case of H storage tanks [49–51]. Also, [52] describes the hydrogen-induced interfacial failure as a major threat to the integrity of coatings and passivation films on metals.

Extensive research has been conducted to understand the mechanisms behind hydrogen-induced blistering in various materials given that the probability of blistering increases if the target material has a low hydrogen solubility [45].

Blisters have been observed in several metals, despite the material crystalline structure. Studies made in [53, 54] show copper as a vulnerable material to blistering, which corroborates the blister’s appearance in the RFQ structures upon low energy hydrogen ions beam and on the samples tested within this work, as it will be seen later on. This vulnerability of copper served as a motivation to study different materials and their response to hydrogen implantation, and also deepen the knowledge in regard to blistering on the copper material. A more detailed review about blistering can be found in section 4.1.

CHAPTER 2

Purpose of Research and Scientific Publications

2.1 Purpose of work

The problems encountered inside the linear accelerator structure at CERN, as outlined in chapter 1 were the fundamental basis that motivated the creation of a dedicated well-structured project to further explore current issues.

Problems such as vacuum breakdowns and blistering are phenomena that have each been subject to thorough investigation, and hence independently addressed. However, there is no indication in the literature of scientific work that correlates both phenomena to understand if the appearance of blistering in a material surface can have an effect when the same surface is exposed to high gradient electric fields.

The existing gap in the literature regarding the interrelation between these phenomena, motivated the work developed in this dissertation, aiming to determine whether surfaces that have undergone hydrogen implantation exhibit altered responses when exposed to high electric fields.

With this purpose, a list of materials have been selected - by trying to match the necessity of endurance to blistering and vacuum arcs - in order to deepen the knowledge of copper and assess alternative material candidates for the manufacturing of a next-generation RFQ. Moreover, this work contributes to deepening the general understanding of material behaviors, potentially helping to enhance accelerator reliability.

The results are summarized in Publications **I**, **II** and **IV**, while Publication **III** discuss new findings about blisters behavior in copper - material currently used in the radio-frequency-quadrupole at CERN and most used worldwide for RF accelerating structures.

2.2 Scientific Publications

2.2.1 Summary of Main Publications

The author was the main contributor of four publications, summarized below. Along the manuscript, the author's publications will be cited according to their roman numerals.

Publication I. Investigation on different materials after pulsed high field conditioning and low-energy H^- irradiation

C. Serafim, R. Peacock, S. Calatroni, F. Djurabekova, A. T. Perez-Fontenla, W. Wuensch, S. Sgobba, A. Grudiev, A. Lombardi, E. Sargsyan, S. Ramberger and G. Bellodi

Frontiers in Physics, Vol. 12, 1308455 (2024)

Experiments to study the high-voltage conditioning process and electrical breakdown statistics have been conducted using pulsed high-voltage DC systems in order to identify materials with high electric field handling capability and robustness to low-energy irradiation. In this paper, we discuss the first results obtained for the three different materials: Cu-OFE, Ti6Al4V and Nb.

Publication II. Effects of H^- low beam irradiation and high field pulsing tests in different metals

C. Serafim, S. Calatroni, F. Djurabekova, R. Peacock, V. Bjelland, A. T. Perez-Fontenla, W. Wuensch, A. Grudiev, S. Sgobba, A. Lombardi and E. Sargsyan

Physical Review Accelerators and Beams, Vol. 28, 013101 (2025)

This work consolidates the findings regarding the investigated materials (Cu-OFE, CuCr1Zr, CuBe2, Ti6Al4V, SS316LN, Nb and Ta) submitted to low-energy (45 keV) H^- irradiation and tested in a pulsed high voltage system. For comparison, the maximum surface electric field was measured for both irradiated and pristine (non irradiated) surfaces of the same material. The effects of irradiation on the surface of the materials, before and after being submitted to high electric fields, were studied with the help of microscopic imaging and chemical analysis. Despite reductions in breakdown field strength post-irradiation, no indications were found that the blisters on the surface have a direct cause in triggering breakdowns during high electric field tests. SS316LN, Ti6Al4V, CuBe2 and CuCr1Zr showed maximum surface electric fields higher than copper, making these promising candidate materials for future RFQs manufacturing.

Publication III. Effect of surface orientation on blistering of copper under high fluence keV hydrogen ion irradiation

A. Lopez Casalilla, C. Serafim, J. K. Kimari, M. Ghaemikermani, A. T. Perez-Fontenla, S. Calatroni, A. Grudiev, W. Wuensch and F. Djurabekova
Acta Materialia, Vol. 266, 119699 (2024)

Structural modifications in the form of blisters have been studied in polycrystalline copper surface exposed to hydrogen in the form of charged ions. Using scanning electron microscopy, it was found that the blistering of the irradiated copper surface does not grow uniformly with ion fluence, indicating that grains with the (100) orientation are the most prone to blistering. Good agreement of experiments with the atomistic simulations reveals the correlation of the delay in blister formation on surfaces with certain orientations compared to the others with the dependence of the hydrogen penetration depth and the depth and amount of vacancies in copper on the orientation of the irradiated surface.

Publication IV. Plasma treated metals after H⁻ irradiation and its effect on vacuum breakdown behavior

C. Serafim, S. Calatroni, F. Djurabekova, M. C. Giordano, M. Himmerlich, V. Bjelland, C. Kouzios, P. Costa Pinto, A. T. Perez-Fontenla, W. Wuensch, A. Grudiev, and S. Sgobba
Physical Review Accelerators and Beams, arXiv:2503.17360 pre-print (2025)

The study extends the latest research by exploring the efficacy of Oxygen Plasma Cleaning (OPC) on metal electrodes irradiated by low energy hydrogen ion beam with the purpose of reducing surface carbon contamination. OPC treatment has been employed on different metals, including copper beryllium (CuBe2), oxygen-free copper (Cu-OFE), and stainless steel (SS316LN). Treated electrodes have been tested for electric field performance under a DC pulsed system and results compared with non-irradiated electrodes and irradiated ones without OPC treatment. The study indicates a significant reduction in carbon content by OPC, enough to allow irradiated materials to achieve performances comparable with the electric field strength of raw surfaces.

All publications follow the open-access article distribution under the terms of the Creative Commons Attribution License (CC BY).

2.2.2 Author's Contribution

Regarding publications **I**, **II** and **IV**, the author was the leading writer for all the original scope of the manuscripts. During the research, the author was responsible for assessing all electrodes during the different stages of the project in terms of microscopic analysis, mainly comprehending scanning electron microscope equipment. Also, the author was responsible to assemble and test the electrodes in the Large Electrode System and analyze the measurements. In terms of sample's irradiation, the author was responsible for assembling and disassembling all the electrodes in the dedicated chamber and prepare all the logistical proceedings before and after testing, in order to maximize the operational time available. The author was responsible for assuring all the procedures were rightly met, from manufacturing to surface treatments to insure the samples were ready for the necessary tests, followed by the management of the different studies. Also, in publication **IV** the author developed the project under study and was responsible for all the coordination among the different teams. Plasma treatments and XPS studies included in this publication were not performed by the author.

Regarding publication **III**, the author was the leading responsible for the experimental part of the research. The author has developed the scope of the study, including sample arrangement, treatments, successfully irradiation assemblies and all the research planning. Moreover, the author was responsible for the analysis made before and after crystallographic mapping in identifying the regions of interest, which were further explored using SEM.

2.2.3 Summary of Secondary Publications

In addition to the four main publications, the author has made contributions in three additional scientific publications, which will not be discussed in the dissertation. While these publications are not part of the main scope of the author research, the knowledge acquired during the doctoral project, specific to microscopic analysis and material science, has allowed the author to further extended his contribution to different projects.

Publication V. Electron Beam Characterization of REBCO-Coated Conductors at Cryogenic Conditions

M. Haubner, P. Krkotić, C. Serafim, V. Petit, V. Baglin, S. Calatroni, B. Henrist, A. Romanov, T. Puig and J. Gutierrez
MDPI, Applied Sciences, Vol. 13, 2765 (2023)

Publication VI. Influence of nanoparticulates and microgrooves on the secondary electron yield and electrical resistance of laser-treated copper surfaces

P. Krkotić, T. Madarász, C. Serafim, H. Neupert, A. T. Perez-Fontenla, M. Himmerlich and S. Calatroni

Physical Review Accelerators and Beams, Vol. 27, 113101 (2024)

Publication VII. Initial high electric field – vacuum arc breakdown test results for additively manufactured pure copper electrodes

A. Ratkus, G. Pikurs, C. Serafim, M. Vretenar, S. Calatroni, T. Torims, V. Bjelland, W. Wuensch, M. Pozzi, M. Pedretti, M. Vedani, T. Romano and R. Peacock

JACoW Publishing, IPAC'23 - Proceedings, ISSN: 2673-5490 (2023)

CHAPTER 3

Materials and Methodologies

3.1 Materials

In terms of RFQ design, the base material of the inner vanes will influence directly the performance, stability and lifetime of the accelerator structure. Parameters such as material's electric and thermal conductivity are crucial in order to minimize power losses and help heat dissipation generated during operations. Also, the material should have good capability for ultra-high-vacuum applications, mechanical strength and good machinability. More information on the mechanical properties of the selected material can be found in Publication **II**. In addition, resistance to radiation-induced damage, becomes equally important, once hydrogen implantation can induce material degradation over time. Materials with higher permeability tend to have a better behavior in accommodating hydrogen in their bulk. This topic is presented in more detailed later on, in chapter 4.

Seven materials were selected for the studies: pure oxygen-free copper (Cu-OFE), UNS type C10100; copper chromium zirconium (CuCr1Zr), UNS type C18150, with approximately 0.1% of zirconium, 1% of chromium and with the rest being copper; copper beryllium (CuBe2), UNS type C17200 with 98 wt% copper and 2% beryllium; stainless austenitic chromium-nickel-molybdenum steel with nitrogen addition (AISI 316LN), UNS type S31653; premium-grade titanium alloy

Table 3.1: Chemical composition (wt%) of the material alloys selected for testing. From Publication **II**.

CuCr1Zr	Cu	Cr	Zr	Si	Fe						
	Rest	0.8	0.09	<0.01	<0.01						
CuBe2	Cu	Be	Co	Ni	Fe						
	Rest	2.0	<0.30	<0.30	<0.20						
SS316LN	Fe	Cr	Ni	Mo	Mn	Si	N	C	P	S	Co
	Rest	17.24	13.31	2.52	1.55	0.41	0.16	0.025	0.023	0.004	0.048
Ti6Al4V	Ti	Al	V	Fe	O₂	C	N₂	H₂			
	Rest	6.06	4.02	0.11	0.11	0.0149	0.003	0.0046			

(Ti6Al4V, grade F-5, 6 wt% aluminum—4 wt% vanadium, UNS type R56400); high purity (99.9%) niobium (Nb), UNS type RRR300 and 99.9% tantalum (Ta), UNS type UNS R05200. The chemical composition of each material alloy can be found summarized in Table 3.1.

3.1.1 Machining and control

For each material, two anodes and two cathodes were manufactured. The functional drawing requirements aimed at achieving a face surface flatness of 0.001 mm, maintaining a surface finish below a roughness (Ra) of 0.025 μm , and localizing the shoulder distance within a tolerance of 0.001 mm. Due to the electrode axial symmetrical geometry and such tight shape tolerance and surface finish requirements, ultra-precision turning has been chosen as manufacturing process. With respect to other processes, the advantage of turning process for the given geometry finishing, was the possibility to perform a final run with a single tool on all key functional surfaces; thus, significantly reduce finishing machining time while at the same time increasing the precision of the final component. The machining was performed on a Hembrug Microturn P100 turning machine, equipped with hydraulic chuck and spindle rotation capabilities of up to 4000 RPM. Where applicable i.e. for non-ferrous metals and alloys such as oxygen-free-electronic copper (Cu-OFE), and copper-chromium-zirconium alloy (CuCr1Zr); monocrystalline diamond (MCD) finishing was applied to meet high surface finish requirements. For electrodes manufactured from niobium (Nb), tantalum (Ta), titanium alloy grade 5 (Ti6Al4V), and stainless-steel (SS316LN), a different approach using adapted tungsten carbide tools was employed.

Due to the typical features of the turning process, cutting speed tends to decrease as the tool approaches the axis of the component, according to the formula $V_c = D_m \pi n / 1000$. For the softer materials such as Nb, this brings additional challenges during the finishing run when the central stud was not being cut but rather formed. This prompted meticulous analysis and adjustments to cutting parameters and tool selection, to ensure optimal results. Another challenge was an excessive abrasive nature of materials such as Ta and Nb, which brings about less satisfactory results in terms of precision and surface finish in comparison to other materials.

Metrology using a Leitz Inifinity CMM machine [55], was performed in all the electrodes after machining in order to evaluate the profile of their surface. A schematic cross-section drawing of a cathode electrode can be seen in Figure 3.1. From this quality control, two main measurements were crucial to validate the electrodes for future testing. First, it is validated if the flatness of the plane Ref. A and plane Ref. B are within the accepted tolerances. The second point is the measurement of the alignment of these two planes which must guarantee a good parallelism of them at the gap size of 10 mm. Validating this parallelism between the two surfaces is crucial in order to avoid misalignment when positioning the

anode and cathode into the LES system, along with a dedicated spacer between them, as shown in Figure 3.3 (a). All the high pulsing tests made with the electrodes, were done using a 60 μm spacer. Any wrong parallelism between Ref. A and B. when positioning the spacer would cause a misalignment and not guarantee the 60 μm gap between the electrodes surfaces.

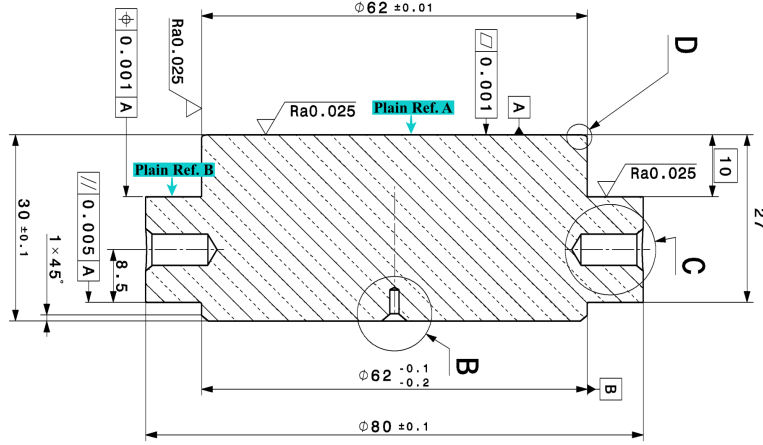


Figure 3.1: Schematic drawing of the cathode electrode showing "Plain Ref. A" - cathode surface which will be exposed to testing, and "Plain Ref. B" - surface of the electrode's shoulder.

3.2 Experimental Testing

3.2.1 Structure of Testing

As mentioned earlier, for each material, two sets of electrodes, i.e. two cathodes and two anodes, were manufactured. SEM analysis served to validate the final surface, before installing electrodes for testing. Figure 3.2 shows the chronological events including the different phases of the studies. In general, the first pair of electrodes is tested as the reference, for high voltage tests endurance using the Large Electrode System (LES) - see section 3.2.3 - while the second pair is irradiated prior to LES testing. Results from those studies are summarized in Publications **I** and **II**.

Furthermore, the same principle of testing was applied for the results included in Publication **IV** and discussed in chapter 5.2. However, for the research conducted in the publication, surface treatments, using a dedicated oxygen plasma environment were used as a middle step between the post irradiation and pre-high voltage tests.

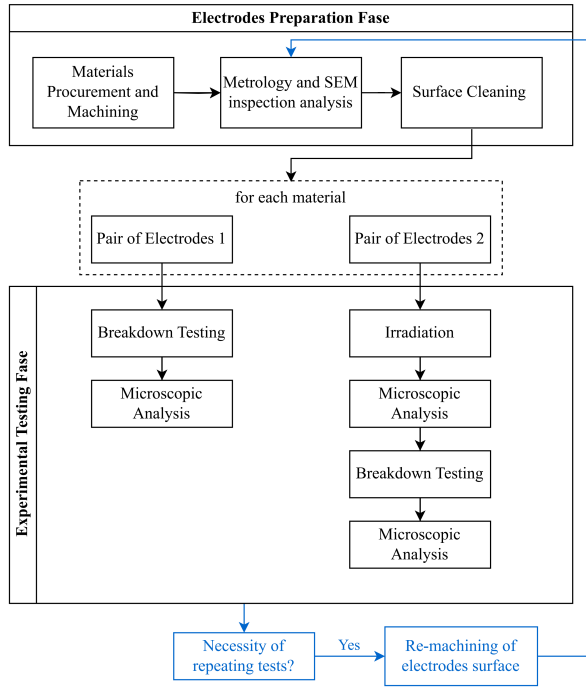


Figure 3.2: Diagram showing the process of electrodes preparation before testing and the different stages during experimental testing.

3.2.2 Irradiation with Hydrogen ions at low energy

A low-energy H^- beam with an energy of 45 keV, mirroring the energy of the beam as it enters the RFQ from the ion source, was utilized to irradiate a cathode made from each material. A dedicated chamber was machined, with an opening flange which connects to the ion source irradiation facility [56]. This chamber allows the mounting of the electrode to be done in order for the main surface to serve as the target for the ion beam. The cathode is secured via ceramic adapters, which are then screwed to the chamber's main body, assuring no conductivity between the stainless steel chamber and the sample and, guaranteeing a precise measurement of the irradiation beam current on the electrode. The irradiation performed, with an approximate duration of 50 hours in different electrodes, resulted in a deposition of 1.2×10^{-19} p/cm² ions in each target.

3.2.3 Large Electrode System

The Large Electrode System (LES) is a dedicated pulsed DC system built for the purpose of applying high-gradient electric fields in a set of electrodes, for the study of conditioning processes and breakdown events triggered from it.

LES has been designed and operated at CERN, with the purpose of replicating RFQ conditioning in terms of electric field. The system geometry and fast repetition rates allow not only for the manipulation of diverse materials but also allow the acquisition of experimental data much faster than RF testing - the differences in terms of testing time to achieve similar final number of pulses can be observed in [57, 58].

The system is composed by a main vacuum chamber, designed to geometrical insert two electrodes with a maximum diameter of 80 mm. The cathode and anode are placed inside the chamber along with a ceramic spacer (Al_2O_3) between them, which guarantees a uniform gap between the two surfaces. A vacuum feedthrough connects the chamber to a pulse generator (MARX), that multiplies by 10 the voltage received by the power supply equipment, limited until 1 kV of power delivery. The pulse generator provides high voltages pulses (until 10kV) to the system, with a pulse length from 1 μs to 1 ms and a repetition rate until 6 kHz [59, 60]. The main vacuum chamber has four window ports positions with a 90 degrees angle between each other and horizontally aligned with the gap between cathode and anode, as seen in Figure 3.3. Two cameras are installed in two view ports in order to capture light that may be emitted during the occurrence of a vacuum arc. A LabView program, developed to triangulate the signal received from the cameras, allows for a real-time monitoring of the breakdowns position on the electrodes surface during testing [61]. The high-vacuum in the chamber is achieved by using a turbo-molecular pump [62] supplying a vacuum in the order of the 10^{-9} mbar. The pressure is constantly controlled also because it is an additional way of identifying breakdowns events. Apart from the light emission and vacuum spikes detection, the most important method to detect a breakdown is by controlling the voltage and current across the electrodes, using in this case a LeCroy oscilloscope. When a vacuum arc happens, there is a sudden drop in voltage and increase in current, caused by the conductive plasma between the two electrodes [63]. The voltage and current behavior can be seen in [64, 65], using the same system. More information regarding the LES system and dedicated studies, primarily made with copper, can be found in [66–68]. The purpose of conducting high pulsing test is to determine the maximum and stable electric field that each material can achieve. This begins by - after electrodes installation and a good high-vacuum is reached - applying a minimal voltage to the system. The increase of voltage is done progressively and in a controlled way to minimize any potential risks to the material's surface. In each conditioning run (voltage ramping step) the initial voltage matches the final voltage of the previous run. Here, it is set a new target voltage, typically targeting for additional 300V (i.e. +5 MV/m in electric field for a 60 μm gap) from the current voltage. Within the run, the increments are done automatically by small increments of 10 V every 100 000 pulses. When reaching the final voltage, a new run with the next target voltage is only set when the current voltage is kept constant for a while and the rate of breakdowns is stable. When a breakdown event occurs and there is a sudden drop in voltage, the system is set to provide steps of voltage increments

until it matches the voltage prior to the breakdown. If the final voltage after a breakdown's recovery doesn't achieve the target voltage defined, it is an indication of a saturation point for the electric field limit sustained by the material under test. Post-testing analysis of the data extracted from the all measurements, allows for the quantification of the vacuum arcs triggered during the all process of conditioning, along with their positions in the surface.

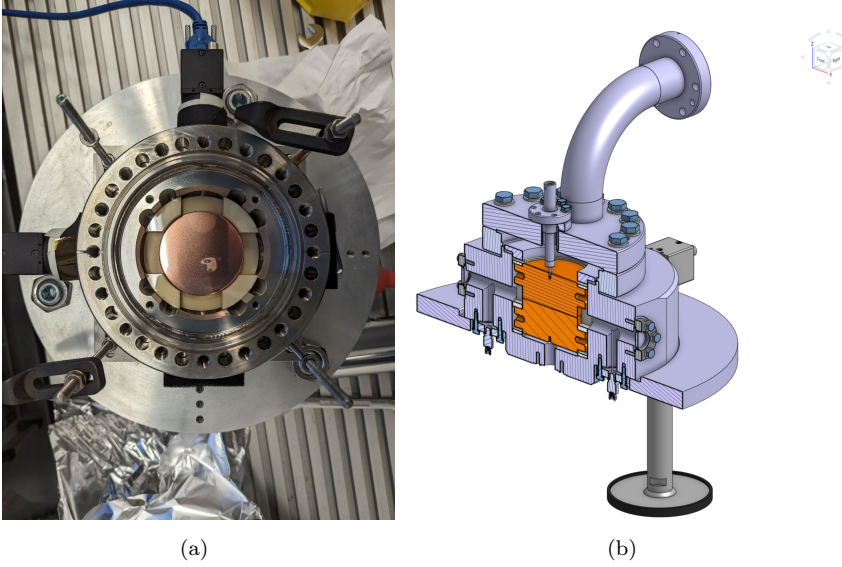


Figure 3.3: (a) Photograph taken on the top view of LES chamber while installing electrodes for testing. The LES chamber is open, with its main flange removed, inside the chamber it can be seen a copper cathode and a ceramic laid on top of the cathode's shoulder before inserting the anode. (b) CAD cross-section image taken on the LES system, showing two electrodes inside.

3.3 Scanning Electron Microscope

Scanning Electron Microscope (SEM) was used as an important microscopic technique, in multiple stages of the research, for the analysis of the electrodes. Analysis were made using the model Σ IGMA from the company Zeiss [69]. Complementary to SEM analysis, optical microscope was also used, generally to acquire mapping of the surfaces and identify features of interest, facilitating afterwards their localization on the SEM. The primary SEM equipment used for all observation is shown in Figure 3.4. The equipment has an electron source with a tungsten filament, responsible for the generation of a beam of electrons and allowing an acceleration voltage of the beam until 30 kV. The Gemini column is the area

where the electrons are emitted, accelerated, focused and deflected toward the sample.

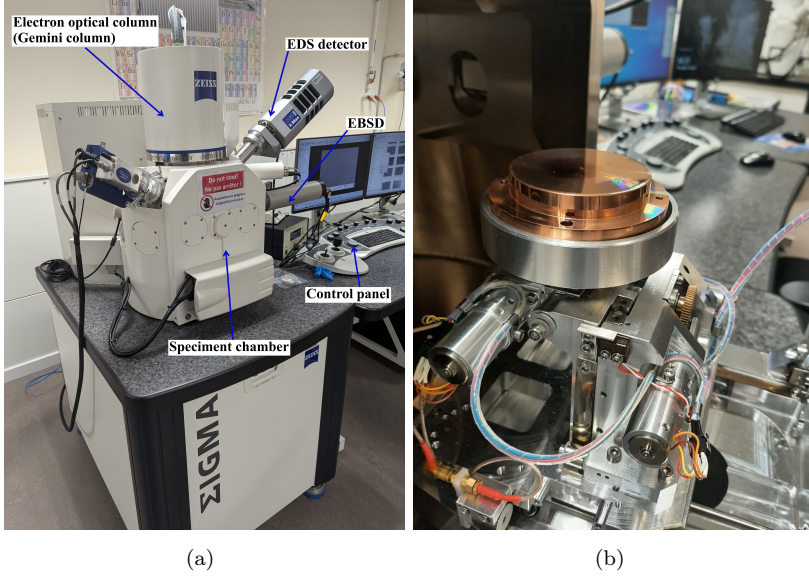


Figure 3.4: Scanning Electron Microscope model Σ IGMA, installed at CERN, part of the Materials, Metrology and Non-Destructive Testing Section within the Engineering Department and Mechanical and Materials Engineering Group (EN-MME-MM): (a) External view of the SEM; (b) SEM with open chamber where a copper electrode is mounted and secured in the sample stage.

Samples are secured in the SEM chamber upon the sample stage, which has a 5 Cartesian motorized axis, including a 360 degrees continuous rotation and a sample tilting between -10 to 90 degrees. For the case of the electrodes, a dedicated platform is mechanically connected between their bottom surface and the chamber stage, allowing for a more controlled positioning and safe operation. For the analysis made on the electrodes, three detectors were mainly used: secondary electron detector (SE), inLens detector (SE2) and Back-Scattered Electron Detector (BSE). The secondary electron detector is installed at 45 degrees from the vertical axis of the beam gun. Secondary electrons are ejected from the outer atomic shell of the sample when the electrons from the primary beam hit and interact with the surface. Typically, the produced electrons have low energies less than 50 eV, providing a high sensitivity to variation in the surface contours, and therefore it becomes an essential technique for the study of topographical information about the surface features. Differently from the SE2 detector, which receives the signal from the side, the BSE detector is positioned below the final lens, seeing the sample from the top. BSE detector was mainly used to

provide material composition information. Given the large dimensions of the electrodes surface, this helped to map the surface for possible contamination, by evaluating the different imaging contrasts. Elements with a higher atomic number, scatter more electrons, translating in a higher brightness when comparing with elements with a smaller atomic number. At last, the In-lens detector, can efficiently detect the secondary electrons emitted directly upwards from the sample, as it is installed directly in the vertical axis coincident with the primary beam path. In-lens detector became useful specially when investigating more superficial information in the surfaces. By using very low accelerating voltages, electrons produced by the interaction with the small depth reveals more sensitive surface details. Scanning electron microscopy was used systematically to analyze all the electrodes and additional samples in our studies. Results regarding these observations are included in Publications **I - IV**.

SEM analysis was complemented with Energy-Dispersive X-ray Spectroscopy (EDS). This chemical analysis allowed to identify qualitatively external elements in the samples. This technique involved bombarding a solid sample with a focused electron beam and measuring the emitted X-ray spectrum to perform localized chemical analysis. The analysis involved identifying the specific energies of X-ray peaks that are characteristic of each element. In this quantitative approach, the mass concentration of each element is approximately proportional to the relative intensity of an X-ray line. The concentrations of elements are quantified by assessing the relative intensities of the lines detected in the spectrum for each element. Additionally, Electron Backscattered Diffraction (EBSD) was used in a particular case to characterize grain crystallographic orientations of small copper samples. During EBSD analysis, the focused electron beam interacts with the sample, causing the electrons to backscatter in a pattern that is characteristic of the crystallographic structure of the sample surface. This diffraction pattern is detected and analyzed by a dedicated software to determine the orientation of the grains, distribution and other textual properties of the material [70]. Due to limitations in sample's geometry to fit the holder for EBSD analysis, dedicated samples were design with dimensions flexible enough to perform not only EBSD, but also to be able to rightly fit for Focused Ion Beam (FIB) and X-ray Photoelectron Spectroscopy (XPS).

3.4 Atomistic Modeling

Molecular dynamics (MD) [71] is a computational tool that allows to simulate the motion of atoms in a material resulting in structural modifications under given external conditions. Atomistic simulations using MD allows to simulate the dynamics of atomic motion under different conditions and therefore providing insights on plastic deformation mechanisms. MD simulations were performed in the studies presented in Publication **III**, in order to explain the difference in the

shapes of the blisters by specific behavior of dislocations within the FCC crystal structure.

We note that the MD method is notorious for its short timescales, which allows to follow the evolution of the atomic system only within a few nanoseconds. This excludes the long-term processes such as diffusion, which may take place on the scale of seconds and even minutes and hence require the use of longer scale computational methods. However, the good agreement between the experiments and the MD results obtained within this thesis confirms that the selected computational method is sufficient to explain the processes of H blistering implying a strong H trapping by vacancies generated during the H ion irradiation. More details are given in section 4.1.

The method is based on numerical integration of Newton's equations of motion for all atoms in the system resulting in new positions and velocities of the atoms at every time step depending on interatomic forces that are computed directly from the applied interatomic potential [72]. It is clear that the choice of the interatomic potential is essential for accuracy of the MD description of material's behaviour under a given external condition. Although there are many models, proposed for describe Cu-Cu interactions, in this work the Mishin embedded atom model (EAM) was used, since it was fit specifically to reproduce mechanical properties of Cu [73]. The forces and energies are computed using the interatomic potential, and based on this, the evolution of the system for the next time step is calculated [74]. Similarly, for H-H interactions an embedded atom model was used following the methodologies outlined in [75–77]. Given the low solubility of H in Cu [78], for simplicity of the model we used a purely repulsive ZBL (developed by Ziegler, Biersack and Littmark) potential [79] for Cu-H interactions. This potential limited the penetration of H atoms into Cu lattice, subsequently improving the efficiency of simulations of plastic deformations at the bubble surface. Further investigation of H-effect on mechanical response of Cu lattice on the H pressure within the bubble may add more details on the processes developed in the Cu-H interface, however, these processes are not within the scope of the present thesis.

Within a model, if atoms move too fast during a single time step, the accuracy of the simulation may be compromised while a very short one will increase computational costs. For this reason, the time-step should be chosen in a way that the simulated outcome remains unchanged for any smaller time steps. The pressure and temperature of the system are controlled using barostats and thermostats algorithms. The control of pressure within the bubbles is done by manipulating the concentration of H atoms in terms of number of H atoms per missing Cu atom. In the study all the cells were relaxed at 600 K adopting the Berendsen thermostat [80] and using a simulated time of 100 ps.

CHAPTER 4

Study of hydrogen implantation in metals

4.1 Formation of blisters

Hydrogen is a light gas well known for its ability to implant into solids. When considering conditions such as low energy irradiation, ion implantation in metals and the consequent bubbles formation are a concern for the material's integrity, inducing detrimental effects and changes on the mechanical properties [81] [82]. Studies made in [83] reported reduction in ductility in copper samples, along with formation of defects such as blisters, dislocations and voids. Blisters have also been associated with embrittlement [84], contributing to severe creep deformation [85–87]. Also, a review presented in [88] reports crack propagation to be associated with blister nucleation.

The theoretical understanding of blistering phenomenon is primarily grounded in the hydrogen diffusion process, trapping of hydrogen atoms, followed by the formation of high-pressure regions that can lead to macroscopic blistering on a metal surface. The latest is, therefore, a final stage, as long before becoming visible on a material surface, nanoscale H bubbles are found to form in a certain depth under the surface.

Blisters have been observed in metal's surfaces despite their crystal structure - some examples can be found in the following references for face-centered cubic (FCC) such as copper [83, 85, 89–95] and aluminum [52, 96–99], and body-centered cubic (BCC) such as iron [86, 87, 100] and tungsten [101–105].

As ions are implanted into the material, they diffuse and accumulate in certain regions. In the literature, the trapping of ions is consensually attributed to several lattice defects. Publications [106] and [93] highlight vacancies, impurities, material dislocations, interstitial loops as the main sources for accumulation and localization of hydrogen within the material. In [81], the role of grain boundaries is extensively studied, emphasizing that the segregation of H atoms in some grain boundaries are due to the larger volume defects at those interstitial sites.

Additionally, [85] attributes the fast growth of bubbles at grain boundaries, possible due to combination of vacancies with preferential diffusion along boundary planes.

Figure 4.1 illustrates the process of blisters formation in a polycrystalline material, since the formation of small voids until a protrusion is visible on the surface. At last, blisters caps can rupture, releasing gas and material detriments to the environment.

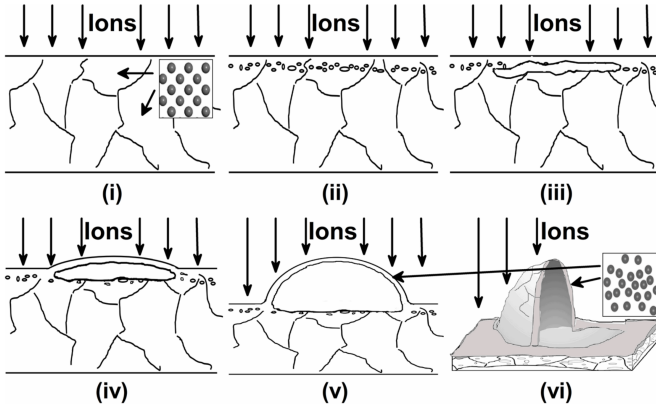


Figure 4.1: Illustration of blisters evolution under ion irradiation adapted from [104].

Hydrogen usually occupies interstitial sites present in the lattice, however ion irradiation can induce abundant vacancies in metals, providing more trapping sites for hydrogen atoms [107]. According to [108] one single vacancy in copper is able to trap up to six hydrogen atoms. As multiple H atoms can be trapped in a single vacancy, the apparent H solubility can be enhanced [84]. The accumulation of H within a monovacancy leads to its expansion, and the followed aggregation of closeby vacancies will lead to a hydrogen-vacancy cluster. The latter, may grow by absorbing more vacancies or coalesce with existing vacancy clusters. The preference for hydrogen to occupy vacancies over other lattice sites comes from the lower potential energy within the vacancy. Vacancies created during irradiation serve as energetically favorable trapping sites for hydrogen atoms - the binding energy of a hydrogen atom in a monovacancy in copper has been calculated to be about 0.24 eV [108]. The strong affinity of H with vacancies is presented in [109], where the vacancy formation energies and their interaction with H are studied for multiple FCC materials. Also, in a study addressing cluster formation via He implantation in tungstan [110], it is explained that cluster growth can be enhanced when an incident ion passes through the cluster and transfers partially some of its kinetic energy, making the cluster hot enough to push out a self-interstitial atom. The continuous trapping of hydrogen, and its

followed recombination as molecular hydrogen, stabilizes the cluster [111], leading to small bubbles with nanometric sizes [112] - typically called blistering initiation or pre-blister cavitation. The nucleation process and growing is explained in detailed in [111, 113].

The structures containing bubbles were first observed in [114], where depth dependence profiles were calculated. This initial phase, has been reviewed in [89], where the author reports different penetration depths for helium ions by different low energies irradiation, concluding that at certain depths blistering starts when the pressure of cavities reaches the yield stress of the material.

Blisters development is known to be dependent on ion fluence and temperature (different growth and distribution of bubbles, as a function of different range of temperature, has been observed in [85]). For the fluence of ions, the higher the fluence, the higher the number of trapped implanted atoms, which leads to pressurized gas inside the bubbles. The continuous coalescence of bubbles and increase of internal pressure, leads to a growth mechanism, towards the surface, based on plastic deformation. Over-pressurized bubbles, as a means of stress releasing from the walls of the bubbles, tend to punch out self-interstitial atoms from the material matrix, resulting in dislocations and dislocation loops. The dislocations motion has been reported to be emitted along the close-packed planes of the host matrix in the slip direction, meaning that blistering will grow differently in materials with different slip systems. The binding energy between hydrogen and dislocations is reported to be less in FCC than in BCC materials [115]. Studies made in [90] and [116] describe blister growth via dislocation emission along the 111 planes in $\langle 110 \rangle$ directions in copper.

Although several studies address blisters and microvoids observations by means of microscopic techniques, while some computational studies try to explain their development, there is still a lack of experimental evidences in the literature, to fully comprehend why these protrusions present on the same material cause different features on the surface.

There are some experimental indications showing a dependence of vacancies and blister formation with surface orientation. For example, in [52] blisters have been observed to grow in aluminum pillars preferentially in specific grain directions. Also, in publication [99] it has been identified variously shaped blisters on polycrystalline Al surfaces, dependent on the grain orientation during exposure to H_2 plasma. In [89], it is proposed that the variation in blister sizes across different surfaces may be linked to channeling directions that facilitate deeper ion penetration. Subsequently, our results in Publication **III** corroborate these findings, demonstrating that the size of blisters varies with surface orientation.

Regarding the materials chosen for testing, with prospects of a future RFQ, it was taken in consideration parameters such as hydrogen diffusion data. Diffusivity describes the interstitial diffusion flux of hydrogen atoms in a bulk material while solubility dictates the amount of hydrogen that the material can retain. In general, high H diffusivity helps in a more uniform distribution of hydrogen

throughout the bulk material. In addition, a high solubility is equally important, as surpassing the solubility threshold can lead to internal pressures that exceed the metal's tensile strength, often helping the development of blisters on the surface. The product of both parameters is expressed as the hydrogen permeability, i.e. it considers not just how much hydrogen can be absorbed, but also how quickly it can move through the entire material. Overall, copper alloys were selected to enhance mechanical properties of the RFQ candidate material compared to pure copper, to increase resistance to blistering, while the remaining alloys with higher permeability were chosen to emphasize its effect on H blistering.

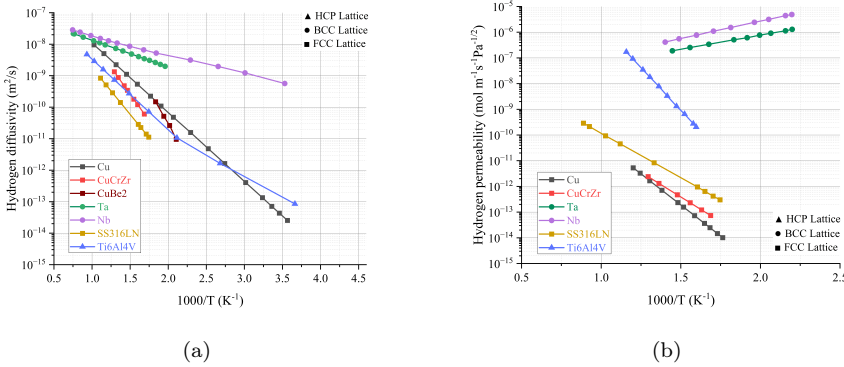


Figure 4.2: Compilation from multiple sources of hydrogen diffusivity (a) and hydrogen permeability (b) in function of reciprocal temperature, for different materials (Cu, CuCr1Zr, CuBe2, SS316LN, Ti6Al4V, Ta and Nb). From Publication **II**.

In the literature, hydrogen diffusivity values for different metals are obtained under controlled and standard conditions, based on factors such as temperature, hydrogen concentration and the intrinsic properties of the metal. In this sense, the coefficients for both hydrogen diffusivity and solubility in different metals will differ upon extreme environments such as irradiation, when many irradiation-induced defects appear [117].

Figure 4.2 shows a compilation of data extrapolated from different sources, representing the hydrogen diffusion and permeability in a material's bulk in function of reciprocal temperature, in a) and b), respectively. While these data don't take in consideration irradiation effects, it gives a baseline understanding of the material response to hydrogen implantation.

Ta and Nb are among the materials with the highest capabilities for hydrogen diffusion with the addition of good solubility. Ta has been reported as one of the materials with the highest resistance to blistering [118, 119]. In contrast, copper

exhibits a relatively low hydrogen diffusivity. Furthermore, the low hydrogen solubility further contributes to a very low overall hydrogen permeability.

When compared to pure copper, CuCr1Zr shows similar hydrogen diffusion characteristics and permeability values, as noted in [120]. Both Cr and Zr serve as strengtheners in the copper matrix, additionally they can also function as trapping sites for hydrogen atoms, which overall translates in an increased hydrogen solubility but decreased rate of hydrogen transport through the lattice and its mobility. The same principle applies with the addition of beryllium in CuBe2. Hydrogen accumulation in Be vacancies was studied in [121] where it was shown that these defects can be effective traps for hydrogen atoms. Titanium alloy stays in a middle term among all materials. The increase of hydrogen diffusivity has been associated with the V addition into the titanium base material [122]. Austenitic stainless steels present high content of elements with a complex chemical composition. SS316LN presents the lower diffusivity among the materials, however, has a high solubility [123]. Hydrogen permeation in different austenitic steels, reported in [124], explains that the hydrogen solubility correlates mainly with the main alloying elements. The presence of Cr and Mo tend to increase solubility, however this effect is not as large as in BCC materials. Body-centered cubic structures, as in the case of Ta and Nb, have in general more interstitial spaces when compared with FCC and hexagonal close-packed (HCP), which favors the mobility of hydrogen atoms.

4.2 Blistering on metal surfaces after low energy irradiation

As explained in section 3.2.2, irradiation was performed in the seven materials mentioned above. Among those, only Cu-OFE, CuCr1Zr and CuBe2 have shown hydrogen blisters visible on the surface while Ti6Al4V, SS316LN, Nb and Ta have shown no effects of blistering on the surface.

Figure 4.3 shows SEM images of copper and copper alloys cathode's surface, after exposure to H- low energy irradiation. For CuCr1Zr, blisters on the surface appear to follow the machining marks of the electrode, as seen in Figure 4.3 (a). This effect has been also seen in the other materials, however less evident, as for the case of CuCr1Zr, the impact region of the ion beam coincided with the center of the electrode, where the machining marks are more pronounced.

Overall, for both CuCr1Zr and CuBe2, blisters showed to have less density when compared with Cu-OFE, which is assumed to be an effect of the additional alloying elements. For Cu-OFE electrode, the shape of the surface blisters as well as their density appear to correlate with the shape of the grains, as seen in Figure 4.3 (c). In an attempt to further investigate these observations, additional studies were carried which are summarized in the next section. Moreover, the effects of

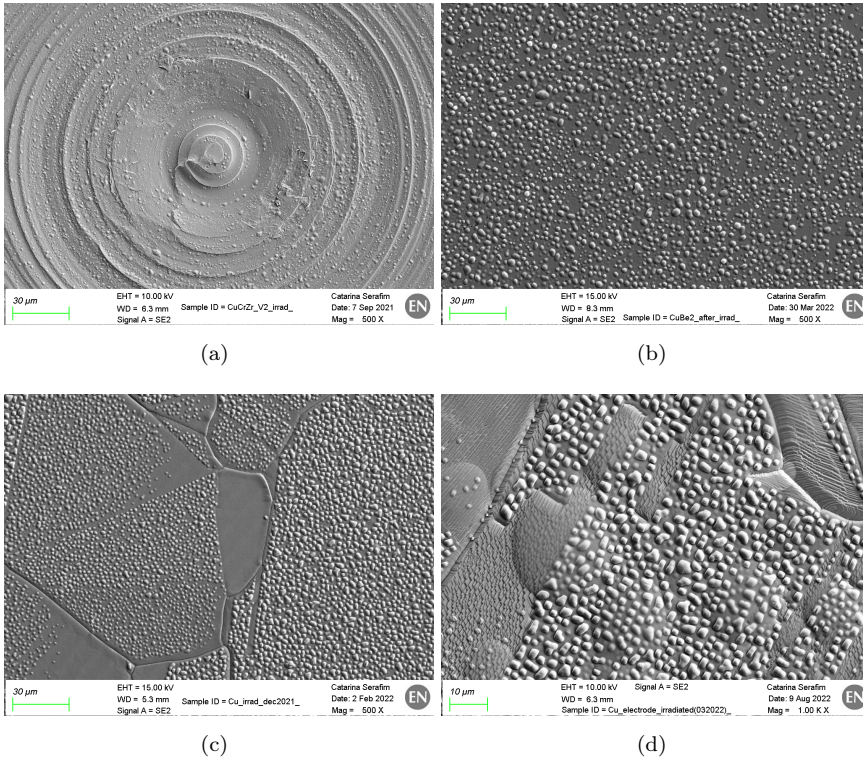


Figure 4.3: SEM imaging after H- 45 keV irradiation of different electrodes surfaces: CuCr1Zr in (a), CuBe2 in (b) and Cu-OFE in (c) and (d). While the same material, (c) and (d) are observations from two distinguished Cu-OFE cathodes.

irradiation when conducting tests with strong electric fields, in all materials, are discussed in the next chapter.

4.3 Blistering effects on irradiated copper samples

4.3.1 Sample testing and observations

A sample made of Cu-OFE was used to further investigate the blistering effects on copper surfaces, which have been reported during the copper electrodes study in Publication I. For this purpose, Electron Backscatter Diffraction (EBSD) technique was used to perform a mapping of the crystal orientation of the copper grains in the center region as illustrated in Figure 4.4. EBSD was done in multiple steps, by performing individual surface mappings, each one with a length of 4.2 mm, high of 2.6 mm and a step sizes between 4 and 10 μ m. Afterward, the same sample was used as a target for irradiation with 45 keV beam of H ions,

resulting in a deposition dose of approximately $1.3 \times 10^{19} \text{ H}^-/\text{cm}^2$ at the high fluence area, imitating the extensive H^- irradiation exposure of the surfaces of the RFQ structure.

The beam was successfully targeted in the region of interest, allowing to study the effects of hydrogen implantation in the different copper grains, previously indexed in terms of crystallographic orientation. Optical microscope was used to image the surfaces pre and after irradiation and find the grains of interest. A Zeiss Crossbeam 540 Focused Ion Beam (FIB) incorporated with a Scanning Electron Microscope (SEM) was used to mill the sample in different spots in order to obtain a cross-section of specific grains.

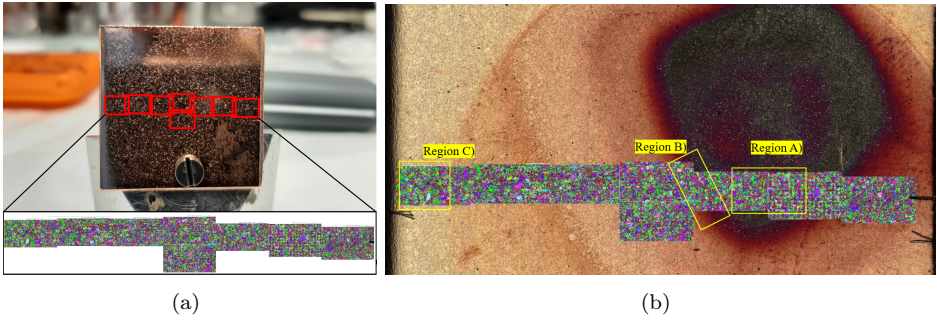


Figure 4.4: (a) Copper sample before irradiation, showing the location where EBSD analysis was done. (b) Optical figure obtained by optical microscope using 50x lens, after irradiation. The darkest contract in the sample shows the highest deposition of particles coming from H^- ion beam. Additionally, the EBSD mapping was overlapped to the correspondent grains. Here 3 regions of interest are highlighted: region A: high fluence; region B: transition region and region C: far away from irradiated spot.

Two areas with different ion beam exposure, i.e. different distances from the center of the beam, were chosen to observe the effect of the H^- exposure on the bubble growth in the sample. The first region, corresponds to the surroundings of the core beam, i.e. region with lower fluence, which has been called transition zone (region B in Figure 4.4). And secondly, a high-fluence irradiation area corresponding to the highest deposition of particles (region A in Figure 4.4). At last, a region outside the irradiation targeted spot was also analyzed for comparison (region C in Figure 4.4).

Figures 4.5 and 4.6 show observations taken in the transition and higher fluence regions, respectively. Analysis were focused on the three preferential low index orientation grains marked in the map with blue (100), red (111) and green (110).

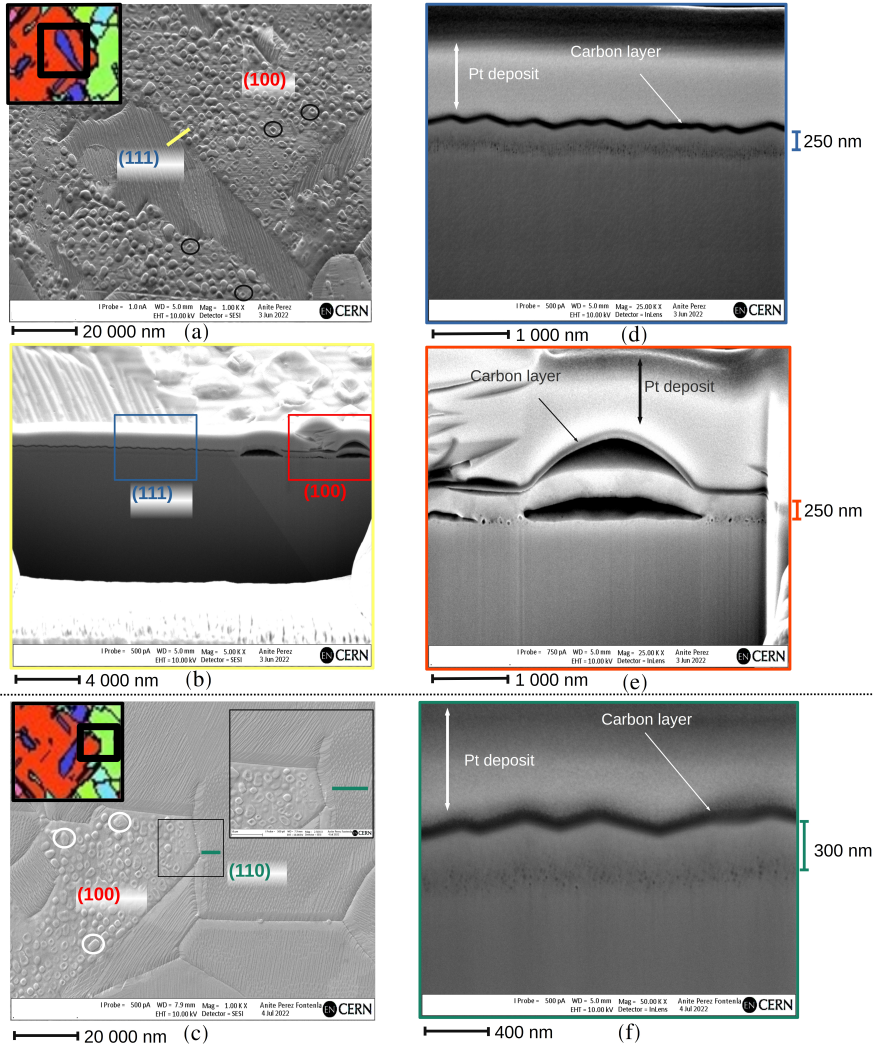


Figure 4.5: SEM images of the irradiated copper surface. (a) The surface of two grains is marked as (111) and (100) and a yellow line marks where the cross-section was performed. Black circles mark some of the dimples. (b) Cross-sections of the two grains (111) and (100) - corresponding to the yellow line in (a), shown in Figures (d-e) respectively. (c) Surface of the two grains marked as (100) and (110). (f) Cross-section of a (110) grain in the transition area shown in (c) by a green line. The areas shown in the cross-sections are marked in red, blue and green for (100), (111) and (110), respectively. The horizontal dashed line separates the two different regions explored at the transition area. A protective layer of platinum (Pt) was deposited on the regions of interest prior to cross-sectioning to preserve the surface integrity and minimize topographical artifacts. From Publication **III**.

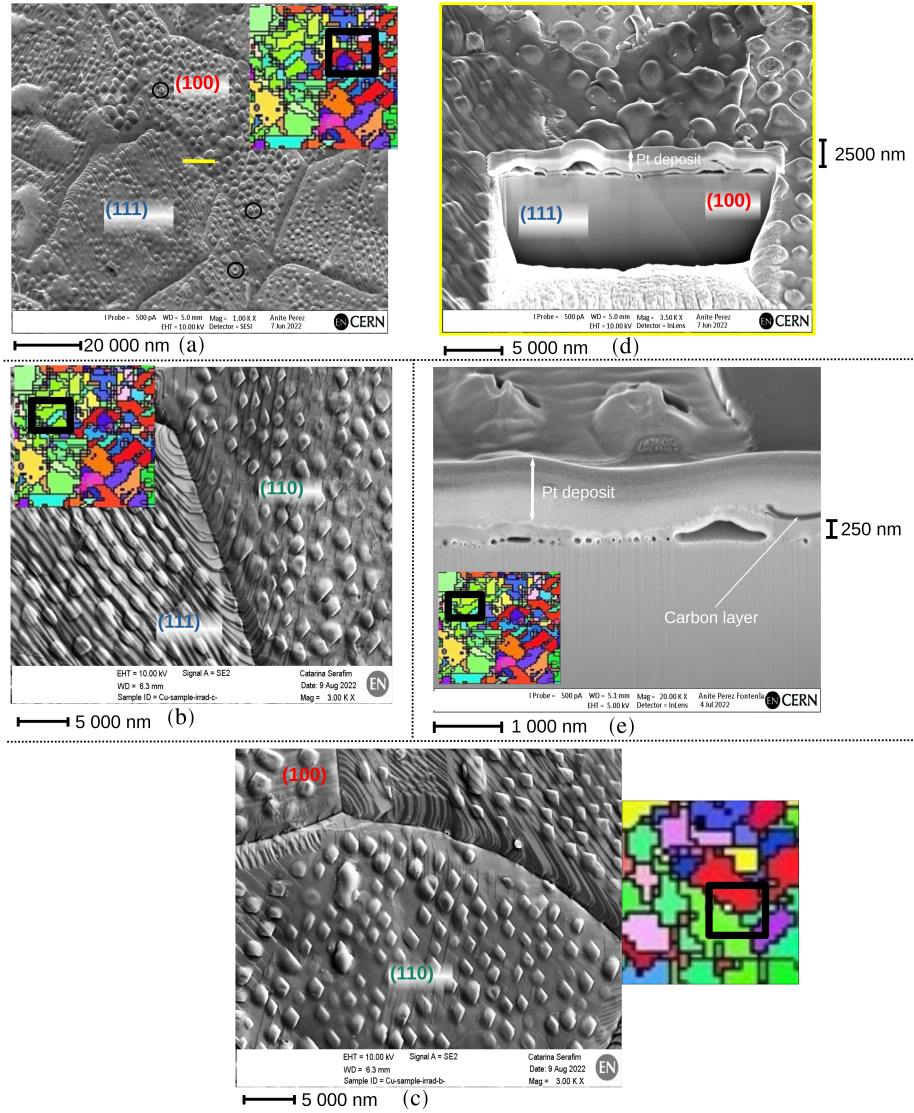


Figure 4.6: SEM images of the irradiated copper at the high fluence area. Surface of two grains explored: (a) (111) and (100), (b) (111) and (110) and (c) (100) and (110). Cross-sections of the two grains (d) (111) and (100), and (e) (110). Vertical and horizontal dashed lines separate the three different regions explored at the high fluence area. EBSD maps of the regions explored can be found in insets of (a), (b) and (c) respectively. From Publication III.

In Figure 4.5 (a) we can see two distinct grains, one with a crystal orientation of (111) and a neighbor with a crystal orientation of (100). In (100) grain blisters are observed well developed in the surface, whereas the (111) and (110) no blisters were identified. These observations were not exclusive to those grains, but generally observed in all the transition regions. Figure 4.5 (b) highlights the specific regions between (111) and (100) grains, with blue and red squares that are magnified in Figures 4.5 (d) and (e), respectively. It was concluded that for both (111) and (100) the initiation phase, the voids start to accumulate beneath the surface at the same approximate depth (250-295 nm). In the (100) grain, these bubbles appear more developed, with some growing significantly larger than others, as detailed in the zoomed-in image of Figure 4.5 (e), resulting in large blisters on the surface. Contrastingly, the bubbles formed in the (111) grain remain in a stage of nanometric scale (between 1 and 10 nm) as shown in Figure 4.5 (d). Meanwhile, the green line in Figure 4.5 (c) marks the cross-sectional view location for the (110) grain. Also, in this grain no blisters have developed further to the surface. However, the initial bubbles beneath the (110) oriented grain have been observed with smaller size and located deeper, at depths of 305 and 335 nm - Figure 4.5 (e).

Figure 4.6 shows the surface with different grain orientations in the region with high irradiation fluence. The zoom-out view of this region in Figure 4.6 (a) highlights again the grain (100) with well developed blisters, and contrarily from what we have seen in the transition region, now the grains (111) and (110) - Figure 4.6 (b) - are seen also with blisters already developed in the surface quite uniformly. We observe again the appearance of small bubbles, that are likely to be the nucleation sites of the large blisters, however, in the high fluence area, the bubbles in the three oriented grains have developed further. The cross-sectional view in Figure 4.6(d) shows bubbles for (111) and (100) grains, forming at a similar depth (approximately 270–280 nm beneath the surface), as in the lower fluence transition area. Qualitative analysis of these grains shows a difference in the shapes of the blisters grown on the two explored grains. While on the (100) grain the blisters have the 90 degree vertices, showing square-like forms, the blisters on the (111) grain are more round, with occasional formation of some better-defined vertices. For (110) grains, the blisters appeared with a clear diamond or rhomboidal shapes, as observed in Figure 4.6 (b) and (c); and the formation of small bubbles within a range of 210 and 330 nm.

4.3.2 Atomistic insights

Experimentally it was consistently observed the formation of blisters with different shapes, for each of the three different orientations along the surface.

Molecular dynamics simulations have successfully reconstructed the process of H bubble growth in a copper lattice. The results showed to be in agreement to what is seen experimentally, where the different shapes have been attributed to

the oriented grains yielding differently under the pressure built up in the formed bubbles.

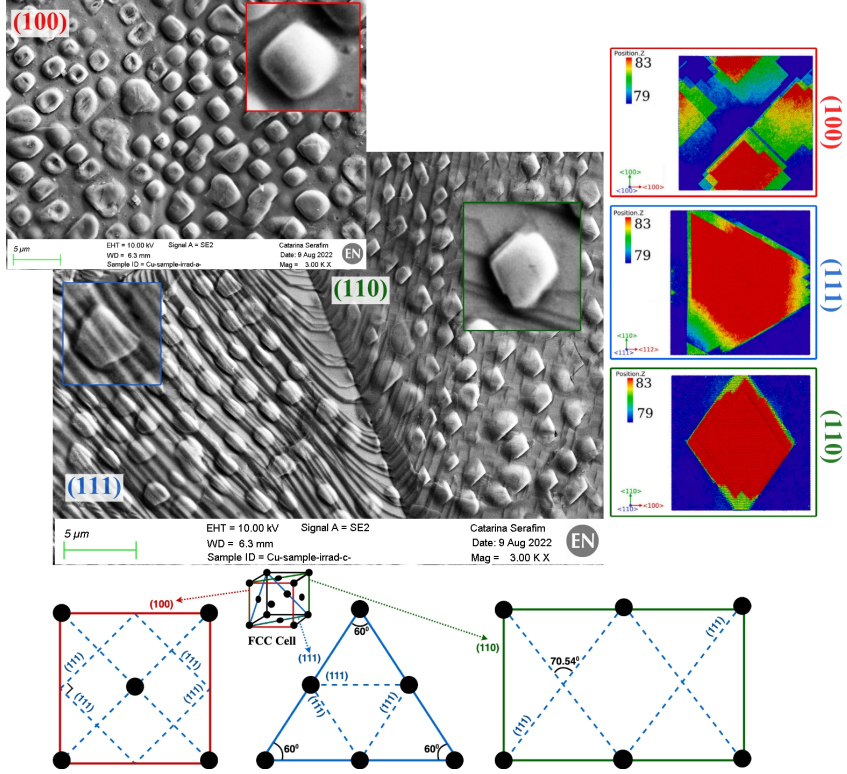


Figure 4.7: Left: SEM images of three surface grains with (100), (111) and (110) orientation showing blistering after H- low energy beam irradiation. Right: MD simulation of cell surfaces top view oriented as (100), (111) and (110) showing different shape's protrusion. Atoms are colored according to their z position in Å. Bottom: schematic of the (111) planes projected (dashed blue lines) on (100), (111) and (110) surfaces. Adapted from Publication III.

Figure 4.7 on the right, shows the top views of the Cu surfaces for the three orientations. The different shapes are explained by the emission of dislocations from the bubble surface along the (111) planes in $\langle 110 \rangle$ directions. For a better visualization, on the bottom of Figure 4.7 it can be seen an FCC unit cell, with the projection of the three planes. Overall the dislocations are forming along the closed-packed plane which intersect the (100), (111) and (110) planes in the form of a square, triangle and rhomboid shape, respectively.

The most remarkable observation was the different times of growth of blisters in regions with different ions fluence. In the transition region, while voids were observed beneath the three orientations, only the bubbles under the (100) surface resulted in well-formed blisters on that surface and no blisters were seen in (111)

or (110) grains. Moreover, in the high fluence region, blisters appear on the surface in all three oriented grains, and with higher density in (100) surfaces. The studies corroborate a direct dependence of ions fluence with blister growth. Additionally, the conclusion that the growth of bubbles is dependent on grain orientation, suggests that the channelling directions in the different surfaces can induce different penetration of the ions.

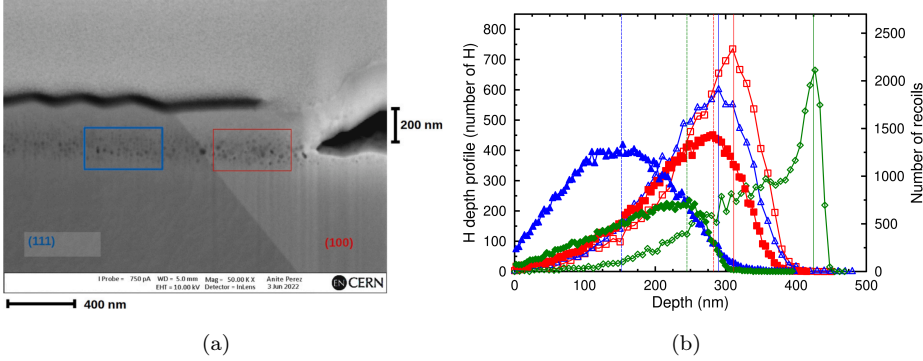


Figure 4.8: (a) FIB cut showing a grain boundary between (111) and (100) grains at the transition area. (b) Simulation using MDRANGE for the H depth profile (open markers) and distribution of recoils with energy above 40 eV (filled markers) for (110) (green), (111) (blue) and (100) (red) grains, as a function of depth. The vertical lines in different colors mark the maximum of each distribution, accordingly. From Publication III.

As discussed, hydrogen atoms are known to accumulate in the vacancies, which can grow larger clusters during prolonged ion irradiation. Vacancy distribution profile for the three orientations has been simulated externally from the author's work (Figure 4.8 (b)).

In these simulations, we observed remarkable difference in the penetration depths of H ions as well as in the vacancy depth distributions in differently oriented grains. The vacancy profiles were estimated from the corresponding recoil generation depth profiles, i.e. the profiles that included all primary knocked-on atoms (PKA) with the energy larger than 40 eV. The threshold energy was selected sufficiently high to produce at least one vacancy. As it is seen in Figure 4.8 the strongest overlap of H ion penetration and the vacancy depth profiles is observed for the grain with the (100) surface orientation. As both profiles practically fully overlap, one can conclude that this leads to the fastest bubble growth under this surface. Additionally, the overlap profiles for (111) and (110) surfaces are much smaller, indicating that only a small part of the implanted ions reached the created vacancies. As such, blister formation in those directions will take longer time to be formed. In summa, the larger the difference between the formation

of vacancies and the H depth profiles, the more fluence is needed to blister the grain.

CHAPTER 5

High pulsing tests on different metals with and without irradiation exposure

5.1 Surface conditioning of electrode materials

The results for all the tested materials in the Large Electrode System are summarized in this chapter. The main focus was to compare the maximum steady state electric field that was reached during the conditioning experiments for each of the studied materials, for the cases of irradiated and non-irradiated pairs. As discussed in 4.1, the tested materials were chosen aiming for the improvement of resistance to blistering upon H irradiation and understand if irradiation exposure would have an effect in respect to materials reaching high gradient surface electric fields.

More information regarding each conditioning along with breakdown positioning images, after testing, can be found in Publications **I** and **II**. Below, the conditioning plots are represented by blue dots and green dashes, respectively, for the electric field and respective numbers of breakdowns for the non-irradiated electrodes. The red dots and cyan dashes have the same representation but for the irradiated electrodes. The electric field values and number of breakdowns can be read on the left and right vertical axes, respectively; while the number of pulses during conditioning is shown in the horizontal axis.

Copper (Cu-OFE) and Copper Alloys (CuCr1Zr and CuBe2)

Non-irradiated copper electrodes have reached a stable field of 80 MV/m. Irradiated electrodes - marked in Figure 5.1 as "Cu Irrad I" - were the first pair of electrodes submitted to irradiation. In this case, that pair reached the same field as the non-irradiated. The results show that irradiation effects on the material had no significance in how the material was able to reach a higher gradient, except for the fact that the number of breakdowns at the end, was approximately

four times higher for the irradiated electrodes comparing with the non-irradiated ones.

Discovery of contamination during irradiation, which will be discussed later in this chapter, have proven to be detrimental for the electric field withstanding capabilities of many materials, however this type of contamination was not present on the first copper irradiated electrodes, which explains their good performance closely comparable with the performance of the non-irradiated copper pair. For this reason, later, in our studies, the process of irradiation and testing a new set of copper electrodes was planned, and the results can be observed in Figure 5.1 marked as "Cu Irrad II". In this case, copper electrodes were able to reach a stable electric field of only 23 MV/m.

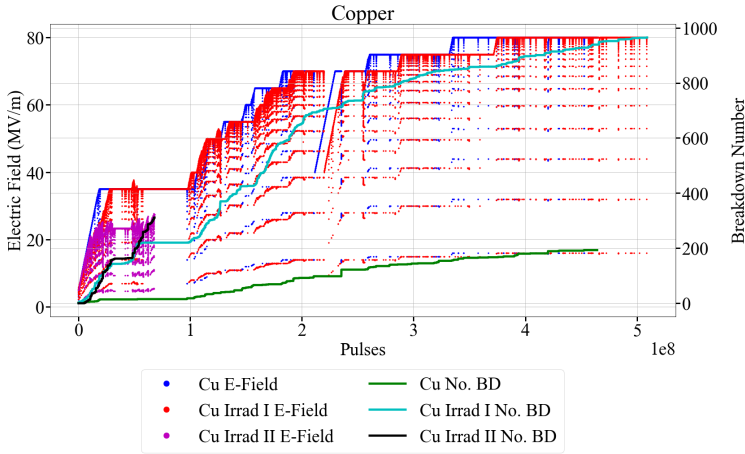
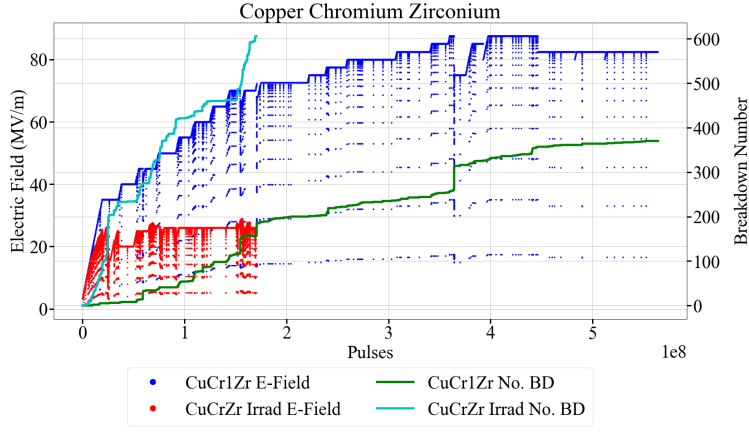
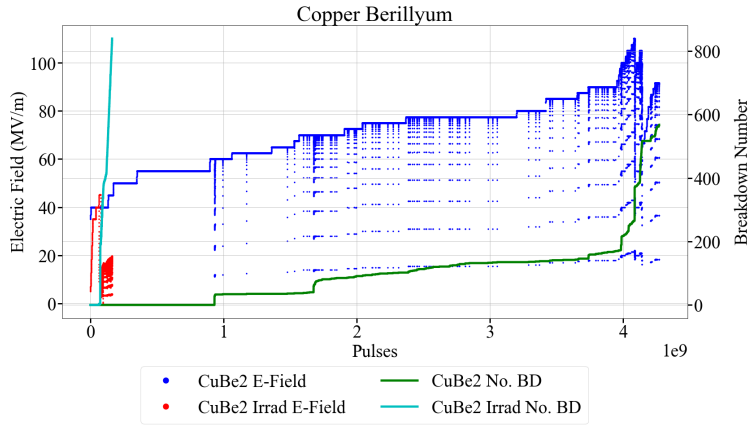


Figure 5.1: Conditioning of the irradiated and non-irradiated pairs of copper electrodes. Adapted from Publication I.

Non-irradiated electrodes of copper alloys had slightly better results than copper electrodes. Copper chromium zirconium had a similar behavior as in the conditioning of copper, reaching a stable surface field of 82.5 MV/m, while copper beryllium had the best value among the three, with a stable electric field of 90 MV/m. Still, for copper beryllium, the maximum electric field has reached the value of 110 MV/m, a field that was not possible to hold due to the sudden appearance of breakdowns clustering in a single location. In contrast with the good results for the non-irradiated copper alloys, the irradiated electrodes presented a very difficult conditioning by presenting a large number of breakdowns and not being able to surpass the surface fields of 29 MV/m and 45 MV/m, for CuCr1Zr and CuBe2, respectively.



(a)



(b)

Figure 5.2: Conditioning of the irradiated and non-irradiated pairs of (a) copper chromium zirconium and (b) copper beryllium electrodes. Adapted from Publication **II**.

Titanium Alloy (Ti6Al4V)

Titanium alloy electrodes have reached a maximum electric field of 110 MV/m. However, the material seemed to present a tendency for breakdowns clustering at these fields. To avoid material's damage, the voltage was reduced, which led to reducing of a stable electric field to the value of 100 MV/m. A decrease of breakdown performance was registered for the irradiated pairs. The irradiated Ti6Al4V electrodes presented the best value, among all irradiated materials, reaching a stable electric field of 90 MV/m.

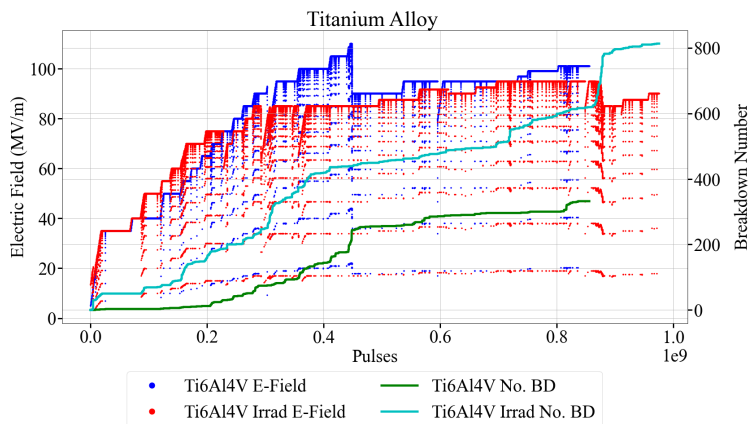


Figure 5.3: Conditioning of the irradiated and non-irradiated pairs of Ti6Al4V electrodes. Adapted from Publication I.

Stainless Steel 316LN (SS316LN)

Stainless steel non-irradiated electrodes were the best conditioned material by sustaining the highest electric field of 120 MV/m. Additionally, no cluster of breakdowns was observed during testing, resulting in a uniform distribution throughout the electrodes surface. For the irradiated pair, the performance was half of what was achieved by the non-irradiated electrodes, with a maximum electric field of 62.5 MV/m.

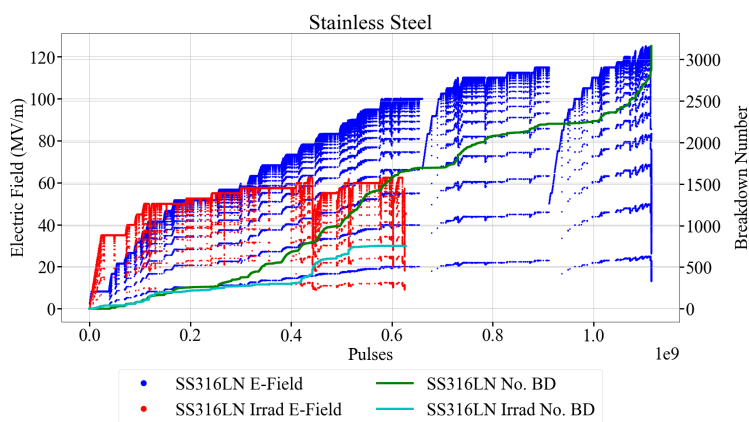


Figure 5.4: Conditioning of the irradiated and non-irradiated pairs of stainless steel electrodes. Adapted from Publication II.

Niobium (Nb) and Tantalum (Ta)

In terms of non-irradiated electrodes, niobium material was able to reach a stable electric field of 80 MV/m with no visible cluster on the surface during the conditioning curve. Tantalum was the material with the smaller performance reaching only 60 MV/m. For both materials, the irradiated pairs had a significant difference when compared with their non-irradiated pairs. For Nb electric field stabilized approximately at 20 MV/m while for Ta it stabilized at 24 MV/M.

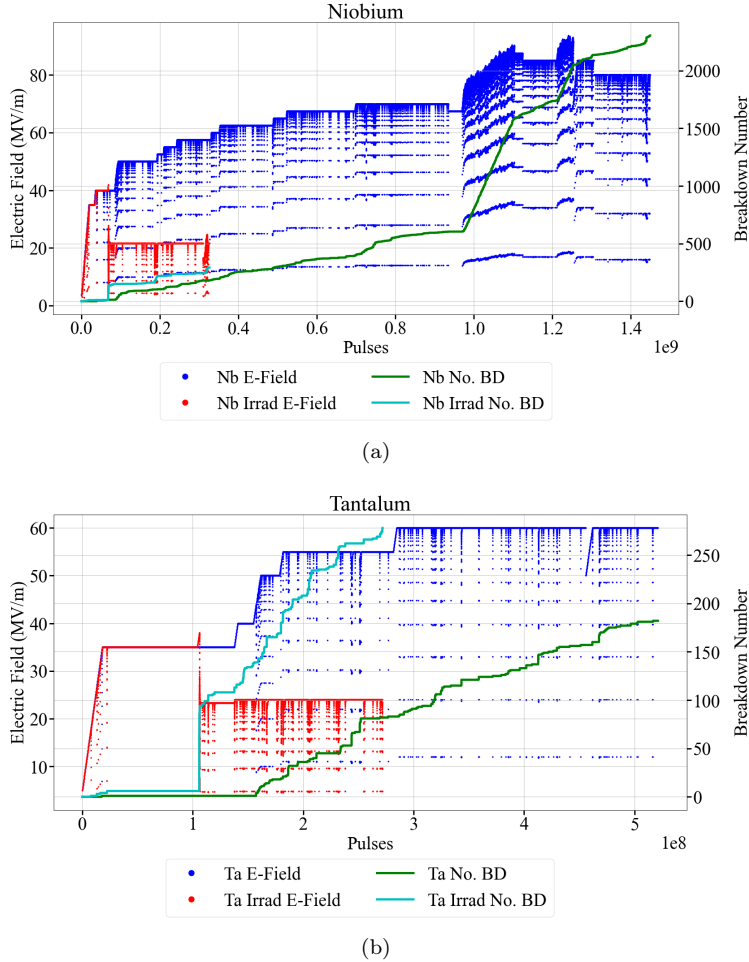


Figure 5.5: Conditioning of the irradiated and non-irradiated pairs of (a) niobium and (b) tantalum electrodes. Adapted from Publication I and II.

5.1.1 Surface Analysis

Microscopic observations, show a breakdown event in the form of a crater on the surface, with splashes of melted material in their surrounding. Topographic features are common for all materials, while the size of the breakdowns is dependent on the applied voltage, with diameters ranging approximately from 1 to 500 μm . For all the non-irradiated materials, the positioning of breakdowns after LES testing, is uniformly distributed throughout the surface of the electrodes, showing no preference for specific locations, however it was observed that when increasing voltage levels too quickly clusters of breakdowns can occur.

Regarding, irradiated electrodes, blistering in the surface of the cathodes after irradiation, was observed, using SEM, in all copper and copper alloy materials, while Ti6Al4V, SS316LN, Nb and Ta did not present any blisters on the surface or any indication of hydrogen implantation damages. However, for all the irradiated pairs, the breakdowns locations after the high voltage pulsing tests, were observed to be localized, with higher density, preferential near and inside the irradiated regions. Such behavior, has been successfully linked not to irradiation damages, but from carbon contamination coming from the irradiation procedure.

In the beginning of the project, the hypothesis that blistering in the surface could be correlated with the breakdown appearance was firstly disproved by analysis made on the first irradiated copper (marked as Cu Irrad I, in Figure 5.1). In this electrode, the irradiation didn't manifest any problems in terms of conditioning of the material. In fact, the distribution of breakdowns in the surface don't seem to have any correlation with the targeted region, as seen in Figure 5.6.

Figure 5.6 shows SEM images, with different magnifications, taken in the irradiated cathode region after LES tests on 'Copper Irrad I' electrodes. In Figure 5.6 (a) the more bright area corresponds to a part of the surface which is covered by blisters. Additionally, the breakdowns show a good dispersion, with no preference to the blistered region. Figure 5.6 (b)-(d) show a vacuum breakdown with an approximate diameter of 150 μm , presenting splashes of molten material. Also, in Figure 5.6 (d) it is visible that the breakdown strength has provoked the explosion of the nearby blisters, which is a common observation to all blistered materials.

In contrast, the latest irradiated copper presented significantly lower performance. As seen in Figure 5.1, the pair "Cu Irrad II" only reached 23 MV/m, and breakdowns were mainly located within the irradiated region. The difference between these two irradiated copper electrodes, has been attributed to small percentages of carbon on the first irradiated copper surface, which allowed those electrodes to reach high electric field. In the first year of research and after the first irradiation was performed, modifications were done in the irradiation set-up used for this project, resulting in a poorer vacuum, over which the author did not have any control. The changes have provoked an increase of hydrocarbons and carbon contamination compared to the first experiment, however the upgraded

set-up was set to more truly mirror the current LINAC4. In this sense, despite the identified carbon contamination, the followed results present to be more relevant as they better represent real operational conditions.

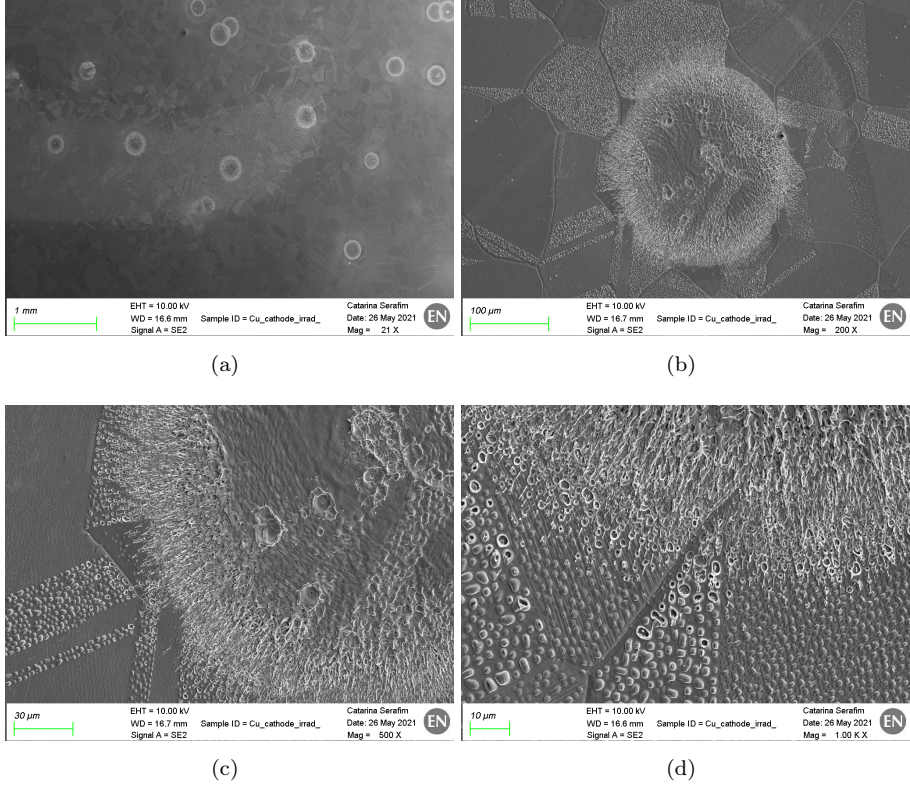


Figure 5.6: (a) SEM imaging, using secondary electron detector, showing partially the irradiated zone which corresponds to the less dark zone (effect caused by blistering) and some of the breakdowns provoked by the high energy pulsing. (b) - (d) SEM imaging with different magnification, using secondary electron detector, showing a breakdown in the transition zone of the electrode. From Publication **I**.

The bad performance of the irradiated pairs was concluded to be due to the presence of carbon in the cathodes surface. EDS analysis made before and after irradiation concluded that carbon contamination happened during the irradiation procedure, and it was consisted in almost all irradiations. While it was not found at the irradiation set-up a contamination source, it is believed that the contamination happens from the beam-induced cracking of the hydrocarbons adsorbed on the surfaces, resulting in deposition of carbon on the targeted regions.

FIB cuts made in the copper sample, discussed in Section 4.3, showed that the

carbon layer present above the bulk surface is in order of the 60 nm for the region with higher deposition of particles. The value of this thickness seems to decrease as we move further away from the main region, as showed in Figure 5.7, until no carbon is detected outside the irradiated zone.

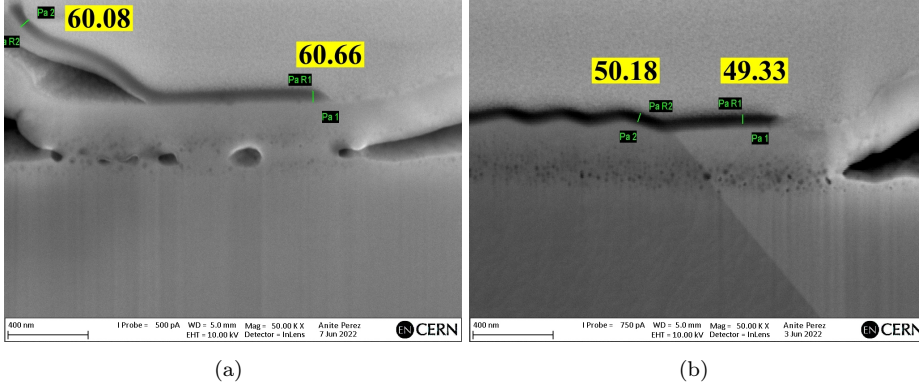


Figure 5.7: Measurements of the carbon layer's thickness present in the copper sample in Section 4.3. Image (a) refers to the region with the higher deposition of H- particles, and (b) to the transition zone.

The presence of carbon as a visible layer, detected using SEM, was observed in copper, copper beryllium and copper chromium zirconium, with all three materials presenting the same behavior, in terms of breakdown occurrence. For Ti6Al4V, SS316LN, Nb and Ta, the carbon was not observed on their surfaces using SEM, however similar quantities of carbon were detected by chemical analysis. These observations are explained by the affinity of these materials in forming carbides, i.e. incorporating carbon into its surface structure rather than forming a distinct layer. On the contrary, copper and copper alloys have lower affinity for carbon atoms allowing them to accumulate on the surface and form a visible layer.

To some extent, the carbon layer presented on the surface seems to act as a protective coating against vacuum arcing, as no breakdowns were found in locations where the carbon layer was still intact. Breakdowns were then observed to have a preference in concentrating in locations where the fragile layer of carbon was cracked and partials of raw surface were exposed. This effect is very well visible in CuBe2 electrodes, presented in Figures 11-13 - Publication II.

The continuous occurrence of breakdown clustering in these restricted exfoliated regions (regions that became free from C), has been identified as the reason preventing to further condition the material's surface to higher electric fields.

Additionally, the size of BDs encountered were in the order of a few μm which is due to the lower voltages applied and possibly due to breakdowns losing energy

when encountering carbon, translating in a smaller impact marks on the metal surface underneath.

The presence of a non-uniform carbon layer in the electrodes surface, was correlated with a consistent reduction in surface electric field for all materials, together with an increase of breakdown clustering in the regions where the layer was damaged. With the purpose of reducing carbon levels in irradiated electrodes, plasma treatment, using pure O₂ (99.999%), was used to clean electrodes after irradiation and before high voltage tests. Results are summarized in the section below.

5.2 Results on the effects of Oxygen Plasma Treatment

With the purpose of addressing the feasibility of Oxygen Plasma Cleaning (OPC) for the removal of carbon, new electrodes of Cu-OFE and SS316LN were machined and exposed to H- irradiation. Afterward, electrodes were submitted to new conditioning studies, to assess if irradiated and free from carbon contamination surfaces could achieve similar electric fields as the non irradiated surfaces. In order to identify the correct duration of treatment, a pilot test was performed in CuBe2 electrodes, where the treatment was divided in various stages, to be able to assess carbon levels using chemical analysis. The observations in regard to this study can be found in Publication **IV**.

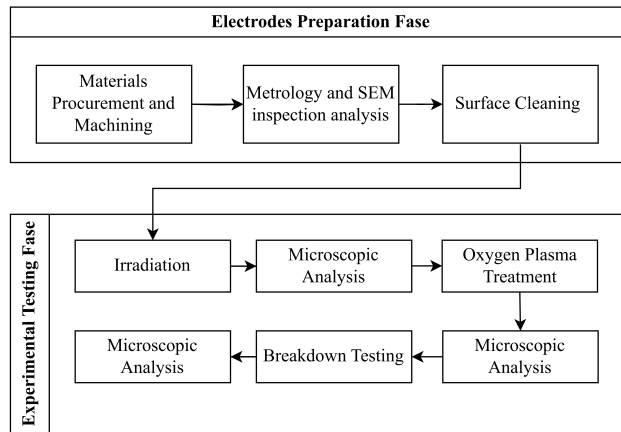


Figure 5.8: Diagram showing the process of electrodes preparation before testing and the different stages during experimental testing, including the new step with oxygen plasma treatment.

OPC showed to be an effective method to remove carbon, allowing to reach percentages of carbon acceptable for ultra-high vacuum applications. After the

treatment, electrodes of Cu-OFE and SS316LN were mounted on the LES system and tested for electric field performance. The new sequence of preparation and testing are represented in the schematic of Figure 5.8. The results for the conditioning tests are shown in Figures 5.9 and 5.10, for Cu-OFE and SS316LN, respectively.

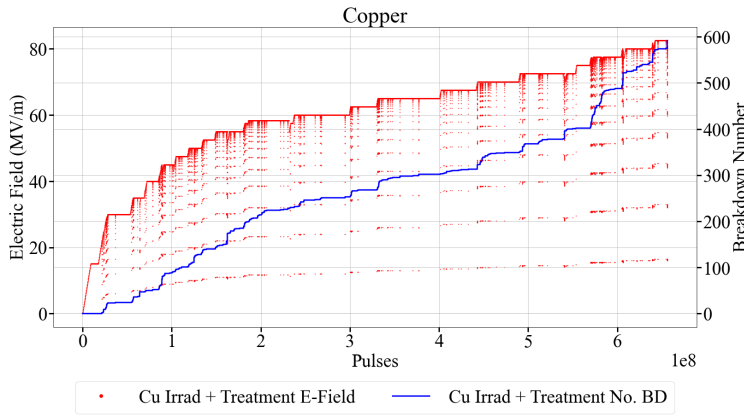


Figure 5.9: Conditioning of the irradiated and plasma treated copper electrodes.

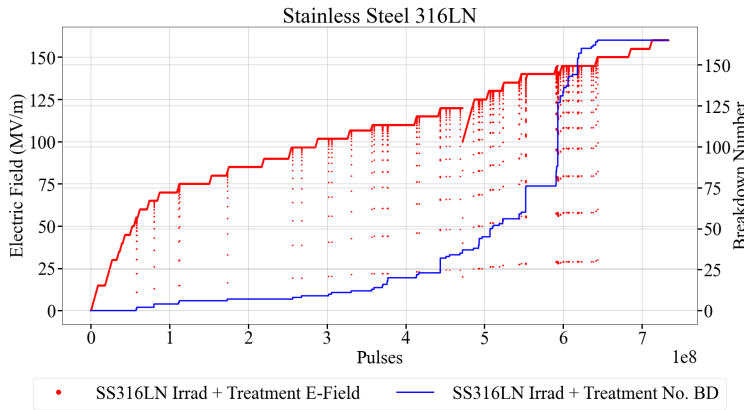


Figure 5.10: Conditioning of the irradiated and plasma treated stainless steel electrodes.

For Cu-OFE, electrodes were able to reach the mark of 80 MV/m, which is comparable with the result obtained for the non-irradiated pair. Moreover, surface analysis showed no evidences of detrimental effects caused by irradiation or plasma treatment.

For SS316LN, the maximum and stable field achieved by the irradiated and plasma treated pair was 160 MV/m. This result shows to be above the maximum electric field reached by the non-irradiated stainless steel electrodes (120 MV/m), meaning that the plasma treatment had an additional effect on the surface, enhancing its capability to sustain higher voltages.

In order to better understand the implications of OPC after irradiation in stainless steel surfaces, dedicated samples were prepared, irradiated and treated with plasma with the same parameters used for the electrodes. These experiments were planned with the purpose of performing additional studies comprehending X-ray Photoelectron Spectroscopy (XPS), taken that its chamber has limited geometrical dimensions, and therefore unable to further study the electrodes.

The XPS results confirmed the removal of carbon induced by the reactive oxygen species in the plasma, corroborating the carbon measurements done by EDS after the treatment. The study has demonstrated that activated oxygen species from the plasma can react with carbon atoms at the surface or break Fe–C and Cr–C bonds to form volatile CO or CO₂, assuring the effective removal of the carbon and the hydrocarbon molecules. Simultaneously, Fe and Cr surface atoms seem to react with oxygen atoms, leading to an increment of the oxidation state of those elements. Results also show that oxygen plasma treatment has further oxidized the non-irradiated sample, when compared with the irradiated one. This is attributed to the fact that for the irradiated region, oxygen species will firstly interact with the carbon before reacting with the bulk material.

The XPS analysis made on this sample showed that the formation of an iron and chromium oxide must have been present on the SS316LN electrodes before installation for breakdown tests. The surface modification has been attributed to be the cause of improving electric field capabilities, by allowing those electrodes not only to reach the highest electric field value, among all the tested materials, but also has made possible to reach those values with the accountability of very few breakdown events - approximately 5% of the total number of breakdowns when compared to the non-irradiated electrodes. More studies will be required to elucidate the effect of oxidation on the dielectric insulation of electrode materials.

The results, in terms of electric field achieved, when tested with LES system are summarized in Figure 5.11, accounting for all the results presented for the non-irradiated, irradiated and irradiated followed by oxygen plasma cleaning electrodes.

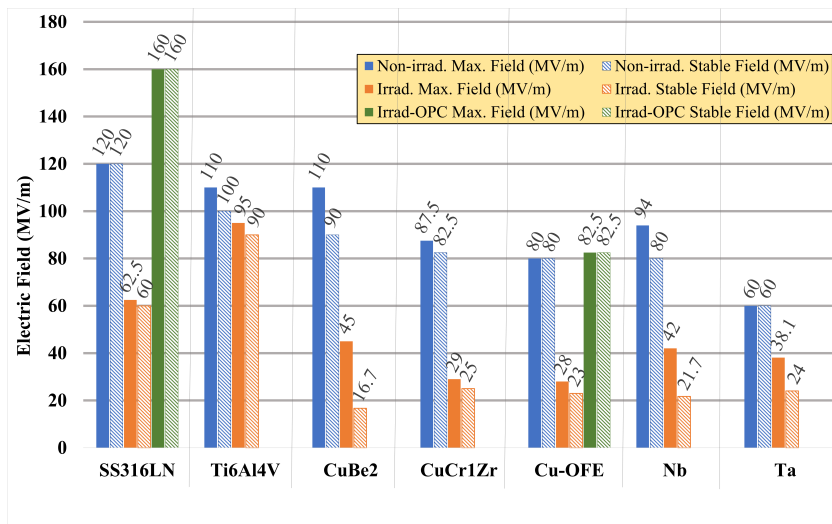


Figure 5.11: Bar plot showing the results for all the tested materials in the LES system, including the results for oxygen plasma treated electrodes. The non-irradiated materials are shown in blue, the irradiated materials in orange and the irradiated and plasma treated in green. The solid and dashed bars correspond to the maximum and stable electric field reached by each material, respectively.

CHAPTER 6

Summary and Outlook

All the milestones of the doctoral project have been fulfilled, with the successful completion of the experimental tests in all proposed materials, both in terms of irradiation and breakdown studies. In terms of non irradiated materials, it was concluded that stainless steel presented the best behavior by achieving stably, the highest surface electric field (120 MV/m). The materials, niobium, copper chromium zirconium, copper beryllium and titanium alloy presented satisfactory results with stable electric fields between 80 and 100 MV/m, values slightly above the ones reached by Cu-OFE electrodes. Taking into consideration that Ti6Al4V has lower thermal and electrical conductivities than copper, a careful design and a more complex assembly process would be required if used for an RFQ. The latter is also true, for niobium and tantalum, which had the more difficult machinability among all materials, making those not ideal for the manufacturing of precise structures. Additionally, tantalum has resulted in the lowest stable operational electric field, reaching only 60 MV/m.

If a material replacement for a future RFQ would have to be chosen, and taking only in consideration breakdown performance, the conducted research suggests that stainless steel would be the material of choice. Also, when compared to the titanium or the copper alloys, SS316LN presents an easier machinability, a wider and more consistent supply availability and is more cost-effective, both in terms of material price and machining expenses. Nevertheless, if one would take in larger consideration thermal and electric conductivity, CuBe2 and CuCr1Zr would both be good candidates with electric field performances above the copper material and with the addition of having higher strength.

For the irradiated materials, all have presented a big decrease in performance when compared with the non-irradiated electrodes. The presence of blistering, as shown on copper and copper alloys, does not seem to have a correlation with the breakdown triggering, nor an effect on the maximum electric field reached. However, it was concluded that such reduced performance is instead associated with carbon, observed on the cathodes' surface after irradiation. The final electric

field achieved in electrodes contaminated with carbon is highly affected by its presence, when comparing with the performance of electrodes that have not been irradiated and free from carbon contamination.

Carbon contamination was identified as a root cause during the thesis work, and its role was not anticipated in the thesis initial planning. The identification of carbon upon hydrogen ions low energy irradiation, and the consequent low performance in terms of electric field achieved, independently on the material used as a target, presents to be a major concern for accelerating structures. As such, oxygen plasma technique was tested as a carbon removal technique. The study concluded to be successful in cleaning contaminated electrodes. The treatment of copper and stainless steel irradiated electrodes, successfully decreased the presence of carbon to levels acceptable for ultra high-vacuum applications. Moreover, when tested on the LES, Cu-OFE showed electric field capabilities similar to surfaces that have not undergone irradiation beforehand, assuring that irradiation exposure and hydrogen blistering do not affect electric field performance. For the case of SS316LN, oxygen plasma treatment has increased iron and chromium oxides above the bulk material, making the electrodes more resistance to breakdown appearance and enabling the holding of higher surface electric fields (160 MV/m).

In terms of future work, additional tests could include the extension of the conducted research to new irradiation campaigns, using different parameters, such as an increase of energy or dose time. Also, re-irradiation of materials that went through high voltage pulsing tests, followed by a reconditioning processes could also bring new insights regarding material behaviors.

More importantly, further testing will be necessary, to explore the role of oxidation in stainless steel surfaces when studying breakdown events. In this study, OPC treatment was performed to an irradiated cathode. Also, taking in consideration that the electric field for the treated stainless steel material surpassed the values obtained for non irradiated stainless steel, the author would suggest, that the treatment is repeated in pristine stainless steel electrodes and done for both anode and cathode. The same principle could be also done for copper non irradiated electrodes. Also, oxygen plasma treatments could be extended to other materials like for copper chromium zirconium, where the additional alloying elements could also have an effect on the oxidation state of the surface after plasma exposure.

At last, the latest research underlines the potential of oxygen plasma treatment, and will hopefully be the first stage of research aiming for the development of a key technology, as a long-term in-situ operational set-up, inside particle accelerators. Such technology could assure the cleanliness and maintenance of inner surfaces of RF devices, prolong their usable lifetime and even increase their performance.

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Sergio Calatroni, Catarina Serafim and Flyura Djurabekova (from left to right) at the 11th International Workshop on the Mechanisms of Vacuum Arcs, in Tahoe City, CA (USA), March 2024.

Annex: Scientific Publications

Publication I



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Investigation on different materials after pulsed high field conditioning and low-energy H^+ irradiation

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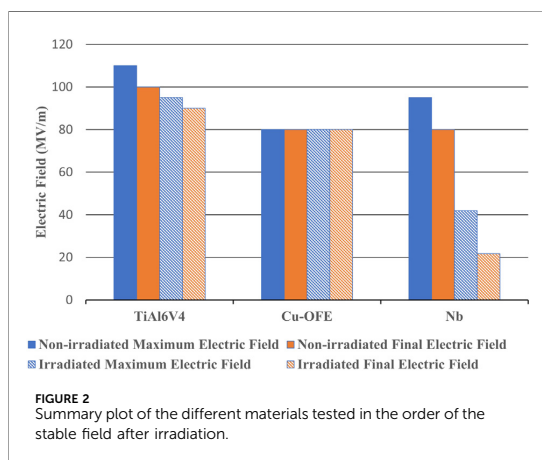
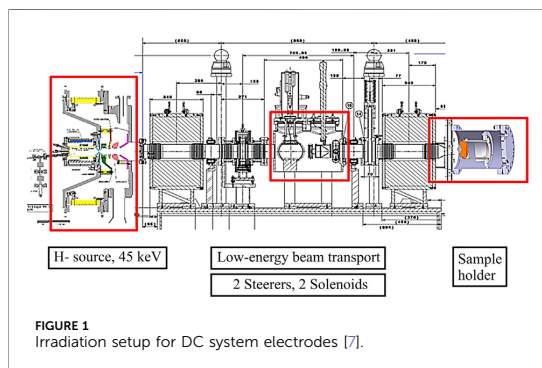
During operation, the radio-frequency quadrupole (RFQ) of the LINAC4 at CERN is exposed to high electric fields, which can lead to vacuum breakdown. It is also subject to beam loss, which can cause surface modification, including blistering, which can result in reduced electric field holding and an increased breakdown rate. First, experiments to study the high-voltage conditioning process and electrical breakdown statistics have been conducted using pulsed high-voltage DC systems in order to identify materials with high electric field handling capability and robustness to low-energy irradiation. In this paper, we discuss the results obtained for the different materials tested. To complement these, an investigation of their metallurgical properties using advanced microscopic techniques was done to observe and characterize the different materials and to compare results before and after irradiation and breakdown testing.

KEYWORDS

Radio-frequency quadrupole, breakdown, blisters, irradiation, electric field

1 Introduction

The first stage of acceleration in the Large Hadron Collider (LHC) at CERN is a linear accelerator known as LINAC4 [1]. H^+ ions are generated by the radio-frequency (RF) source and pass through the low-energy beam transport (LEBT) to the radio-frequency quadrupole (RFQ). An endoscopy of the LINAC4 RFQ showed damage of the copper surfaces and signs of breakdown, in particular at its entrance where high beam losses can be expected [2]. To better understand this problem, tests were conducted to gain more knowledge of the effects of low-energy irradiation on field holding capabilities, on possible surface blistering, and its consequences on the breakdown phenomena. A vacuum breakdown is a discharge across a gap in a circuit, typically occurring when the voltage between two conductive electrodes becomes high enough to ionize the surroundings and allow the flow of current. In the case of our system, a breakdown can be triggered by applying a potential difference between the two electrodes separated by a given gap, under vacuum. When applying a high voltage potential, if the electric field on the electrode surface is high enough, the emissions of neutrals and their sequential ionization will form a conductive plasma within our gap. This plasma will serve as a bridge between the two electrode surfaces, and the emission of electrons from the cathode surface will result in an exchange of charge between the two electrodes [3]. More



detailed information about the process behind the formation of a vacuum breakdown has been reported in multiple research works [3–6]. The vacuum breakdowns from this process are visually observed as craters on the material surface with an order of magnitude of tens of micrometers. Their size of the craters is directly dependent on the magnitude of the electric field applied.

The study of the breakdown phenomenon in linear colliders is highly important, as an increase in the accelerating gradients, and consequently, the increase in the electric fields on the base-material surfaces will increase the probability of the occurrence of a breakdown. For a better understanding whether beam irradiation could have a consequent effect in triggering breakdowns, tests were conducted on pairs of anode and cathode electrodes of different materials that were manufactured for the purpose of the studies. Their breakdown handling capabilities were tested in a dedicated pre-existing pulsed high-voltage set-up [4], the large electrode system (LES). Detailed information about the test conditions can be found in Section 2. For comparison, a pair of non-irradiated electrodes of each selected material was also tested in this system.

For the study of the effects of irradiation, and of the material properties at its origin, a test stand that replicates the low energy beam transport in the LINAC4 tunnel at the CERN was used, as seen in Figure 1. In this test stand, a specific hardware was developed to

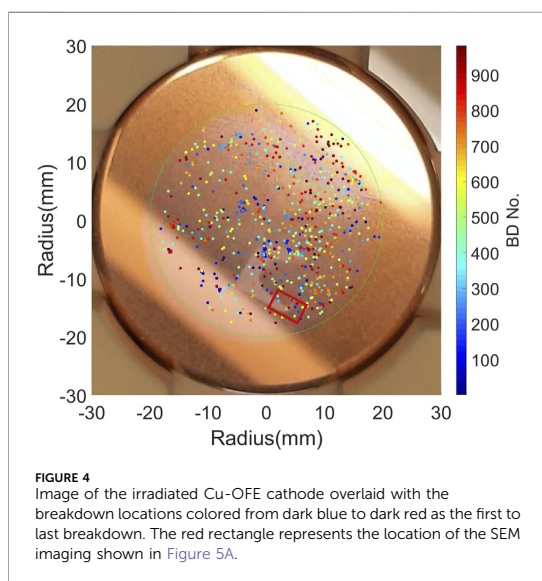
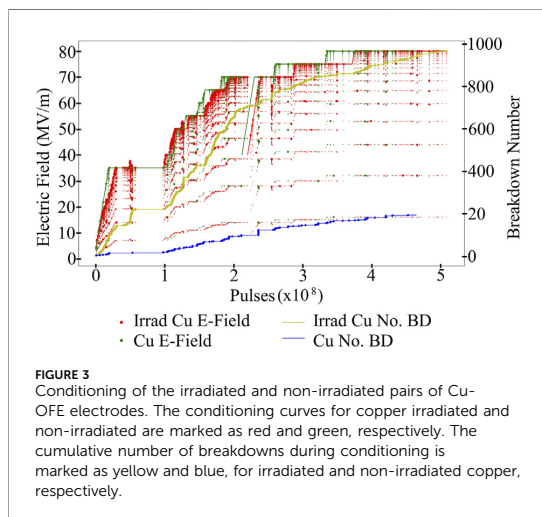
use a cathode as the target for irradiation and allowing for a rapid turnover for various irradiation runs.

Irradiating a material with H^- ions can lead to various effects on the surface material. The outcomes depend on factors such as the type of the material, the ion dose, and the energy level of the ions. The irradiation may cause changes in the surface morphology and composition of the metal, as well as induce structural and chemical changes in the metal lattice. Ion implantation has been reported to enhance properties such as hardness, wear resistance, or corrosion resistance [8]. Depending on the metal type, irradiation with hydrogen ions can lead to hydrogen embrittlement. Hydrogen atoms can diffuse into the metal lattice, affecting its mechanical properties and making it more susceptible to cracking and fracture [9, 10]. Depending on the diffusibility and solubility factors of each material, H^- ions will have different rates of diffusion into the material lattice, and consequently, some materials can have surface modification from the irradiation, with blistering appearance, increasing the roughness of the surface, as we have seen in copper. Surface modification of materials due to the blistering phenomenon caused by hydrogen retention is a known problem [11]. Blistering is dependent on many factors, such as the radiation dose (minimum dose required for the appearance of blisters), the ion energy, the temperature of the target, the angle of incidence [7], and the metallurgical properties of the material. In the case of the RFQ, the energy of the incident H^- beam at its entrance, where most beam losses are localized, is 45 keV. This corresponds to a range of approximately 250 nm in copper, with the H possibly accumulating under the surface and leading to blistering. All electrodes underwent systematic metallurgical analyses, before and after irradiation, and after LES testing, as detailed in this paper.

2 Methodology

A list of candidate materials was carefully drafted for the manufacturing of a future RFQ with better performance. In this paper, we will focus on the results of three different materials: oxygen free electronic-grade copper (Cu OFE, UNS C10100) as the reference employed for the current RFQ fabrication, high purity (99.9%, RRR300) niobium (Nb), and a premium-grade titanium alloy (Ti6Al4V, grade F-5, 6 wt% aluminum—4 wt% vanadium, UNS R56400), forged in an α – β range with a final α -microstructure.

The materials were selected based on their usability for meter-long high gradient RF cavities and their potential resistance to blistering and breakdown phenomena. Nb and Ti grade 5 were chosen in particular for their high hydrogen diffusivity, which should prevent accumulation of hydrogen and thus blistering. Ti grade 5 should also provide comparatively easier machinability. The machining of the electrodes was performed with high precision tooling. After machining, the electrodes were submitted to metrology testing to assure that all the requirements are within the stipulated tolerances. After this, the electrodes have been submitted to a cleaning process. For the case of Cu, a thermal treatment equivalent to the brazing cycle employed for RFQ fabrication was applied, with a heat up ramp rate of 100°/h up to 795°C, dwell time of 6 h at 795°C and 100°/h up to 835°C, and dwell



time of 45 min at 835°C. The natural cooling rate was used in the furnace.

Irradiation was performed at CERN using a low-energy H^+ beam at 45 keV. Each irradiation had a duration of approximately 52–54 h, with a beam pulse duration of 600 μ s, a repetition rate of 0.83 Hz, and a peak pulse current of 20 mA, which resulted in a deposition of 1.2×10^{19} H^+ p/cm² on the target, corresponding to approximately 10 days of beam losses during RFQ operation [12].

The high-voltage testing was performed on the electrodes exposed to irradiation and on electrodes that were not exposed to irradiation. This allowed comparing whether the irradiation had a significant impact on the performance of each material in reaching a maximum and stable field.

The pulsed DC LES consists of two high-precision machined electrodes placed 60 μ m apart in vacuum on the order of 1×10^{-8} mbar. A Marx generator was used to apply pulses of voltage up to 10 kV, pulse lengths between 1 μ s and 1 ms, and repetition rate up to 6 kHz [3]. This system is used for the study of conditioning and vacuum breakdown phenomena. The instrumentation has the ability to detect breakdowns using voltage and current signals, measure pressure spikes, and emitted light used to determine the location of each breakdown during operation [13].

To replicate conditions occurring in the RFQ as closely as possible while keeping testing time to a minimum, a pulse length of 100 μ s and a repetition rate of 200 Hz were used. Once conditioned, pulse length dependence tests were also done up to the pulse length of the RFQ of up to 900 μ s; these did not show a clear dependence of pulse length on the breakdown rate for pulse lengths over 100 μ s [14]. To replicate the electric field of 34 MV/m of the RFQ, the LES was first conditioned to 35 MV/m before increasing the field in steps to find the limit [2]. The gap dependence effect [15] is a possible explanation for the higher electric fields achieved in the LES over the RFQ. The summary plot in Figure 2 shows the materials tested, the maximum field reached, and the final stable field.

In order to inspect the state of the electrodes between each test, microscopy equipment was used. The samples were analyzed by using a digital microscope from KEYENCE and a scanning electron microscope (SEM) (Sigma) from Zeiss, equipped with secondary electron (SE), InLens (Inlens), Everhart–Thornley SE (SE2), backscattered electron (AsB), and electron backscattered diffraction (EBSD) detectors. The results from the observation help in understanding the development of blistering, if any, created on the surface from the irradiation and a possible correlation with the location of the breakdowns from the LES.

3 Results

3.1 Oxygen-free electronic copper (Cu-OFE)

Cu-OFE achieved the second highest stable electric field of the materials tested after irradiation, achieving 80 MV/m. The non-irradiated pair achieved the same stable electric field, suggesting that the irradiation did not have a significant impact, if any, on the performance of Cu-OFE.

Cluster in breakdowns with respect to pulses occurred multiple times. To try to reduce the damage to the electrodes when clusters occurred, the target field was reduced to the previous stable point and pulsed before continuing to be increased. It can be seen from the conditioning chart shown in Figure 3 that the irradiated pair had a larger number of breakdowns at the start, which decreased during conditioning to a similar level as that of the non-irradiated pair, suggesting that it conditioned away any breakdown-inducing features caused by the irradiation.

Figure 4 displays the breakdown locations on the irradiated electrode where clusters occurred in different areas of the beam halo and not at all of the beam center area, suggesting that blisters are not the only cause of or may not have any effect on breakdowns. It is possible that the clusters on the halo are a result of the irradiation

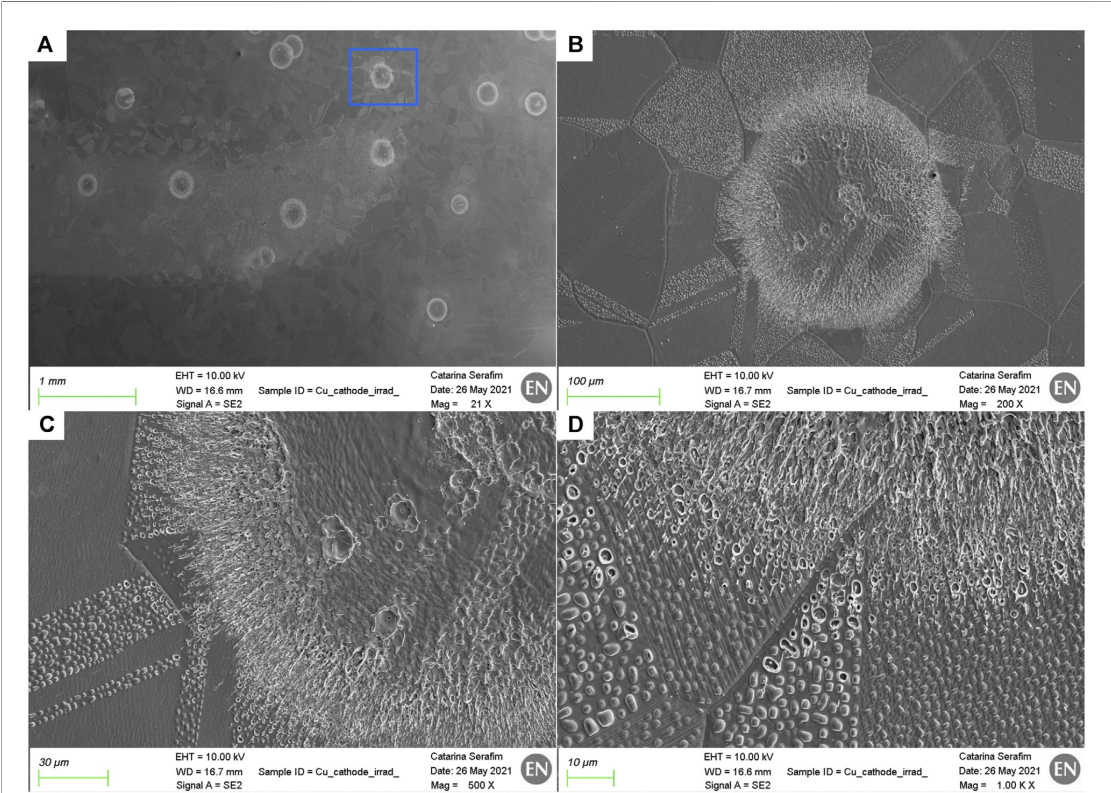


FIGURE 5 (A) SEM imaging, using the secondary electron detector, showing partially the transition zone (the irradiated zone corresponds to the zone less dark) and some of the breakdowns provoked by the high energy pulse. (B, C, D) SEM imaging with different magnifications, using the secondary electron detector, showing a breakdown in the transition zone of the electrode. The location of this breakdown is marked with a blue rectangle in (A).

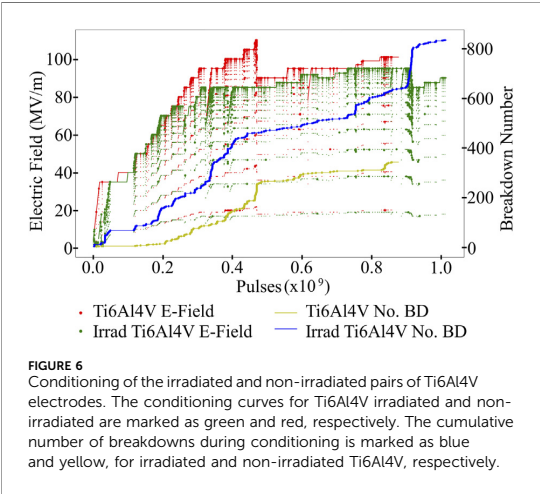
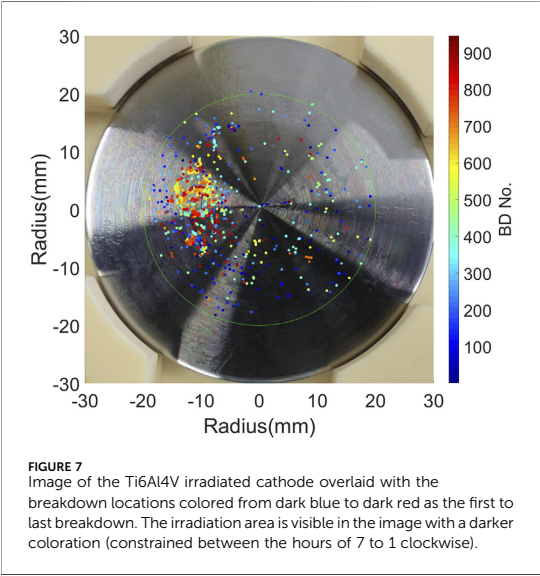


FIGURE 6 Conditioning of the irradiated and non-irradiated pairs of Ti6Al4V electrodes. The conditioning curves for Ti6Al4V irradiated and non-irradiated are marked as green and red, respectively. The cumulative number of breakdowns during conditioning is marked as blue and yellow, for irradiated and non-irradiated Ti6Al4V, respectively.

process as the non-irradiated electrode had no cluster of this sort, with breakdowns being dispersed over the surface.

Observations from the SEM equipment confirmed that the low-energy beam irradiation caused the appearance of blisters on the Cu-OFE electrode's surface. These blisters are concentrated on the impact zone. It is visible that the blisters in the areas with the maximum deposition of beam have a higher density in quantity compared with zones where the beam was less intense.

Figure 5A–D show the results of Cu-OFE after the electrode had been irradiated with the H^- beam and then subjected to high electric field pulsing in the LES. We can observe from Figure 5A that the breakdowns are well-distributed on the surface and do not seem to be correlated with the irradiated zone (zone less dark due to the blistering effect). Figures 5B–D show a breakdown in the transition zone, designated as the area where we start to see a decrease in the density of blistering. In this zone, it is visible that only some grains are affected by blisters. The fact that the phenomenon of blistering is more evident in just some of the grains may be correlated with the grain orientation of the material. Figures 5B, C also suggest that the



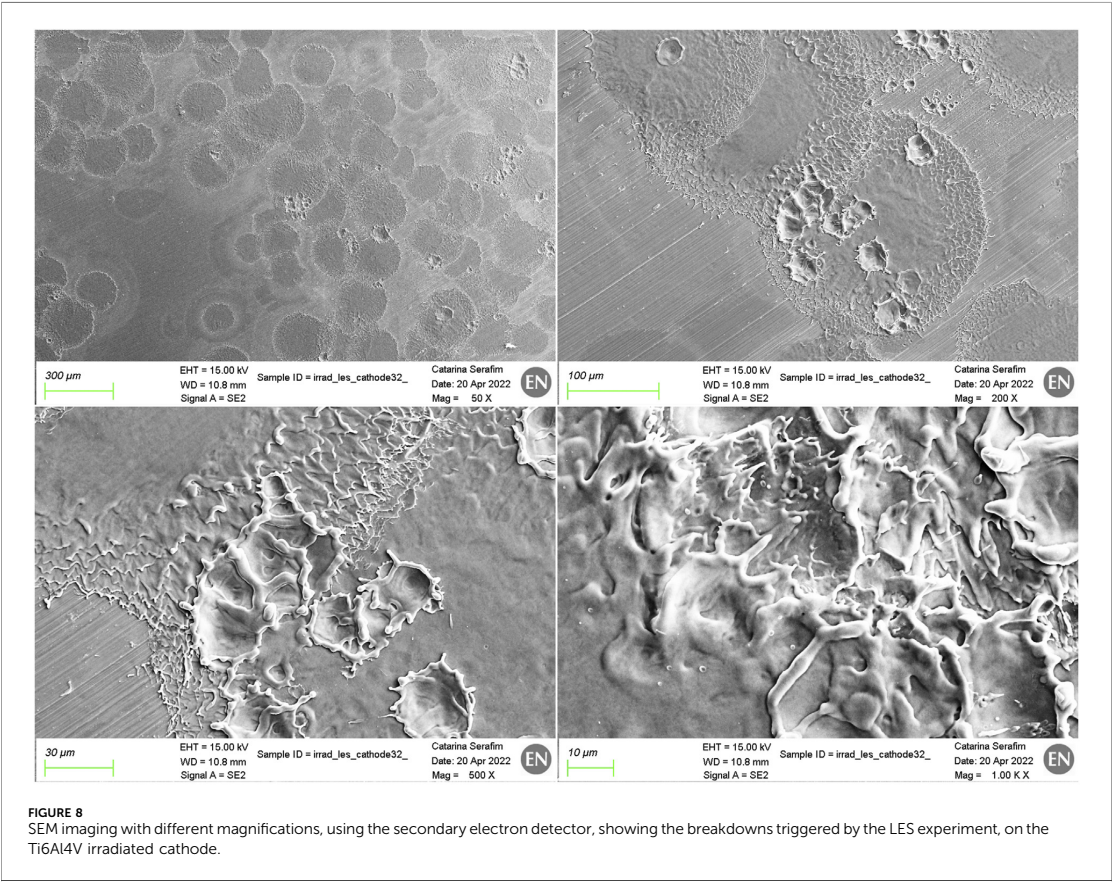
grain orientation may play a role not only in the appearance of blisters but also in their emerging shapes. Additional studies will be performed to understand this correlation.

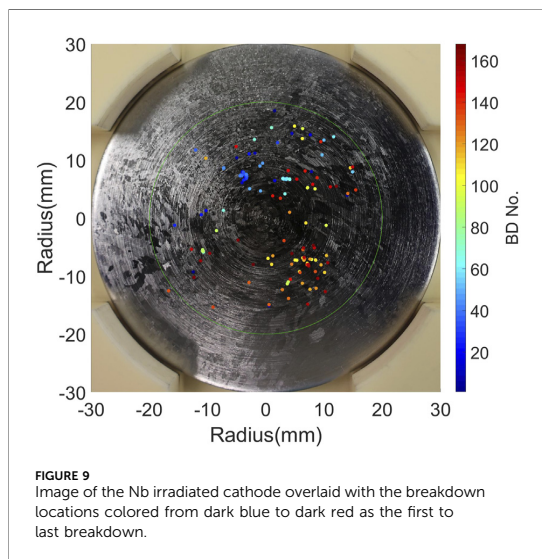
The breakdowns have a circular shape between approximately 100 μm and 200 μm , with splashes of melted material on their surroundings. The heat generated from the plasma formed during a breakdown has been shown to be significant enough to melt some of the blisters close to it, as shown in [Figure 5D](#).

3.2 Titanium alloy (Ti6Al4V)

Concerning the LES experiment after irradiation, the Ti6Al4V electrodes have reached a stable field of 90 MV/m. Furthermore, the Ti6Al4V electrodes have shown a slight decrease in the breakdown performance due to irradiation—the pair of Ti6Al4V non-irradiated electrodes that was tested in the LES reached the average value of 100 MV/m. The conditioning of each pair can be seen in [Figure 6](#).

Both pairs of Ti6Al4V electrodes exhibited a significant decrease in the operating field due to a temporal cluster of breakdowns that required a reduction in the electric field to reduce the risk of additional clusters. As this was a feature during the conditioning





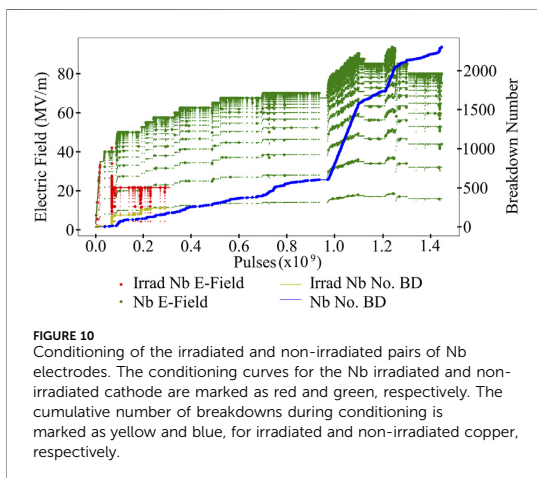
of both pairs, it would suggest that this is a property of Ti6Al4V rather than a spurious event. This may mean that Ti6Al4V has a tendency to accrue surface damage if conditioned too far. Overall, Ti6Al4V performed very well and was able to re-gain most of the previously achieved electric field without any further issues and maintain a stable field. The irradiated Ti6Al4V had a larger breakdown rate (BDR) at the start of conditioning, which then reduced, suggesting a strong conditioning effect of the irradiation area that improved the performance. Figure 7 shows the breakdown locations for the irradiated Ti6Al4V electrode, where the higher concentration of breakdowns appears to be constrained in the irradiation area.

Figure 8 shows the breakdowns on the irradiated Ti6Al4V cathode on the surface. After irradiation, there was no evidence of modification of the surface structure due to irradiation nor appearance of blistering. Discoloration was seen, with a visible difference between the beam center, halo, and non-affected areas. The breakdown craters are similar in diameter to Cu, between 100 μm and 200 μm , due to the high field reached in the LES. No particular physical material defects were observed in these electrodes, which could explain why the irradiation area of the electrode presents a higher number of breakdowns.

3.3 Niobium (Nb)

Nb displayed similar results to those of Ti6Al4V with respect to physical defects and appearance after irradiation. The beam center area and halo for Nb can be seen in Figure 9. Figure 10 displays the conditioning plot for the Nb electrodes.

The irradiated pair had a large cluster of breakdowns upon reaching 42 MV/m during conditioning. This reduced the electric field, and the pair was unable to recover; they settled at a stable field of approximately 23 MV/m. The non-irradiated pairs did not experience any significant clusters and were able to achieve much

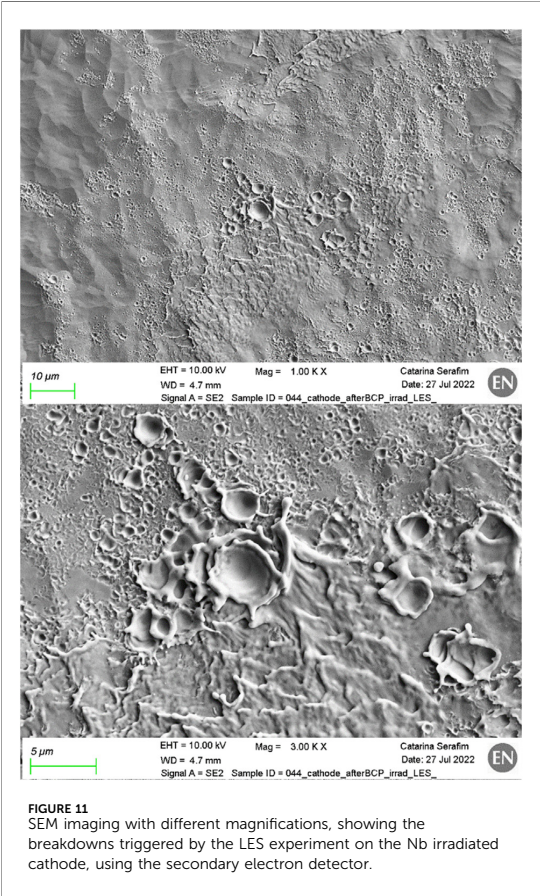


higher fields, reaching a stable field of 80 MV/m. This considerable difference in the field values seems to have been caused by effects from the irradiation experiment. However, microscopy observations have shown no particular features in the surface or blistering effects that can be correlated with the decrease in performance. Investigations are ongoing to ascertain if this can be attributed to chemical surface modifications. Figure 11 shows some breakdowns on the Nb irradiated electrode. The breakdowns are smaller and less deep when compared with those of the Cu-OFE and Ti6Al4V electrodes, due to the smaller field achieved.

4 Conclusion

After irradiation with 45-keV H^+ particles, only Cu has shown blistering on the surface, as expected from hydrogen diffusivity. The affected areas where the blisters have appeared are indeed coincident with the footprint of the beam. During the high-voltage testing after irradiation, Cu and Ti6Al4V have shown the best performance in terms of reaching a stable field. Table 1 displays a summary of the materials tested, the maximum and stable field reached, and the BDR per pulse at the stable field given, where highlighted rows indicate the irradiation before testing. The stability at a specific field was determined based on the BDR, clusters in breakdowns with respect to pulses, occurrence of multiple breakdowns within a single pulse as determined by the cameras, and proximity to a previous limit causing a large cluster. It can be seen that all materials reached relatively high fields with only irradiated pairs being restricted, suggesting this as an effect of irradiation.

The good results from the non-irradiated and irradiated pairs of Ti6Al4V electrodes in the LES make us conclude that the irradiation did not induce any major decrease in performance. However, it may have led to some instabilities, causing a decrease in the obtainable field if run close to the limit. Taking only in consideration the experimental results from this study, it can be concluded that Ti6Al4V was the best material tested so far, with the highest number in both stable and maximum fields reached. However, taking into consideration that this material has lower thermal



and electrical conductivities than copper, a careful design and a more complex assembly process would be required if used for an RFQ.

Copper gave the second-best results and appeared to reach the same field with an initial increase in the number of breakdowns in the irradiated electrode that appeared to condition away. This study suggests that the blistering phenomenon does not present a significant impact on the breakdown appearance or conditioning performance. Copper is currently used for the L4 RFQ and is well-established within the field; therefore, it would not require any manufacturing changes.

Nb had a significant reaction to the irradiation by causing a large and unpredictable cluster in breakdowns, from which it was not possible to recover from. The inferior performance of the material in terms of the reachable high field for the irradiated pair of electrodes, with the additional downside of being difficult to machine, leads us to exclude it from the list of possible materials for a future RFQ.

Finally, it should be underlined that in all the electrodes, some deposition of carbon on the surface was observed after irradiation. Further investigations are under way to better understand the source of the carbon and to avoid it in future experiments. If the carbon is inherent in the irradiation from the LINAC4 source, then it will also

TABLE 1 Summary of the stable, maximum field reached and the BDR at the stable field for each material. Rows highlighted indicate that the pair was irradiated before testing.

Material	Stable field (MV/m)	Maximum field (MV/m)	Stable BDR
Ti6Al4V	100	110	6.04×10^{-7}
	90	95	1.58×10^{-7}
Cu-OFE	80	80	3.13×10^{-7}
	80	80	7.5×10^{-7}
Nb	80	94	1.66×10^{-6}
	21.7	42	4.09×10^{-7}

be expected in the operating conditions of the RFQ. These future studies will also try to assess whether any correlation exists between the presence of carbon in the electrodes surface and the breakdown phenomenon. Additionally, the discoveries observed regarding the different blisters' growth on the different grains of Cu-OFE are being further explored. As these electrodes have dimensions which are incompatible with those of the current EBSD equipment, dedicated samples are under study, with proper geometric dimensions, in order to be mounted in the dedicated chamber for irradiation and to perform EBSD analysis. This analysis will help us identify the orientation of each grain and further investigate how it affects blistering caused by H^- ion implantation.

It should be noted that in the case of the electrodes, the entire irradiation was done before testing. On the other hand, in the RFQ, this occurs throughout running, and depending on whether irradiation occurs faster or slower than the rate of conditioning, it could influence the stability of the structure. This is most relevant for pairs of electrodes that reach similar electric fields when comparing irradiated and non-irradiated electrodes. Re-irradiating or constant irradiation may affect the performance or the achievable field. Tests are planned for conditioning irradiated electrodes and then re-irradiating and re-conditioning to see how this impacts the performance.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

Author contributions

CS: conceptualization, data curation, formal analysis, investigation, methodology, project administration, writing—original draft, and writing—review and editing. RP: Formal analysis, Investigation, Methodology, Writing—original draft, and Writing—review and editing. SC: project administration, supervision, validation, and writing—review and editing. Walter WW: project administration, supervision, validation, and writing—review and editing. FD: project

administration, supervision, validation, and writing–review and editing. AF: investigation, resources, supervision, validation, and writing–review and editing. SS: resources, supervision, validation, and writing–review and editing. AG: project administration, resources, supervision, and writing–review and editing. AL: project administration, resources, and writing–review and editing. ES: project administration, resources, and writing–review and editing. SR: project administration, resources, and writing–review and editing. GB: project administration, resources, and writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Publication II

Effects of H^- low beam irradiation and high field pulsing tests in different metals

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This work studies the suitability of a set of different materials for manufacturing more efficient and durable radio-frequency quadrupole (RFQ) structures compared to that currently used in many linear particle accelerators, traditionally made out of copper. RFQs are susceptible to vacuum breakdowns caused by the exposure to high electric fields, resulting in surface degradation. Additionally, a further limitation of present-day copper RFQs is surface blistering under hydrogen ion beam exposure, due to beam halo losses. Irradiation is associated with a further reduction of the breakdown field strength of the metal surface thereby affecting the overall efficiency of the RFQ. The investigated materials, Cu-OFE, CuCr1Zr, CuBe2, Ti6Al4V, SS316LN, Nb, and Ta, were submitted to low-energy (45 keV) H^- irradiation and tested in a direct-current (dc) system with pulsed high voltage. For comparison, the maximum surface electric field was measured for both irradiated and pristine (nonirradiated) surfaces of the same material. The effects of irradiation on the surface of the materials, before and after being submitted to high electric fields, were studied with the help of microscopic imaging and chemical analysis. Blistering caused by H^- irradiation has been observed in all copper and copper alloy materials. Despite reductions in breakdown field strength postirradiation, no indications were found that the blisters on the surface have a direct cause in triggering breakdowns during high electric field tests. SS316LN, Ti6Al4V, CuBe2, and CuCr1Zr showed maximum surface electric fields higher than copper, making these promising candidate materials for future RFQs manufacturing. This paper focuses on the results with CuCr1Zr, CuBe2, SS316LN, and Ta, complementing and expanding previous work exploring Cu-OFE, Nb, and Ti6Al4V.

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I. INTRODUCTION

The radio-frequency quadrupole (RFQ) is an important section within low-energy linear ion accelerators. Due to the radio-frequency (rf) component of the RFQ, which allows beam focusing, bunching and accelerating, it is possible to achieve high ion beam intensities in a very compact structure. An RFQ has a geometry of four electrodes, called “vanes,” which form the rf cavity; detailed information about the vane fabrication, machining, and brazing can be found in [1].

During the RFQ operation, the possible occurrence of rf electric breakdowns is a factor that can diminish the performance of the structure, leading to beam losses, and limit the lifetime of the RFQ. The increase of breakdowns in the RFQ cavities is correlated with their maximum surface electric field [2]—in the case of the RFQ at CERN LINAC4, the surface field in the structure is around 35 MV/m [3]. This becomes a limitation in the current RFQs and in the future developments for the reduction in size of these complex structures, as smaller dimensions mean a higher vane voltage and therefore higher surface electric fields that can give rise to higher breakdown rates. In the literature, there are no indications that breakdowns are associated with one single material property, and as reported in [4], there is not yet a fully comprehensive explanation of how they can be predicted.

A further important aspect of RFQs is the problems linked to their exposure to accelerator beams. Typically, when the structures are exposed to low-energy hydrogen ions irradiation (in case of proton or H^- beams), hydrogen

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ions can accumulate beneath the material's surface and recombine into molecular hydrogen. As hydrogen accumulates, bubbles are formed and the increase of their pressure inside the material may lead, depending on the material, to the formation of blisters on its surface. This phenomenon is known as blistering and is strongly dependent on the energy and flux of the beam, temperature, and material properties [5]. Blistering can affect the mechanical properties of the materials leading to surface degradation and failure, which will consequently affect the operation efficiency and longevity of the accelerator components. To try to minimize the surface damage caused by blisters, material properties such as permeability, diffusivity, and solubility were taken into consideration when choosing the materials to be tested in this study.

This work is based on the motivation to tackle these two main problems, which have been the primary concern in RFQ's material degradation within the first years of operation, by studying different materials and potentially finding better alternatives for future RFQ developments in terms of high electric field strength and beam loss resilience. Until now, no studies have been conducted to understand whether the blistering effects on the RFQ surface could be potentially linked to the appearance of vacuum breakdowns. In this study, this question is addressed by combining two different set of tests, with the first being high voltage dc pulsing, in a dedicated setup which enables us to replicate RFQ surface electric fields and study the breakdowns triggered from it in a controlled environment. And second, H^- low-energy irradiation in order to see if the irradiated materials perform differently from the nonirradiated materials when submitted to the high-voltage test. The mentioned tests were made on electrodes from various materials (Cu-OFE, CuCr1Zr, CuBe2, Ti6Al4V, SS316LN, Nb, and Ta). For each material, two pairs of cathode and anode were machined with requirements aimed at achieving a face surface flatness of 0.001 mm and maintaining a surface finish below 0.025 μm of roughness. In essence, the copper alloys have been selected for their stronger mechanical properties compared to copper while retaining basically a similar behavior with respect to hydrogen. The other materials have been selected for their very high diffusivity, with Ti6Al4V having high mechanical strength. Stainless steel sits across the two categories: the interest for testing stemming from the fact of having displayed the highest field-handling capabilities in [6] and being a common construction material in particle accelerator technology. Detailed information about the materials can be found in Sec. II A. Details on the experimental setups and procedures are reported in Sec. II B. Complete experimental results are reported in Sec. III, noting that some preliminary results were reported in [7] and are presented here again for the sake of giving a complete picture of this study. Finally, it should be emphasized that it is the first time that such testing is performed with the chosen materials.

II. MATERIALS AND METHODOLOGY

A. Materials

In total, seven materials were chosen to conduct the research: pure oxygen-free copper (Cu-OFE), UNS¹ type C10100; copper chromium zirconium (CuCr1Zr), UNS type C18150, with approximately 0.1% of zirconium, 1% of chromium, and with the rest being copper; copper beryllium (CuBe2), UNS type C17200 with 98 wt% copper, and 2% beryllium; stainless austenitic chromium-nickel-molybdenum steel with nitrogen addition (AISI 316LN), UNS type S31653; premium-grade titanium alloy (Ti6Al4V, grade F-5, 6 wt% aluminum-4 wt% vanadium, UNS type R56400), forged in an α - β range with a final α -microstructure; high purity (99.9%) niobium (Nb), UNS type RRR300% and 99.9% tantalum (Ta), UNS type UNS R05200. The chemical composition of each material alloy can be found summarized in Table I.

1. Physical and mechanical properties

The choice of material, in terms of RFQ design, is crucial as it will significantly influence the efficiency, stability, and lifetime of the machine. Several parameters were taken into account when choosing the materials. Electric conductivity is important, as higher conductivity minimizes power losses, which means that more rf power is used for accelerating the beam, instead of dissipating as heat. A material with higher thermal conductivity is simultaneously as important, as the structure integrity of the vanes depends partially on the capability of the material to dissipate the heat generated by the rf power and beam interactions. During operation, RFQ vanes also experience mechanical stress caused by thermal expansions of the material and electromagnetic forces. For this reason, having a material with high mechanical strength in order to prevent deformations can help maintain the precise geometry of RFQ vanes. Material properties for the thermal and electric conductivity and mechanical strength are listed in Table II, according to the cited literature.

If one would focus only on electric and thermal conductivities, Cu-OFE or the Cu alloys would typically be the materials of choice due to those superior values. In comparison with the high-purity oxygen-free copper, the thermal conductivity of CuCr1Zr stays a bit below. However, this alloy is commonly used instead of copper for applications that require a higher mechanical strength, hardness, and thermal stability [8]. Also, it presents high electric conductivity, the second biggest among all chosen materials. The addition of Cr can improve the high mechanical strength of the alloy, and according to [25], it consequently promotes the reduction of dislocations in the material. CuBe2, showing lower values in the copper

¹UNS stands for Unified Numbering System, typically used worldwide as an alloy designation system.

TABLE I. Chemical composition of the selected material alloys (wt%).

CuCr1Zr	Cu Rest	Cr 0.8	Zr 0.09	Si <0.01	Fe <0.01						
CuBe2	Cu Rest	Be 2.0	Co <0.30	Ni <0.30	Fe <0.20						
SS316LN	Fe Rest	Cr 17.24	Ni 13.31	Mo 2.52	Mn 1.55	Si 0.41	N 0.16	C 0.025	P 0.023	S 0.004	Co 0.048
Ti6Al4V	Ti Rest	Al 6.06	V 4.02	Fe 0.11	O ₂ 0.11	C 0.0149	N ₂ 0.003	H ₂ 0.0046			

family for thermal and electric conductivity, represents a good compromise by having very good mechanical properties and hardness, with the highest mechanical strength among all materials. Its thermal expansion closely matches the steels, including the stainless grades [26,27].

Ti6Al4V combines low density, high strength, and excellent corrosion resistance. This alloy has one of the highest mechanical strength values and lower thermal expansion, which is also important to assure that possible structural vanes can remain stable under varying thermal stress, and superior corrosion resistance in many harsh environments. Also, SS316LN has similar characteristics. The high achievable breakdown field of stainless steel material, reported in [6], represented a good indicator that this material could be a good candidate for the study, even with lower thermal conductivity when compared with copper and copper alloys. The presence of chromium in steels has been associated with a smaller dislocation mobility [6]. Pure Cr particles are known to provide high mechanical strength by dislocation motion inhibition to the material [25,28]. Both of these materials, Ti6Al4V and SS316LN, also offer good machinability but require careful handling when compared with copper and copper alloys, which are easier to machine into complex shapes as required for the RFQ vanes.

In terms of mechanical properties, Ta and Nb fall short when compared with all the other materials and additionally have difficult machinability due to their ductility. On the other hand, both Ta and Nb represent the strongest materials in terms of hydrogen embrittlement and therefore

have been chosen to better explore their behavior in environments involving hydrogen ion beams. This brings us to one of the most relevant parameters that were also taken into account when choosing the materials, which is the ability of hydrogen diffusion in the material lattice.

2. Hydrogen diffusivity

It is well known that hydrogen diffusion in metals is highly associated with a decrease in mechanical and structural properties, due to the occurrence of phenomena such as hydrogen embrittlement or blistering.

Interstitial diffusion happens when the hydrogen atoms diffuse into the bulk material and occupy the interstitial sites in the metal lattice. The diffusivity, i.e., the hydrogen diffusing flux along the metallic material, follows Fick's law: $J = -D\nabla c$, where J is the flux of hydrogen atoms, and D and ∇c are the diffusion coefficient and concentration gradient, respectively, of hydrogen in the metal. D is a key characteristic of the migration of hydrogen in a metal, which is a quantitative characteristic of the rate of diffusion [29]. This thermodynamic parameter, follows Arrhenius dependence on temperature, according with Eq. (1), where D_0 is a constant, E_d is the activation energy of diffusion (J/mol), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K) [29].

$$D = D_0 \exp(-E_d/RT). \quad (1)$$

Another key factor of the process is the solubility factor in the bulk material, describing the maximum amount of hydrogen that can be dissolved in a metal lattice. The quantification of solubility is usually expressed as the Sievert's constant which is defined by the equation: $K_s = c/\sqrt{p}$, where c is atomic gas concentration in the bulk volume and p is the partial pressure of hydrogen gas [30]. Like diffusivity, also Sieverts's constant shows an Arrhenius dependence on the temperature [Eq. (2)]:

$$K_s = S_0 \exp(-E_s/RT). \quad (2)$$

At last, permeability (ϕ) quantifies the ability of hydrogen to enter and move within the material, and it is given by the linear relation of the two concepts of diffusivity and solubility:

TABLE II. Compiled properties of the selected materials at room temperature (300 K) [8–24].

Material	Electrical conductivity (MS/m)	Thermal conductivity (W/mK)	Mechanical strength (MPa)
Cu-OFE	58–60	386–394	220–410
CuBe2	6–8	105–120	1100–1380
SS316LN	1.4	14–17	485–690
Ti6Al4V	2.3	6.7	900–1120
Nb	6.3	53.7	275
Ta	7.7	57.5	180–240

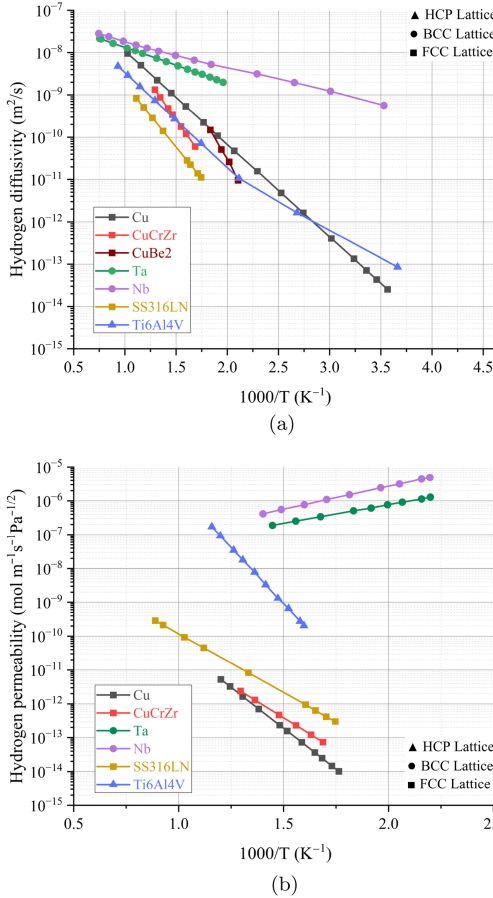


FIG. 1. (a) Compilation of hydrogen diffusion for different materials in function of reciprocal temperature, taken from different sources. Cu—[34], CuCr1Zr—[29], [25], CuBe2—[35], SS316LN—[29], Ti6Al4V—[36,37], Ta—[30], and Nb—[38], [30]. (b) Compilation of hydrogen permeability for different materials in function of reciprocal temperature, taken from different sources. Cu—[25], SS316LN—[29], CuCr1Zr—[29], [39], Ta—[40], Nb—[41], and Ti6Al4V—[42].

$$\phi = K_s D = D_0 S_0 \exp[-(E_d + E_s)/RT]. \quad (3)$$

As hydrogen from beam bombardment accumulates inside the metal lattice, if its amount exceeds the solubility limit, the internal pressure within the material can exceed the tensile strength of the metal, resulting in the formation of blisters in the material surface. Data extrapolated from different sources have been compiled together, as shown in Fig. 1, with (a) and (b) representing the hydrogen diffusion and permeability in a material's bulk in function of

reciprocal temperature, respectively. Both coefficients for each material follow an Arrhenius-type equation. According to the literature, results for the same material can have substantial variability in terms of order of magnitude, as both diffusivity and permeability coefficients will vary from the purity of the material, contamination, and the measurement technique used in the experiments. Hydrogen diffusion is moderated by many factors, such as the size and accessibility of interstitial sites in the material, which differs from lattice to lattice, binding energy of H in the lattice, temperature, and impurities.

The copper alloys follow a similar behavior as Cu, which is expected as Cu is the main element of their composition. The hydrogen permeability of CuBe2 was not found in the literature, however, as just mentioned, this alloy should follow very closely the Cu permeability. Ti6Al4V also follows a similar behavior as pure Ti alpha based, more results can be found in [30–33].

As mentioned, Ta and Nb are among the chosen materials for testing, with the highest hydrogen diffusion capabilities. According to [43], Ta is one of the materials with the highest resistance to the formation of blisters. In [44], it is explained that because of good hydrogen dissolution, blisters are not observed. Reference [45] also reports a decrease in the activation energies for hydrogen diffusion in both niobium and tantalum at low temperatures. The small values for activation energies in Nb and Ta have been associated in part, with their body-centered cubic (bcc) lattice type, which favors the mobility of hydrogen atoms, as bcc crystal lattices have in general more interstitial spaces, when compared with a hexagonal close-packed (hcp) or a face-centered cubic (fcc) structures.

Copper has a relatively low-hydrogen diffusivity, which can cause the appearance of blisters in the surface due to the low rate of hydrogen atoms through the lattice. The additional low-hydrogen solubility consequently results in a very low-hydrogen permeability, even lower than austenitic steels. However, Cu has a higher diffusivity when compared with austenitic steels [46].

CuCr1Zr and CuBe2, copper based alloys, have similar diffusion characteristics when compared with pure copper. However, the addition of alloying elements can reduce the overall mobility of hydrogen ions by also introducing defects or trapping sites for hydrogen. According to [25], the permeability values for CuCr1Zr remain close to the ones in pure copper, but the addition of chromium has been associated with an increase in solubility and a decrease in the hydrogen transport through the lattice (diffusion). Both Cr and Zr, which act as strengtheners in copper, also can act as site traps for H atoms, making the trapped atoms less likely to contribute to the diffusion process.

CuBe₂, being an alloy with approximately 98% Cu, the majority of the diffusion species should be copper [47], so in terms of diffusion, the behavior of CuBe₂ should be similar. The small addition of beryllium has been studied in [48], which reports that the addition of Be to Cu causes the hydrogen permeability to decrease by a factor of 3 (relative to pure Cu) in the temperature range of 700 – 500 °C. Studies made in [49] demonstrated that at least five atoms of hydrogen can be accommodated in a monovacancy, indicating that vacancies in beryllium are efficient hydrogen traps. Additionally, the diffusion and solubility behavior of CuBe₂ has been reported in [35], showing that in terms of diffusion, CuBe₂ exhibits similar results when compared with pure oxygen-free copper and higher diffusion rate than the 300-series austenitic stainless steels.

For titanium, [32] reports that the presence of β phase in Ti grade 5 alloy seems to be enough to dissolve hydrogen without producing either hydride precipitation or cracking. The vanadium addition in the alloy, with different concentrations, has been studied in [50]. It has been concluded that the diffusivity of hydrogen increases with the addition of V in the Ti base material. On the other hand, the presence of aluminum is associated with a decrease in diffusivity and solubility of hydrogen in the alloy [51,52]. Ti6AlV4 has a α microstructure, with a hcp structure. This type of crystal lattice generally has less interstitial sites available for hydrogen diffusion when compared with bcc crystal lattices.

Austenitic stainless steels present high content of elements with a complex chemical composition. SS316LN presents a low diffusivity and high solubility of hydrogen due to its fcc structure [53]. Reference [54] explains that the alloy compositions do not influence the hydrogen permeability but affects the hydrogen diffusion process, i.e., diffusivity appears to depend on the alloy. The presence of Cr and Mo tends to reduce H diffusivity and to increase solubility; however, this effect is not as large as in bcc materials. In a study about hydrogen permeation in different austenitic steels, Ref. [55] explains that the hydrogen solubility correlates mainly with the main alloying elements, concluding that solubility is higher when Cr content increases and the content of Ni decreases. Also, N has been reported to increase solubility. More information about diffusion process, along with diffusion, solubility, and permeability parameters, in stainless steels can be found in Refs. [54–57].

In this paper, we will be focusing on the results of CuCr1Zr, Ta, CuBe₂, and SS316LN, and only briefly summarize for completeness of the results of Cu-OFE, Ti6Al4V, and Nb which have been covered in [7].

B. Experimental setups: Irradiation and LES system

The Large Electrode System (LES) is an experimental setup that allows the test of the samples under high-gradient electric field. The purpose of such a system comes from the need to replicate rf conditions as close as possible, to study

breakdowns appearance in a way which is less expensive and less time consuming compared to rf test operations [58]. The LES enables the testing of one pair of cathode-anode electrodes using high-voltage short pulses. The vacuum chamber where the electrodes are inserted allows for an ultrahigh vacuum and is connected to a Marx generator that provides high-voltage pulses up to a repetition rate until 6 kHz. Measurements of current and voltage are taken from the connected oscilloscope. The main chamber has four apertures/windows which enables the external installation of cameras. Currently, two CCD cameras are installed in order to capture the light emitted from the individual breakdowns, software triangulation is used to extrapolate the exact position where the breakdown took place on the electrode surface and with the help of a data acquisition system create a mapping of the events location during conditioning. More information regarding the LES system, the breakdown localization technique, and details on the standard procedure that is followed for progressively increasing the electric field (“conditioning”) can be found in [59]. For the present experiments, testing in the LES system is done by applying pulses of 100 μ s and a repetition rate of 200 Hz to stay closer to the RFQ conditions while aiming at attaining a maximum breakdown rate of 10^{-5} per pulse as in the standard conditioning experiments.

The aim of manufacturing two pairs of cathode-anode for each material allowed us to use one to irradiate the cathode before submitting it to high-field pulsing tests in the LES chamber. It is commonly accepted that the cathode surface determines the development of breakdowns in the LES system [60]. The nonirradiated pairs are also tested, representing the reference results for the material in question. Comparison between the irradiated and non-irradiated pairs, in terms of performance in reaching an electric surface field, is studied.

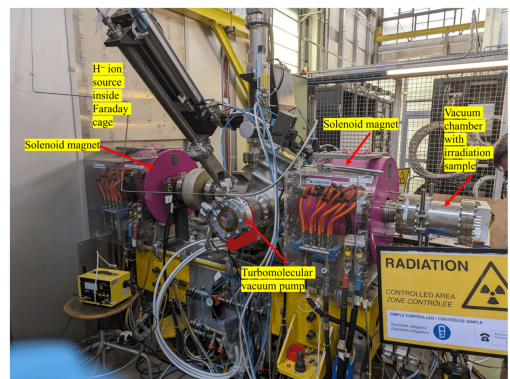


FIG. 2. Photograph of the irradiation setup at CERN, Geneva. The ion beam travels from the left to the right, having a chamber at the end dedicated for the mounting of one electrode.

Figure 2 shows the ion source irradiation facility used to irradiate all the samples. The electrodes are mounted using a dedicated chamber installed at the end of the structure. Specific details about the irradiation apparatus can be found in [3]. In the current RFQ at CERN, It has been reported that the maximum deposition of particles in the structure during operation is approximately 2×10^{11} p/s/mm² [3]. Taking into consideration this value and the beam loss profile along the RFQ, parameters for the irradiation of the samples under study were chosen. Low-energy H⁺ beam at 45 keV, corresponding to the energy of the beam entering the RFQ from the ion source, was used to irradiate one cathode of each material, each one with a duration of approximately 50 h. The pulse duration, repetition rate, and peak current were 600 μ m, 0.83 Hz, and 20 mA, respectively. This irradiation resulted in a deposition of 1.2×10^{19} H⁺ ions in each target over the entire irradiation, which represents approximately 10 days of beam losses during RFQ operation.

C. Microscopic techniques

SEM observations were the main techniques used to have a comprehensive inspection of the surface status in all electrodes. After manufacturing and metrology, SEM observations were done to validate the final surface, before installing electrodes for testing.

Due to the profiling of blistering, breakdowns, and surface roughness under study, secondary electron detector in the SEM was the most used to study the topography of our samples. This detector is installed at a 45° from the vertical axis of the beam gun of the SEM, allowing for more topographical features to be detected. Apart from SE2, inLens detector, which is more sensitive to low-energy electrons and installed in the same vertical axis as the beam, was used when a more superficial analysis was needed. Finally, back-scattered electron (BSE) detector, which detects variations in atomic number, leading to different intensities of the signal, was used to identify the presence of different elements apart from the sample's material. Different elements are represented with different levels of brightness, showing the lighter elements with a darker contrast. As our electrodes have a superficial area of approximately 2800 mm², using BSE detector proved to be very useful in scanning large areas of the surface. All the SEM analysis was complemented with energy-dispersive x-ray spectroscopy (EDS). This chemical analysis technique allowed us to identify qualitatively external elements that may be present in the surface of the electrodes.

III. RESULTS AND DISCUSSION

A. Conditioning results

Table III shows the results from all the materials tested in this project, and for each material, the maximum and stable

TABLE III. Summary table specifying the maximum and stable field reached by all the tested materials, including results from [7].

Material	Irradiation	Maximum field (MV/m)	Stable field (MV/m)
SS316LN	No	120	120
	Yes	62.5	60
CuBe2	No	110	90
	Yes	45	16.7
CuCr1Zr	No	87.5	82.5
	Yes	29	25
Ta	No	60	60
	Yes	38.1	24
Ti6Al4V	No	110	100
	Yes	95	90
Cu-OFE	No	80	80
	Yes	80	80
Nb	No	94	80
	Yes	42	21.7

field that irradiated and nonirradiated electrodes have been able to achieve. In most of these experiments, the conditioning process has been performed manually, where small increments of voltage are applied only after the previous target field is reached and stable.

The following plots show the conditioning results for copper beryllium, copper chromium zirconium, stainless steel, and tantalum. In each plot, four different curves can be seen. The extent of the entire conditioning process can be read on the horizontal axis, as the cumulative number of pulses. The blue curve represents the applied electric field during the conditioning process for the nonirradiated material, while the magenta curve has the same representation for the irradiated material. These two curves are composed with dots—each dot shows the current electric field which is registered at every 100 000 pulses. The electric field for these curves can be read in the left vertical axis, calculated from the ratio between the voltage applied and the physical gap in use (60 μ m in this cases). When observing the curve, sudden drops in electric field can be seen. These drops represent a breakdown or a multiple breakdowns event on the material surface. After a breakdown happens, the recovery of voltage is set, corresponding to the same level of voltage prior to the breakdown, and the system automatically increases voltage back to this target—for more information regarding the voltage behavior upon a vacuum arc, consult Ref. [59]. The cumulative breakdown events are counted during the process and can be read through the right vertical axis. The curves in orange and green represent the cumulative number of breakdowns (No. BD) during the conditioning tests for the nonirradiated and irradiated materials, respectively.

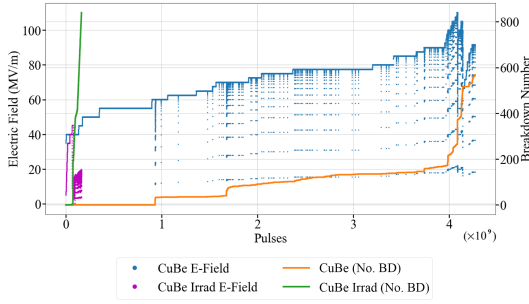


FIG. 3. Conditioning of the irradiated and nonirradiated pairs of CuBe2 electrodes.

1. CuBe2

Figure 3 shows the conditioning for CuBe2 electrodes irradiated and nonirradiated.

For the nonirradiated electrodes, a maximum field of 110 MV/m was reached. However, at high fields, breakdowns started to cluster at a specific location, where it appeared to be impossible for the field to remain stable. Taking into consideration that the stable field was directly affected by this cluster of breakdowns, a retest on new CuBe2 nonirradiated electrodes will be done in the future to assess whether the maximum and stable field can achieve higher results. In contrast with the results above, the irradiated pair has only reached a maximum field of 40 MV/m after approximately 100 million pulses as seen by the magenta curve in Fig. 3. The high number of breakdowns (green curve) at that field resulted in a sudden drop in voltage, leading to an unrecoverable condition. The irradiated electrodes did not recover back to the earlier maximum voltage, instead, the stable field ended up at approximately 17 MV/m.

2. CuCrIZr

Nonirradiated CuCrIZr has reached a maximum field of 87.5 MV/m, as shown in Fig. 4. After reaching the maximum value, the electrodes experienced a sudden decrease in the field to 75 MV/m, and consequently, a big increase in the breakdown rate. After this, a retry of stepping up the voltage was done. The electrodes were able to reach the maximum field again and hold it for a longer period but ended up stabilizing at 82.5 MV/m. For the irradiated CuCrIZr, this pair of electrodes has reached a maximum stable field of 26 MV/m. There was not any breakdown cluster registered during conditioning or observed in the surface analysis; however, the majority of the breakdowns were concentrated in the irradiated area.

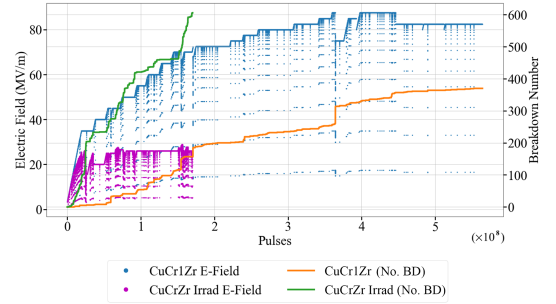


FIG. 4. Conditioning of the irradiated and nonirradiated pairs of CuCrIZr electrodes.

The deposition of particles from the irradiation is visible in Fig. 6(b) in the darkest circle region.

3. SS316LN

Figure 5 shows the conditioning for the irradiated and nonirradiated SS316LN electrodes. Stainless Steel nonirradiated electrodes have shown very good results in terms of conditioning, being the material that has reached the highest electric field, among all the tested materials.

During conditioning, the high voltage cable between the Marx generated and the connection to the chamber broke 2 times, due to the maximum voltage supported by the cable. In Fig. 5, this can be observed in the two reconditioning events at approximately 0.65 and 0.9 billion pulses in the blue dots. After replacing the cable with one that could hold the applied voltages, the electrodes were able to reach a maximum field of 120 MV/m. On the other hand, the irradiated electrodes only reached a stable field of 60 MV/m. When trying to increase the voltage applied, the electrodes reach the maximum field of 62.5 MV/m, but without being able to stabilize in that field and resulting in a

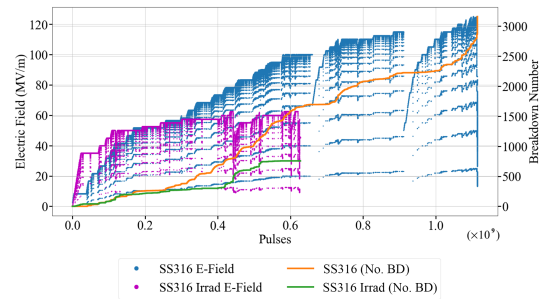


FIG. 5. Conditioning of the irradiated and nonirradiated pairs of SS316LN electrodes.

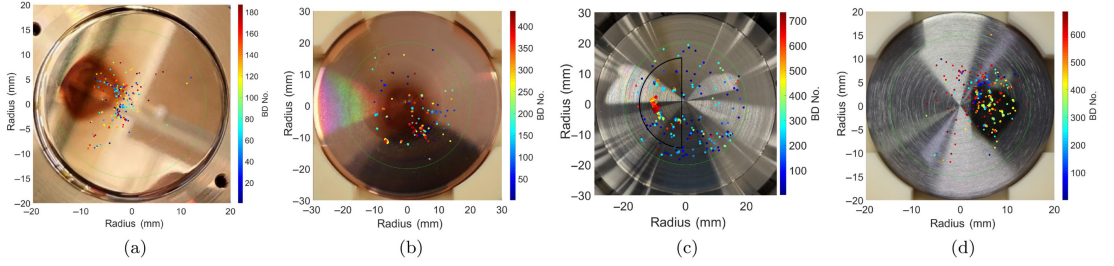


FIG. 6. Images taken before closing the chamber of the different irradiated cathodes overlaid with the breakdown locations after conditioning. Breakdowns are colored from dark blue to dark red as the first to last breakdown. (a) CuBe2, (b) CuCr1Zr, (c) SS316LN, (d) Ta. The green circles in all figures represent the coincident surface diameter of the anode electrode. The irradiated targeted regions can be seen as a darker color on the electrode surfaces. For the case of SS316LN, the irradiated region is not well distinguished and it has been marked with a black half-circle.

significant increase in the number of breakdowns. From Fig. 6(c), it can be seen that the large increase in breakdowns is locally coincident with the irradiated region. The irradiated region corresponds to the darkest half-circle seen on the left part of the electrode surface.

4. Ta

Figure 7 shows the conditioning of the irradiated and nonirradiated Ta electrodes. For the nonirradiated, the maximum and stable field reached was 60 MV/m. For the irradiated pair, the maximum field reached was 35 MV/m; however, after just 10^7 pulses, the field dropped to around 23 MV/m and was unable to recover from that value. After the conditioning, no cluster was observed on the surface of the electrodes; however, the effects of irradiation are very clear, showing the concentration of breakdowns mainly in the impact zone of the H^- beam. Figure 6(d) shows the locations of the breakdowns in the irradiated cathode, in which it can be observed that a larger quantity of breakdowns are concentrated in the irradiation zone.

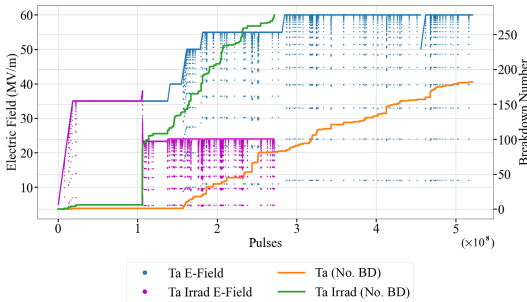


FIG. 7. Conditioning of the irradiated and nonirradiated pairs of Ta electrodes.

B. Microscopic observations and discussion

For all the nonirradiated materials, microscopic analysis has shown that the breakdowns from the LES tests are uniformly distributed throughout the surface of the electrodes. Also, breakdowns shapes and size are in accordance with the results reported in [7]. SEM observations confirmed blistering on the surface coincident with the irradiated region. For the copper based materials, i.e., CuBe2 and CuCr1Zr blistering caused by the poor hydrogen diffusion in the material is visible, as was the case for pure Cu-OFE. Blistering on the copper electrodes, as previously studied, can be seen in [7]. The beam density distribution follows a Gaussian distribution which results in more particles arriving at the center of the targeted region compared with the outer regions (for copper based materials in which blisters are observed, the nonuniformity of beam density is well observed by the different density of blisters). The distribution of the energy profile in all irradiation is uniform in the entire targeted region, which means that each ion reaches the surface with 45 keV. Copper was the material in which studies have been made to understand the penetration depth and the effects of irradiation in terms of blistering, where it was concluded that the penetration depth for the H ions (approximately between 250 and 300 nm) is independent of the beam density distribution. More information regarding the blistering effects in copper can be found in [61].

As expected, the good diffusion of hydrogen in Ta is confirmed with no blistering appearing on the surface after irradiation, as was also previously observed in Nb and Ti6Al4V. The same behavior happens for SS316LN; however, the nonappearance of blisters cannot be attributed to its hydrogen diffusion coefficient of the material but rather to the high-strength characteristics of this material [62].

For CuCr1Zr, it is observed that the blisters seem to follow the machining marks of the surface, as shown in Fig. 8(a). This effect is more visible in the center of the electrode surface, where the machining grooves are more

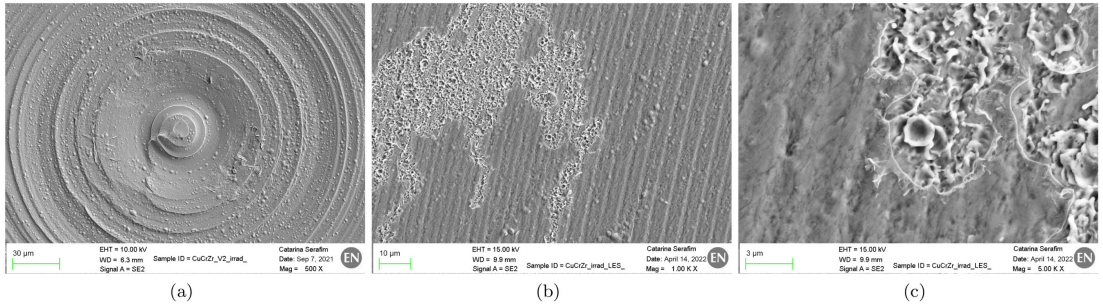


FIG. 8. SEM imaging, using secondary electron detector, of (a) center of CuCr1Zr electrode's surface after H^- beam irradiation and before LES testing. (b), (c) breakdowns in CuCr1Zr after H^- beam irradiation and LES testing.

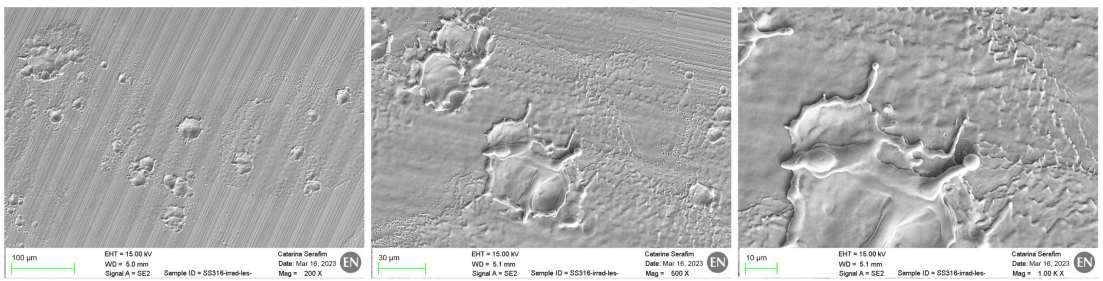


FIG. 9. Breakdown images, using secondary electron detector from SEM with different magnification, of SS316LN electrode after H^- beam irradiation and LES testing.

pronounced. Figures 8(b) and 8(c) shows the surface of the same electrode, after conditioning test. In Fig. 8(b), it can be seen a different contrast in surface coloring: the whiter region has a more rough surface where the multiple breakdowns are located. The more magnified Fig. 8(c)

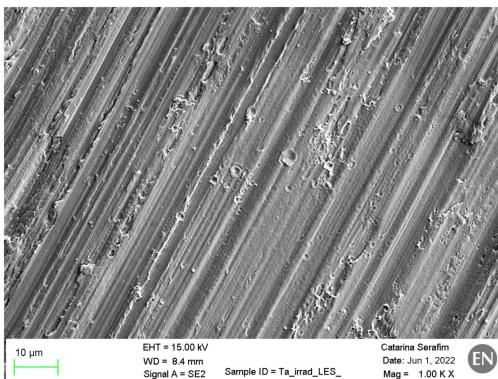
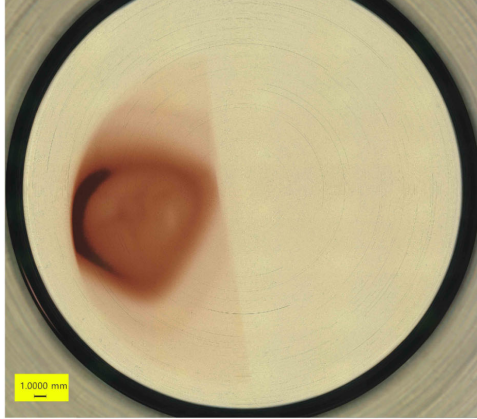


FIG. 10. Breakdown image, acquired using SEM secondary electron detector, on the tantalum electrode after H^- beam irradiation and LES testing

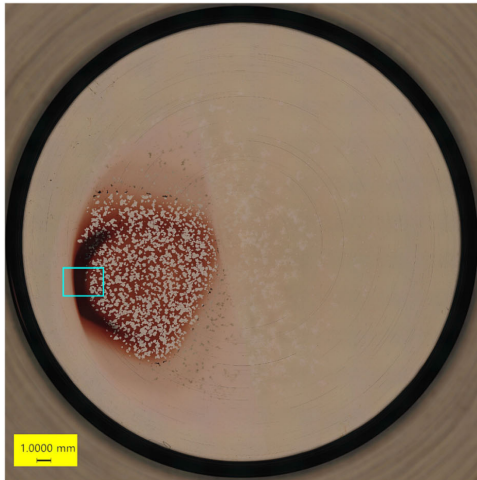
shows the contours of a carbon layer surrounding the edges of the small breakdowns. More detailed findings regarding the carbon effects are discussed below.

In all the irradiated materials, breakdowns have dimensions between 1 and 50 μm , in the irradiated regions, proportional to the electric surface field that was achieved, see [63] for comparison. Figures 9 and 10 show the breakdowns inside the irradiated region of SS316LN and Ta electrodes, respectively. The sequential vacuum arcs and the spots temperature rise lead to local melting, forming craters on the material surface, typically with splashes of molten material in its surroundings. This behavior has been reported before in the specific case of stainless steel in [64]. The irradiated SS316LN was the one with a better response to irradiation of all the materials described in this section, not only reaching the highest electric surface field (60 MV/m) but also for being able to hold that same field without suddenly dropping in voltage. Also, stainless steel was the only material in which breakdowns dispersed more from the irradiated region. Nevertheless, such good response, does not exclude the main fact that the 60 MV/m reached by the irradiated SS316LN corresponds to half of the electric field reached by the nonirradiated SS316LN.

In all irradiated materials, the problem in reaching a stable field is predominant. The big difference between the



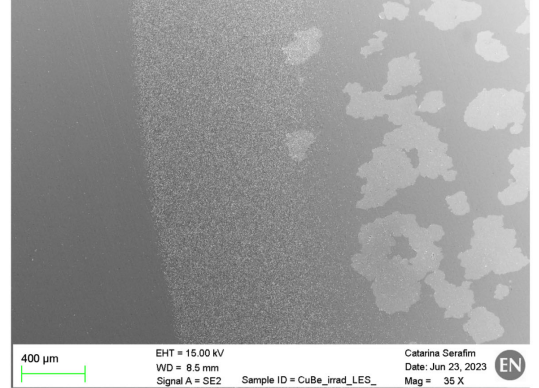
(a)



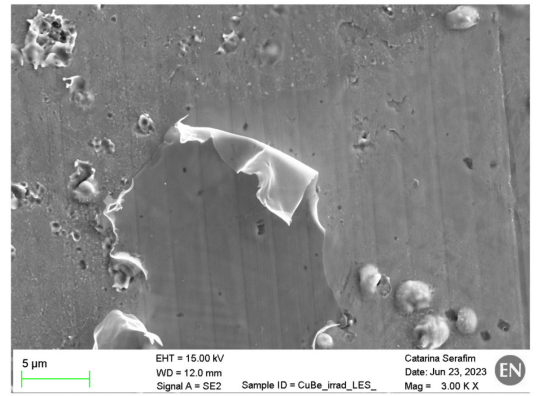
(b)

FIG. 11. Optical microscopy imaging of (a) CuBe2 cathode after being exposed with irradiation and before conditioning test; (b) CuBe2 cathode after being exposed with irradiation and after conditioning test. Blue square indicates the location of Fig. 12 on the surface of the electrode.

values of surface electric field between the irradiated and nonirradiated pairs can only mean that irradiation has a direct cause in decreasing the conditioning process. The cause does not seem to be correlated with the blistering effect, as blisters are not observed in Ta or SS316LN. Based on surface characterization of all the materials made before LES testing, no defects on the surface were found that could explain the poor performance. Cu-OFE results covered in [7] are another indication of the nonrelation of the blistering effect with the breakdowns appearance. Chemical analysis was performed in the different stages of all testing, leading to the conclusion that a carbon



(a)



(b)

FIG. 12. (a) SEM imaging using secondary electron detector, with 35× of magnification, of CuBe2 cathode after irradiation and LES test. (b) SEM imaging using secondary electron detector, with 3000× of magnification, of CuBe2 cathode after irradiation and LES test, showing a layer of C partially removed from the surface.

contamination happened after irradiation procedure. EDS was performed at multiple points of the surface inside and outside the irradiated regions of the different cathodes. From this, it was observed that a higher amount of C coincident with regions where we have more deposition of H^- particles, and the C percentage diminishes as we go further away from the irradiated region. Values ranged between 5% and 12% in weight, in contrast with the nonirradiated regions in which only 1%–2% was observed.

The cause of the carbon presence in all the irradiated surfaces might be attributed to contamination from the irradiation process, possibly from ion-induced cracking of residual hydrocarbon gases onto the surfaces. The presence of this superficial carbon has provided unusual conditioning behaviors in LES tests, not yet seen until the current date.

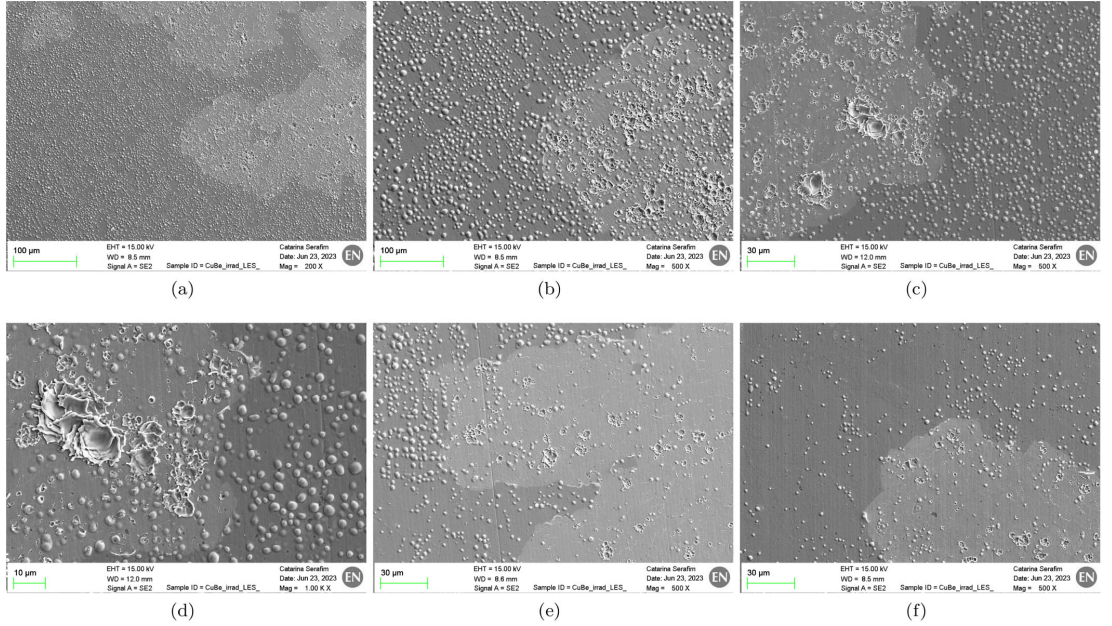


FIG. 13. (a)–(d) SEM imaging, using secondary electron detector, of CuBe2 cathode after irradiation and LES test. The regions in focus were taken where there was the highest deposition of particles from irradiation. (e),(f) SEM imaging, using secondary electron detector, of CuBe2 cathode after irradiation and LES test. The regions in focus were taken in the transition zone.

In Ta and SS316LN materials, when using SEM imaging, the presence of a carbon layer goes almost unnoticed. However, for CuBe2 and CuCr1Zr, the layer of carbon that has been formed on the surface is very visible. Below, we share images of CuBe2 cathode after irradiation and conditioning test using the LES system.

Figure 11(a) shows an optical image of the surface of the cathode electrode after it has been exposed to irradiation. The irradiated region is shown with a darker coloration, forming a half-circle shape, coincident with the gasket used during irradiation to limit the irradiated spot in the target. The darkest C-shape is where we had the highest deposition of particles, and it is where the highest density of blisters is found. After irradiation, LES tests were performed with this electrode. Figure 11(b) shows the state of the surface after the test, where the appearance of white spots covering the irradiation zone and its surroundings was observed.

Further analysis, using SEM and EDS, confirmed that the white regions represent the regions where carbon has been removed from the surface, designated as exfoliated regions. In SEM imaging, exfoliated regions appeared with a lighter contrast compared with the rest of the darker surface, as shown in Fig. 12(a).

The carbon layer is a fragile and thin layer, measured to have approximately 60 nm of thickness in the regions with higher ion deposition [61]. Figure 12(b) shows the carbon

layer peeling out from the surface (machining marks of the electrode surface are visible beneath the C layer). It becomes difficult to access the origin for the removal of the carbon. Analysis made postirradiation and pre-LES testing showed the carbon layer contamination without signs of degradation or cracking, which proves that the different regions where carbon has been removed appeared during the high voltage tests. At this stage, it is hypothesized that the initial stress from a vacuum arc or high-voltage exposure could have initiated a crack on the C layer, from which it triggered a peeling effect enhanced by the vacuum environment. Also, outgassing coming from the electrode could originate additional stress against the C layer, provoking cracking and peeling.

Additionally, it has been observed that breakdowns, from the high pulsing test, are only concentrated inside these exfoliated areas. This result is common for all the different regions: either in regions where there was more deposition of particles and therefore more density of blisters per area [Figs. 13(a)–13(d)], or in transition zones, where there is a decrease in blister's density as we move further from the high-density zone [Figs. 13(e)–13(f)]. This result may bring further insights to the scientific community of vacuum breakdowns studies, since it has not been yet fully understood the mechanisms that triggers the appearance of a breakdown. From the current results, we can summarize the following observations: (i) in an irradiated sample that

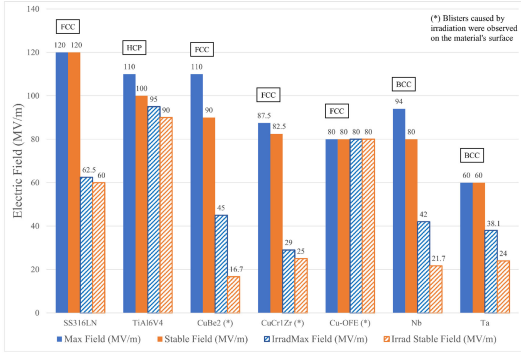


FIG. 14. Bar plot showing the results for all the tested materials in the LES system. The solid bars represent the results of nonirradiated electrodes. The lined bars represent the results for the irradiated electrodes. The blue and orange colors represent, respectively, the maximum and stable electric field achieved during testing.

has been contaminated with carbon, the number of breakdowns in the irradiated region is much bigger than the number of breakdowns in the nonirradiated region; (ii) in post-LES testing observations, breakdown sites were not observed in regions that still had a carbon contamination layer, and regions where breakdown sites were observed did not have a carbon contamination layer—the carbon removal happened during high pulsing field test; (iii) the final electric field achieved in electrodes contaminated with carbon is highly affected by its presence, when compared with the performance of electrodes that have not been irradiated and free from carbon contamination; (iv) the presence of blistering on the surface does not seem to have a correlation with the breakdown triggering, nor an effect on the maximum field reached.

Accounting for the results presented here and in [7], the final summary of all the materials in terms of surface electric field, when tested with LES system, was compiled together in Fig. 14, showing the results from all materials in order of best stable field achieved.

IV. CONCLUSIONS

We have measured the maximum field attained by several materials in the LES pulsed dc high-voltage system at a constant breakdown rate. Taking into consideration only the tests of nonirradiated materials, SS316LN shows to be the best material in reaching the highest and stable surface electric field (120 MV/m). Of the copper alloys, CuBe2 attains the highest performance reaching 90 MV/m. As a reference, standard Cu-OFE electrodes typically reach about 80 MV/m. As the main purpose of this study is to find a better substitute material for the manufacturing of an RFQ, the interest comes to materials

that can perform better than copper, which is the material traditionally used.

All of the irradiated materials have presented a big decrease in performance when compared with the non-irradiated electrodes. Blistering, as shown in copper alloys, does not seem to be directly correlated with this reduction. The reduced performance is instead associated with a carbon layer observed on the cathode's surface after irradiation. This may require further investigation regarding the role of carbon in the breakdown studies. For future testing, ways to remove the carbon layer from the electrodes surface are being investigated, which is not simply feasible with standard cleaning processes used in accelerator vacuum technology such as degreasing.

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The authors declare that the research was conducted in the absence of any commercial or financial relationship that could be construed as a potential conflict of interest.

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Publication III



Full length article

Effect of surface orientation on blistering of copper under high fluence keV hydrogen ion irradiation

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ABSTRACT

Copper and hydrogen are among the most common elements that are widely used in industrial and fundamental research applications. Copper surfaces are often exposed to hydrogen in the form of charged ions. The hydrogen ions can accelerate towards the surface, resulting in an accumulation of hydrogen below the surface. Harmless in low concentrations, prolonged hydrogen exposure can lead to dramatic changes on copper surfaces. This effect is visible to the naked eye in the form of blisters densely covering the exposed surface. Blisters are structural modifications that can affect the physical properties of the surface including, for example, vacuum dielectric strength.

Using scanning electron microscopy we found that the blistering of the irradiated polycrystalline copper surface does not grow uniformly with ion fluence. Initially, only some grains exhibit blisters, while others remain intact. Our experiments indicate that grains with the {100} orientation are the most prone to blistering, while the grains oriented in the {110} are the most resistant to it. Moreover, we noticed that blisters assume different shapes correlating with specific grain orientation.

Good agreement of experiments with the atomistic simulations explains the difference in the shapes of the blisters by specific behavior of dislocations within the FCC crystal structure. Moreover, our simulations reveal the correlation of the delay in blister formation on surfaces with certain orientations compared to the others with the dependence of the hydrogen penetration depth and the depth and amount of vacancies in copper on the orientation of the irradiated surface.

1. Introduction

The interaction of hydrogen with metals has attracted much attention recently because of various energy technology solutions, such as energy storage, future nuclear fusion power plants, hydrogen fuel cells and oil refining [1–4]. One of the major challenges in the use of hydrogen is hydrogen-induced degradation, corrosion, cracking and blistering [5,6]. Similarly, in technological applications related to particle accelerators or fusion power plants, metal surfaces can also be extensively exposed to hydrogen in the form of protons or negatively ionized atoms. One of the most detrimental effects that metal surfaces can experience under these conditions is blistering. The mechanisms behind blistering have been extensively studied in many materials to prevent malfunction or failure of devices exposed to hydrogen or noble gas ions [7]. These light species create defects in the lattice that can accumulate at grain boundaries or other lattice imperfections [8–10].

Under hydrogen ion irradiation, vacancies formed in atomic collisions with the bulk lattice atoms are capable of accommodating more than a single hydrogen atom [11–13]. Accumulation of multiple hydrogen atoms within a vacancy leads to expansion of the vacancy into a larger vacancy cluster that can accommodate even more hydrogen atoms [14], eventually resulting in stable bubbles at least 1.5 nm in size [15] and larger. On the surface, these bubbles are observed in the form of blisters [16–20].

Blistering is a phenomenon that has been observed in many metals regardless of their crystalline structure, body-centered cubic (BCC) or face-centered cubic (FCC). For example, tungsten, which is one of the most studied BCC metals because of its application for plasma-facing components in future nuclear fusion power plants, remains susceptible to the adverse effect of blistering [21–24] despite its otherwise superior properties, such as high melting point, good thermal conductivity, low

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thermal expansion, and high strength at high temperatures. Moreover, this effect has been reported in many other BCC metals such as V [25], Nb [26], carbon steel [27–29] and Fe [30–32]. FCC metals, such as Al [6,33–38] and Cu [18–20,39–42], experience blistering under different conditions of temperature, ion energy and fluence. For increasing the durability of these materials, hence improving their performance, it is important to understand the mechanisms of blistering in metals in order to mitigate its effects, since the properties of these materials change when exposed to light gas species [43,44]. This effect is particularly interesting in Cu, a metal that has a wide range of applications, including natural gas pipelines, the electronics industry, architecture and the storage of nuclear fuel waste [45–47]. It is also one of the most widely used metals in accelerator technologies because of its high electrical and thermal conductivity, and mechanical properties [48]. More precisely, Cu is used in radio frequency quadrupoles (RFQ) which act as injectors of protons from the source in the Large Hadron Collider (LHC) [49] and in neutral beam injectors in the International Thermonuclear Experimental Reactor (ITER) [50]. A proper understanding of blistering is crucial to avoid the frequent replacement of expensive components and disruption of regular operation of these devices.

Surface modifications in the form of protrusions can be seen in a microscope on metal surfaces. In H_2 atmosphere the protrusions were observed on both Al [38] and Ni [51] surfaces. Moreover, the shapes of these protrusions on Al surface were found to be different on the grains with different orientations, when the surface was exposed to low energy and high fluences molecular H_2 plasma [52]. These protrusions were shown to have square, circular and triangular shapes on the {100}, {110} and {111} surfaces, respectively. The conditions of exposure to hydrogen beams, i.e. energy and fluence, may play a role in the final surface modification. Some discussion related to plastic deformations in FCC lattices due to hydrogen accumulation under the surface is offered to explain the shapes of the protrusions. However, the proposed model does not provide sufficient atomic level insight into the effect of crystallographic orientation at any stage of protrusion development in these materials.

Computational methods, such as molecular dynamics (MD) [53], which simulate explicitly the dynamics of atomic motion under different external conditions, can provide crucial insights on mechanisms of plastic deformations as well as explain the dependence of the studied processes on crystallographic orientations of the material structure. For instance, valuable insights on the mechanisms of small gas bubbles growth in abundance of He and H atoms were obtained in Ni [54] and Cu [42,55]. However, the bubble growth near the surface which can result in surface blisters in FCC metals has not been yet addressed with an atomistic level detail.

Simulating the entire process of blister formation at the surface with MD methods is infeasible due to the size and time scale limitations. Generally, the binary collision approximation (BCA) methods are considered to fit better for the studies of implantation of light ions into a target [56–58]. The information about the ion depth profile and vacancy concentration, which is easily available from these calculations, can be used to model the size of forming blisters. Nevertheless, these models do not consider the crystal orientation as a parameter important for the blistering process, although it was shown to be significant for Ni [51] and Al [38,52]. For Ni, a lower density of blisters was observed for (100) grains compared to (111) ones. Similarly, for Al pillars [38], larger density of blisters were observed for (111) planes than in (100), and no blister was found in (110) planes of the pillars. Some authors [59,60] studied the effect of the crystal orientation on the penetration of He in Cu for several energies in the range of tens of keV. Moreno and Eliezer [59] have reported the observed dependence of the size of blisters on surface orientation, attributing this dependence to the different He depth profiles in different directions in Cu and CuBe. Unfortunately, the reported difference in He depth profiles is insufficient to explain the experimental results in the present work.

To explain blister formation in W [61–63], Au [64] and Ni [65], the defect formation (in terms of displacements per atom) was considered in combination with the depth profile of gaseous ions of different incident energies. Some details on bubble growth mechanisms were obtained in Fe [66] and Al [67], highlighting the importance of the interaction of H with the created vacancies. However, in these studies, the crystal orientation of the matrix as well as the effect of the surface were not included.

In the present study, the blisters were observed in radio-frequency quadrupole (RFQ) structures, which are the first accelerator element downstream the H^- ion source in the LHC injector chain at CERN. Here the stray beam of the H^- ions impacts the copper surfaces at the RFQ entrance with energies between 45 keV and 3 MeV. During the LHC runs, the surface is exposed to the beam for very long time, which becomes sufficient to cause severe deformation of the surface. To study this process, we used a combined experimental and theoretical approach to explain the non-uniformity of shapes and sizes of blisters covering the polycrystalline copper surface under prolonged exposure to H^- ion beam of 45 keV energy.

2. Methods

2.1. Experimental methods

In our experiments, we used Cu-OFE (oxygen-free electronic-grade copper, UNS C10100) electrodes that were prepared by diamond machining from a multi-directional forged bar [68]. The shape of the electrodes used in this work is compatible with the large electrode system described in detail in Ref. [42,69]. After machining, the degreased electrodes underwent the thermal treatment (835 °C, with the annealing ramp of 100 °C/h) applied for 20 min. This imitates the vacuum brazing cycle employed in the fabrication of the actual RFQ.

The irradiation of the sample was performed at CERN using an identical twin H^- source that injects into the operational RFQ. The sample was installed in a vacuum downstream of the source with a fixture, permitting beam incidence perpendicular to the sample surface. Beam energy was 45 keV at a fluence of $\sim 1.3 \times 10^{19} H^-/cm^2$ with an exposure time of 40 h, and a duty cycle of about 0.1% at a repetition rate of 1 Hz.

According to Ref. [70], H^- is fully ionized into H^+ within less than 1 atomic diameter after entering the copper surface, and calculations show that H^+ at 45 keV has a Bragg peak at a depth of about 300 nm.

Prior to irradiation, the sample was analyzed using electron backscatter diffraction (EBSD), where the orientation of the different grains can be detected with a certain range of accuracy. This allows us to follow the effect of the incoming irradiation in the differently oriented grain, and obtain information from it. For more information see Figure S1 in Supplementary material Section A.1.

Blisters on the sample were imaged by using a Scanning Electron Microscope (SEM) model Sigma from Zeiss. Additionally, Focused Ion Beam (FIB) milling was performed to obtain the cross-sectional view of the grains using a Pt protective layer.

2.2. Computational methods

In our computational studies, we performed MD simulations using the PARCAS code [53]. We used the embedded atom model (EAM) interatomic potential, developed by Mishin et al. [71] (Mishin potential) to describe the Cu–Cu interactions. We also used an EAM potential for the H–H interactions, following the works in Refs. [72–74], while the purely repulsive ZBL potential [75] was used for the Cu–H interactions. The use of a repulsive potential is motivated by the low solubility limit of H in Cu [76]. Moreover, in this approximation, we were able to generate sufficient pressure that is exerted at the walls of the void within an MD cell [42], while missing the occasional appearance of H atoms in interstitial positions within the Cu lattice.

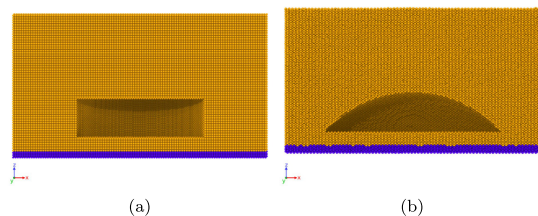


Fig. 1. Slice of the different simulation cells. In blue the fixed layer at the bottom. (a) Disk-shaped void and (b) hemisphere-shaped void. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

All cells in our simulations were of the same size, which was ~ 30 nm in the x - y directions and 15 nm in the z -direction, containing $\sim 1\,040\,000$ atoms. The generated cell was relaxed at 600 K and 0 kbar (NPT) [77] with periodic boundary conditions in all directions for 50 ps. The main simulations of this study were performed using periodic boundary conditions only in the x - y direction, while the cell in the z -direction had an open surface at its top. The cell was rotated to align the z -axis with one of the low-index crystallographic directions $\{100\}$, $\{110\}$ and $\{111\}$ to imitate differently oriented grains. At the bottom of the cell, a fixed atomic layer prevented the cell from moving during the simulations (see Fig. 1, blue slabs). After the surface was opened, the cells in all three orientations were additionally relaxed for 100 ps at 600 K in NVT using the Berendsen thermostat [77]. The same temperature using the Berendsen thermostat was applied in all the remaining simulations, which were performed for 100 ps of the simulated time.

In the prepared cells of three orientations, we inserted two types of voids in the shape of a disk and a hemisphere (see Fig. 1). These shapes were selected to imitate the shapes found in the SEM images of the bubbles grown in Cu during the extensive H^- irradiation (see Fig. 3). Moreover, the chosen geometries can enhance the interaction of the void with the surface to compensate for the limited timescale of MD simulations. For consistency, we kept the volume of all the created voids the same ($\sim 7 \times 10^3 \text{ nm}^3$) regardless of their shapes. All bubbles were positioned 9 nm below the surface measured from the top of the bubble.

The pressure within the bubbles was controlled by the concentration of H atoms in terms of $n_{H/Vac}$ (the number of H atoms per missing Cu atom). The H atoms are randomly distributed within the void at a distance not shorter than 0.09 nm, which is larger than the bond length predicted by the H-H potential [74]. Although we simulated the bubbles with the different concentrations of the H atoms, we were able to observe structural modifications only under the pressure of 20 kbar ($n_{H/Vac} \approx 1.2$). To ensure the sensible result within 100 ps, we increased the H concentration to $n_{H/Vac} = 2$ (30 kbar) as in [42], while performing only one test simulation with $n_{H/Vac} = 1.2$ for the disk-shaped bubble, which was located closer to the surface than other bubbles (see Supplementary material Section A.2). We also show in the Supplementary material Section A.3 that under the pressures which we use in the current simulations, the likelihood of formation of H_2 molecules is low, while in experiments, under the lower pressures and longer time scales the gas may consist of molecules. We observe how the hydrogen contained in the bubble is in atomic state, being this pressure enough to not allow the formation of H-H bonds.

The solubility of H in Cu, at similar conditions to these reproduced in our computational study (600 K and 20 kbar) is very low [76]. Hence we can assume that the H atoms present in the Cu lattice accumulate in a void, which allows us to focus on the response of the material to the hydrostatic pressure of the hydrogen gas within the bubble.

For visualization of the results, we used the Open Visualization Tool (OVITO) [78].

To estimate the hydrogen depth profile for different crystallographic orientations, we additionally used the MDRANGE code [79], which is an MD code efficiently calculating ion range profiles and their lateral straggles within the recoil interaction approximation (RIA). For instance, the code was successfully applied to calculate the channeling maps in materials with different crystal structures [80]. In this approximation, solely the forces acting between the ion and the target atoms are considered, disregarding the further evolution of the cascades that involve interactions amongst the target atoms. Statistically significant results were obtained by running 10 000 simulations of 45 keV H impacts for each low-index crystallographic orientation of the copper surface. Since these simulations are limited to the interactions of the impacting ions only, it is not possible to obtain directly the number of produced vacancies to be compared between the different crystallographic directions. Both distributions of the produced defects and the ion range were obtained with the help of a more conventional binary collision approximation approach, using the CASWIN code [81] simulating 50 000 impacts of 45 keV. Although the crystal structure is not taken into account in these simulations, we use them to correlate the vacancy and the primary recoils depth distributions generated by the passing hydrogen ions in Cu. More detail on the CASWIN simulations can be found in Supplementary material A.4.

3. Results and discussion

In this section when discussing the experimental results, we will refer as blister to those bubbles of large size (larger than hundreds of nm) and not entirely rounded, that are formed close to the surface and leave track at the surface. If the bubbles are rounded and the size smaller than the called blisters, we will simply use bubble. However, in the computational results, we will use the term protrusion to name this effect at the surface, since the scale of the computational results differ from the experimental ones.

3.1. Blister shapes and sizes on polycrystalline Cu surface under different h ion fluence

The orientation of the grains on the Cu surface was determined before irradiation using the EBSD technique. The full map of the analyzed region can be seen in Supplementary Figure S1. We see the overall prevalence of the blue, green and red colors on the map, which indicate the preferential orientation of the grains is in one of the low-index directions, such as $\{111\}$ (blue), $\{110\}$ (green) and $\{100\}$ (red). To verify the effect of the H^- exposure on the bubble growth in the sample, we selected two different areas with varying exposures to the ion beam, i.e. at different distances from the center of the beam. These areas are shown in Figure S1: in blue a transition area between the core of the beam and the halo, and in magenta a high fluence irradiation area corresponding to the beam core.

Fig. 2 shows a section of the transition area of the Cu surface exposed to the H^- ion irradiation for 40 h reaching the fluence of $\sim 1.3 \times 10^{19} \text{ cm}^{-2}$. Here we selected the regions within the transition area (i.e. the low fluence) across two grains with notably different orientations ($\{111\}/\{100\}$ in Fig. 2a and $\{100\}/\{110\}$ in Fig. 2c according to the EBSD map). In Fig. 2a we observe the formation of dimples in the center of several blisters. The appearance of dimples in these blisters can be due to a larger hydrogen pressure inside them, inducing a stronger plastic deformation at the center over the surface, where the stress is higher. This causes a more deformed region of the blister at the top. A FIB-SEM from Zeiss was used to mill the sample to obtain the cross-sectional views of the two grains in question. Visualizing the sample, we systematically observe a thin black layer which corresponds to carbon, and it is observed in all the grains considered (see for instance Fig. 2d). The carbon layer results from the surface cracking of hydrocarbons in the residual gas of the vacuum of our irradiation facility. This phenomenon is known to occur upon electron or ion

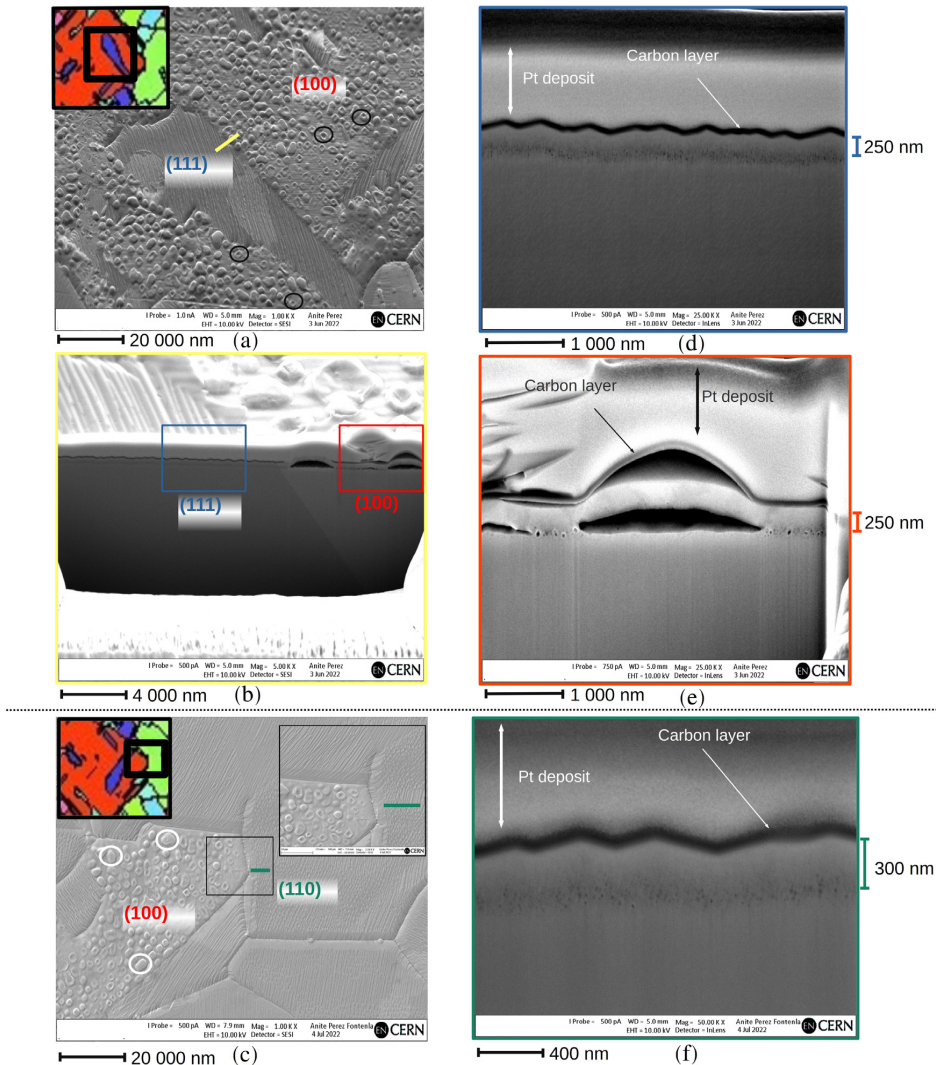


Fig. 2. SEM images of the Cu surface irradiated by H^- ions up to a dose of $\sim 1.3 \times 10^{19} H^-/cm^2$ at the transition area. (a) The surface of two grains is marked as (111) and (100). A yellow line marks where the cross-section was carried out. Black circles mark some of the dimples. (b) Cross-sections of the two grains (111) and (100) (corresponding to the yellow line in (a)), shown in Figures (d–e) respectively. (c) Surface of the two grains marked as (100) and (110). Inset: Zoom of the boundary region between the two grains. (f) Cross-section of a (110) grain in the transition area shown in (c) by a green line. A Zeiss Crossbeam 540 Focused Ion Beam (FIB)/Scanning Electron Microscope (SEM) was used to perform the cross-section on the sample. Imaging was performed using InLens Secondary Electron Detector at 10 keV and various magnifications. The areas shown in the cross sections are marked in red, blue and green for (100), (111) and (110), respectively. The horizontal dashed line separates the two different regions explored at the transition area. EBSD maps of the regions explored can be found in insets of (a) and (c) respectively. For a view of the complete EBSD map, see Figure S1b. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

surface irradiation also in high vacuum environments, such as scanning electron microscopes or plasma fusion experiments. In Fig. 2b, the blue and red squares outline the regions that are zoomed in Figs. 2d and 2e, respectively, while the green line in Fig. 2c indicates the area where the cross-sectional view was obtained for the (110) grain found on the same surface as the grains shown in Fig. 2a (for a detailed location of the grains see EBSD map in Figure S1a).

In Fig. 2a and 2c, we clearly see that blisters of approximately square shapes are fully developed on the (100) grain, while no trace of blister formation is seen in the same images on the (111) and (110) grains. Nevertheless, in Fig. 2c we observe that close to the boundary between (111) and (110) grains, some blisters exhibit almost

rhomboidal shape and the height of them is not as prominent as in other parts of the grain. Besides, we observe different shapes due to the coalescence of blisters (marked in white in Fig. 2c). In the cross-sectional image of the grain (see Fig. 2b), we see a layer of small bubbles grown at the same depth (about 250–295 nm) under the surface of both grains. However, in the (100) grain, the bubbles are more developed with some of them growing much larger than the others (see a zoom-in image in Fig. 2e), which result in big blisters on the surface. We note that the shape of the blisters is close to hemispherical, with a fairly flat bottom part. Moreover, in Fig. 2e, we observe dual blistering, which corresponds to a secondary blister formation caused by the accumulation of hydrogen between the substrate and the C layer

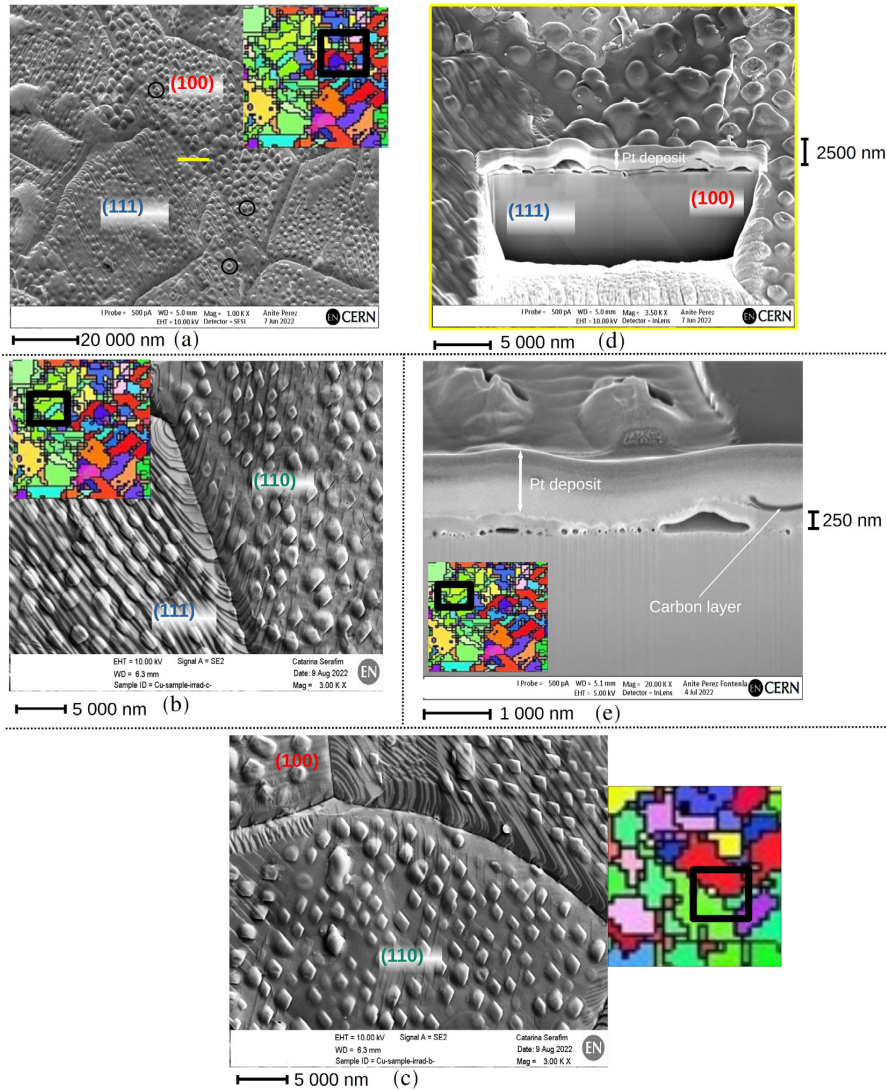


Fig. 3. SEM images of the Cu surface irradiated by H^- ions up to a dose of $\sim 1.3 \times 10^{19} H^-/cm^2$ at the high fluence area. Surface of two grains explored: (a) (111) and (100), (b) (111) and (110) and (c) (100) and (110). Cross-sections of the two grains (d) (111) and (100), and (e) (110). A Zeiss Crossbeam 540 Focused Ion Beam (FIB)/Scanning Electron Microscope (SEM) was used to perform the cross section on the sample. Imaging was performed using InLens Secondary Electron Detector at 10 keV and various magnifications. Vertical and horizontal dashed lines separate the three different regions explored at the high fluence area. Black circles mark some of the dimples. EBSD maps of the regions explored can be found in insets of (a), (b) and (c) respectively. For a view of the complete EBSD map, see Figure S1c.

deposited during irradiation. Surprisingly, the bubbles grown in the (111) grain are only in an initial state of nanometric size (see Fig. 2d). The bubbles under the surface in the (110)-oriented grain are grown deeper (305 and 335 nm under the surface) and even smaller (see Fig. 2e and note the different scale bar). Additionally, we observe that at the non-yielded grains a roughness pattern (i.e. faceting) is present, especially noticeable from the undulations in the carbon layer (see Fig. 2d and 2f). Faceting is a consequence of the thermal treatment on the sample, and it has been previously observed for copper [82,83]. The role of the surface patterning on the plastic deformation of the top Cu layer can influence the process of blister formation. Nevertheless, a detailed investigation into this specific effect lies beyond the scope of this work, and we will investigate this effect in the near future.

Fig. 3 shows the surface with different grain orientations in the region of the high irradiation fluence. The zoom-out view of this region in 3a shows that the surface, including the grains with [111] orientation, is covered by blisters quite uniformly. Again, here we observe dimples in the (100) grain, some of them resemble small holes. In the latter, the hydrogen pressure could have caused the yield of the blister at the center. Yet again, we see well-developed blisters on the (100) grain, while on the (111) grain, the blisters are weaker and developed to a lesser extent than on the (100) grain. However, a qualitative analysis of these grains shows a difference in the shapes of the blisters grown on the two explored grains. While on the (100) grain the blisters have the 90° vertices, the blisters on the (111) grain are more round with only occasional sharpened features. Moreover, in Fig. 3a, it is clear

that the coverage density of blisters on the (111) grain is smaller than that on the (100) grain. The stronger magnification in Fig. 3b shows some formation of better-defined vertices in the shape of the blisters on the (111) grain. Furthermore, we observe that (111) grain exhibits some striation at the surface that combines with the blistering. In the same image of Fig. 3b, we see well-developed blisters in clear diamond-like or rhomboidal shapes on the (110) grain as well as in Fig. 3c. A quantitative analysis will be required to obtain precise information on the density and shape of the blisters in the differently oriented grains.

The cross-sectional image of these grains shown in Fig. 3d reveals that the bubbles under the surfaces in both grains form at approximately the same depth as in the transition area (low fluence, shown in Fig. 2b), about 270–280 nm, while in this high fluence area, the bubbles are developed further in the (111) grains. We observe again the appearance of small bubbles, that are likely to be the nucleation sites of the large blisters, and as the fluence increases they develop into similar blisters as in the (100) grain. We observe that these blisters have rather hemispherical or disk-like shapes. Similarly, in Fig. 3e, we also observe the formation of blisters in the area of the high fluence, which have remarkable rhomboidal shapes of the blisters appearing at the surface. We also see the formation of small bubbles within a range of 210 and 330 nm.

3.2. Simulation of surface protrusions grown on cu surfaces with different orientations above pressurized h bubbles

In the experimental images shown in Figs. 2 and 3, we observe the formation of bubbles of different shapes from small rounded to large flat-faced and hemispherical ones that are more expanded in the direction of the surface. We also notice that small rounded bubbles tend to grow at an early stage of bubble formation, while the large bubbles, which usually result in surface blisters, are observed at later stages when the irradiation fluence is much higher. Although the small bubbles may interact with the surface as well, the deep positioning of these bubbles as well as the corresponding absence of visible change of surface morphology motivated us to study the effect of hydrogen accumulation in the bubble of only two shapes, the disk-like and hemispherical. These specific shapes allowed us to construct an MD model of a bubble with a large top area to achieve sufficient shear stress resulting from the effect of the gas pressure within the bubble and the presence of a nearby open surface [84,85].

We show the top views of the Cu surfaces with three different orientations, see the left column in Fig. 4 for the (100) surface (Figs. 4a and 4g), the middle column for the (111) surface (Figs. 4b and 4h) and the right column for the (110) surface (4c and 4i) after 100ps of the relaxation run in the NVT ensemble at 600K since a bubble of either disk-like (the upper row (4a–4c)) or hemispherical (the third row from the top (4h–4j)) shape was placed beneath it. In the second and fourth rows of Fig. 4, we show the corresponding snapshots of the structures shown in the row above, but at different times. These times were selected to show more clearly the stacking faults that were formed by Shockley partial dislocations emitted from the surface of the bubbles. The images in Figs. 4d and 4j are tilted for a better illustration of the stacking faults, while the other images are shown from the top. In these images, only the atoms with the centrosymmetry parameter more than 5 are shown for clarity. Showing only these atoms for each orientation, the formation of the surface protrusion is more visible.

In Fig. 4 we see that the large bubbles beneath the surfaces with all three orientations have resulted in protrusions with remarkably different shapes. However, all shapes of protrusions are aligned with {111} planes. This alignment and a large number of stacking faults between the bubbles and the open surface indicate that the protrusions originate from plastic deformation in Cu as a result of the interaction of hydrostatic pressure within the bubble and the open surface. Moreover, we see that the shapes of protrusions correlate with the orientation of the surface stronger than with the shape of the bubble, since regardless

of the latter the shape of the protrusions are almost similar for (100), (111) and (110) surfaces (Figs. 4a and 4g, Figs. 4b and 4h, and Figs. 4c and 4i, respectively).

The most remarkable shape of square protrusions, we indeed observe on the (100) surface, which is in good agreement with most of the blisters at the surface of Fig. 2. Although none of the {111} planes is perpendicular to this surface, yet we clearly see two squares that are formed not directly above the bubble but slightly to the side from it. Unfortunately, the current size of the simulation box was too large to obtain a full protrusion of the squared shape within a reasonable computational time. To enable such a shape, we reduced the size of the simulation cell by placing the bubble closer to the surface but reducing the concentration of the H atoms ($n_{H/Vac} = 1.2$). These results are presented in Supplemental material Section A.2. Moreover, the complex dislocation-mediated interaction of the disk-shaped bubble with the (100) surface can be viewed in the online video 100-DISK-N2.MP4.

In Fig. 4d one can see the dislocation reaction that led to the formation of the protrusion. Here we clearly see that the stacking faults (between the two Shockley partials) extended from the bubble towards the surface in four {110} directions on the {111} planes. The stacking faults intersect the (100) surface at the angle of 45°. The intersecting lines from four {111} planes form a square on the (100) surface as it is explained in the schematic, see Fig. 4m. Here we highlight in red the (100) surface where a protrusion is formed by the dislocations moving along four {111} planes in {110} directions. The dashed blue lines on the red (100) surface show the intersection lines, which form the final square shape observed in Fig. 4a. A slight offset from the position of the bubble is explained by the dislocations emitted from different random locations on the bubble surface and since they expand to the open surface at 45°, the shift of the location of some protrusion emitted from the bubble is expected. However, these shifts are unlikely to play a significant role in the shape of macroscopic protrusions, while the straight angle of the vertices of the final protrusion above the bubble will persist as the main feature of the protrusion on this surface.

A triangular protrusion appeared on the (111) surface can be seen in Fig. 4b. This differs from the close-to-circular shape of blisters seen in the experiment, see Fig. 3. The circular shape of a protrusion we observed on the surface above the bubble with the lower pressure ($n_{H/Vac} = 1.2$), see Supplementary material Section A.2. However, we explain this circular shape of protrusion by the low gas pressure that was insufficient for the surface to yield. We note that the height of the protrusion is not uniform with the elevation that increases towards the center of the protrusion right above the under-surface bubble. This indicates the dilation of the bubble under the inner pressure as a result of the elastic response of the lattice. Consequently, when the pressure is increased and the bubble is placed deeper under the surface, we observe significant plastic deformation of the lattice in the form of dislocation network in the region between the bubble and the surface (see movie 111-DISK-N2.MP4). However, overall we can see that the triangular protrusion is the product of stacking faults growing from the bubble surface as shown in Fig. 4e. The stacking fault is forming along the three {111} planes which intersect the (111) surface in the form of a triangle (for more detail, see Fig. 4m). On the much larger scale of the experimental bubbles, one can expect the formation of a protrusion with a circular shape. This conclusion is in line with the plastic response of Cu surface to accumulated H pressure under the surface. Yet we note that the bubbles must build up higher H pressure inside before the surface with the {111} orientation can yield.

In Fig. 4c, we observe that the (110) surface yields forming a rhomboid-shaped protrusions. This result is in remarkable agreement with the experiment, see Fig. 3. Here, the stacking faults grow straight to the surface along the {111} planes that are perpendicular to the (110) surface. These planes form the angles approximately 71° and 109°, which are exactly the same angles of vertices of the obtained protrusions in our MD simulations (see Fig. 4c and 4f) and of the blisters in experiment, see Fig. 2. The angles and corresponding planes

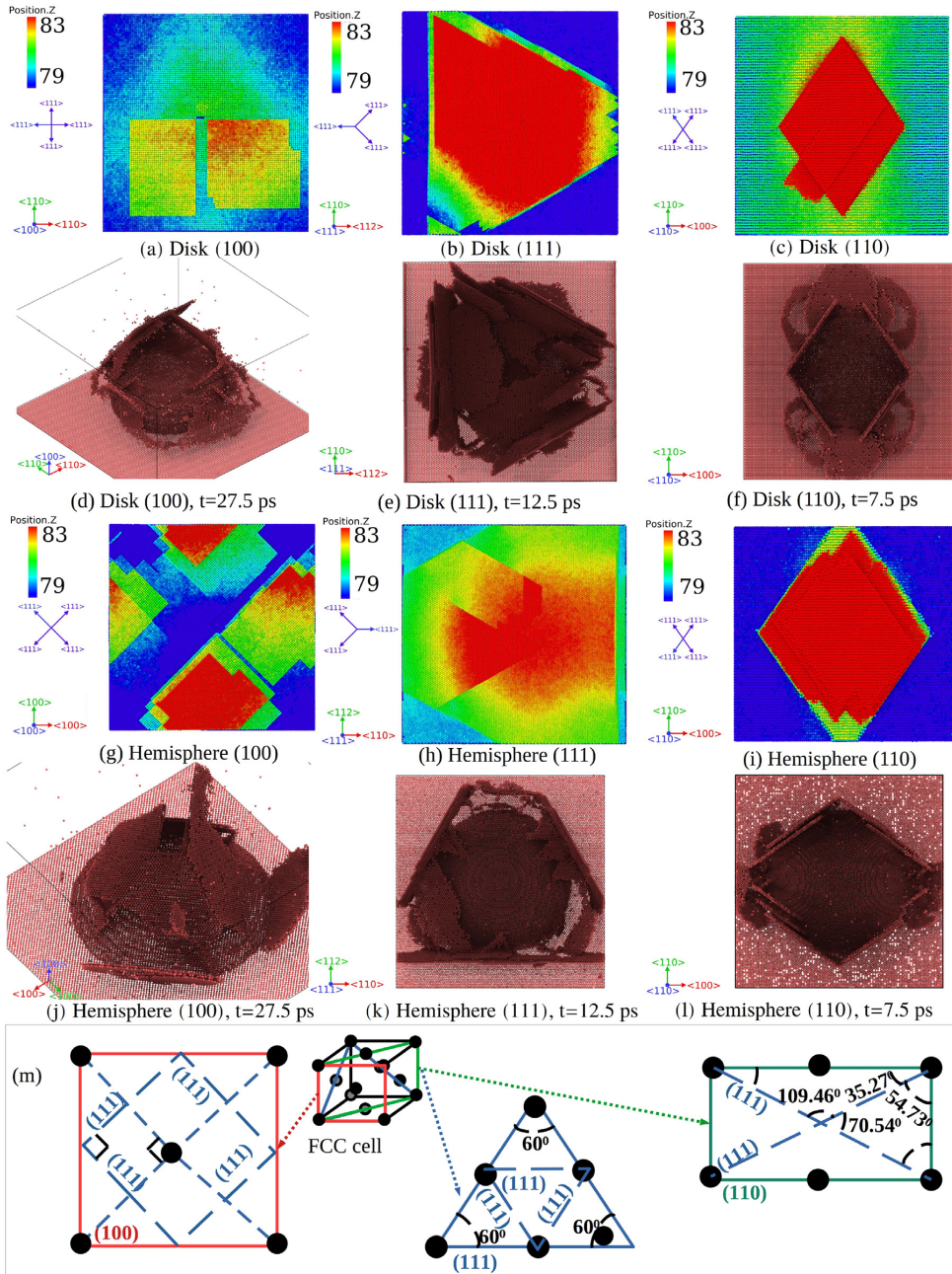


Fig. 4. Final configurations (after 100 ps) of surfaces for disk-shaped (a, b, c) and hemispherical-shaped bubbles (g, h, i) using (100), (111) and (110) surfaces orientation, respectively, under $n_{H/Vac} = 2$. The directions normal to {111} planes projected onto the differently oriented surfaces are marked in blue. Atoms are colored according to their z position in Å. The lower limit corresponds to the initial level of the surface in each case, and upper limit is chosen for an easier visualization of the protrusion. Top view of cells surfaces at different times for disk-shaped (e, f, g) and hemispherical-shaped bubbles (j, k, l) oriented as (100), (111) and (110), respectively, under $n_{H/Vac} = 2$. The view corresponding to (100) surfaces (a, d) has been tilted for improvement of clearness. Atoms located at the surface and those with centrosymmetry parameter (CSP) [86] smaller than 5 are omitted for clarity. (m) Schematic of the {111} planes projected (dashed blue lines) onto (100), (111) and (110) surfaces.

are explained in more detail in Fig. 4m. This shape of protrusion was previously observed by Pohjonen et al. [87]. For a more detailed view of the process see the online video 110-DISK-N2.MP4.

Although the overall shape of protrusions grown from the hemispherical bubble (Figs. 4g–4i and 4j–4l) are similar to the corresponding protrusions from the disk-shaped bubble, the closer comparison of the

two cases reveals some differences. For instance, on the (100) surface we observe the protrusions in the form of terraces, i.e. multilayered formations that stand out from the surface much stronger than in the case of the disk-shaped bubble. It is clear that the uneven top (curvature) offers a larger area for sufficient shear stress to build up along the {111} slip planes under the hydrostatic pressure in the bubble and vicinity of the open surface facilitating emission of dislocations, compare Figs. 4a and 4g. Note the different lateral orientation of the simulation box which explains the 45° rotation of the protrusions with respect to one another on both (100) surfaces. For a detailed view of the growing dislocations see the online video 100-HEMISPHERE-N2.MP4. The same explanation holds for the hemispherical bubble under the (111) surface, see Fig. 4h. The protrusion on this surface is much less clear with many triangular shapes standing out. This is due to more frequent sites where the dislocations can be emitted. Unfortunately, the size of the cell did not allow us to continue this simulation even longer, but we observe the tendency towards a more circular shape of the protrusion compared to the disk-like bubble. To follow the complete process of dislocation emission in this case, see the online video 111-HEMISPHERE-N2.MP4.

The protrusion on the (110) surface, see Figs. 4i and 4l, appears in the rhomboidal shape, similarly to the protrusion from the disk-shaped bubble, however again, the size of this protrusion is larger. We also clearly noticed that the protrusion is also terraced as in the case of the (100) surface. This is a direct consequence of the curvature of the top of the bubble. For a detailed view of the process see movie 110-HEMISPHERE-N2.MP4.

From our MD simulations, we conclude that blisters that grow on Cu surface exposed to high fluence H irradiation can be explained by plastic deformations caused by strong H pressure that builds up in the bubbles grown under the surface. The protrusions in the form of blisters, visible on experimental surfaces, grow in our simulations via dislocations emitted from the bubble surface along the {111} planes in <110> directions. This explains the difference in the shapes of the blisters on the grains of different orientations.

We draw attention that the bubbles under the {110} surface resulted in a surface protrusion at the earliest time compared to the protrusions on the {111} and {100} surfaces. In fact, the latter yielded a protrusion the latest among the three orientations, see the times of the frames in the images showing the stacking faults in Fig. 4. Hence, the difference in dislocation behavior under the surfaces with different orientations cannot explain the experimental result. From the plastic deformation point of view, it is rather counter-intuitive to see the first blisters on the {100} surface, while the {111} and {110} yield much later, i.e. at much higher fluences.

Furthermore, another effect could contribute to the earlier appearance of blisters on the real {100} surface: the difference in the rate of adatom diffusion between the low-index surfaces. The activation energy of migration of an adatom on the {100} surface is ~0.4 eV [88,89], while on the {110} surface it is 0.2–0.27 eV [90,91], and on the {111} surface only 0.04 eV [92,93]. The much faster diffusion on the {110} and the {111} surfaces could facilitate the dissolution of the initially formed atomic steps before they can develop into blisters; while on the {100}, the slower diffusion makes the steps more persistent. Any difference in atom step stabilities arising from surface diffusion considerations is likewise beyond the reach of the time scales of our MD simulations and, experimentally, only large blisters are noted at the surface.

4. Role of crystal orientation on h accumulation under the irradiated surface

Quiros et al. [52] have reported the formation of blisters of different shapes on Al surface depending on the orientation of the grain during the exposure to H₂ plasma, which was also explained by plastic deformation at the formed under-surface bubbles. The shapes of the

blisters that the authors observed on Al polycrystalline surface only partly resemble those that we observe in our experiments because of the different experimental conditions: H₂ plasma exposure compared to the ion beam with a much lower ion flux and much higher energy of tens of keV compared to hundreds of eV in plasma irradiation. We also note that the stacking fault energy in Cu lattice is lower [94] than for Al [95], which may lead to the formation of different shape protrusions, in particular, on {110} surface.

The most striking observation in our experiments emerges from the comparison of the two regions of the irradiated surface: with the low (transition area) and the high (middle of the irradiated region) ion fluences. In the transition area of our sample (see Fig. 2a) we see the well-developed blisters only on the (100)-oriented grain, but not on the (111)-oriented grain, at least, with the resolution of the SEM image. Comparing the images in Fig. 2d–2f, we see small bubbles at approximately the same depth under all three surfaces, while the large bubbles are formed only under the (100) surface. It has been suggested by Moreno and Eliezer [59] that the difference in the size of the blisters on different surfaces can be related to the channeling directions that can induce the deeper penetration of the ions. In Fig. 5a we plot the channeling map for H ions in Cu that was generated by using the MDRANGE [96] code. Indeed we see that the [110] direction exhibits the strongest channeling effect, $R_{\text{mean}} = 353 \pm 1$ nm, since this is the direction with the close-packed {111} planes along it. However, the analysis of this map does not explain the difference in blister formation between the surfaces with the {111} and {100} directions. On the contrary, the penetration of H ions in the [100] direction is slightly deeper than in the [111] one, $R_{\text{mean}} = 271 \pm 1$ nm and $R_{\text{mean}} = 255 \pm 1$ nm, respectively. Moreover, the lateral straggling cannot have a significant effect on the bubble growth, since it is fairly similar, in our simulations of the channeling map, it is 68.8 ± 0.1 and 69.4 ± 0.1 nm, respectively for (100) and (111).

We will now take a closer look at the dynamics of radiation damage under 45 keV H⁺ ion irradiation. Since the H atoms have high binding energy to vacancies [97,98], they are known to accumulate in the vacancies, which can grow larger clusters during prolonged ion irradiation. If the H ions stop near a vacancy cluster, they can be trapped in it, forming bubbles [99]. Therefore, we now look at the distributions of vacancies in Cu and analyze their correlation with the H depth profiles during the 45 keV H⁺ ion irradiation using the BCA code CASWIN [81]. In Fig. 5c we show the H depth profile (olive color) and the vacancies depth distribution (black color), which have maxima at similar depths with about 50 nm separation. In addition, we plot the depth distribution of the primary recoil atoms (the atoms of the target that are knocked-on directly by impacting hydrogen ion) with the energy not less than 40 eV. The energy was selected to be sufficient to create at least one vacancy in copper (according to Refs. [100,101] the threshold displacement energy for Cu is 33 eV). We see that both vacancy and primary recoil depth distributions are very similar, with a small shift towards the surface of the maximum of the vacancy depth distribution. In the CASWIN code, the crystal structure of the target material is not taken into account. Therefore, it is not possible to observe the dependence of defect distributions or depth profiles of implanted species on the crystallographic orientation of the irradiated target. For this purpose, we used the MDRANGE code, which can simulate the penetration of the H ions in a specific direction in the Cu crystal structure. For computational efficiency, the MDRANGE code does not follow the evolution of the full cascade, which would allow to obtain the vacancy depth distribution directly. Instead, the MDRANGE records the primary recoils, which can be used to assess the shape of the vacancy depth distributions in the specific directions as we saw from close comparison of the two curves in the simulations by means of the CASWIN BCA code.

The results of these calculations are shown in Fig. 5d.

In Fig. 5d we see that the ion depth profiles (open symbols) and the primary recoil profiles, i.e. the profiles of vacancy distributions (filled

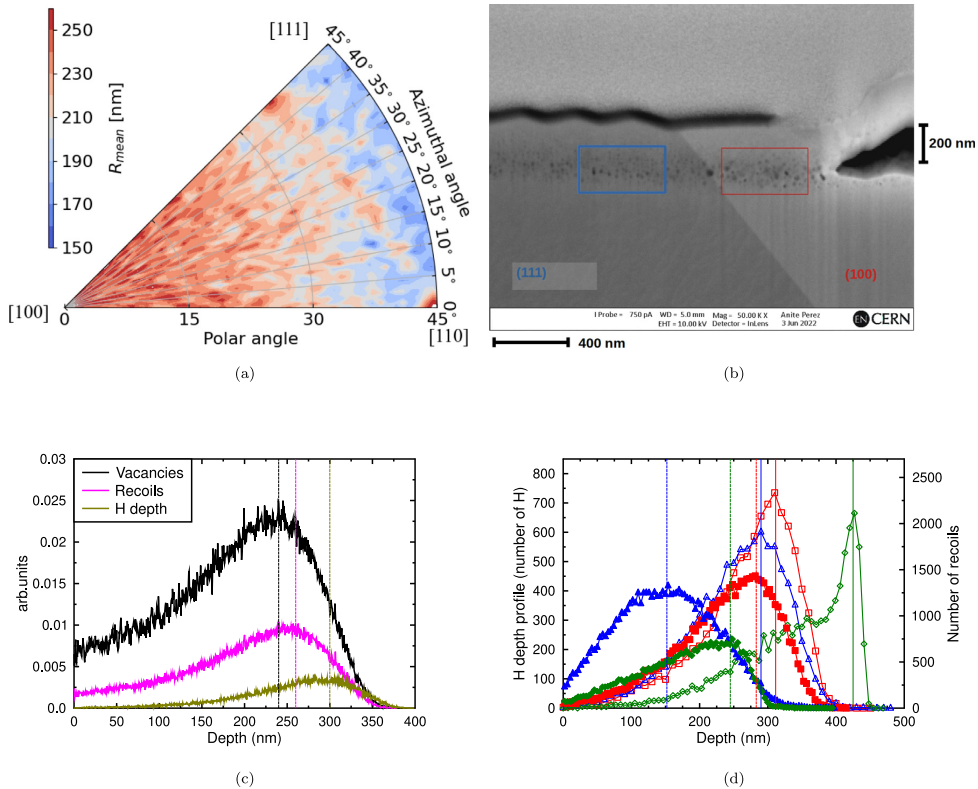


Fig. 5. (a) Channeling map for the 45 keV H ion irradiation of Cu calculated using the MDRANGE code [102]. The map is colored according to the mean H penetration depth (in nm, see the color bar) for each crystallographic direction identified by the pair of the polar and azimuthal angles. The main crystallographic directions are indicated at the corners of the map. The plot is generated with the polar and azimuthal angular steps of 1° , and each point is the average obtained for 100 impacts. (b) Zoom-in of grain boundary between (111) (blue) and (100) (red) grains at the transition area. The rectangular zones marked in each grain are of the same area. (c) Vacancies (black), recoil atoms with the energy above 40 eV (magenta) depth distributions as well as the H depth profile (olive) obtained by the CASWIN code, averaged over 50 000 H ion impacts. The y-axis shows the probability density depth distribution per ion impact. Black, magenta and olive vertical dashed lines mark the maxima of vacancy, recoil and H depth distributions, respectively. (d) H depth profile (open markers) and distribution of recoils with energy above 40 eV (filled markers) for (100) (square), (111) (triangle) and (110) (diamond) as a function of depth in MDRANGE averaged over 10 000 ion impacts. The recoil profiles are used to model the vacancy profile shown in (c). Vertical lines of different colors mark the maxima of the distributions of the corresponding colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

symbols), are strongly dependent on the crystallographic direction (see Fig. 5c, where vacancies are created a slightly closer to the surface than recoils). Comparison of both profiles, the ion depth profile and the primary recoils, for each orientation separately, reveals that only the profiles obtained in the [100] direction (red open and filled squares) have peaks located at approximately the same depth with only ~ 12 nm of separation. This means that both profiles practically fully overlap, i.e. the accumulation of H in this direction occurs almost at the same depth as the created vacancies. The largest overlap of both profiles leads to the fastest bubble growth under this surface.

The ion depth profile in the [111] (blue open triangles) is similar to that in the [100] direction, but the vacancies are formed much closer to the surface. The overlap of both profiles in this direction is smaller since the peaks are separated by ~ 140 nm. However, the depth of the maximum overlap is fairly close to that of the bubble growth depth in the [100] grain, the small bubbles are visible in Fig. 5b at approximately the same depth as the much larger ones that have grown in the [100] grain.

Finally, in the [110] direction, the H depth profile is the largest. We see that the separation between the peaks in this direction is larger than in the [111] direction, ~ 180 nm, and the peak height is smaller when compared to the peaks of the primary recoils generated but the ions in other directions. Since the ions in this direction move along

the close-packed {111} planes, i.e. in the planar channels (see the red region in the [110] direction in the channeling map in Fig. 5a), they generate fewer recoils with sufficiently high energy, which produce a lower number of vacancies. The smaller peak of the primary recoils along with the specific shape of the ion depth profile (due to channeling effect the majority of ions reach almost the maximal penetration depth) the overlap is very small and the bubble growth dynamics in this direction is remarkably slow. These simulation results explain why in experiments we see in the transition area, where the fluence is lower, only the blisters on the [100] grains and not on the other two grains, although the plastic deformation around an under-surface pressurized bubble is expected to yield faster in the grain of the (110) orientations, which have the slip {111} planes oriented perpendicular to the {110} surface.

Our results show that the discrepancy in penetration depths along the different directions of the incoming ions is not sufficient to explain the orientation-dependent blister formation in FCC materials [59]. Nevertheless, we observe that after high ion fluences, blistering occurs everywhere when the damage produced close to the surface is filled with hydrogen. Once hydrogen atoms occupy the created vacancies, the latter may continue growing via the loop punching mechanisms [42]. Then, after the coalescence of small bubbles into big blisters, the effect is noticed at the surface similarly as it is seen in Figs. 3d–3e and 4.

This process happens faster in (100) grains and slower in (111) and (110) grains. Consequently, the larger the difference in depth between the H depth profile and the formation of vacancies, the more fluence is needed to blister the grain.

5. Conclusions

In this work, we report the non-uniform blistering of a polycrystalline copper surface under the high fluence 45 keV negative hydrogen ion irradiation. The morphology analysis of the surfaces irradiated with two different ion fluences revealed that the shape of the blisters grown on different grains was different and correlated with the crystallographic orientation of the grain surface. Moreover, the whole surface of the areas irradiated to high ion fluence was densely covered with blisters fairly uniformly, while at lower fluence the coverage was highly non-uniform: well-developed blisters were seen only on some grains, while the other grains remained flat.

To obtain the insights into mechanisms of copper surface blistering, we carried out a set of molecular dynamics simulations to show how the surface of the differently oriented grains yields under the pressure built up in bubbles formed in copper during the hydrogen ion implantation. The shape of protrusions obtained from the bubbles placed under the surface with different orientations is in good agreement with the shape of blisters observed in experiments. We also were able to explain the delay for blistering on {111} and {110} oriented surfaces compared to that of {100} orientations, when we explicitly considered the crystal structure of copper. We revealed that the difference in blistering is not associated with the difference in the penetration depth of the implanted ions as it was proposed earlier but by the degree of the overlap of the hydrogen depth profile and the vacancy depth distribution. This conclusion is consistent with our experimental observation of the fastest blister growth on the grains of {100} orientations, in which the overlap of depth distributions of the implanted hydrogen atoms and the vacancies created due to ion impacts was the strongest.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.actamat.2024.119699>.

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Publication IV

Plasma treated metals after H- irradiation and its effect on vacuum breakdown behaviour

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Vacuum breakdown in accelerator structures is a critical challenge that occurs under high electric fields. In environments subjected to hydrogen ion irradiation or high beam losses, such as in Radio-Frequency Quadrupoles (RFQ), residual hydrocarbons from the vacuum may result in carbon contamination of the metal surfaces from charged particle induced cracking. Under these conditions, it has been assessed that surface carbon contamination leads to a decrement of the surface electric field holding properties. This study extends the latest research by exploring the efficacy of Oxygen Plasma Cleaning (OPC) on metal electrodes irradiated by low energy hydrogen ion beam with the purpose of reducing surface carbon contamination. OPC treatment has been employed on different metals, namely copper beryllium (CuBe2), oxygen-free copper (Cu-OFE), and stainless steel (SS316LN). Treated electrodes have been tested for electric field performance in a DC pulsed system and results compared with non-irradiated electrodes and irradiated ones without OPC treatment. The study indicates a significant reduction in carbon contamination by OPC, enough to allow irradiated materials to achieve performances comparable with the electric field strength of raw surfaces. Moreover, it has been observed that stainless steel samples had some alteration in the surface chemistry that enhanced the material's ability to sustain high electric fields while decreasing vacuum arcing events. Notably, OPC treated SS316LN electrodes surpassed the performance value of untreated ones, demonstrating the potential of plasma treatments in extending the operational performance of accelerator components.

I. INTRODUCTION

Vacuum arcing has been identified as a main concern in high gradient RF accelerators structures. The breakdown appearance is due to high electric fields between metal surfaces, as is the case for example of the CERN Radio-Frequency Quadrupole (RFQ), the first element of the injection chain of the Large Hadron Collider (LHC). Multiple studies have tried to explain the appearance of vacuum breakdowns using both atomistic simulations and experimental testing [1–8]. According to the literature, breakdown appearance is dependent on material properties [9, 10] making the choice of materials for RF applications a major factor to be exploited. This work follows on the experiments conducted on dedicated test electrodes in regard to materials studies for breakdown resistance of irradiated surfaces. The main aim of those experiments, reported in [11, 12], was to find a more suitable material for RFQ manufacturing, since copper - material currently in use - has suffered some degradation over the years due to breakdowns and hydrogen implantation in the form of blistering [13], caused by the continuous operational exposure to a hydrogen ion beam. While vacuum arcs are still yet to be fully comprehended, especially in terms of event's initiation, the current studies will hopefully bring new additional contributions to

the field of research. Carbon contamination has been recognized to be the cause of decrease of electric field holding performance in irradiated electrodes [12]. It has been discovered that the surface becomes contaminated by a carbon layer, possibly due to the cracking of hydrocarbons present in the accelerator vacuum. Carbon contamination has been a well-known issue during ion beam irradiation, however the potential risks associated with it have not been fully recognized. Awareness of this problem is emphasized in [14], where the authors discuss this effect in steels.

With the prospect of eliminating carbon from irradiated surfaces, an Oxygen Plasma Cleaning (OPC) technique has been explored on irradiated electrodes, aiming to remove the carbon contamination. Plasma cleaning is a versatile technique widely utilized across various industrial sectors, including semiconductors, biomedical applications, aerospace, and advanced material processing [15–18]. This technique is particularly valuable where precision, cleanliness, and minimal surface damage are critical. Recently, plasma cleaning has been adopted for specialized applications in particle accelerators - oxygen plasma or mixtures of oxygen and argon have been employed to effectively remove hydrocarbon contamination from components such as beam line optics [19, 20], accelerator vessels [21], copper cavities [22] and superconducting accelerating cavities [23], significantly improving vacuum operational stability. Beyond carbon and hydrocarbons decontamination, OPC induces other effects, such as the formation of superficial oxide layers [24–27].

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This is particularly impactful for materials where the oxide formation deriving from the oxygen plasma treatment has been reported to modify and often improve wettability, adhesion and dielectric properties [28–30]. Studies made in [31, 32] report strong oxidation of stainless steel surfaces in the form of iron and chromium oxides, upon plasma-based ion implantation, without any degradation of the surface aspect. Chromium oxides via oxygen plasma treatments have been associated in [33] with improvement of corrosion resistance while retaining a considerable electrical conductivity. Also, [34] explores the effects of RF plasma treatments in stainless steel, observing that O_2 environments produce high valence oxide states along with increased thickness of oxide film and a roughness decrease in a nano scale.

In this work, high voltage tests were conducted on plasma treated electrodes, with the aim of comparing results between plasma treated and non-treated surfaces, in terms of breakdown behavior and electric field holding performance. CuBe2, Cu-OFE and SS316LN electrodes were the materials selected to conduct the experiments as it will be discussed later on. Microscopic techniques using Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) were primary used to analyze all the material's surfaces during the different experiments. Moreover, X-ray Photoelectron Spectroscopy (XPS) was used to additionally explore possible changes in surface chemical composition.

II. METHODOLOGY AND MATERIALS

A. Tested Materials

Seven materials were studied as candidates for the manufacture of future Radio-Frequency-Quadrupoles. Among those materials, covered in [11] and [12], titanium grade 5 (Ti6Al4V), stainless steel AISI 316LN (SS316LN) and copper beryllium (CuBe2) were the three materials that have better responded to high voltage pulsing tests, being able to achieve high electric fields (above 100 MV/m) and presenting good resistance to sustain vacuum arcing. Preliminary plasma cleaning tests were carried out on existing copper beryllium (UNS type C17200 with 98 wt% copper and 2% beryllium). After the proven feasibility of the experiment, two materials were chosen for machining new electrodes, namely pure oxygen-free copper, UNS type C10100 (Cu-OFE), as it presents nowadays the most common material in terms of RFQ manufacturing, and stainless austenitic chromium-nickel-molybdenum steel with nitrogen addition (AISI 316LN), UNS type S31653, as it was the material with the highest electric field attained in the previously mentioned tests. In addition, when compared to the titanium or the copper alloys, SS316LN presents an easier machinability, a wider and more consistent supply availability and is more cost-effective, both in terms of material price and machining expenses.

B. Irradiation and Breakdown Testing

Prior to oxygen plasma treatment, irradiation using low energy H^- ions at 45 keV was performed in the cathode's surface for each material. For comparability, the irradiation has been set identically to the one reported in [12]. In terms of the main chronology of the events, electrodes from the different materials start from being exposed to irradiation, followed by plasma treatment, and at last installed for breakdown testing on the Large Electrode System (LES) [6, 35–38]. The LES aims to apply high pulsed DC fields to a pair of electrodes (cathode and anode) with a small gap (60 μm) between the two surfaces. By controlling the voltage applied between anode and cathode, it is possible to monitor vacuum arcing triggered during the process. After sample installation and after a vacuum in the order of 10^{-8} mbar is reached, the process of conditioning starts by applying small levels of voltage. From here, the voltage is gradually increased, in accordance with the material's response to the consequent breakdowns. Operational maximum field is typically measured at a steady-state average breakdown rate of 10^{-5} . The system allows for breakdowns real-time monitoring, along with positioning on the surface, while controlling voltage control. Additional information about the components and measurements techniques will not be described in this publication, as they have been addressed in detailed in [12].

C. Oxygen Plasma Treatment Set-up

The plasma cleaning treatments were performed in a dedicated test bench, which is shown in Figure 1. The experimental set-up consists of the following components: a DN100 stainless steel vacuum vessel to house the treated samples, an oxygen-fed plasma source, and a turbomolecular pump mounted on a DN60 transition to maintain constant pressure. The plasma source employed is an inductively coupled plasma (ICP) RF sources branded ibss Group, operating at 13.56 MHz and an RF excitation power P_{RF} ranging from 10 to 300 W. The gas, pure O_2 (99.999 %), is injected in the ignition chamber of the plasma source and the active species are extracted through an orifice to the volume to be cleaned. Completing the set-up are: a membrane gauge for the pressure reading, a quartz crystal microbalance coated with amorphous carbon as a reference for the etching rate, and a viewport for visual inspection of the samples.

During the treatments, the chamber pressure was kept at 4×10^{-3} mbar. The other process parameters were adjusted based on the electrodes being treated. For the pilot test, the CuBe2 cathode was treated at 60 cm away from the plasma source, with plasma source powered at 50 W, and for a total treatment duration of 6 hours, split in tranches of 75, 105, and 180 minutes for intermediate inspections. Based on findings regarding carbon removal rates from the irradiated surfaces, subsequent

treatments for the remaining two electrode pairs (Cu-OFE and SS316LN) were set to a fixed 6-hour duration. As precautionary measurement, the samples were placed at closer distance (30 cm) and the P_{RF} increased from 50 W to 100 W to ensure complete carbon removal. The plasma cleaning efficiency as function of chamber pressure, plasma source power and distance from the source outlet were the subject of a study that will be published elsewhere. In this work, the treatment parameters were selected to maximize the carbon removal rate while maintaining a conservative ion energy and minimize the physical sputtering of material from the sample and ion implantation.

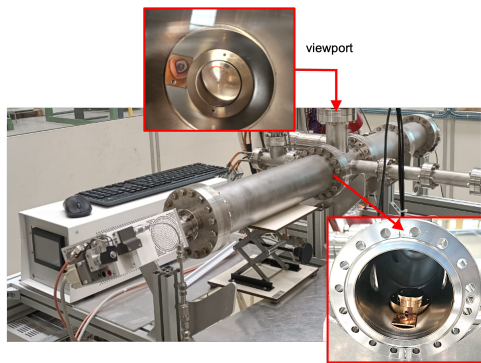


FIG. 1. Photograph showing the main treatment chamber, in which an electrode is installed. The upper small photograph shows the viewport of the system, allowing visualization of the sample during operation. The lower small photograph shows the position of the CuBe2 electrode before closing the flange of the system.

III. RESULTS AND DISCUSSION

A. Plasma Treatment of a rough surface: CuBe2 electrodes

Recent results, published in [12], showed that for irradiated materials the capability of reaching high electric fields has been limited by the carbon content present at the cathode surface. Standard wet surface cleaning methods, using either solvents or detergents as it is common practice for UHV applications [39], are not effective in removing amorphous carbon. Therefore, a new approach has been tested, by using OPC. This method would also have the advantage that it could be applied in-situ on existing RFQ structures, in case carbon-contamination from irradiation would degrade operational performance.

CuBe2 has been irradiated and tested in the LES system. For this part of the study, the same irradiated CuBe2 electrodes were chosen to conduct a pilot test in carbon removal after LES testing using OPC. In order to understand what would be the ideal time of treatment,

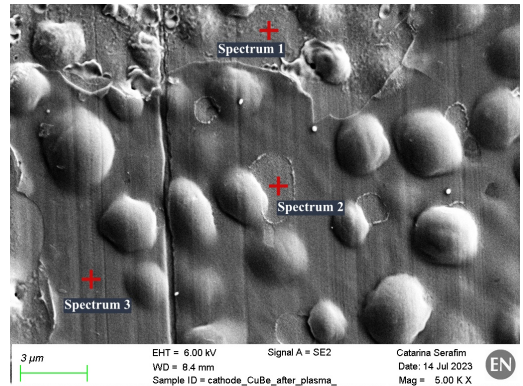


FIG. 2. Scanning electron microscope imaging of the CuBe2 cathode's surface after the 1st plasma treatment, with identification of the location of the different EDS measurements points.

TABLE I. Measurements of carbon content by EDS analysis made on CuBe2 cathode's surface, in different stages of the plasma treatment and on the locations visualized in Figs. 2 and 3.

		C (wt%)
75 minutes of treatment	Spectrum 1	0.49
	Spectrum 2	3.46
	Spectrum 3	12.23
360 minutes of treatment	Spectrum 4	10.98
	Spectrum 5	4.02
	Spectrum 6	0.97
	Spectrum 7	0.10
	Spectrum 8	9.98
	Spectrum 9	3.16
	Spectrum 10	0.43

without compromising the surface of the electrode, the procedure was divided as mentioned above in three treatments of 75 + 105 + 180 minutes. Between each treatment, SEM and EDS analysis were performed to assess the surface and carbon state.

After the first 75 minutes, SEM observation showed already that in some regions the CuBe2 surface was beginning to be exposed - see for example, regions marked as 'Spectrum 2' in Figure 2. An additional 105 minutes of treatment clearly showed that the carbon content has been reduced significantly, with the EDS values showing approximately a decrease of one third in comparison with the treatment before. However, these first two treatments, showed to be not sufficient in removing the carbon content in the CuBe2 surface.

Figure 3 shows the surface state after a final treatment with additional 180 minutes. The main image, represents a region with higher blister concentration, where breakdowns from LES experiment can also be seen. The image was acquired using backscattered detector, providing information about the locations with existing carbon in

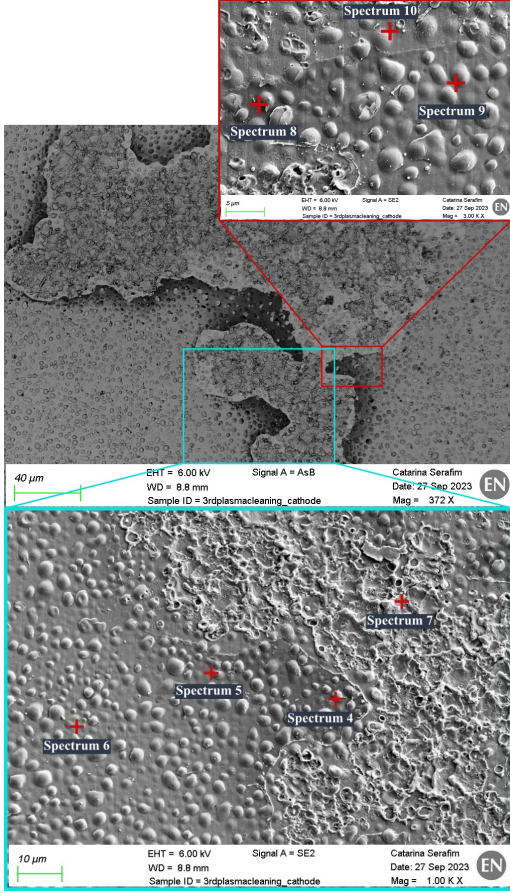


FIG. 3. Scanning electron microscope imaging of the CuBe2 cathode's surface after 360 minutes of plasma treatment, with identification of the location of the different EDS measurements points.

a darker coloration. EDS measurements were done in multiple locations (blue and red images). The carbon layer has proven to be difficult to be completely removed from the regions contouring the edges of the pre-existing breakdowns craters, possibly due to copper vaporization during vacuum arcing events. Apart from these specific regions, the full treatment proved to be successful in removing the carbon, with final concentrations staying below 1 wt%.

Taking in consideration, that the plasma treatment method was aimed to be used further in our studies on surfaces free from breakdowns and minimal roughness, 360 minutes (6 hours) was the time chosen for the duration of treatment for future electrodes.

1. Re-conditioning of CuBe2 electrodes after plasma treatment

Figure 4 represents the results from the different LES testing, made in CuBe2 electrodes. The explanation regarding the different conditioning curves can be found in subsection III B 1. The plot shows the conditioning of CuBe2 irradiated (pre-plasma treatment) and non-irradiated electrodes from publication [12], plotted simultaneously, with the new result of the conditioning test made with the plasma treated CuBe2 in magenta. Again, it should be emphasized that this is the same pair of electrodes that was previously exposed to high voltage pulsing test after irradiation (dark blue curve). The results from the new conditioning show a dramatic difference in terms of higher electric field achieved, by being able to reach a maximum of 95 MV/m and a stable field of 92 MV/m, almost 6x more than the irradiated electrodes without plasma treatment (approximately 17 MV/m). This result stays however slightly below the electric field reached by the non-irradiated electrodes (red curve), where the maximum field was 110 MV/m.

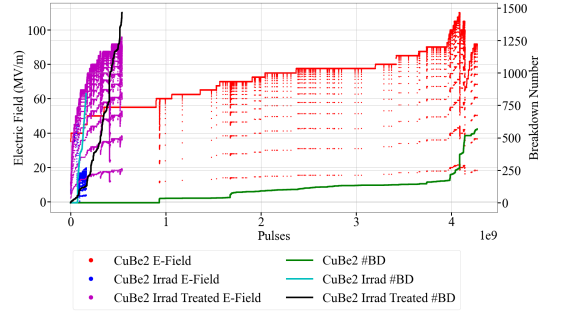


FIG. 4. Overlap of the different conditioning plots of LES tests on CuBe2 electrodes (non-irradiated, irradiated and irradiated and plasma treated).

The small difference is possibly attributed to the carbon content that was not removed in some of the regions on the cathode surface. Additionally, the roughness of the surface in both cathode and anode, due to the breakdowns from the previous test, may have contributed to a more hard process of conditioning, which could also explain the higher number of breakdown events for the irradiated and treated electrodes when compared with the total number of breakdowns from the non-irradiated electrodes test.

The smaller vacuum arcs from the first conditioning can be observed inside the red squares in Figure 5 in contrast with a breakdown from the 2nd conditioning, where a single breakdown reached diameters in the order of 300 µm. This difference in size is due to the lower energy discharged at lower fields, see [40]. Figure 6 shows the mapping of the surface using an optical microscope,

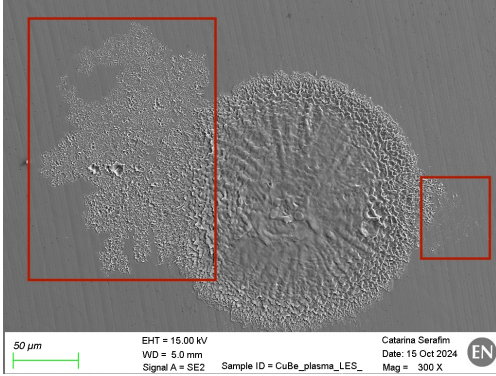


FIG. 5. SEM image using secondary electron detector with 300x magnification showing small breakdowns caused by the 1st conditioning test (inside the red squares) and a single bigger breakdown (event during the 2nd conditioning test).

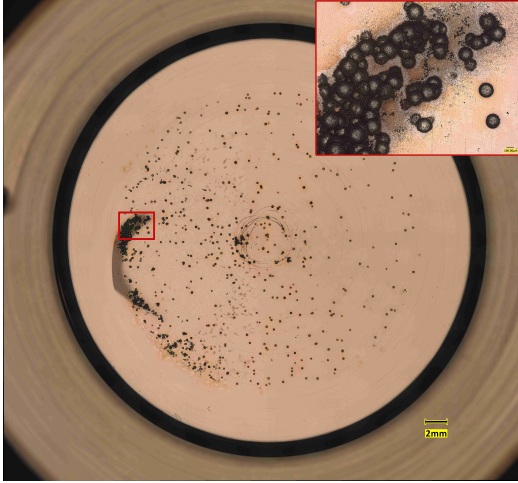


FIG. 6. Optical image of CuBe2 cathode surface and zoom in region in red, after retest on the LES system (2nd conditioning).

in which the C-shape mark on the left, visible on the surface, is the optical effect caused by the blistering (irradiated region). The small black dots dispersed in the surface correspond to the breakdowns from the 2nd conditioning. For comparison of the previous surface states, please see Figure 11 from [12].

While a good dispersion of breakdowns in the surface is observed, a few clusters have been identified in the irradiated region. These breakdown clusters, that were formed during the second conditioning experiment, are coincident with the surface regions in which carbon was not removed from the plasma treatment (as seen in Fig-

ure 3). In the second conditioning, the presence of traces of carbon seemed to attract vacuum arcing to those specific locations, leading to an increase of more than 2x the total number of breakdowns when compared with the non-irradiated electrodes.

B. Plasma treatment of pristine irradiated surfaces: Copper and Stainless Steel

New electrodes of Cu-OFE and SS316LN were machined, irradiated and submitted to a treatment of 6 hours of OPC. For copper, the carbon layer present on the electrode surface after irradiation is very clearly observable when using SEM. In some regions, this carbon layer has been broken, showing some flakes partially peeling from the copper surface - the effect is visible in Figure 8.

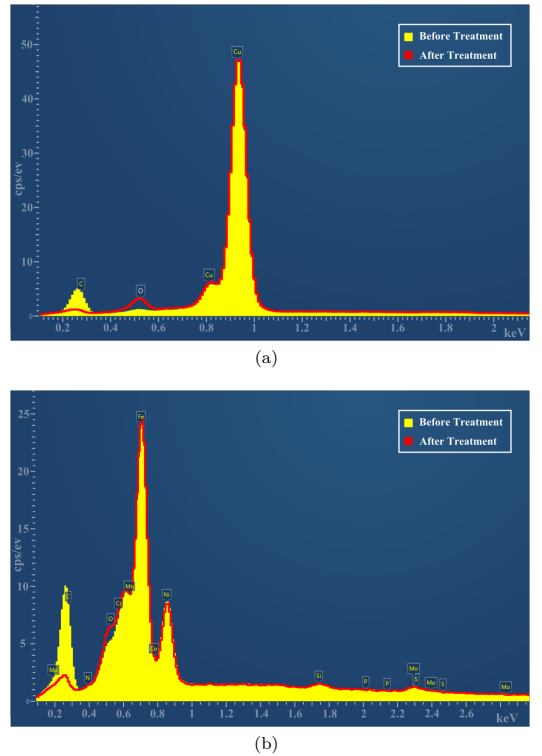


FIG. 7. EDS spectrum analysis for (a) Cu-OFE and (b) SS316LN, showing the elements present in the surface before plasma treatment (yellow) and after plasma treatment (red).

In SS316LN, the presence of the carbon contamination doesn't create a distinguished carbon layer, as seen in copper and copper beryllium. SEM and optical microscopic analysis show no indication of a layer formation

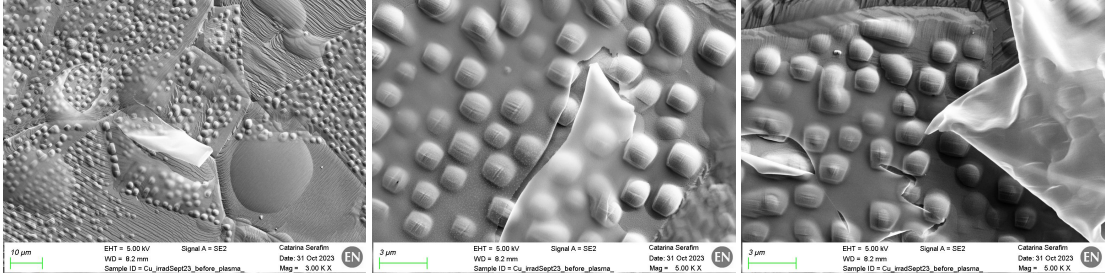


FIG. 8. SEM images using secondary electron detector showing the state of the surface of Cu-OFE electrode after irradiation and before OPC. In the images, the blistering caused by the H implantation in Cu-OFE is visible, additionally the formation of a thin carbon layer upon the surface is clear, which has been broken and is laminating from the surface. Also in the left image, some bubbles are visible, an effect caused by the implantation of hydrogen between the copper surface and the carbon layer.

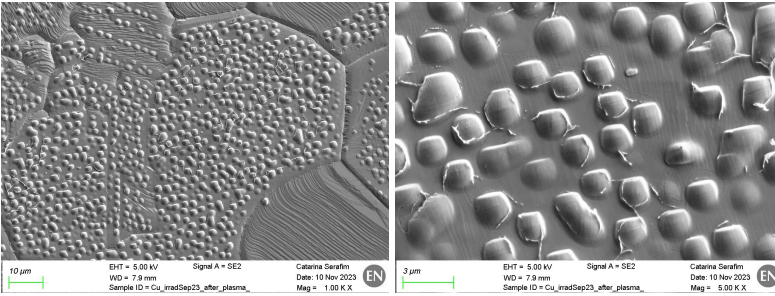


FIG. 9. SEM images using secondary electron detector showing the state of the surface of Cu-OFE electrode after irradiation and after oxygen plasma cleaning. After OPC, bubbles on the surface are no longer visible and the continuous layer of carbon was removed, however, some carbon residuals are still visible at high magnification (right image).

above the surface, however EDS measurements in multiple regions inside the irradiated region confirmed the same percentages of carbon as on copper - between 8-12 wt%. EDS analysis were done after irradiation, before and after plasma cleaning. The treatment proved to be very effective in removing the carbon, where EDS analysis in different locations consistently measured carbon below 1 wt% for both materials.

In Cu-OFE some residuals of the carbon layer were still visible on the copper surface, see Figure 9. According to EDS analysis, these showed no significant carbon contamination, while prolonging the treatment to further cleanliness could have had increased the surface oxidation on the surface. Figure 7 shows the EDS elements spectrum for (a) Copper and (b) SS316LN, before and after plasma cleaning, where quantitative differences in the carbon peak are visible. After plasma treatment, an increase of oxygen content in both samples is also evident, which confirms the oxidative nature of the treatment.

1. Conditioning Results

The plots in Figures 11 and 12 include three different set of conditioning tests, for three different pairs of electrodes. The conditioning curves represent the continuous increase of voltage for one pair of electrodes, which is

translated in electric field (left vertical axis). The breakdowns during the process are visible via sudden drops in electric field, followed by a rapid recovery to voltage levels previous to the breakdown. From this point the voltage is kept during a certain number of pulses until a new increase of voltage is set. The conditioning curves are represented in red (non-irradiated electrodes), dark blue (irradiated electrodes) and magenta (irradiated and plasma treated electrodes). The respective cumulative number of breakdowns during the conditioning are represented in green, cyan and black and can be read through the right vertical axis.

Copper (Cu-OFE)

Figure 11 shows simultaneously the LES testing results for three different Cu-OFE electrodes. The conditioning of Cu-OFE irradiated and treated electrodes is shown in the red curve in Figure 11. Both Cu non-irradiated and irradiated plasma treated have reached the mark of 80 MV/m.

When tested with high pulsing voltages in the LES, irradiated electrodes (without any plasma treatment) have only stably reached 23 MV/m - dark blue curve in Figure 11. For the latter, surface analysis have shown breakdown to be positioned in the irradiated region, following

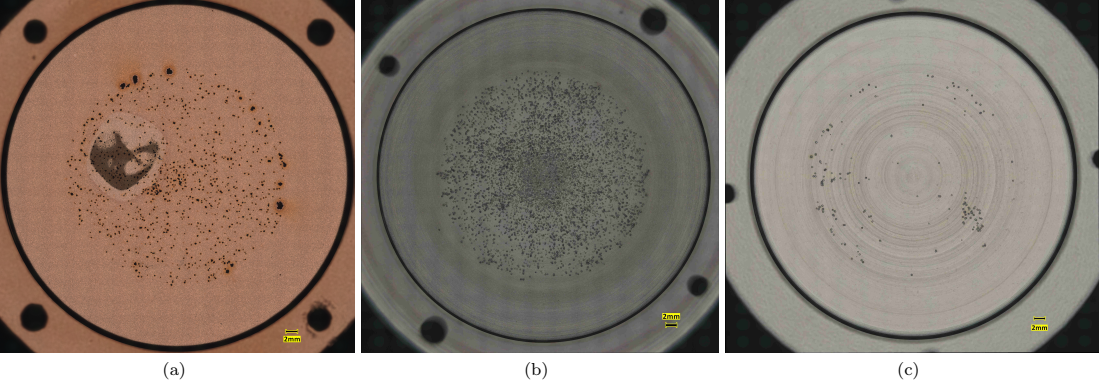


FIG. 10. Optical image of three different cathodes after LES testing: (a) irradiated and plasma treated Cu-OFE cathode surface, (b) non-irradiated SS316LN cathode surface, and (c) irradiated and plasma treated SS316LN cathode surface.

the same behavior as the CuBe2 irradiated electrodes reported in [12].

Stainless Steel (SS316LN)

SS316LN non-irradiated electrodes were among the studied materials in [12], being the material that presented the best results in terms of conditioning performance. The irradiated pair, however, has shown to be being able to achieve only 60 MV/m (dark blue curve). For the case of the SS316LN electrodes irradiated and plasma treated, the conditioning results, have not only reached the maximum electric field mark of the non-irradiated electrodes (120 MV/m - red curve), but have surpassed it, by reaching a maximum and constant field of 160 MV/m (magenta curve). The irradiated and treated electrodes have registered until the end of testing less than 200 breakdowns (black curve). It is the first time in breakdown testing that, for this level of electric fields, such a small number of total breakdowns is registered. For comparison, the non-irradiated electrodes have registered more than 3000 breakdown events.

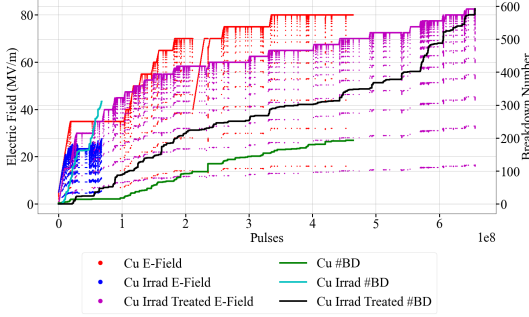


FIG. 11. Overlap of the different testing conditioning made in three different Cu-OFE electrodes (non-irradiated, irradiated and irradiated and plasma treated).

The irradiation didn't provoke sudden and agglomeration of vacuum arcs in specific locations or any decrease in performance when compared with the non-irradiated pair (results as well as surface imaging are very similar to the ones reported in [11]). The final state of breakdown dispersion is shown in Figure 10 (a): the distribution of breakdowns is quite uniform all over the surface, showing no extraordinary events on the blistered irradiated region. Some small clusters have been observed on the edges of the tested surface, however apart from the concentration of multiple breakdowns, no additional features have been found.

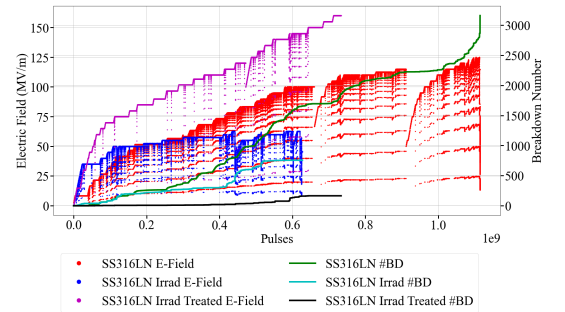


FIG. 12. Overlap of the different testing conditioning made in three different SS316LN electrodes (non-irradiated, irradiated and irradiated and plasma treated).

Figure 10 includes optical micrographs of the status after high voltage testing for both cases: (b) non-irradiated and (c) irradiated, where the notorious difference in breakdown on the surface are visible. Irradiation on SS316LN material, have produced no blistering seen in the surface. Dark coloration has been observed after irradiation, and associated with the carbon content. After plasma treatment, the irradiated spot was no longer visible on the surface, leaving no traces of irradiation. Additionally, after high voltage testing, SEM imaging showed no defects on the entire surface apart from the breakdowns. The latest, have reached large round crater diameters in the order of $500\text{ }\mu\text{m}$, due to the large fields experienced during the testing.

The difference in both electric field performance and breakdowns events suggests that the plasma treatment, aimed to remove the carbon contamination from the stainless steel cathode, has produced an additional effect on the electrode's surface. Additional studies on the effects of OPC in SS316LN surface were therefore performed, as discussed in the next section.

C. Analysis of chemical composition on plasma-treated SS316LN samples

To explore what the implications of the oxygen plasma treatment on the irradiated surfaces are, three $40\times 40\text{ mm}^2$ SS316LN samples were prepared for XPS analysis. Sample *i* was partially masked and then irradiated using the irradiation test stand with the same parameters used for the electrodes described above.

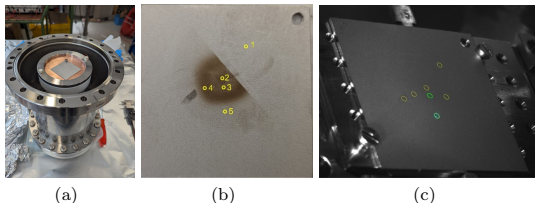


FIG. 13. (a) SS316LN sample *i* mounted onto the target chamber before installation chamber and irradiation. (b) Photograph of sample *i* after H- irradiation and before the plasma cleaning, including markings of regions where XPS analysis was performed. (c) Sample *i* after plasma treatment, mounted inside XPS chamber with identification of the measurement points.

Figure 13 (a) shows the target sample mounted in the irradiation chamber. After confirmation of the presence of a carbon layer as found on the electrodes by EDS, the sample underwent the same oxygen plasma cleaning treatment as before. Figure 13 (b) shows a photograph of the sample *i* after irradiation. The beam-exposed region is visible by its dark coloration. Figure 13 (c) shows the same sample inside XPS chamber after the plasma treat-

ment, where the irradiation marks are no longer visible. For comparison, two additional samples had been prepared and characterized in parallel. Sample *ii* was not irradiated, but treated by OPC after degreasing. Additionally, sample *iii*, called reference sample, was not submitted to any irradiation and/or treatment other than degreasing and was stored under primary vacuum until the XPS analysis was performed.

Figure 14 includes the main core level spectra of the most relevant elements on the surfaces: iron ($\text{Fe } 2p_{3/2}$), chromium ($\text{Cr } 2p_{3/2}$) and oxygen ($\text{O } 1s$) from the XPS characterization of the three samples. The green and blue spectra represent different measurements on the irradiated sample after plasma cleaning, in the irradiated and non-irradiated region, respectively. The red data represents the degreased and oxygen plasma treated sample *ii*, and the orange spectra are representative for the sample that was only degreased (without irradiation nor additional treatments). We have calculated the elemental composition assuming a homogeneous distribution of all elements by fitting all spectra using CasaXPS version 2.3.24 [41] with the algorithms implemented therein considering the electron analyzer transmission function. For all spectra, a Shirley-type background correction was performed, and the elemental sensitivity factors that are based on the cross-sections reported by Scofield [42] and taking into account an inelastic mean free path (IMFP) of the emitted electrons, which depends on their kinetic energy: IMFP proportional to $E_{kin}^{0.7414}$ [43], are considered.

Most significantly, the XPS results confirm the removal of carbon induced by the reactive oxygen species in the plasma [21] as shown based on the EDS analysis. The C surface content of the degreased sample was 25 at.% and typical values for irradiated samples with carbon layer are above 90 at.%. The plasma treatment reduced the amount of the surface carbon to below 10 at.%. As the samples had to be transferred through air prior to surface characterization, such trace amounts are not avoidable due to readsorption of hydrocarbon molecules from ambient air. Figure 14 (a) includes the Fe/Cr and Fe/O ratios of all four sample preparation stages. It is evident that the plasma treatment not only leads to further oxygen uptake and oxidation but also strongly depletes the chromium content at the surface, which is typically high for stainless steel samples. This change could be linked to a preferred oxidation of iron leading to redistribution of Cr to subsurface regions, or due to the possibility of creation of oxygen ions in the source that could sputter the outermost surface of the sample.

When analyzing the spectral signatures of the samples, it is clearly visible that the surface is stronger oxidized after the plasma treatment. The $\text{Fe } 2p_{3/2}$ state at 706.8 eV, which is clearly present on the degreased surface and is linked to metallic Fe^0 species at the surface [44], is almost absent for all other samples. Instead, the main contribution is from iron oxide (with an intensity maximum at 710.2-710.9 eV). The spectral shape

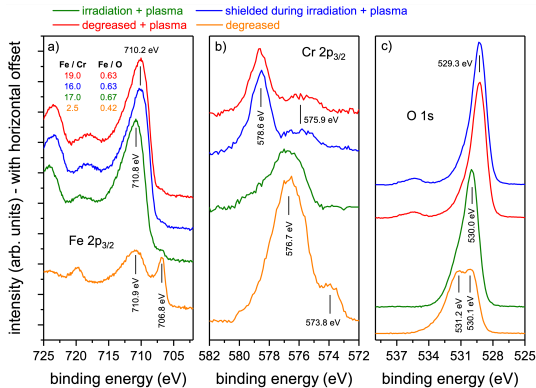


FIG. 14. X-ray photoelectron spectra of SS316LN after different surface preparation procedures as indicated in the legend – (a) Fe $2p_{3/2}$, (b) Cr $2p_{3/2}$, and (c) O $1s$ state, respectively. The inset in (a) shows the elemental ratios of Fe/Cr and Fe/O.

resembles the spectrum of Fe_2O_3 in Ref. [45]. One has to mention that the binding energy values of the core levels for the irradiated samples after plasma cleaning are 0.6–0.7 eV higher than those of both surfaces that were only plasma-treated without prior irradiation. This indicates a difference in work function at the surface, which leads to a global shift of the BE of the core levels. Indeed, when measuring the work function of a degraded sample prior and after plasma oxidation, we found an increment of 0.7 eV. This has to be kept in mind when comparing relative differences in the core level binding energies for the samples. The degraded samples exhibit the presence of hydroxide and hydrocarbon surface adsorbates with a state in the O $1s$ spectrum at 531.2 eV in addition to the metal-oxide peak at 530.1 eV. The Cr $2p_{3/2}$ state of the degraded samples exhibits a minor metallic component (Cr^0) around 574 eV [46], while the main chromium content is in the form of Cr_2O_3 (Cr^{+3}) with a representative peak at 576.7 eV [44, 47]. For the irradiated sample, the carbon layer and other adsorbates were efficiently removed by the plasma treatment and the surface is composed of Fe_2O_3 and Cr_2O_3 . However, the plasma process even further oxidized the non-irradiated steel surface. While the Fe $2p$ spectra are comparable, the dominating state at 578.6 eV in the Cr $2p_{3/2}$ spectrum, additional to the shifted Cr^{+3} feature of low intensity at 575.9 eV, indicates the formation of CrO_3 (Cr^{+6}) at the surface [48, 49].

When considering that the activated oxygen species of the plasma can react with carbon atoms at the surface or break Fe–C and Cr–C bonds to form volatile CO or CO_2 , the effective removal of the carbon layer and the hydrocarbon molecules is assured. Simultaneously, Fe and Cr surface atoms with free valence electrons can react with oxygen atoms, leading to an increment of the oxidation

state up to Fe^{+3} and Cr^{+6} . On the bare stainless steel samples, this is well demonstrated by the measurements. However, for the irradiated sample, the oxygen plasma could not directly interact with the metal surface but was first etching the carbon layer during the plasma process. The process time seems to have been sufficient to remove this layer completely, while the surface chromium atoms did not undergo full oxidation, as it is the case for the exposure of the non-irradiated samples to the plasma.

IV. CONCLUSIONS

Carbon contamination has been identified upon low energy irradiation with H ions, which translates in major concerns for accelerating structures, as surface carbon has been associated, independently of the material under testing, as the main cause for reduction of the maximum achievable electric surface fields. This study has demonstrated the efficiency of OPC in removing carbon contamination from metal surfaces. For the preliminary study case of CuBe2, it has been observed that the treatment was less effective, due to the fact that the electrodes were pre-exposed to vacuum arcing events while presenting carbon on the surface. However, for newly irradiated electrodes of Cu-OFE and SS316LN, the treatment successfully decreased the presence of carbon to levels acceptable for ultra high-vacuum applications. When tested for breakdown performance, treated CuBe2 and Cu-OFE showed electric field capabilities similar to surfaces that have not undergone irradiation beforehand, assuring that irradiation exposure and hydrogen blistering do not affect electric field performance. This is also true for SS316LN electrodes, where oxygen species from OPC have also caused a strong oxidation of the surface in the form of iron and chromium oxides. The strong oxidation in SS316LN samples after OPC seems to enhance breakdown resistance and enable the holding of higher electric surface fields, possibly through the increase of the work function.

Further testing will be necessary to explore the role of such oxidation in stainless steel surfaces when studying breakdown events. To date, planning is being developed to assess SS316LN plain electrodes with OPC (without any irradiation exposure) in comparison with untreated ones, both as cathode and anode, for future DC testing, including detailed electron field emission measurements. Future work will also focus on optimizing OPC parameters to further enhance the efficiency of carbon removal. At last, this research underlines the potential of oxygen plasma treatment as a key technology to be developed as a long-term *in-situ* operational set-up inside particle accelerators, assuring the cleanliness and maintenance of inner surfaces of RF devices that could prolong their usable lifetime and even increase their performance.

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VI. CONFLICT OF INTEREST

The authors declare that the research was conducted in the absence of any commercial or financial relationship that could be construed as a potential conflict of interest.

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