EXECUTIVE SUMMARY OF THE THESIS

Laser cleaning of rhodium-coated mirrors from fusion-relevant boron and boron-tungsten contaminants

LAUREA MAGISTRALE IN NUCLEAR ENGINEERING - INGEGNERIA NUCLEARE

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1. Introduction

The continuous year-over-year increase in energy demand in a global warming scenario makes the transition towards clean energy sources of primary importance. In particular, magnetic confinement nuclear fusion, through the development of tokamak machines like ITER and DEMO, represents a promising long-term solution for safe and stable electricity production without long-lived radioactive waste.

During operation, to retrieve information on the plasma behavior by analyzing the electromagnetic radiation emitted by it, optical diagnostic systems play a crucial role. The most critical components of those systems are the First Mirrors (FMs), since they are placed inside the vacuum vessel directly facing the thermonuclear plasma to guide the light to the diagnostic systems, which are located outside a bioshield due to their vulnerability. To guarantee accurate measurements, the mirrors must maintain a high specular reflectivity over the UV-vis-NIR spectral range while withstanding harsh conditions such as high thermal loads, high-energy neutron irradiation, and fluxes of particles coming from the plasma. Rhodium (Rh) is a strong candidate material for these components due to its optimal optical properties, which are stable under thermal loads [3].

Among the critical aspects during tokamak operation, the Plasma-Wall Interaction (PWI) is an inevitable phenomenon, which causes physical sputtering and erosion of First Wall (FW) materials. The eroded species migrate inside the plasma and are subsequently redeposited in regions far from their origin; in particular, redeposition of FW species on the first mirrors forms contaminant layers that degrade the mirror's optical properties. Thus, to ensure reliable optical diagnostic measurements, the development of a periodic *in-situ* mirror cleaning technique is necessary.

Recently, the ITER Organization revised the project baseline [1], which now foresees a full tungsten (W) first wall and the use of boronization as a wall conditioning technique, since boron (B) is an optimal oxygen getter to mitigate impurities. Thus, B and W are expected to be the main constituents of the FM contaminant layers. In this context, the previous mirror cleaning studies [2] conducted on contaminant species (carbon and beryllium) that are no longer foreseen as FW materials, require updating. Indeed, there is a lack of experiments regarding the optical degradation caused by B and B/W mixed contaminants on first mirrors, and regarding the efficacy of cleaning techniques on these specific layers.

1.1. Thesis objectives

This thesis investigates, at the laboratory scale, the impact of boron (B) and mixed boron-tungsten (B/W) coatings on the reflectivity of nanocrystalline rhodium samples, and the subsequent restoration of their optical properties through laser cleaning. To achieve this, the research first focuses on producing and characterizing these tokamak-relevant coatings to quantify the specific reflectivity degradation they induce on the mirrors. The study then assesses the effectiveness of pulsed laser cleaning for the selective removal of these contaminants by conducting a comparative analysis between infrared (1064 nm) and green (532 nm) laser wavelengths. Finally, the overall reflectivity recovery and the morphology of any remaining coating residues are evaluated, while rigorously assessing the mirror's structural integrity to evaluate and minimize laser-induced damage.

2. Methods

In this experimental work is has been exploited the same nanosecond Pulsed Laser Deposition (ns-PLD) apparatus for the production of both the rhodium mirror samples and the boron containing contaminants. Moreover, the same laser device has been employed also for the cleaning procedures.

2.1. Sample production and contamination

Pulsed Laser Deposition (PLD) is a versatile thin-film production technique based on the laser ablation of a solid target placed on a motorized holder, in a vacuum chamber with a controlled atmosphere. The vaporization of the target surface caused by the interaction with a focused high-intensity laser generates a plasma plume of ablated species that expand and deposit onto the substrate. The thickness and morphology of the deposited film are highly dependent on the variety of selectable deposition parameters.

The experimental setup employed in this thesis includes a Q-switched Nd:YAG laser delivering 7-10 ns pulses at either 1064 nm (IR) or 532 nm (green) wavelengths, focused with an inclination of 45° on the target surface. For the production of mirrors, a Rh target was employed, while for the contamination, the target was made of sintered boron, with the addition of a piece of tungsten for the mixed B/W coatings. The background pressure is controlled by pumps and gas injection flow-meters.

2.2. Laser cleaning

The cleaning procedures exploited the same laser system of the PLD process, with the key difference that the mirrors were placed at the target position for direct irradiation. An important modification from the PLD setup was the removal of the focusing lens. Avoiding a focused beam was crucial to prevent excessive laser fluence that would damage the mirror substrate and compromise both the uniformity and selectivity of the cleaning process. As a result, the laser on the mirror formed an elliptical spot with a semi-major axis of 5 mm and a semi-minor axis of 3 mm.

2.3. Characterization

Characterization of the samples has been made both after sample production and after cleaning, with the main objective of correlating the reflectivity properties with the surface morphology and atomic composition of the samples.

Scanning Electron Microscopy (SEM) was employed to acquire surface and cross-sectional images, with a resolution reaching nanometric dimensions thanks to the use of electrons as probes on the samples. Through the reconstruction of the backscattered electron (BSE) or the secondary electron (SE) signals, detailed images for the analysis of surface morphology can be obtained. The interaction between the electron beam and the sample also induces the emission of characteristic X-rays. Analyzing their energy and signal intensity via Energy Dispersive X-ray Spectroscopy (EDXS) provides information regarding the film atomic composition. To extract quantitative data, such as mass thickness and atomic composition, the EDDIE software was employed, which uses a reference-free method; thus eliminating the need for a standard homogeneous reference sample [4].

Finally, to assess the degradation and subsequent recovery of the mirrors' optical performance, measurements in the spectral range between 300 nm and 2500 nm were conducted using a PerkinElmer UV-vis-NIR spectrophotometer equipped with a 150 mm Spectralon integrating sphere. This allowed for the measurement of both the hemispherical (total) and diffuse reflectance, while the specular component was derived by subtraction: $R_{\text{spec}} = R_{\text{tot}} - R_{\text{diff}}$.

3. Production of mirrors and contaminants

3.1. Rh samples

Highly oriented nanocrystalline rhodium samples, whose morphology is shown in Figure 1, were produced on silicon substrates via PLD using as deposition parameters: 1064 nm laser wavelength, high vacuum, 16 J/cm^2 fluence. In particular, two dimensions of squared mirrors were produced. Large samples (side of 26 mm) centrally positioned on the substrate holder reached 320-390 nm thickness in 30 minutes of deposition; this dimension was specifically required for spectrophotometric measurements. Instead, small samples of 11 mm side length were positioned peripherally reaching 300 nm thickness in 60 minutes. These were subsequently employed for damage threshold tests and for trial cleanings.

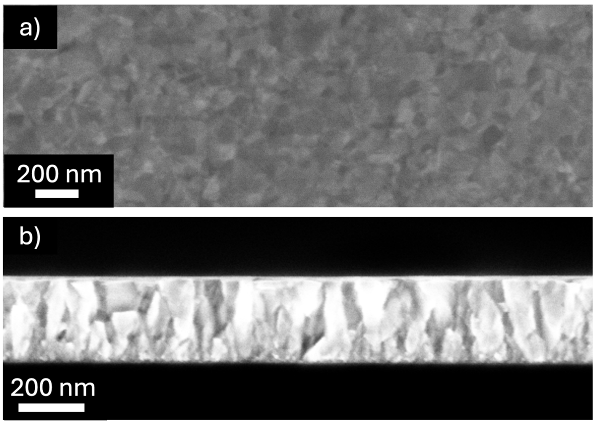

Figure 1: SEM images of the Rh mirrors: (a) top view and (b) cross-section view.

Optical characterization via UV-vis-NIR spectrophotometry required an analytical correction (dividing the raw data by the Spectralon reflectance) to remove integrating sphere artifacts caused by the highly specular nature of the mirrors. The corrected data demonstrated optimal optical performance, showed with the blue line in Figure 3: specular reflectance ranged from 65–78% in the UV-visible spectrum and rose to 95% in the infrared. The diffuse reflectance remained close to zero over the entire spectral range. This indicates a smooth surface, without scattering defects, which confirms the excellent optical performance required of the samples to be representative of tokamak first mirrors.

3.2. B contaminants

Boron was selected as the main material composing the ITER-relevant contaminants on mirrors since the boronization layer will be the first one to be eroded during tokamak operation.
Using PLD under high vacuum conditions (10^{-3} Pa), with a 532 nm laser wavelength, and a 7.4 J/cm^2 laser fluence, compact amorphous B coatings were deposited onto the previously produced Rh mirrors. SEM characterization showed a flat surface morphology, with a film thickness on the larger sample ranging from 160 nm at the edge to 200 nm at the center due to PLD plasma plume geometry. EDXS analysis combined with the EDDIE software measured an atomic composition of 85.7% boron and 14.3% oxygen, and a mass thickness of 35 µg/cm^2 corresponding to a density of 1.75 g/cm^3.
Spectrophotometric measurements demonstrated that the boron layer (purple line in Figure 3 (a)) severely degrades specular reflectance of the pristine rhodium. The coating acts as a dielectric thin film, inducing a strong interference pattern. The total reflectance in the orange-yellow spectrum around 585 nm drops below 10% due to an interference minimum, while the blue-violet region corresponds to a maximum, giving the sample a purple appearance. The diffuse reflectance remained below 2.5%, indicating that the surface remained smooth.
Attempts were made to produce porous boron coatings by injecting argon gas into the vacuum chamber to work with a background pressure of 5 Pa and 10 Pa. However, these trials resulted in chemically unstable coatings that started to oxidize immediately after exposure to ambient air. Due to this instability, the deposited films are highly non-reproducible samples and, moreover, are not representative of the high vacuum tokamak environment. Thus, these coatings have been considered unsuitable for optical degradation measurements or laser cleaning tests.

3.3. B/W coatings

To take into account the tungsten impurities originating in the regions where the boron conditioning layer is eroded rapidly, mixed B/W coatings were produced by adding a small tungsten piece to the boron PLD target.
SEM analysis confirmed that the co-deposition

was uniform, yielding a compact, flat film between 130 nm and 150 nm thick. EDXS data, analyzed with EDDIE, showed that the atomic percentage of tungsten was higher in the center of the sample (approximately 16% of W) compared to the edge (containing 10.7 % of W). This can be explained by the higher directionality of the tungsten plasma plume compared to the boron one. The mass thickness was approximately 55 µg/cm^2 at the center and 99 µg/cm^2 at the edge, corresponding to densities of 4.25 g/cm^3 and 6.6 g/cm^3 respectively.

The presence of tungsten drastically shifted the optical behavior of the coating from a dielectric to a metallic one. Specular reflectance of the film (purple line in Fig. 5 (a)) is between 30% and 50% in the whole spectrum. Furthermore, the interference pattern, which characterized the B coating, is completely suppressed due to the presence of W, which reduced the light's skin depth. The diffuse reflectance (purple line in Fig. 5 (b)) remained close to zero, indicating that the surface of the coating is smooth.

4. Laser cleaning of contaminated mirror samples

The laser cleaning procedures were performed in vacuum to replicate future *in-situ* tokamak cleaning. The employed methodology to achieve uniform laser irradiation of the larger mirrors is a partial horizontal superposition of vertical cleaning scans, which ensured the same number of laser shots per point of the sample (N_p). In the results discussed below, N_p is fixed to 20 to ensure sufficient spatial overlap of the pulses while limiting cumulative irradiation to preserve the mirror's integrity.

To determine the upper limit to the selectable laser fluence, damage tests were conducted on pristine rhodium mirrors. The result is that fluences exceeding 850 mJ/cm^2 caused microscopic melted areas and cracking along the nanocrystalline grains. Consequently, a fluence of approximately 750 mJ/cm^2 (350 mJ per pulse) was established for all the following cleaning scans. At this fluence, neither the IR (1064 nm) nor the green (532 nm) laser wavelengths caused damage to the mirrors.

For both the B and the B/W coatings, a comparison between the cleaning performance of the two laser wavelengths has been made.

4.1. Cleaning of B coatings

Initial trials on smaller mirrors demonstrated some important results: the IR wavelength produced unsatisfactory cleaning, leaving behind both pieces of non-ablated film and melted residues. Conversely, the green wavelength gave optimal results, completely ablating the B coating and revealing the underlying intact Rh mirror. Furthermore, the trial cleanings also proved that a double scan on the same sample leaves the mirror intact.

Applying the multiple scan pattern to the larger mirrors, the cleaned mirrors whose SEM images are shown in Figure 2 were obtained. The discrepancy observed in the cleaning trials in confirmed.

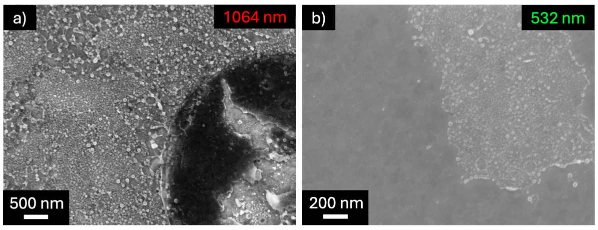

Figure 2: SEM images of the boron coated mirror after cleaning. (a) IR-cleaned mirror, (b) mirror cleaned with the green wavelength.

Visually, the IR-cleaned mirror exhibited opaque stripes, particularly in the thicker central region of the coating. SEM analysis confirmed that the laser failed to ablate the coating uniformly, leaving a highly rough surface characterized by cracked boron fragments and areas covered by melted residues (Fig. 2 (a)). Thus, optical recovery, presented with red lines in Figure 3, was poor. Specular reflectance remained 10–20% below pristine levels in the infrared range and remained between 20–55% in the UV-VIS range. Furthermore, the diffuse reflectance spiked to 8–10% across the spectrum, indicating a tenfold increase from the pristine values, due to light scattering caused by the rough residues. Mean surface roughness was extrapolated from diffuse reflectance data using the Total Integrated Scattering (TIS) method and Bennett's relation, obtaining a value of about 35.77 nm, compared to a pristine mirror value of 2.74 nm.

The mirror cleaned with the green wavelength appeared visually restored, with only faint traces of the laser scan path. SEM revealed that

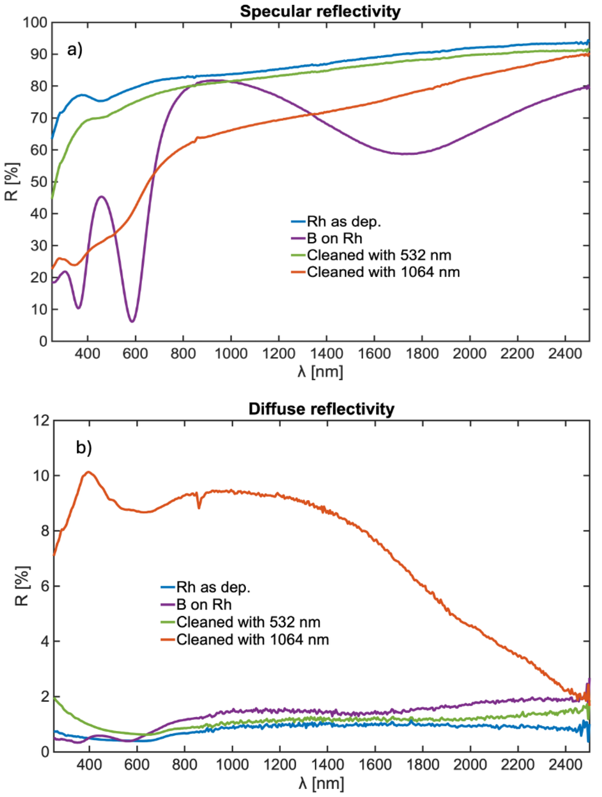

Figure 3: Specular (a) and diffuse (b) reflectance of the Rh mirror: as-deposited (blue line), coated with boron (purple line), and cleaned with the IR (red line) and green (green line) wavelengths.

the coating was largely ablated, leaving only nanoscale melted droplets organized in stripes, which are compatible with subsequent laser shots in a scan. These droplets formed on the large mirror but not on the trial mirrors because the coating on the larger mirror was 50–70 nm thicker, thus making it more difficult to ablate. Despite these nanoscale residues, optical recovery, presented with green lines in Figure 3, was excellent. Specular reflectance recovery exceeded 90% in the visible and IR spectra, and diffuse reflectance remained below 2%. The specular reflectance recovery in the UV range was lower because shorter wavelengths are more easily scattered by nanoscale residues. The extrapolated mean surface roughness was 3.93 nm, close to the pristine value.

The difference in cleaning efficacy between the two wavelengths can be attributed to the interference pattern, since 532 nm (green) is close to an interference minimum of the B layer, resulting in higher energy absorption, while the IR wavelength (1064 nm) is mainly reflected since it is close to a reflectance maximum.

4.2. Cleaning of B/W coatings

To assess tungsten's impact, B/W contaminated mirrors were cleaned using the same parameters used for pure B coatings (750 mJ/cm^2, 20 pulses per point). Initial trials with the green wavelength revealed incomplete ablation, leaving nanoscale melted residues.

Regarding the impact on larger mirrors, the cleaning results were the opposite compared to the performance on the boron coating. The IR wavelength partially succeeded in the coating removal, but micrometric-sized melted areas on the Rh mirror were found, shown in Fig. 4 (a). The specular reflectivity (red line in Fig. 5 (a)) reached 70–85% in the IR range, but only 25–55% in the UV-vis spectrum. The melted residues increased roughness to 7.83 nm.

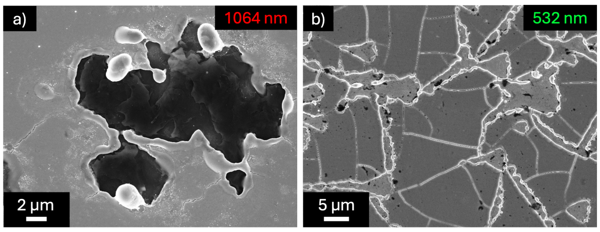

Figure 4: SEM images of the B/W coated mirror after cleaning. (a) IR-cleaned mirror, (b) mirror cleaned with the green wavelength.

On the other hand, the green wavelength severely degraded the mirror, making the specular reflectance drop below the contaminated value (green line in Figure 5 (a)). The coating in the central region fractured into large non-ablated fragments (Fig. 4 (b)) , while in other regions melting of the coating occurred. Damage to the Rh substrate via melting also occurred. The combination of these residues and damage raised the diffuse reflectance (green line in Figure 5 (b)) up to 19%, with a surface roughness of 54.8 nm.

The main results obtained with the presence of tungsten regard the modification of the laser-material interaction. In particular, the metallic behavior suppressed the interference fringes and changed light absorption by the film; in fact, the IR light was absorbed better by the B/W film rather than the B one and thus was able to cause ablation. Moreover, higher tungsten

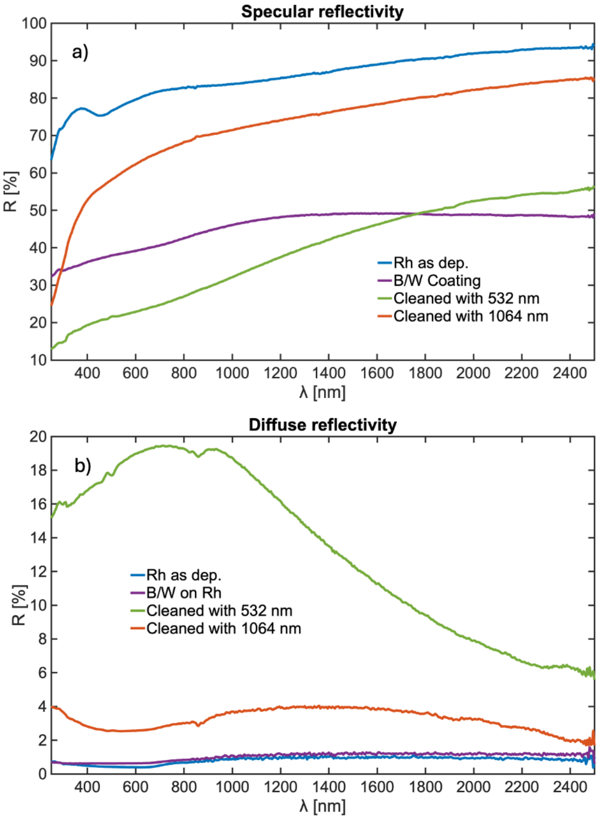

Figure 5: Specular (a) and diffuse (b) reflectance of the Rh mirror: as-deposited (blue line), coated with mixed boron and tungsten (purple line), and cleaned with the IR (red line) and green (green line) wavelengths.

concentrations in the center of the sample caused the coating to fracture under thermal stresses rather than ablate. In areas with lower tungsten concentration, the coating melted instead, also transferring heat to the Rh mirror. In fact, the interaction between the coating and the mirror reduced the mirror's damage threshold.

5. Conclusions

To reflect ITER's new material baseline, this study successfully exploited ns-PLD to produce nanocrystalline rhodium mirrors coated with compact, fusion-relevant pure boron and mixed boron-tungsten (B/W) contaminants. The efficacy of laser cleaning was subsequently evaluated using IR (1064 nm) and green (532 nm) wavelengths.

The experimental results highlighted that the first laser pulse dictates the overall cleaning success; if the energy is insufficient for complete ablation, it induces nanoscale melting that makes subsequent removal difficult. Furthermore, the presence of a contaminant layer lowers the intrinsic laser damage threshold of the underlying Rh mirror. For pure B coatings, which exhibit dielectric properties and strong thin-film interference, the green wavelength achieved excellent restoration with nearly 90% visible and near-infrared reflectance recovery.

Conversely, adding just 10–16% tungsten gave the coating a metallic behavior that completely suppressed the interference pattern, making the B/W layers difficult to clean without transferring heat to the substrate. The green wavelength caused Rh melting on B/W coated samples, and while the IR wavelength performed slightly better, it still left melted residues. Thus, a satisfactory cleaning procedure for B/W coatings was not achieved. To advance First Mirror laser cleaning, future research must focus on optimizing cleaning parameters for thinner deposits (below 100 nm) to prevent mirror melting, lowering the laser fluence for B/W coated mirrors, and investigating UV laser wavelengths that are in general better absorbed by metallic coatings. Additional development should include the use of fs-PLD to reproduce porous contaminants and study the mirrors' resistance to repetitive contamination-cleaning cycles.

References

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