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IMPACT OF THE Cu SUBSTRATE SURFACE PREPARATION ON THE MORPHOLOGICAL, SUPERCONDUCTIVE AND RF PROPERTIES OF THE Nb SUPERCONDUCTIVE COATINGS *

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Abstract

Nowadays, one of the main issues of the superconducting thin film resonant cavities is the Cu surface preparation. A better understanding of the impact of copper surface preparation on the morphological, superconductive (SC) and RF properties of the coating, is mandatory in order to improve the performances of superconducting cavities by coating techniques. ARIES H2020 collaboration includes a specific work package (WP15) to study the influence of Cu surface polishing on the SRF performances of Nb coatings that involves a team of 8 research groups from 7 different countries. In the present work, a comparison of 4 different polishing processes for Cu (Tumbling, EP, SUBU, EP+SUBU) is presented through the evaluation of the SC and morphological properties of Nb thin film coated on Cu planar samples and QPR samples, polished with different procedures. Effects of laser annealing on Nb thin films have also been studied.

INTRODUCTION

Thin film technology moves the surface preparation from Nb to Cu, because the Nb thin film cannot be chemical treated. For the Nb on Cu resonant cavities two principal copper cleaning and polishing treatments were studied: one is the electropolishing (EP) and the other one is the chemical polishing with SUBU solution [1-4]. The influence of surface preparation is deeply studied in bulk Nb cavities and it is responsible for the main performances advancement. Similar considerations can be done for Nb on Cu cavities, because the morphology and the roughness of the copper surface are replicated by the Nb growing film. Moreover, there exist studies that show a direct correlation between copper surface preparation and Nb films SC properties [5]. A better understanding of the surface effects and their impact on the thin film and later on rf-properties of the coating is mandatory in order to improve the performances of superconducting (SC) cavities by coatingtechniques, and it's the goal of the present work.

Operatively the effect of copper polishing has been studied through the evaluation of the morphological and superconductive properties of Nb thin film coated on the polished copper planar samples. The cleaning and polishing procedures were carried out at CERN and Italian Institute of Nuclear Physics - Legnaro National Laboratories (INFN). At CERN 25 copper planar samples were treated with SUBU solution as reference, at INFN other 25 samples were divided in 4 different batches, one for each treatment investigated: SUBU solution, EP, SUBU+EP and Tumbling. On 15 out of the 50 treated copper planar samples, a 3 µm thick Nb film deposition was done. The deposition processes were carried out at Science and Technology Facilities Council - Daresbury Laboratory (STFC), University of Siegen and INFN, 5 samples each, using the same procedure and parameters. Samples treated in the same cleaning and polishing batch were coated in more than one laboratory, in order to minimize the role of the deposition facility on the SC film properties. Laser treatment was also tested as post-treatment on 5 coated samples, at Riga Technical University (RTU).

Surface characterization on Cu samples and Nb film was done after each process (polishing, film coating, post treatment, etc.), directly by the partner involved in the process. At this stage, superconductive characterizations were carried out at IEE Bratislava and consist in magnetic moment vs. field and temperature measurements. Nb coatings were also characterized by thermostimulated and photothermostimulated exoelectron spectroscopy at RTU. The interpretation of the results requires additional research to understand the nature of the introduced defects and physics of TSE/PTSE in Nb and for that reason are not reported on this paper. More information in [6]. More superconductive characterizations are planned in the next year, at Saclay Nuclear Research Centre (CEA) with a local AC-magnetometer, at STFC with a radiofrequency cathode and at Helmholtz-Zentrum Berlin (HZB) and CERN on Quadrupole Resonator (QPR)'s sample in order to have more information about the correlation between polishing treatment and superconductive properties. On Fig. 1 the samples flow is schematized.

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SAMPLE PROCESS	#	C1	C7	C10	L1	L19	L20	L10	L13	L16	L23	L18	L21	L9	L4	L8
Sample production	1	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN
Sample labeling	2	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN	CERN
Sample shipping	3				to LNL	to LNL	to LNL	to LNL	to LNL	to LNL	to LNL	to LNL	to LNL	to LNL	to LNL	to LNL
SUBU Polishing Process	4	CERN	CERN	CERN	LNL	LNL	LNL									
EP Polishing Process	5							LNL	LNL	LNL						
EP+SUBU Polishing Process	6										LNL	LNL	LNL			
Tumbling Cleaning procedure	7													LNL	LNL	LNL
Surface characterisation	9				LNL	LNL	LNL	LNL	LNL	LNL	LNL	LNL	LNL	LNL	LNL	LNL
Sample shipping	10	to U.Siegen	to STFC	to LNL	to U.Siegen	to STFC		to U.Siegen	to STFC		to U.Siegen	to STFC		to U.Siegen	to STFC	
Nb coating	11	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL
Sample cutting	12	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL
Surface characterisation	13	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL	U.Siegen	STFC	LNL
Sample shipping	14	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE	to IEE
SC magnetization characterisation	15	IEE	IEE	IEE	IEE	IEE	IEE	IEE	IEE	IEE	IEE	IEE	IEE	IEE	IEE	IEE
Sample shipping	16			to RTU			to RTU			to RTU			to RTU			to RTU
Laser post-treatment	17			RTU			RTU			RTU			RTU			RTU

Figure 1: Samples workflow scheme of the present work. For each sample are reported all the process done and the treatment facility.

EXPERIMENTALS

On this section are described all the processes reported in the sample workflow scheme of Fig. 1.

The samples have a size of 53mm x 53 mm and comes all from the same OFE copper sheet (rolling machining), The samples were cut at CERN. The polishing procedures were carried out at CERN and INFN. At CERN 25 copper planar samples were treated with SUBU solution as reference, at INFN other 25 samples were divided in 4 different batches, one for each treatment investigated: SUBU solution, EP, SUBU+EP and tumbling. For all the processes, except tumbling, 40 µm of material removing was agreed on in order to have comparable results. Unlike chemical and electrochemical polishing, tumbling smooths the surface without etching.

15 samples (3 for each batch) were coated with a Nb film via magnetron sputtering in 3 different coating facilities and then characterized. This paper refer only on these 15 samples. The polishing protocol used for the different treatments has been standardized as reported in Table 1 and differ for each treatment basically only for the polishing step.

Table 1: Standard Polishing Protocol Used

#	Treatment	Solution	Time (min)
1	Degreasing	NGL 1740 ultrasounds	5
2	Activation	H_3NO_3S, 5 g/l	3
3	***Polishing***	***Treatment depending***	***-***
4	Passivation	H_3NO_3S, 20 g/l	1
5	Rinsing	Demineralized water	1
6	Spraying	Ethyl alcohol	-
7	Drying	Nitrogen gas	2
8	Packing	Wafer boxes under N_2	-

Chemical Polishing (SUBU5)

Chemical polishing with SUBU solution is a standard process in the copper cavity preparation of Nb on Cu superconductive radio frequency (SRF) cavities [1-4].

The polishing agent is SUBU5, a solution developed for LEP2 at CERN [7, 8]. SUBU5 is a mixture of sulfamic acid (5g/l), hydrogen peroxide 32% (50ml/l), n-butanol 99% (50ml/l) and ammonium citrate (1g/l); the working temperature is 72°C. 6 samples were treated by chemical polishing: 3 at CERN and 3 at INFN. The protocol and the set-up adopted were identical and are reported in Table 1 and Fig. 2 respectively. Treatment time was different, since SUBU erosion rate strongly depends on the sample surface / solution volume ratio.

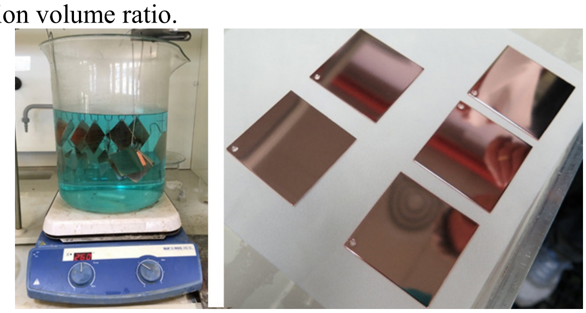

Figure 2: On the left the copper samples during the chemical polishing in SUBU5 solution at CERN. On the right, the polished samples at INFN.

Electro-Polishing

The second treatment evaluated in this work is electropolishing (EP). The electrolyte used was a mixture of phosphoric acid and butanol in a volume ratio of 2 : 3. EP of copper for resonant cavities is described in [9].

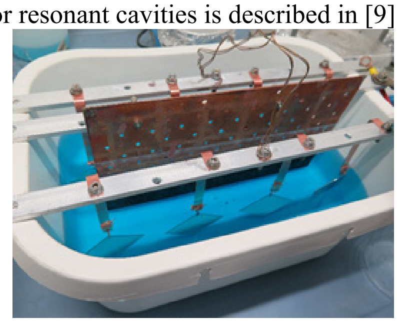

Figure 3: Configuration used for the EP of the copper samples at INFN. A central copper cathode, and 4 copper samples in each side.

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The EP was done at room temperature and without bath agitation in order to prevent difference between the 8 samples (Fig. 3). Since no agitation was present the process current was driven at low current in order to avoid high bubble evolution.

EP + SUBU

Cavities surface preparation on ALPI linac at INFN-LNL [1] and LHC at CERN [3] consisted in a double process. First a deeply etching with EP and then a SUBU for the surface finishing. A similar process was replicated in this project in order to identify potential advantages in use a combined polishing treatment in respect to the single polishing techniques (SUBU and EP).

Tumbling

Tumbling has been applied to to Nb/Cu cavities at LNL for ALPI QWR [1] and it is a common treatment in Nb bulk cavities [10]. Tumbling effectively removes irregularities like scratches and especially any roughness at electron beam weld seams. Tumbling is also needed for removing the fissures in the initial surface preparation of hydroformed and spun cavities.
For this project, the samples was treated at INFN with a Turbula 3D Powder mixing machine (Fig. 4). Samples were kept in a sample holder to prevent bending and two different media were used in order to obtain the best results in terms of surface smoothing.

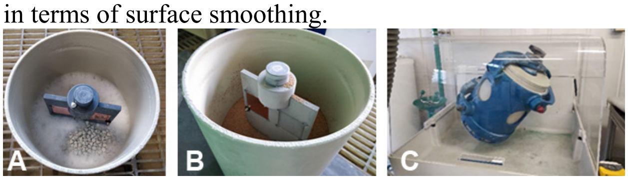

Figure 4: Pictures of the Set-up of the tumbling polishing procedure. A) Sample holder, B) Allumina embedded in ureic resin, C) Coconut powders, D) Tumbling barrel filled with alumina media and Rodastel30 bath, E) Tumbling barrel filled with coconut powders, F) Turbula tumbling machine

Nb Film Deposition

The Nb deposition was carried out by STFC, INFN and University of Siegen using the parameters reported in Table 2. Each facility has been coated one sample for each treatment, for a total of 15 samples, as reported on Figure 1.

Table 2: Parameters set for the coating of Nb thin films on Cu using DC magnetron sputtering.

Parameter	STFC	U.Siegen	INFN
Base pressure @ 650 °C (mbar)	$<10^{-9}$	$1.22\text{x}10^{-5}$	$< 9\text{x}10^{-8}$
Deposition T	650 °C	650 °C	650 °C
Current density (mA/cm^2)	22	15	27
Target power (W)	≈ 400	≈ 400	≈ 750
Discharge gas	Kr	Ar	Ar
Disch. P (mbar)	$1.5\text{x}10^{-3}$	$1.5\text{x}10^{-2}$	$5\text{x}10^{-3}$
Substrate rotation	4 rpm	n/a	No
Thickness	10 µm	3 µm	3 µm

All the samples has been coated via magnetron sputtering. Although the deposition configuration is different from one centre to another, the deposition parameters were set to be comparable. The procedure and the applied deposition parameters in all three deposition facilities are shown in Table 2.

Laser Post Treatment

Laser irradiation of Nb / Cu samples was performed in Ar atmosphere by the fundamental frequency of Nd:YAG laser (λ=1064 nm). The samples were irradiated with different intensities of laser radiation (I=140MW/cm^2 – 320 MW/cm^2) with spot diameter 1 mm. The pulse duration was τ= 6 ns. The focused laser beam was scanned over the sample surface at different speeds of 0.1 – 0.5 mm/s and a step 0.3 mm.

RESULTS AND DISCUSSIONS

Cu Morphological Characterization

Five different characterizations were done at INFN to evaluate the copper surface after the polishing: optical inspection, reflectivity, , SEM and EDS.

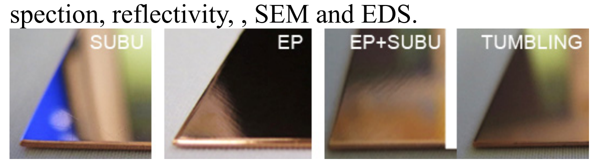

Figure 5: Copper surface after the polishing treatments.

From a simple optical inspection (see Fig. 5) significant difference are visible. The SUBU samples present a mirror like surface, EP samples presents a mirror like surface with a diagonal texture due to the oxygen evolution during the EP process and the absence of a bath agitation. In the EP+SUBU samples, SUBU process reduced the texture, but did not remove it completely. Tumbling samples present a shining surface (but not mirror like as SUBU and EP samples) with small scratches visible only examining the sample from a certain angle. Reflectivity characterization present similar values for all the treatments (64-66 %), except Tumbling one, that present a lower reflectivity (52 %), confirming the visual inspection.

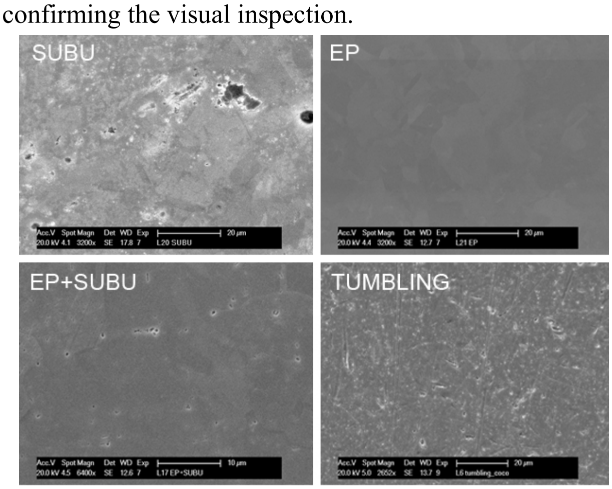

Figure 6: SEM micrographs of the four treatments evaluated.

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The SEM characterization (Fig. 6) shows a very smooth surface in the EP sample. SUBU produce pitting on the surface, visible also in the EP+SUBU sample. On the other hand, SEM micrographs confirm the presence of a large amount of scratches and defects on the surface of tumbling sample. EDS characterization was also done on each samples and no visible contaminations appear.

Nb Morphological Characterization

AFM measurements were performed in non-contact mode for roughness evaluation. Scan area was 5 x 5 µm. Three successive scans on different sample spots where taken. The scans (reported in Table 3) show a high deviation of roughness on the three measured spots in case of sample SUBU (CERN). In fact, the measurements should be correlated with SEM surface micrographs, since the AFM scan maps only a very small fraction of the overall sample surface.

Table 3: Summary of AFM measurements performed on three different spots of the Nb coated sample. Ra value is the average of three measurements.

Treatment	AFM - Roughness (Ra) [nm]
SUBU5 (CERN)	21 ± 12.1
SUBU5 (INFN)	6.3 ± 1.2
EP	11.5 ± 0.7
EP + SUBU5	14.2 ± 2.4
Tumbling	18.3 ± 1.5

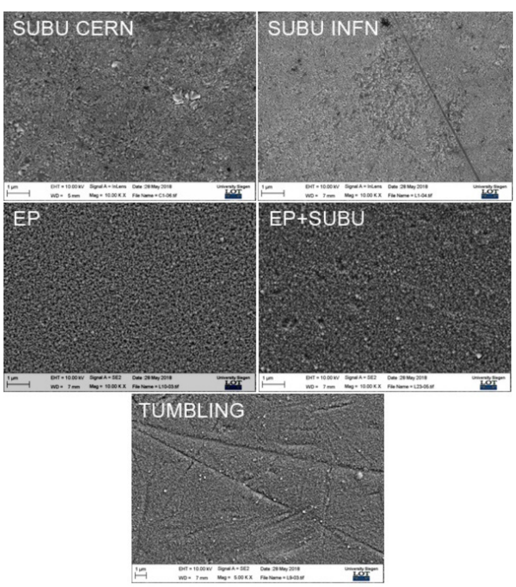

Figure 7: SEM micrographs of the coated sample surface (plan view). All samples deposited with Nb at UniSiegen.

Figure 7 shows SEM investigations of all five samples. It becomes obvious that on the SUBU samples two different grain structures can be observed. That is, areas with lower grain size and lower roughness, and areas with higher grain size and, therefore, higher surface roughness.

The findings correlate with the SEM investigations of the uncoated substrate: it is shown that the SUBU pre-treatment leads to anisotropic etching of the different grain orientations on the polycrystalline Cu substrate. This, in turn, leads to different growth mechanisms of the deposited film. Another phenomenon of the SUBU treatment revealed by the SEM investigations is pitting which leads to areas with very high roughness values and high deviation of these values. The EP, by contrast, shows less deviation of Ra which also correlates with the SEM investigation. The lowest roughness values are measured on SUBU samples provided by INFN. This is in contrast with the before mentioned findings. However, the inspected area by AFM is small. If the measurement does not cover one of the areas showing high roughness due to the above-mentioned effect, the result is reasonable.

Nb SC Properties Evaluation

Small measurement samples of approximately 2 mm x 2 mm were cut from the deposition samples (53x53 mm^2) to characterise the superconducting properties of the Nb films. After cooling down the sample below T_c in zero applied field, the magnetic moment m of the measurement sample was measured in dependence on monotonically increasing applied field B, recording the so-called virgin magnetization curve. The applied field was oriented perpendicular to the flat face of the sample. The main characteristic determined was the first flux entry field B_{en}, detected as the applied field at which the virgin magnetization curve starts to deviate from the linear Meissner-state dependence.

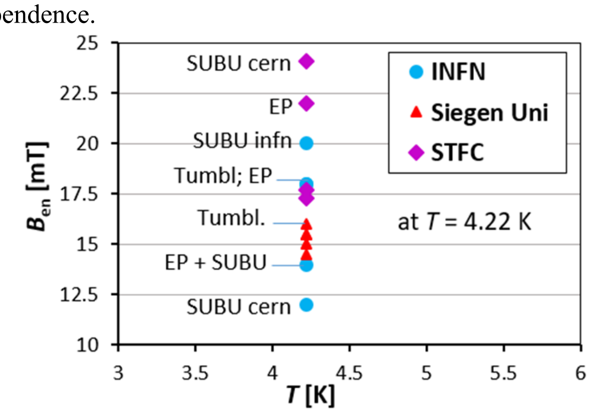

Figure 8: First flux entry field B_{en} determined at 4.22 K for the Nb samples deposited at INFN Legnaro, University of Siegen and STFC Daresbury.

The cutting process surely created certain damage at the edges of the measurement samples, however, the same procedure was followed and the same cut-off machine was used in preparation of all the investigated samples. We thus assume the damage was comparable in all the cases and the determined B_{en} values can be used to relatively compare the samples' properties. Similarly, due to practically identical dimensions of the samples, the geometry-related effects should have the same impact on the determined values. The results of the first flux entry field determination are summarised in the Fig. 8.

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Nb Laser Post Treatment

The AFM characterizations of non-irradiated and laser irradiated samples summarized in Table 4, show that the surface roughness decreases dramatically after irradiation.

Table 4: AFM Roughness Comparison Between Nb Coated Samples before and after Laser Irradiation

Treatment	**Ra** Non irradiated	**Ra** Irradiated
SUBU5 (CERN)	9 nm	1 nm
SUBU5 (INFN)	9 nm	7 nm
EP	12 nm	5 nm
EP + SUBU5	13 nm	3 nm
Tumbling	25 nm	13 nm

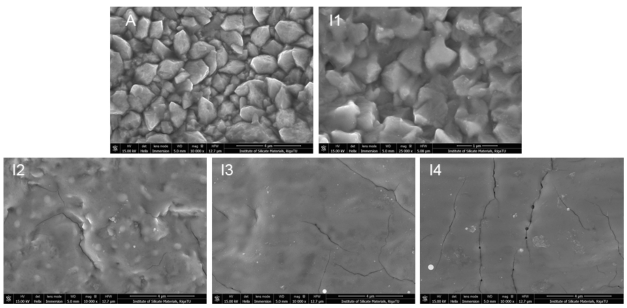

Figure 9: SEM images of Nb/Cu sample before irradiation (A) and after irradiation by Nd:YAG laser with intensities: I_1 = 140 MW/cm^2; I_2 = 170 MW/cm^2; I_3 = 253 MW/cm^2; I_4 = 320 MW/cm^2.

SEM images of non-irradiated and irradiated samples are shown in Fig. 9. Before the irradiation, Nb/Cu surface consists of nano-crystals with sizes ranging from 300 nm to 2 µm. After the irradiation, nanocrystals become smaller and surface becomes smoother due to its melting with increasing of laser intensity. Evaporation takes place at the intensity 320 MW/cm^2. However, cracks appear on the irradiated surface at 253 MW/cm^2 and higher intensities. XRD patterns of non-irradiated and irradiated Nb/Cu sample has shown the increase of crystallite size from 25 nm to 31 nm and the decrease of lattice constant a_0 from 3.370 Å to 3.289 Å. Superconducting properties of the samples were investigated, as well. In Table 5, the flux entry field B_{en}, determined applying the 2% relative difference criterion before and after the irradiation by laser depending on Cu surface preparation methods at 4.22 K is shown.

Table 5: First Flux Entry Field B_{en} Determined at 4.22 K for the Nb Coated Samples before and after Laser Irradiation

Treatment	B_{en} Non irradiated	B_{en} Irradiated
SUBU5 (CERN)	12 mT	17.0 mT
SUBU5 (INFN)	20 mT	23.7 mT
EP	18 mT	18.8 mT
EP + SUBU5	14 mT	15.5 mT
Tumbling	18 mT	19.1 mT

The temperature distribution in the irradiated Nb/Cu structure was calculated by solving the Stefan problem. We consider the two-phase Stefan problem, since certain part of the material is melted. Assuming the known parameters of bulk Nb and Cu, the numerical solution suggests that only the Nb layer can be partly melted during a nanosecond laser pulse, the underlying Cu being not melted. It is because the heat diffusion length in Nb (about 0.38 µm for pulse duration τ = 6 ns) appears to be much smaller than the 3 µm thickness of the Nb layer. Longer pulses (1 µs to 10 µs) are required for melting of Cu.

CONCLUSIONS

Five surface treatments techniques: SUBU, EP, EP+SUBU, Tumbling and Laser Polishing, prepared in 3 different Institutions on an identical planar substrate was investigated. Based on the morphological characterization, the main conclusion is that the most promising procedures are EP, as a pitting free technique. SUBU provides the lowest roughness, but pitting is more dangerous from RF point of view. Superconducting Properties of Nb films shows a slight difference between deposition facilities rather than different surface preparation. RF test are mandatory for a better comprehension of the substrate effect on the final properties of Nb film coating. RF measurements at Helmholtz-Zentrum Berlin (HZB) on Quadrupole Resonator (QPR)'s sample are already planned.

Laser post-treatment first results are very promising. Laser radiation show the capability to reduce dramatically the surface roughness and to increase the field of first entry in all the samples treated. The mechanism is still under investigation.

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