

Mo-99 2015 TOPICAL MEETING ON MOLYBDENUM-99 TECHNOLOGICAL DEVELOPMENT

AUGUST 31-SEPTEMBER 3, 2015
HILTON BOSTON BACK BAY
BOSTON, MASSACHUSETTS

PVD-based Manufacturing Process of Monolithic LEU Foil Targets for ⁹⁹Mo Production

Tobias Hollmer, Winfried Petry
Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II)
Lichtenbergstraße 1, 85748 Garching – Germany

ABSTRACT

The complete fabrication of the cylindrical LEU foil target was demonstrated using a newly developed manufacturing method. Hereby, the uranium as well as the interlayer material is coated directly on the inside of the outer cladding cylinder. This process was realized by a cylindrical magnetron enhanced PVD technique (sputtering). The set-up was extensively parametrized and an algorithm was developed, which allows the calculation of the grown layer thickness in real time or to simulate different sputter procedures. By adjusting the process parameters, the mechanical properties of the produced foils, their thickness homogeneity and the material utilization were optimized. In this way, self-supporting uranium foils with a good mechanical strength and a high thickness homogeneity were produced. By the application of a suitable interlayer material, these uranium foils were easily separable from the aluminum cladding. The material utilization of the uranium sputter process was above 90%.

1. Introduction

^{99m}Tc is the most widely used radioisotope in nuclear medicine for diagnostic imaging worldwide. It results from the beta minus decay of ⁹⁹Mo, which is mainly produced by fission of ²³⁵U in irradiation targets using high-flux nuclear reactors. The monolithic cylindrical LEU target provides a multitude of advantages over conventional dispersion targets, such as the higher uranium density or the minimization of highly radioactive liquid waste during processing. To make the fabrication of these targets industrially feasible, a novel manufacturing process was developed. In contrast to conventional production techniques where the uranium foil is pre-produced by rolling or casting [1,2], in this process the uranium foil is directly produced in the outer cladding cylinder by PVD deposition. Thereby, a cylindrical uranium sputter target is evaporated by a bombardment of argon ions. In the same way, the interlayer material, which allows a separation of the uranium foil from the cladding after irradiation, can be deposited. To realize this process, an advanced cylindrical sputter device was developed. The necessary ions are generated by a low pressure dc plasma. To increase the ionization density, the plasma is

magnetron enhanced, meaning that the electrons are trapped in the plasma region by an additional magnetic field. To produce the necessary cylindrical uranium targets for the sputter procedure, a casting process was developed. Using an arc melting furnace, sputter target with a high density of 98.8% in average and a good surface quality were produced. In a final step, the successful assembly of the coated target was demonstrated. Therefore, a hydraulic forming device was built and successfully tested. The principle of the developed manufacturing process and the dimensions of the irradiation target are shown in figure 1. The dimensions were slightly altered from the original Y-12 design to metric units in order to simplify the machining of components.

The following paper will focus on the coating process. For further details and a description of the casting process and the target assembly, reference is made to [3].

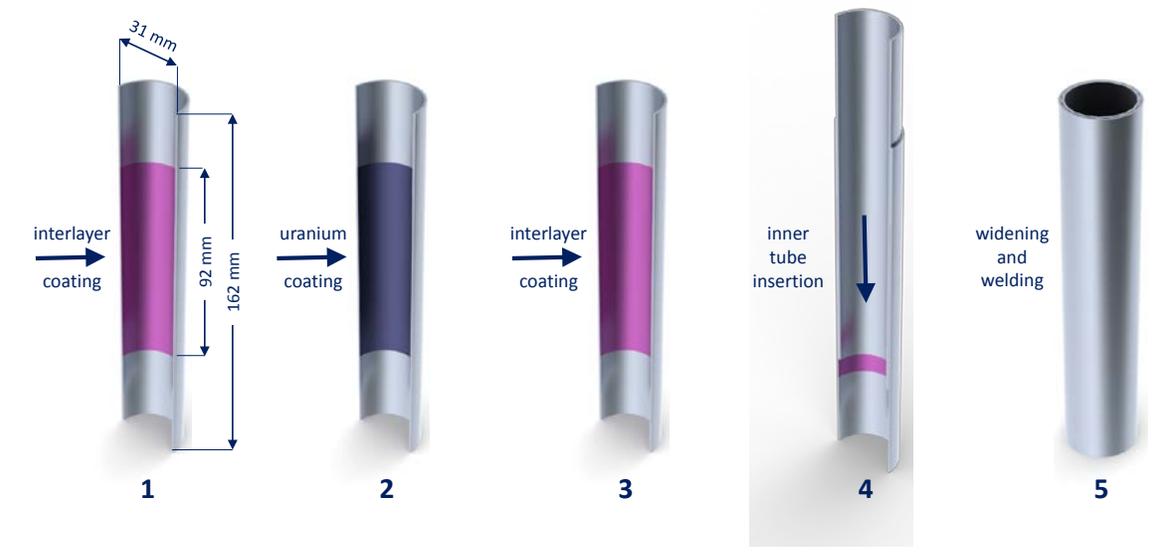


Figure 1: The irradiation target manufacturing procedure by PVD coating.

2. Instrumentation

A schematic of the sputter apparatus is shown in figure 2. It consists of a cylindrical PVD target (a), which is mounted in a water cooled heat sink (b). The target is electrically isolated from the heat sink and connected to a dc power source, providing up to 800 V and 2 kW. On both ends of the sputter target, a ceramic electron reflecting surface (c) is attached. Due to an electrostatic charge, these surfaces trap the plasma generating electrons in the volume around the target. In this way the plasma is well localized and its ionization density is significantly increased.

The sputter source can be moved along the central axis of the substrate (d), the outer cladding cylinder. To prevent the outer ends of the cladding cylinder to be coated, re-usable aluminum coating shields (e) are installed.

All these components are located inside a vacuum vessel, which allows the establishment of a suitable argon process atmosphere. The process pressure is determined by a dynamic equilibrium

between a controlled argon inflow and a constant outflow using a two stage pumping system. The vacuum vessel is surrounded by a magnetic coil (f), which both provides a magnetic field of up to 120 mT for the magnetron PVD process and allows to control the substrate temperature. Latter is realized by the coils' ohmic heating and a PID controller, which controls a cooling water flow through the coil. This allows the adjustment of the coil temperature from 20°C to 90°C.

Due to the design of the sputter device, both the magnetic field and the gas pressure show a dependency on the position of the sputter source. Since these two parameters have a strong influence on the sputter process, the position dependency is eliminated by a PLC controlled adjustment of field and pressure according to the sputter source position. Thereby, a uniform sputter process and, as a result, a homogenous layer thickness can be realized.

To allow a safe handling of the uranium and to prevent the produced samples from oxidation, the set-up is mounted on a glove-box with a highly pure argon atmosphere. The complete sputter process is PLC controlled and can be performed fully autonomously.

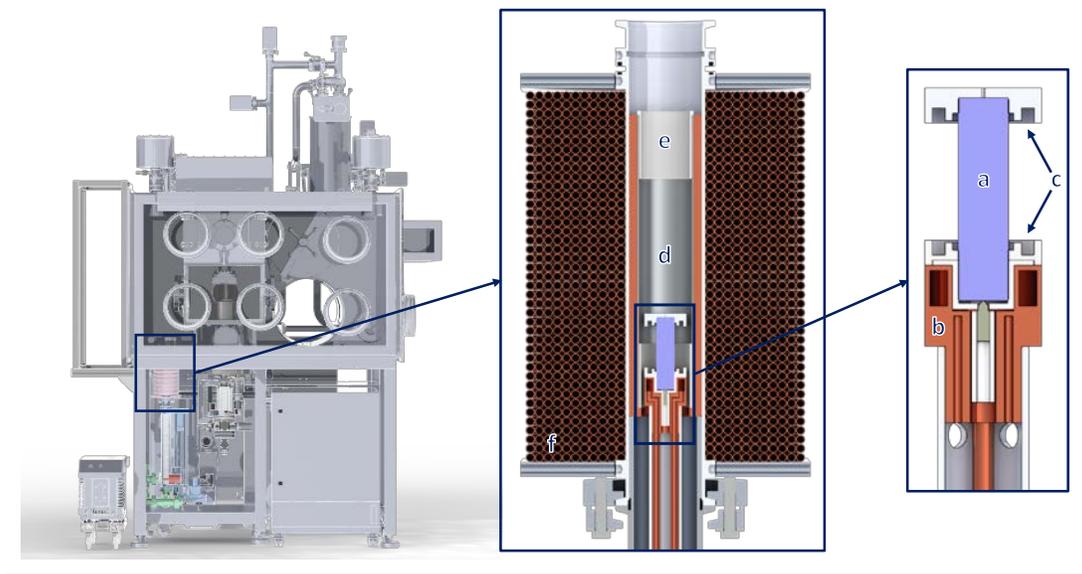


Figure 2: The cylindrical PVD device.

3. Process parameters and results

To make the PVD process feasible for the irradiation target production, it was aimed to produce uranium foils with a high mechanical strength and homogeneity. Due to the desired possibility to disassemble the target after irradiation, the produced foils need to be self-supporting and separable from the substrate. Furthermore, the sputter process has to be fast enough to allow the irradiation target production in a reasonable amount of time. These four objectives (layer quality, homogeneity, adhesion and sputter rate) can be controlled by following adjustable process parameters: sputter power, magnetic field, gas pressure, the application of an interlayer and the movement of the sputter source. The dependency of all these parameters is shown in figure 3.

Before performing the coating experiments with uranium, the sputter device was extensively parameterized using copper as surrogate material. Due to a similar melting point of both

materials, their layer formation in the PVD process is comparable. Therefore, the optimal process parameters gained for copper could successfully be transferred to the uranium sputter process.

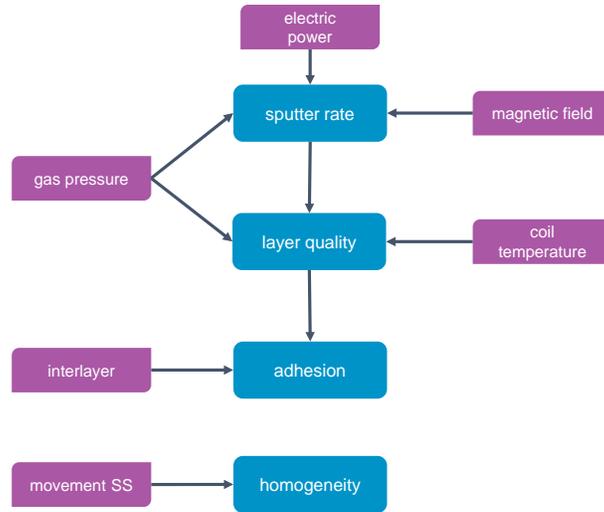


Figure 3: Objectives of the PVD process (blue) and their dependencies on the adjustable process parameters (purple).

Sputter rate

The sputter rate is defined as the eroded mass per time. It is influenced by the applied electric power, the gas pressure and the magnetic field. The magnetic field traps the plasma generating electrons on cycloidal-like path around the sputter target. Up to a certain point, a higher field strength leads to a more efficient trap of the electrons in the system. This increases their residence time in the plasma and, therefore, the ionization density. Due to the higher ionization density, more ions are created and the sputter rate increases. Therefore, a high field strength is preferable. The applicable field however, is determined by the limited cooling of the coil. In the given set-up, a magnetic field of 85 mT proved to be the ideal compromise between high sputter rate and possible heat dissipation. Therefore, the magnetic field strength was kept constant in all experiments.

The gas pressure is indirectly proportional to the sputter rate. At high pressures, the mean free path of the sputtered target atoms is reduced. This causes a higher residence time in the plasma region, which leads to an increased ionization probability of the target atoms. In this case, the target atoms are accelerated back towards the target and the effective sputter rate is reduced. Therefore, the gas pressure was kept as low as possible. Limiting factor is the stability of the plasma. At low pressures, the necessary voltage to sustain the plasma increases. This leads to more electric arcs and, therefore, a low stability of the process. As a compromise, the pressure was fixed to 0.035 mbar.

The main parameter to influence the sputter rate is the applied electric power. Following formula has proven to accurately describe the dependency of the sputter rate R on the electric power P and electric current I

$$R = aP \frac{I}{I + b} \quad (1)$$

The parameters a and b are material specific and were determined by comparing the measured mass difference of the sputter target before and after the coating procedure with the calculated mass difference

$$m = \int R(t)dt \quad (2)$$

In the current set-up with a magnetic field of 85 mT and a pressure of 0.035 mbar, the parameters were determined to be $a = 0.120 \frac{mg}{W \min}$ and $b = -50.99 mA$ for uranium. The consideration of the electric current in equation (1) increases in accuracy significantly compared to a simple linear dependency on P . By using equation (1), the maximum deviation between the measured and the calculated values stayed below 1.6% for sputtering uranium. Figure 4 shows a comparison between the measured and the calculated values. For comparison, the simple linear dependency on P is also shown.

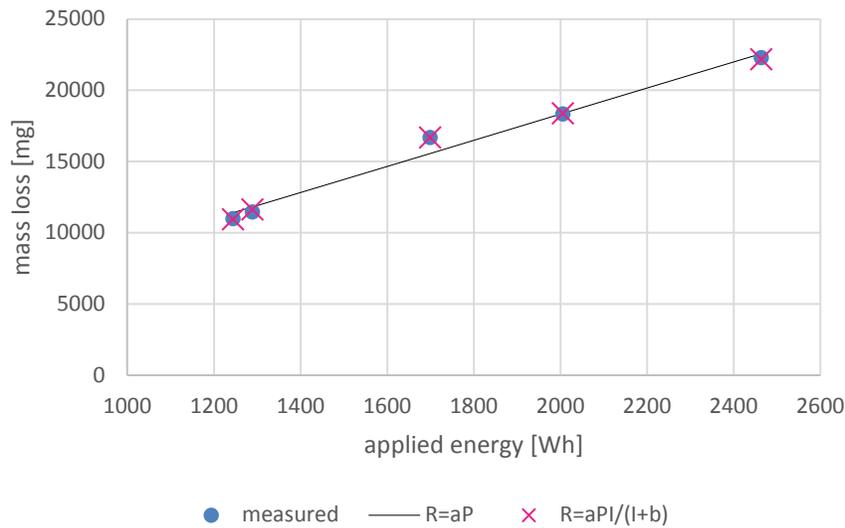


Figure 4: Comparison of the calculated and the measured target mass loss for different uranium sputter procedures.

In the current set-up, the maximum sputter rate is determined by the limited cooling of the sputter target. In case of uranium, the maximum power was set to 90 W to prevent the sputter source from damage. However with an improved cooling system, significantly higher powers can be achieved. The sputter rater can be further improved by using krypton instead of argon as

sputter gas due its better mass ratio to uranium. With these two measures, the necessary time to produce an irradiation target can be reduced from currently 24 h to 8 h.

Layer quality

The quality of the deposited layers depends on the type of layer growth. The deposited layer on the substrate grow by successive nucleation of atoms on previous deposited material. Layers deposited atom-by-atom, like sputter coating, generally grow in a columnar structure. The form of the columnar growth mainly depends on the mobility of the adatoms. In a given system, this mobility can be controlled by the substrate temperature and the inert gas pressure. A high substrate temperature and a low gas pressure, lead to more compact and denser layers, what results in a higher mechanical strength. Since the gas pressure was kept constant, as detailed in the previous section, the important parameter for the layer quality is the substrate temperature. This temperature can be influenced in two ways: the temperature created by the magnetic coil and, due to the low target substrate distance, the intensity of the sputter plasma. Latter is controlled by the applied electric power.

It could be shown that the uranium layer quality strongly depends on the substrate temperature. While at low temperatures the deposited layer are brittle and tend to crack when exposed to air, layers deposited at high temperatures show a high mechanical strength and no signs of cracking. Good results were achieved, when using a coil temperature of 90°C and a sputter power of 90 W. The actual substrate temperature could not be determined, but is significantly higher than the 90°C due to the heating caused by the plasma. A microscopy of an aluminum-uranium-aluminum multilayer deposited with these settings is shown in figure 5. As one can see, the layers show no signs of cracking or inhomogeneities. The separation of the upper aluminum layer is caused by a contraction of the mounting resin used to prepare the microscopy sample.



Figure 5: Microscopy of a sputtered Al-U-Al multilayer.

Homogeneity and material utilization

As described in chapter 2, the dependency of the sputter parameters on the position of the sputter source was electronically eliminated. Therefore when using constant sputter parameters, the layer homogeneity only depends on the movement of the sputter source.

The layer thickness F can be calculated by

$$F(z) = \frac{\epsilon_c}{2\pi\rho r_i} \int f(z, z_s(t))R(t) dt \quad (3)$$

where z is the axial position of the substrate, z_s the position of the sputter source, R the sputter rate according to equation (1), ρ the material density, r_i the inner diameter of the substrate cylinder and ϵ_c the coating efficiency. The coating efficiency is given by the mass of the material deposited on the substrate compared to the total eroded mass. This efficiency is mainly determined by the material deposited on the electron reflecting surfaces. The function f is the deposition distribution of the sputter source. f is a normalized, material dependent function and describes the thickness distribution of the deposited material. It showed that this distribution can well be described by following formula

$$f(z, z_s(t)) = \frac{mm}{4c} \left[\frac{c - (z - z_s(t))}{\sqrt{(c - (z - z_s(t)))^2 + d^2}} + \frac{c + (z - z_s(t))}{\sqrt{(c + (z - z_s(t)))^2 + d^2}} \right] \quad (4)$$

with c and d being material dependent variables. These variables were determined by measuring the thickness distribution resulting of a non-moving sputter source by microscopy. At a pressure of 0.035 mbar and a magnetic field of 85 mT the parameters were determined to be $c = 12.26 \text{ mm}$ and $d = 3.98 \text{ mm}$.

The calculation of the thickness using equation (3) was validated by comparing sputtered thickness distributions with calculated ones. Figure 6 shows a typical sputter procedure of uranium and the resulting thickness distribution. The plot shows both the measured values and the values calculated according to equation (3). As one can see, both distributions are in very good accordance. Therefore, the formalism can not only be used to follow the grown layer thickness distribution in real time but also to simulate different movements of the sputter source. It showed that very homogenous layer can be produced when using a constant up and down movement of the sputter source during the coating procedure. In the given example, the resulting thickness shows a high homogeneity with a maximum deviation of less than 1.6% in the range from -30 mm to +30 mm.

The material utilization of the coating process is defined by the material loss on the coating shields (figure 2, e) and the coating of the electron reflecting surfaces (c). Latter is given by ϵ_c in equation (3), which is approximately 95%. The material loss on the coating shields can be determined by the maximum oscillation of the sputter source. Up to a movement from -35 mm to +35 mm, no significant coating appears. At a normal movement from -45 mm to +45 mm, the average material utilization is approximately 92%. However, the deposited uranium on both the electron reflecting surfaces and the coating shields can be removed. By recycling this material in the sputter target production, the material utilization can be increased above 95%.

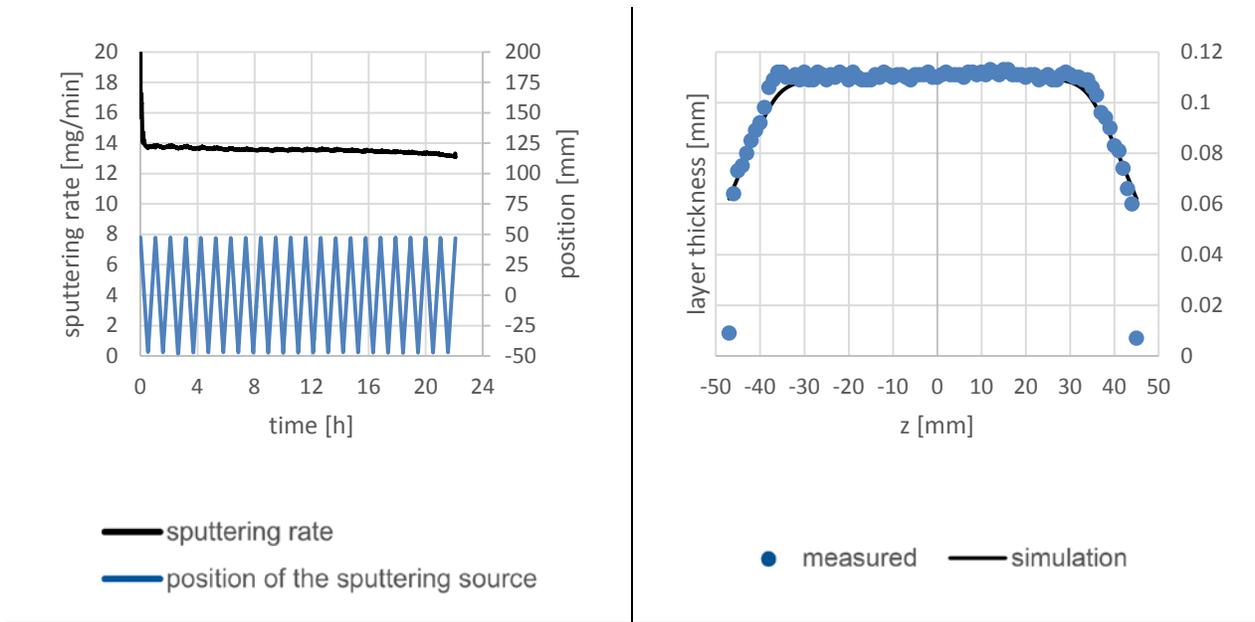


Figure 6: Typical uranium coating procedure and resulting thickness profile.

Adhesion

The adhesion of sputtered layers can be controlled in two ways: by its layer quality and/or by applying a suitable interlayer. Layers with a poor quality also show a poor adhesion to the subjacent substrate. This can be used to produce separable foils by first coating a layer with poor quality followed by a layer with high quality. This approach was tested with copper layers. It showed that the layers could easily be removed, however the removal was not free of residues.

To control the adhesion of the uranium layers, experiments with aluminum and graphite interlayers were performed. In case of aluminum, the interlayer was sputtered in the same way as the uranium layer. In contrast, the graphite was applied by spraying and a subsequent drying step. In both cases, the uranium layers are easily removable without any residues. As an example, a sputtered Al-U-Al multilayer is shown in Figure 7. The outer aluminum layer has a thickness of approximately 20 μm , the uranium layer of 140 μm and the inner aluminum layer of 5 μm . After the coating process, the substrate cylinder was cut in shorter segments, cut open on one side and bent up. The resulting uranium foil came off easily from the outer aluminum layer, while the inner aluminum layer stuck to the uranium. The uranium foil showed a good mechanical strength and flexibility. After an exposure to air of approximately 30 minutes, the foil showed a tarnish typical to uranium (see figure 7). However, no signs of mechanical impairment due to oxidation could be observed; even after an exposure time of several days.

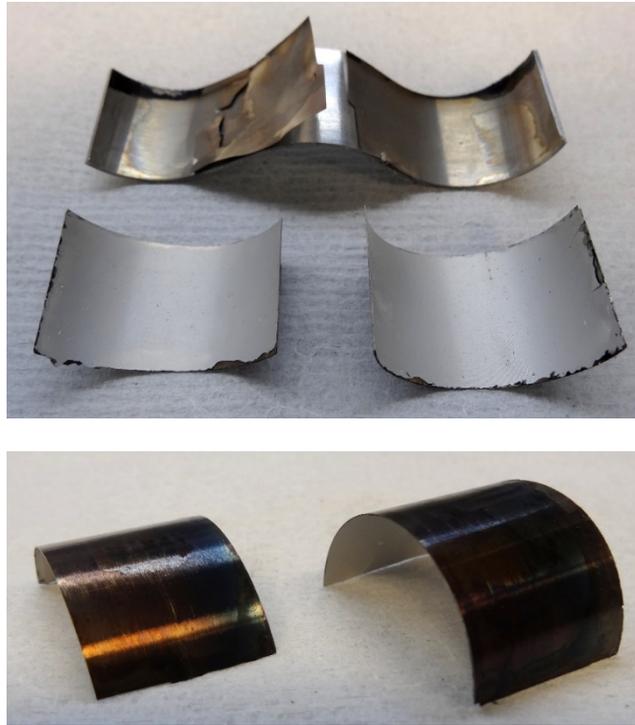


Figure 7: Sputtered uranium foil with two aluminum interlayers.

5. Conclusion

Within the presented work, a complete PVD based manufacturing process of cylindrical LEU foil targets was demonstrated. Figure 8 shows the developed process from a potentially oxidized uranium ingot to a completely assembled and welded irradiation target. A detailed description of the single manufacturing steps can be found in [3].

It was the aim of this study, to demonstrate the feasibility of PVD coating for the production of cylindrical LEU foil targets. Therefore, a demonstration PVD reactor was developed, which allowed to study the relevant sputter parameters. The apparatus was extensively characterized and, in this way, the process could be well understood. The developed theoretical description of the layer thickness is based on only four different material parameters and allows the simulation of different movement profiles and a real-time process observation.

A major requirement for the feasibility of the presented manufacturing technique is the separability and the mechanical stability of the produced foils. As described in chapter 4, the mechanical strength of the foils mainly depends on the coating temperature. By applying sufficient values, mechanically stable uranium foils were produced. These foils were self-supporting and showed no mechanical impairment due to oxidation.

It was also demonstrated that the adhesion of the uranium layer to the substrate can successfully be controlled by the usage of a suitable interlayer. Experiments were performed using aluminum and graphite. In both cases the produced foils were easily separable from the subjacent substrate.

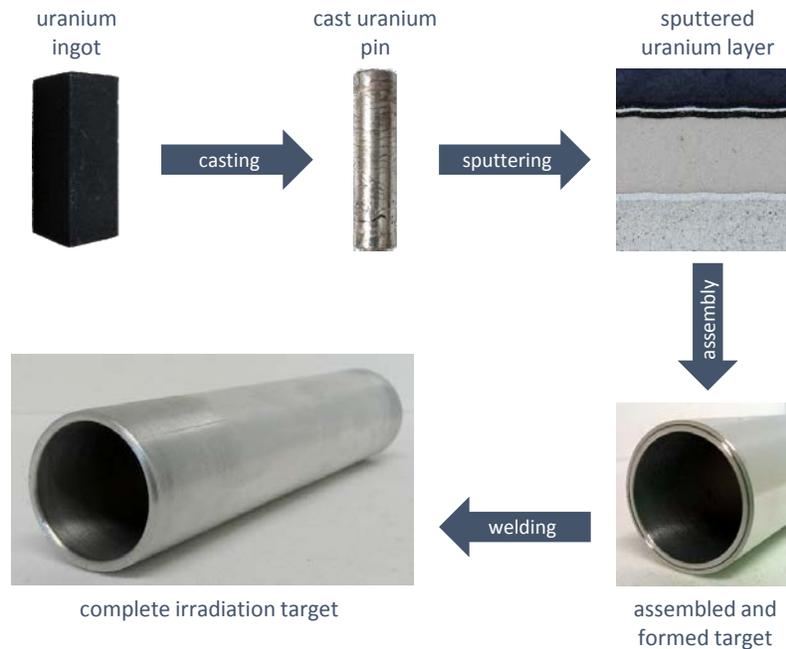


Figure 8: The complete irradiation target manufacturing process by PVD coating.

The developed coating process features three major benefits. The first benefit is its high degree of flexibility. Thickness, length and mass of the uranium foil and the interlayer material can easily be modified. This can be used to optimize the irradiation target and the overall cost efficiency. A second important advantage is the high material utilization. For the uranium pin casting an efficiency of 95% was achieved. Together with the maximum sputter efficiency of 92% for uranium, this results in an overall efficiency of 87%. These numbers do not consider any material recovery from the electron reflectors, which would lead to a further increase. A third advantage of the presented technique, is the high degree of automation. After loading the target and the substrate in the PVD reactor, the process is PLC controlled and fully autonomous.

In summary it can be concluded that the presented technique proved to be suitable for the irradiation target manufacturing. Therefore, further development will take place, which is oriented towards an industrial application.

6. References

- [1] L. Jollay, J. Creasy, C. Allen, G. Solbrekken, "Equivalent Fission Mo-99 Target without Highly Enriched Uranium", Mo-99 Topical Meeting, Santa Fe, USA, 2011.
- [2] C. Kim, "KAERI Recent Activities on Research Reactor Fuel", IWG consultancy meeting, Vienna, Austria, 2010.
- [3] T. Hollmer, "Development of a PVD-based manufacturing process of monolithic LEU irradiation targets for ^{99}Mo production", PhD thesis, Technische Universität München, Germany, 2015.