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E-PLATE: Electrostatic Powder pLating for Accelerator TargEts

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Electrostatic Powder pLating for Accelerator TargEts

Project plan

	WP1. Building automated deposition system
0	WP2. Deposition of targets for cross-section measurement experiments
Q	WP3. Study of new factors influencing deposition
••	WP4. Validation of upgraded technique on Mo
	WP5. Analysis of results
	WP6. Presenting results

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WP 1. AUTOMATED DEPOSITION SYSTEM CONSTRUCTION

Choice of the automatable power supply

According to evaluation based on the technical details, convenience of automation and final cost of the unit, the Spellman SL60N60/230 with eSL Ethernet option was chosen.

Design of the remote-control system

The PC-based automation system based on LabVIEW was chosen in order to have maximum flexibility for any further changes in control system.



Remote control by TeamViewer

Laptop:

FIGURE 1. CCD CAMERA SETUP FOR REMOTE POWDER MOTION CONTROL

For the remote control of the process the distant on-line method of the process observation was used: the BOSCH VBC-255-51 color CCD camera (all pieces borrowed) with USB video adapter attached to the PC controlling the process. Further remote control is realized by TeamViewer. Two software programs were used to observe and acquire the video: ArcSoft Showbiz (licenze) and Deput By NHC (free).



FIGURE 2. TEAMVIEWER SCREEN DURING THE PROCESS OBSERVATION ON DISTANT PC

Purchase of the components

The Spellman SL60N60/230 with eSL Ethernet option HV power supply and a list of electronic components required for automation has been purchased.

System installation

New Vacuum system

The vacuum system originally used for the HIVIPP deposition (Figure 2a) was composed mainly of aged recovered units (Alcatel 5400 turbomolecular pump with controller, Varian SH-100 scroll pump).



2018-beginning 2019



(a)

(b)

FIGURE 3. EVOLUTION OF THE PUMPING GROUP

We have met a number of problems related to the use of the recovered components. Fortunately, the other group at LNL lab has borrowed us for 6-12 month an automatable pumping group, which we are using for the depositions at the moment.

The Item[®] aluminium profile support was designed and realized in the mechanical workshop of LNL in order to install the new vacuum system, required working space for a glove-bag (see Figure 2b).

The actual vacuum system comprises ACP28 (Pfeiffer) primary pump, MAG W 600 P (Oerlikon) turbomolecular pump, pneumatic gate-vale of HVA, pneumatic valves from SMC, set of vacuum meters and corresponding controllers. A "transition" between the chamber and the gate valve was realized in LNL mechanical workshop and the vacuum was tested before the installation in the system (Figure 4).



FIGURE 4. "TRANSITION" TESTING BY LEAK-DETECTOR

A new feedthrough was purchased in order to correspond to the maximum voltage (60 kV) supplied by the new HV power supply Spellman SL60N60/230.

In figure 5 the general scheme of the components is illustrated.



FIGURE 5. PUMPING SYSTEM SCHEME

A linear manual actuator was installed and connected to the new sample holder system in order to open and close the cylinder before the process.

In Figure 3b the whole new system photo is shown.

Sample-holder

The sample-holder for HIVIPP deposition is a particular issue, requiring attention. Originally the sample-holder repeating the concept proposed by Isao Sugai in his first papers on HIVIPP deposition Ver. 0 was used (see Figure 6).



FIGURE 6. VER.0 SAMPLE-HOLDER: DISMOUNTING AFTER DEPOSITION

The main limitations of the sample-holder Ver. 0 include:

- No pumping inside cylinder \rightarrow low vacuum
- No centring of substrates and a cylinder
- No guaranty of planarity \rightarrow Powder can escape
- Difficult to assemble (2 people are required)

For this reason, a new version Ver.1 (see Figure 7) has been designed (L. Pranovi) and realized (LNL mechanical workshop).



FIGURE 7. SAMPLE-HOLDER DESIGN VER.1

In order to improve the vacuum inside the cylinder, a manual linear actuator was connected to the upper part of the sample holder Ver.1. According to the realized test, the vacuum was improved during the cylinder opening. Once the vacuum was tested, the power supply was connected to the electrodes and several HV tests were performed on the new sample holder. 30 kV voltage was reached at 10 mm electrodes distance with cylinder in vacuum.

However, some considerations should be highlighted:

- a cleaned environment is necessary in order to avoid dust that causes sparks; the cleaning procedure of sample holder pieces includes washing in ultrasonic bath with TICKOPUR RW 77 (Dr H Stamm Gmbh.) soap, rinsing in water, EtOH, drying.
- to increase the voltage a conditioning is absolutely required (see HV automation).



FIGURE 8. SAMPLE-HOLDER VER.1 INSIDE THE VACUUM CHAMBER

The Ver. 1 sample-holder has allowed to obtain the following improvements:

• Vacuum inside cylinder thanks to the linear actuator attached to the upper electrode

- Centring the cylinder and substrates
- Versatility for different size of cylinder (height and diameters)
- Improving insulation outside the cylinder
- Easily removable electrical connection
- Gripping holder for easy and safe extraction by means of parallel clamp
- Compact design to fit the DN100 viewport



FIGURE 9. SAMPLE-HOLDER VER.1 OPENING AND CLOSING

The sample-holder with cylinder and powders is placed inside the vacuum chamber through the CF100 fast-opening view-port using a dedicated parallel clamp to keep together the assembly.



FIGURE 10. PARALLEL CLAMP TO PLACE THE ASSEMBLY INSIDE THE CHAMBER

HV power supply automation

The LabView control system was designed from scratch. In the present form, it allows full access to the control and diagnostics of the high voltage generator. The control strategy is based on the readings of the actual values of voltage and current. The operator is able to set a ramp based on a series of steps, whose duration and voltage increase can be constant, or user defined. A linear function allows to have a constant voltage steps that holds for a duration that is increasing as long as the total voltage is increasing. This is necessary in order to give the conditioning of the apparatus: the higher the voltage the longer the duration of the step. The definition of the step can be seen on Figure 11a.



FIGURE 11. (A) DEFINITION OF VOLTAGE STEPS ON THE CONTROL SYSTEM. (B) TYPICAL VOLTAGE RAMP FOR A DEPOSITION.

The next Figure 11b shows a typical voltage ramp used for a powder deposition. It can be seen how the voltage step up is constant, but the duration of each steps increases as long as the total voltage is increasing.

It must be noted that the set voltage of each step is not defined a priori: the voltage step is added to the last read voltage instead of the last set voltage. This allows efficient conditioning, based on the actual status of the experiment. This can lead to unpredictable duration of the ramp, but on the other hand it allows more efficient diagnostics.

The data recording of long experiments can result into a too large file, leading to problems on the data analysis.



FIGURE 12. TYPICAL DEPOSITION PROCESS LOGGING IN THE LABVIEW PROGRAM INTERFACE.

For this reason, the operator can manually modify the rate of data stamp, having more data in the part of the experiment that are of interest. Moreover, the operator can set a

maximum file size: once the open file reaches this size it is closed, and a new file is opened. This avoids the generation of too large files.

Finally, the LabView program is opened to the inclusion of a DAC to read other parameters from the experiment, such as pressure, temperature and the likes. This feature will be implemented in the near future, to allow interlock or more complete data analysis.

Safety interlocks of the high voltage power supply are not in the LabView program: for safety system it has to be a real signal, Normally Open or Normally Closed. This interlock is part of the power supply hardware, only monitored by the LabView program.

WP 2. DEPOSITION TARGETS FOR THE CROSS-SECTION MEASUREMENT EXPERIMENTS Ti enriched targets deposition.

Ti-48, Ti-49 and Ti-50 enriched targets preparation is necessary for the measurements of the cross-sections of the nuclear reactions ⁴⁸Ti(p,2p)⁴⁷Sc and ^{49,50}Ti(p,x)⁴⁷Sc planned in the framework of the INFN CSN5 project PASTA (2017-2018).

A batch of **Ti-48** enriched targets was realized using HIVIPP technique and has been successfully used for the cross-section measurement experiments at the Arronax facility (Nantes, France).

Unfortunately, the enriched powder material properties change a lot from batch to batch and purchased **Ti-49** and **Ti-50** isotopic powders from **Oak Ridge National Laboratory** appeared to be completely different from previously used **Ti-48** from **TRACE** (by the same supplier - Oak Ridge National Laboratory). The material received was not in the requested form of metallic powders, but in the form of metal sponge of different size and shape, up to 2 mm pieces (Figures 13,14).



FIGURE 13. POWDERS OF TI-48 FROM TRACE (PRODUCTION OAK RIDGE), TI-49 AND TI-50 FROM OAK RIDGE NATIONAL LABORATORY



FIGURE 14. SEM OF TI-48 AND TI-49 POWDERS

The HIVIPP deposition has been realized using the smallest fraction of enriched ⁴⁹Ti. Very few material (0-0.6 mg/cm²) has been deposited. Figure 15 reports the result of the SEM analysis of the obtained deposit. It was different from Ti-48, since it was not uniform, containing powders agglomerates.



FIGURE 15. SEM ANALYSIS OF THE ⁴⁹TI ON AL TARGET: NOT UNIFORM

After this test, the idea of reducing the powder size was considered. Being a high plasticity metal, Ti can not be milled at the r.t. However, there is information in the literature on successful milling at the temperature of the liquid nitrogen. We have tested (unfortunately without positive results) manual mortar powders size reduction in liquid nitrogen. It is evident that even treating powders manually in liquid nitrogen, the temperature is higher due to heat exchange with air and mortar. The evolution is an automatic ball milling at low temperature. The only commercially available ball milling machine using a jar with continuous liquid nitrogen flux in the jacket is the Retsch Gmbh CryoMill.

After a successful test of ^{nat}Ti cryomilling at the Verder Scientific exposition-laboratory (Retsch official representative) the CryoMill machine was purchased by LARAMED LNL funds, since it is able to resolve the problem of pre-treatment, absolutely necessary for the enriched powders material in the case of further utilization not only for HIVIPP deposition, but also for the other target preparation methods (pressing, sintering, etc.). The cryomill was installed at INFN-LNL in October 2018 and a set of tests was performed starting form ^{nat}Ti metallic flakes (Figure 16) in order to optimize the protocol before using the enriched material.



FIGURE 16. TI-NAT FLAKES (LEFT) AND THEIR SEM IMAGE (RIGHT)

The optimized cryomilling procedure resulted in small (5-70 μ m) and ^{nat}Ti powder of irregular shape (not spherical, not flatted) (see Figure 17). Low amount of Fe contamination (~5% at.) is present in the milled powder because of stainless steel jar and sphere utilized. In future, for the enriched Ti, a dedicated zirconia jar and sphere will be used to avoid Fe contamination.



FIGURE 17. TI POWDERS AFTER OPTIMIZED CRYOMILLING PROCEDURE STARTING FROM TI-NAT FLAKES

Obtained ^{nat}Ti powder was successfully utilized for HIVIPP deposition (15kV, 40h, 1cm cylinder height) onto AI substrates of 100 μ m, resulting in targets with deposited density of about 4 mg/cm² (8 μ m). At the moment the activity on Ti is stopped, we plan the cryomilling and further deposition of the targets of enriched Ti -49 and Ti-50 at the beginning of 2020.

WP 3. INFLUENCE OF NEW FACTORS ON THE DEPOSITION PROCESS

Different Mo-nat powders

In order to separate fractions with different powder size, the powder was manually sieved using appropriate sieves (Giuliani s.r.l.) with net openings of 60, 40 and 20 μ m.

The verification of the efficiency of the manual sieving was made in July 2018 using already available (box already opened, means exposed to atmosphere) Mo powder of 170 mesh, of 99.5% purity, spherical (Alpha Aesar, Lot. Q18A033). Then new Mo powder with "equal specifications" was purchased in order to start the experiments according to DOE, with new and not oxidized powder.

Purchased natural Mo powders of 170 mesh (should correspond to <90µm), 99.5% purity, spherical (ABCR, Lot. 1379824) was purchased and sieved manually in controlled atmosphere (Ar glove bag). In Figure18 different fractions are shown. The SEM images (Figure 19) revealed that the shape of the powder is sponge-like (and far from spherical, as it was declared), so it was difficult to control the powder size. According to EDS analysis the powders after sieving was characterized by about 10-30 at. % of oxygen.



40 μm < x < 50 μm FIGURE 18. SEM OF DIFFERENT FRACTIONS OF SIEVED ABCR (ORIGINALLY 170 MESH) MO POWDERS



FIGURE 19. SEM: SPONGE-LIKE SHAPE OF ABCR MO POWDER

First depositions were carried out using **ABCR powder (size 50<x<70)** on Cu substrates with different surface finishing, as laminated and mechanically lapped, in order to see the behaviour of sponge-like Mo powders and verify if the roughness of the substrates influences the deposited amount (Table 1).

TABLE 1: MO-NAT ABCR POWDERS DEPOSITION ON DIFFERENT CU SUBSTRATES

Exp	Parameters	Deposited density (by weighing)					
#		up	low	average			

43	- - -	Cu laminated Cylinder h=1cm Time: >30 h set V: 25 kV	0.84±0.14 mg/cm ² (0.82±0.13 μm)	2.01±0.16 mg/cm ² (1.9±0.16 μm)	1.43±0.16 mg/cm ² (1.36±0.16 μm)
44	- - -	Cu lapped Cylinder h=1cm Time: >30 h set V: 25 kV	1.1±0.14 mg/cm ² (1.07±0.14 μm)	1.45±0.15 mg/cm ² (1.4±0.14 μm)	1.28±0.15 mg/cm ² (1.24±0.14 μm)

It should be noted that average deposited density of the targets realized onto not treated and mechanically polished copper is comparable, the difference is in the range of the error. Since we did not observe significant improvement using mechanically polished copper, for the further experiments as laminated copper was used as the substrate.

The SEM images (Figure 20) reveal that the deposit is uniform and follows the substrate roughness. Already in previous depositions, we have noted that the microstructure of the deposits repeats the powder size. From the SEM images at higher magnification (Figure 20 right) it can be observed that the size of the particles deposited is of the order of several microns. This means, that only these particles, composing the sponge-like powders (see Figure 19) are acting. And sieving of the sponge-like powders agglomerates (ABCR) does not allow to obtain the "probe particles" of different size for the HIVIPP process. The mechanical behaviour of such agglomerates of powder is not predictable.



FIGURE 20 : SEM COMPARISON OF MO DEPOSITION ONTO LAMINATED AND LAPPED CU SUBSTRATES

Therefore, a new bottle of Mo powder (Alpha Aesar 170 mesh, spherical, Lot. Q18A033) was borrowed from another LNL group in order to anticipate a new purchase procedure (requiring time!) and to start the experiments according to the DOE.

Two different bottles of Alpha Aesar Mo powder 170 mesh (<90 μ m), 99.5% purity, spherical, were available (Lot. n. Q18A033 and Lot. n. D24L18). The powder of Lot. n. Q18A033 (new) was sieved in controlled atmosphere (Ar filled glove bag) in order to prevent the oxidation of the powder. Instead, the sieving of the powder of Lot. n. D24L18 (already opened) was

realized in air. In this way, different powder size, not oxidized powder and oxidized powder were prepared.

The resulted fractions are well distinguished, but the net openings of the sieves do not correspond to the declared values: $60 \mu m$, $40 \mu m$, $20 \mu m$ (see Figure 21).



Figure 21. SEM of Mo powder Alfa Aesar Lot. N. Q18A033 sieved.

The oxygen amount was measured by EDS and, unfortunately, the powder sieved in controlled atmosphere appeared to be already oxidized (oxygen amount ~40%). The fraction of the different sizes of the powder are shown in Table 2.

TABLE 2: PARTICLE SIZE FRACTIONS						
	Mo powder Alfa Aesar Lot. N. Q18A033	Mo powder Alfa Aesar Lot. N. D24L18				
Shape	Spherical bulk	Spherical sponge-like				
X>70	30,4%	71,7%				
50 <x<70< th=""><th>67,1%</th><th>9,7%</th></x<70<>	67,1%	9,7%				
40 <x<50< th=""><th>2,5%</th><th>13,8%</th></x<50<>	2,5%	13,8%				
X<20	0%	4,7%				
Oxygen amount	~40%	~58%				

In addition, despite the same characteristics declared, the powder shape is different between the two different Lot. Numbers, as it can be visible in the SEM images (Figure 22).

FIGURE 22: MO 170 MESH POWDERS SHAPE FROM DIFFERENT COMPANIES.

Originally, the spherical, bulk-like powder (Alfa Aesar 170 mesh, spherical Lot. **Q18A033**) was chosen for DOE experiments since the size can be clearly distinguished and they are not agglomerates.



FIGURE 23: REDUCTION SYSTEM USING HYDROGEN OVERPRESSURE

After the analysis, this powder was considered as **oxidized powder** (because the oxygen amount was >40 at. % according to EDS). Thus, in order to get the **not-oxidized powder** a reduction was needed. Fortunately, during the TECHNOSP CSN5 project we have developed a method and experimental set-up for Mo reduction, starting from MoO_3 powders [1]. The set-up comprising the H₂ batch overpressure reactor and the reduction thermal cycle are presented in Figure 23.

First reduction tests were carried out for 4 hours starting from Mo powder (Alfa Aesar, 170 mesh, spherical, Lot. Q18A033) sizes >70 (80) and 40 < x < 50 (40).

The reduction process did not modify the shape of the powder and the oxygen amount decreased to \sim 15% with respect to >40% of the starting powder.

First block of experiments according to DOE: spherical Mo powders

Therefore, the new DOE plan we have followed is described in the following tables.

	Feeters	Lower level	Central point	Higher level			
	Factors	(-)	(0)	(+)			
X 1	Electric field, E (kV/cm)	5	10	15			
X ₂	Powders size (µm)	40(±10)	60(±10)	80(±10)			
X 3	Powders reduction, tred 950°c (h)	0	2	4			
X ₄ Cylinder height, h (cm)		1	1.5	2			
		deposition time ~40 h					
		substrate roughness: laminated $R_a=0.5\mu m$					
	Fixed parameters	substrate oxidation level: as it is					
	rixed parameters	vacuum level: 1 x 10 ⁻⁶ mbar					
		powder amount ~100 mg					
		substrate thickness: 250 µm					

TABLE 3: DOE: FIXED PARAMETERS AND STUDIED FACTORS.

materials: Mo (99,5%) on Cu (99,9%)

TABLE 4: FRACTIONAL FACTORIAL DESIGN								
Run	Exp #	X ₁	X ₂	X ₃	X4			
1	48	-	-	-	-			
2	51	+	-	-	+			
3		-	+	-	+			
4	47	+	+	-	-			
5		-	-	+	+			
6	50	+	-	+	-			
7	49	-	+	+	-			
8		+	+	+	+			
9		0	0	0	0			

The first 1/2 Fractional Factorial Design of Experiments is illustrated in Table 4.

In Table 5 the summary of realized experiments is presented.

TABLE 5: MO ALFA AESAR SPHERICAL POWDERS DEPOSITION EXPERIMENTS										
		Factors								ing, [mg/cm²]
Exp #	X ₁	El. Field [kV/cm]	X2	Powder size [µm]	X3	Powder red time [h]	X4	Cylinder height [mm]	Y1 - Low	Y ₂ - Up
47	+	15	+	80	-	0	-	10	0,2±0,13	0±0,13
48	-	5	-	40	-	0	-	10	0,15±0,13	0,02±0,13
49	-	5	+	80	+	4	-	10	0,065±0,13	0,065±0,13
50	+	15	-	40	+	4	-	10	0,065±0,13	0,11±0,13
51	+	15	-	40	-	0	+	20	0±0,13	0±0,13

The "deposited" quantities were in the range of the error. Thus, it was concluded that **spherical Mo powder was not deposited** on the Cu substrates in different conditions (cylinder height, electric field, powders size).

SEM and EDS analysis (see Figure 24) of the deposited substrates were realized and had proven significant surface modification but almost no deposition (according to the EDS map a low quantity of Mo is distributed on both deposited-right and not deposited-left part). According to EDS analysis, the "deposited" area contained 69% Cu, 1.5% Mo, 6.5% Si and 23% O (at. %). Si presence is probably related to the traces of quartz, indeed the quartz cylinder in depositions with spherical Mo powders was becoming opaque. The explanation could be, that we were not able to reduce completely the MoO₃ on the surface of the Mo spherical powder and it behaved as an abrasive agent.



FIGURE 24: SEM-EDS ANALYSIS OF THE MO SPHERICAL DEPOSITION ON CU-49UP

The conclusion that the spherical shape of the powders is not favorable for the HIVIPP deposition was made. For this reason, the set of the experiments with spherical Mo powders was interrupted (see Table 4) and an approach to modify the shape of the Mo powders was developed.

Shape modification of Mo powders: cryomilling

Fortunately, working with Ti powders for the WP 2 we have found a method to modify the shape of the powder by the CryoMill (Retsch Gmbh.) purchased by the LNL-INFN LARAMED group (see Figure 25).



FIGURE 25. RETSCH GMBH CRYOMILL SCHEME (A) AND EXPERIMENTAL SET-UP AT LNL-INFN (B).

The milling test was realized using the same Mo natural powders Alfa Aesar, 170 mesh, spherical, lot. Q18A033, described in Table 6.

TABLE 6: MO CRYOMILLING EXPERIMENTS							
Mo cryomill test #	6	3	4				
Milling procedure	1 cycle (7min cooling, 3min intermediate cooling, 3min milling, tot mill 3min)	3 cycles (7min cooling, 3min intermediate cooling, 3min milling, tot mill 9min)	6 cycles (7min cooling, 3min intermediate cooling, 3min milling, tot mill 18min)				



From SEM images, it is visible that the powders obtained using just 1 milling cycle still contains spherical particles, instead after 3 or 6 milling cycles the powders shape is acceptable. However, in order to obtain different powders size fractions "3 cycles" milling procedure was chosen for further utilization. No any agglomerates were observed.

The new powder fraction sizes after sieving are presented on the figure 26. The bigger size fraction ($x>100 \ \mu m$) was excluded, since the particles are too much flattened. Other three fractions are used for the experiment's realization according to a current DOE plan.



Figure 26. SEM of sieved cryomilled Mo powder Alfa Aesar Lot. N. Q18A033.

Second block of experiments according to DOE: non-spherical Mo powders

The second 1/2 Fractional Factorial Design of Experiments is illustrated in Table 7.

Based on the powder's analysis the factor X_2 levels have been changed a bit. Based on the experience from the previous deposition experiments the following factor X_1 upper level has been decreased, since 15kV/cm was difficult to guarantee experimentally in case of 2cm cylinder height. Also, the powders amount (fixed parameter) 50 mg was defined.

The chosen studied factor levels and fixed parameters are presented in Table 8.

TABLE 7: DOE: FIXED PARAMETERS AND STUDIED FACTORS.

	Factors	-	0	+		
X 1	Electric field, E (kV/cm)	5	9	13		
X ₂	Powders size (µm)	10	30	50		
X 3	Powders reduction, tred 950°c (h)	0	2	4		
X 4	Cylinder height, h (cm)	1	1.5	2		
		deposition time ~40 h				
		substrate roughness: laminated $R_a=0.5\mu m$				
	Fixed parameters	substrate oxidation level: as it is				
		vacuum level: 1 x 10 ⁻⁶ mbar				
		powder amount ~50 mg				

substrate thickness: 250 µm
materials: Mo cryomilled, Cu (99,9%)

The experiments with cryomilled Mo powders have been started. Just three experiments of the set have been realized (see Table 8). However, it can be said that in opposite to a spherical shape (starting material was the same!) the **Mo powders of irregular shape is successfully deposited** on copper by HIVIPP technique.

		NITC
		NLS.

	Factors							Output weighting, [mg/cm ²]		
Exp #	X1	El. Field [kV/cm]	X ₂	Powder size [µm]	X3	Powder red time [h]	X4	Cylinder height [mm]	Y1 - Low	Y2 - Up
54	+	13 (13kV)	-	20	-	0	-	10	2.0±0.2	2.79±0.19
55	+	13 (26kV)	-	20	-	0	+	20	0.82±0.13	0.46±0.13
57	+	13 (13kV)	+	50	-	0	-	10	0.58±0.13	1.3±0.15



FIGURE 27: SEM-EDS ANALYSIS OF THE MO CYROMILLED DEPOSITION ON CU-55UP

As it was realized before for the Alfa Aesar spherical Mo powders deposition, in Figure 27 an EDS map of the deposition of Mo cryomilled on copper is presented. The deposited layer can be observed. According to the EDS analysis, the "deposited" area contained 41% Cu, 47% Mo and 12% O (at. %).

We have found that powders shape is critically influencing the HIVIPP deposition (even if this aspect was not originally considered the parameters to study). There is no definitive explanation of this phenomenon, however, is can be related to the following aspects:

- the charge distribution on the irregular powders shape leading to a higher energy of the flying particle with respect to the spherical one;
- presence of a uniform and hard oxide layer (which, probably, was not completely reduced) on the surface of a bulk spherical Mo powder vs creating of new active non oxidized surfaces during cryomilling.

It should be said that our deposit of Mo on copper substrate (2.8 mg/cm² or \sim 2.7 µm calculated for bulk-like Mo density) is already as twice as higher than the maximum achieved by the group of I. Sugai (see Figure 28).



FIGURE 28: GRAPH REPRESENTING DEPOSITED THICKNESS VS DEPOSITION TIME BY I. SUGAI WITH POINT PRESENTING OUR LAST RESULT

WP 4. FINAL UPGRADED TECHNIQUE

WP4 will be realized after the WP3 is completed (in the second part of 2019). However, the preliminary high-power irradiation test of several Mo on copper HIVIPP deposited targets has been realized.





FIGURE 29. PROTON BEAM IRRADIATION TEST AT 17.6 MEV OF NATMO ON CU HIVIPP DEPOSITED TARGETS

The irradiation tests of 43_L , 44_L , 43_{UP} , 44_{UP} Mo natural targets on copper backing have been performed by ACSI TR19 cyclotron at Sacro Cuore Don Calabria Hospital, Negrar. The

irradiations have been realized for 2 min (in order to reach the thermal equilibrium of the target and minimize the activation) using 17.6 MeV proton beam of about Ø10mm and increasing the beam current in each following irradiation from 10 to 50 μ A (see Figure 29). The 50 μ A 17.6 MeV proton beam with the spot of Ø10mm corresponds to heat powder density of 1.1kW/cm².

No visual modification or damage of the targets occurred during irradiation. In order to acquire the photos, the targets have been stored in the hot-cell to leaves them decaying and then have been photographed. The signs of oxidation of Mo can be observed in the targets. This is related to the water presence in the helium gas cooling circuit (to cool down the target from the front) due to f the cooling system of the cyclotron solid target.

The fact that the HIVIPP deposited targets withstand the heat powder density of ~1kW/cm², guarantee that, from the point of view of target quality, HIVIPP technique can be a promising solution for the realization of the targets for radioisotope production (where such elevated currents and corresponding heat loads are normally used).

WP 5. ANALYSIS

SEM analysis of deposited targets

SEM was used for the analysis of both powders (sieved, milled, reduced) and deposited targets.

For example, on the Figure 30 the SEM microstructure of the Mo cryomilled powders deposited using different cylinders height keeping the other deposition parameters equal. The deposits at higher cylinder height are smoother that is even more evident on the upper sample. Probably because the process is less influenced by the electric field non-uniformities related to the surface roughness both original and modified during deposition.

FIGURE 30. SEM OF MO-NAT ON CU TARGETS DEPOSITED USING CRYOMILLED POWDERS

RBS analysis of the targets.

Prepared targets were analysed using the Rutherford Backscattering Spectrometry (RBS) method. Since the HIVIPP deposited samples have extremely high roughness, both superficial and interfacial (intermixing with the substrate), their RBS analysis appeared to be a challenge!

TABLE 7. RDS EXE ENTREMIS AT A 12000 ENE INFIT A COLLETATION				
Data	Samples type			
24.10.17	⁴⁸ Ti on Al			
06.12.17	⁴⁸ Ti on Al			
01.02.18	⁴⁸ Ti on Al			
17.01.19	Mo on Cu			
16.05.19	Mo on Cu (planned)			
29.05.19	Mo on Cu(planned)			

TABLE 9: RBS EXPERIMENTS AT AN2000 LNL-INFN ACCELERATOR

In total 18 targets of two types were analysed by RBS:

- 14 *type T* targets of Ti-48 enriched isotope from TRACE, deposited on 25 μm aluminium backings 99% purity (AN2000 irradiation runs on 24.10.17, 06.12.17, 01.02.18).
- 4 **type M** targets of natural Mo of 99.4% purity deposited on 250 µm copper backings of 99.9% purity (AN2000 irradiation run on 17.01.19)

A proton beam of 1 mm diameter at 1.8 MeV and 10-20 nA current intensity, delivered by the LNL AN2000 Accelerator, was used in order to measure the deposition profile.

A Silicon surface barrier detector, placed backward at 170 degrees and covering 2 msr of solid angle, was used to measure the energy of the scattered ions. The spectra were recorded with charge integration of 10-20 μ C.

In order to allow an easy comparison each spectrum was re-binned off-line to 3 keV/ch.

The analysis was made following the method suggested by Leavitt et al. [2], modelling the target deposition depth in successive layers of different composition. The simulated composition refers to the backing and deposited material, and to the oxidation level of the deposited one. While in [2] the total composition is considered a free parameter constant within the layer, in the present simulation the rate of change, of the deposited material, as a function of depth is the free parameter within the layer.

The beam straggling effect broadening the energy distribution was considered using the Chu [3] correction factor.

FIGURE 31. TYPICAL TYPE T TARGET SIMULATION: TI-48 ON AL

The type T targets were strongly oxidized, and the oxygen yield was corrected, for the non-RBS effects, following the Gurbich [4] approach. In this target type also the simulation impurities in the ⁴⁸Ti isotope and AI backing were considered.

In the case of type T targets thickness < $350 \mu gr/cm^2$, also the aluminium backing shows a yield influenced by nuclear reaction effects. In this case the experimental yield of a free Al backing was used instead of the full RBS calculation.

Two type T targets were also scanned in order to verify their homogeneity, which resulted to be better than 15%.

Sample	Ti deposited density by	Deposited density by RBS, µg/cm ²				
	weighting, µg/cm ²	Ti	0	Total		
251	970 ± 140	741	176	917 ± 92		
25u	710 ± 140	729	162	891 ± 89		
261	260 ± 130	377	102	479 ± 48		
26u	390 ± 130	406	104	510 ± 51		
271	580 ± 140	609	183	792 ± 79		
27up	580 ± 140	602	180	782 ± 78		
301	1070 ± 140	744	32	776 ± 78		
30u	2200 ± 170	524	41	565 ± 57		
311	400 ± 130	370	59	429 ± 43		
31u	330 ± 130	273	53	326 ± 32		
321	600 ± 140	668	161	829 ± 83		
32u	530 ± 140	420	100	520 ± 52		
331	670 ± 140	642	25	667 ± 67		
33u	400 ± 130	360	42	402 ± 40		

TABLE 10: RBS VS WEIGHTING DATA: DEPOSITED TI-48

In the case of type M targets, the oxidation is very low, and the effect is negligible, the Cu contribution was calculated assuming pure Cu and no secondary effects (impurities, multiple scattering, etc.).

The final simulated spectrum was obtained by calculating the individual RBS contribution of ⁴⁸Ti, Mo or Cu and the non-RBS for O and AI on each layer.

In order to obtain the best fit of the measured spectra the free parameters were optimized by using the Microsoft Excel Solve procedure, were the target cell was the sum of weighted squared residuals between the experimental and the calculated data. Following this procedure, the total amount of target material can be extracted and compared with the value previously obtained by weighting.

FIGURE 32. TYPICAL TYPE M TARGET SIMULATION: MO ON CU

While the type T spectra are fitted including the data above 500 keV, in the type M case the calculation does not include only the region below 1200 keV.

In the figures the experimental data is shown in yellow, the deposited material in red, the oxygen contribution in gray, the Al or Cu (backing) in blue, while the sum of all in black.

Figure 31 shows a typical type T simulation. Table 10 reports the results of the analysis of the 14 titanium targets. Figure 32 shows a typical type M simulation. Table 11 shows the obtained results for the Mo targets. An estimated RBS error of 10% is reported.

TABLE 11: RBS VS WEIGHTING DATA: DEPOSITED MO-NAT ON COPPER

Sample #	By RBS, mg/cm ²	By weight, mg/cm ²		
43L	2.05 ± 0.20	2.01 ± 0.16		
43U	1.20 ± 0.12	0.84 ± 0.14		
44L	1.63 ± 0.16	1.45 ± 0.15		
44U	1.18 ± 0.12	1.10 ± 0.14		

In summary, the RBS shows to be a well-suited method for target characterization when deposition thickness ranges in 0.2 to 5 mg/cm². The examined portion of the target is very

narrow (about 1 mm²) and scanning measurements are necessary in order to verify the target homogeneities.

WP 6. PRESENTING RESULTS

The E-PLATE project was successfully presented at three international conferences:

- H. Skliarova, S. Cisternino, G. Cicoria, M. Marengo, S. Carturan, P. Martini, A. Boschi, C. Rossi Alvarez, V. Palmieri, J. Esposito. *TECHN-OSP: Molybdenum target preparation techniques for cyclotron-based Technetium-99m production*. Symposium on Technetium and Other Radiometals in Chemistry and Medicine (TERACHEM 2018), Bressanone (BZ), Italy, September 26-29, 2018 (oral presentation).
- H. Skliarova, S. Cisternino, L. Pranovi, <u>P. Antonini</u>, G. Pupillo, L. Mou, J. Esposito, C. Rossi Alvarez. *High energy Vibrational Powder Plating for cyclotron target deposition*. 41st European Cyclotron Progress Meeting, Dubna, Russia, 2-6 September 2018 (poster).
- <u>H. Skliarova</u>, S. Cisternino, G. Cicoria, M. Marengo, J. Esposito, C. Rossi Alvarez, V. Palmieri. State of art of cyclotron solid target preparation at INFN-LNL for production of medical radionuclides in the framework of LARAMED project. 17th International Workshop on Targetry and Target Chemistry (WTTC17), Coimbra, Portugal, August 27-31, 2018 (oral presentation).

Here it should be noted the particular interest from Prof. J. Engle of University of Wisconsin led to the INFN-DOE Summer student project proposal on E-PLATE project in 2019 (competition is ongoing).

The **E-PLATE project was mentioned** also in the following **conference presentations** (aspects related to Ti targets preparation):

- <u>G. Pupillo</u>, A. Fontana, L. Canton, F. Haddad, H. Skliarova, S. Cisternino, P. Martini, M. Pasquali, A. Boschi, J. Esposito, A. Duatti, L. Mou. *Nuclear Cross Section Measurements of the Theranostic Radionuclide Sc-47: Preliminary Results of the PASTA Project.* Oral presentation. 2018 European Nuclear Physics Conference, Bologna, Italy, September 2-7, 2018
- <u>G. Pupillo</u>, L. Mou. P. Martini, M. Pasquali, J. Esposito, A. Duatti, C. Rossi Alvarez, H. Skliarova, S. Cisternino, A. Boschi, L. Canton, A. Fontana, T. Sounalet, F. Haddad. *Cyclotron-based production of the theranostic radionuclides* ⁶⁷Cu and ⁴⁷Sc. 15th Varenna Conference on Nuclear Reaction Mechanisms, Villa Monastero, Italy, June, 11-15 2018

peer reviewed publications:

- J. Esposito, D. Bettoni, A. Boschi, M. Calderolla, S.Cisternino, G. Fiorentini, G. Keppel, P. Martini, M. Maggiore, L. Mou, M. Pasquali, L. Pranovi, G. Pupillo, C. Rossi Alvarez, L. Sarchiapone, G. Sciacca, H. Skliarova, P. Favaron, A. Lombardi, P. Antonini, A. Duatti. LARAMED: A Laboratory for Radioisotopes of Medical Interest. Molecules, vol. 24, no. 1, p. 20, Jan. 2019
- H. Skliarova, P. Buso, S. Carturan, C. Rossi Alvarez, S. Cisternino, P. Martini, A. Boschi, J. Esposito. Recovery of Molybdenum Precursor Material in the Cyclotron-Based Technetium-99m Production Cycle. Instruments 2019, 3, 17

and scientific reports:

- J. Esposito, G. Keppel, G. Pupillo, L. Mou, M. Pasquali, P. Martini, M. Gobbo, M. Calderolla, P. Favaron, H. Skliarova, S. Cisternino, L. Sarchiapone, A. Boschi, M. Maggiore, C. Rossi Alvarez, G. Fiorentini, A. Duatti. *Progress of the LARAMED Project*. LNL Annual Report-2017, 2018, p.114
- G. Pupillo, L. Mou, H. Skliarova, S. Cisternino, J. Esposito, L. Canton, A. Fontana, P. Martini, M. Pasquali, A. Boschi, C. Rossi Alvarez, A. Duatti. PASTA Project Production with Accelerator of Sc-47 for Theranostic Applications. LNL Annual Report-2017, 2018, p.128

One LNL Annual report was dedicated to E-PLATE project:

• H. Skliarova, S. Cisternino, L. Pranovi, P. Antonini, J. Esposito, C. Rossi Alvarez. System for accelerator target deposition with High Energy Vibrational Powder Plating (HIVIPP) method. E-PLATE Project. LNL Annual Report-2017, 2018, p.188.

MILESTONES AND DELIVERABLES CONTROL

TABLE 12: MILESTONES, DELIVERABLES

Name	Description	Starting time	Deadline 2018	Realized	
M1	Realization of automated deposition system	01.01.18	31.07.18	100%	
M2	First block of experiments with different Mo deposition parameters	01.08.18	31.12.18	50% (interrupted)	
M3	Second block of experiments with different Mo deposition parameters	01.01.19	30.06.19	20%	
M4	Process mathematical model	01.08.18	30.09.19	0%	
M5	Test of Mo maximum thickness deposition	01.10.19	31.12.19	0%	
M6	Cyclotron test of Mo target	01.01.19	31.12.19	50%	
D1	New system installation (no automation)	01.04.18	31.05.18	√	
D2	Automated deposition system	01.01.18	31.07.18	√	
	Ti-nat targets on AL foil	01.09.17	01.11.17	\checkmark	
D3	Ti-48 targets on AL foil	01.10.17	01.04.18	√ ý	
D3	Ti-49 targets on AL foil	16.04.18	08.06.18	Moved to	
	Ti-50 targets on AL foil	16.04.18	08.06.18	year 2020	
	Cr-nat targets for METRICS	13.11.18	11.12.18	cancelled	
	Cr 52,53 targets for METRICS	01.01.19	30.04.19	cancelled	
D4	Mo on Cu target of max thickness	30.09.19	31.10.19		
D5	Manual for the HIVIPP deposition system	01.11.19	31.12.19		
D6	Protocol of the deposition	01.11.19	31.12.19		
D7	Final report of the activities and results	01.10.18	30.11.19	✓ report 1st year	

FIGURE 33. GANT CHART OF THE PROJECT

[1] H. Skliarova, P. Buso, S. Carturan, C. Rossi Alvarez, S. Cisternino, P. Martini, A. Boschi, J. Esposito. Recovery of Molybdenum Precursor Material in the Cyclotron-Based Technetium-99m Production Cycle. Instruments **2019**, 3, 17.

[2] J.A. Leavitt et al., in: Handbook of Modern Ion Beam Materials Analysis, eds. J.R. Tesmer, M. Nastasi, C.J. Maggiore, J.C. Barbour and J.W. Mayer, Materials Research Society, Pittsburgh, PA (1995), chap. 4.

[3] Chu, W.K. Calculation of energy straggling for protons and helium ions. *Phys. Rev.* A **1976**, 13, 2057–2060.

[4] A.F. Gurbich, Nuclear Instruments and Methods in Physical Research Section B129 (1997) 311