

THIN NITRIDE LAYERS AS PERMEATION BARRIERS

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ABSTRACT. Permeation barriers represent one of the crucial fields in materials development for thermonuclear fusion. Primary objective of the barriers is to suppress the permeation of hydrogen isotopes (mainly tritium) from future thermonuclear fusion facilities. Secondary objective is to reduce hydrogen retention in structural materials, potentially also improving their corrosion resistance. Expected reactor conditions put high demands on the material, as well as on the final barrier quality. Key properties are tritium permeation reduction, absence of defects (especially cracks), high-temperature stability and corrosion resistance, and compatibility with structural materials (mostly ferritic-martensitic steels). Regarding industrial scale production, ability of the deposition method to coat large complex surfaces is desirable. Thin nitride layers, identified as promising permeation barriers, were prepared by diffusion-based nitridation and physical vapour deposition (PVD) and characterized.

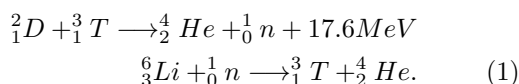
KEYWORDS: permeation barriers, nitride layers, PVD coating, permeation measurement.

1. INTRODUCTION

Nuclear fusion is an appealing means of energy production that can resolve growing energy demands of the mankind. Facing inevitable exhaustion of fossil fuels and growing awareness of climate changes caused by greenhouse gases emissions, it is obvious that current means of energy production need to be replaced. Renewable sources (e.g. solar, hydro, wind or geothermal power) are not expected to be capable of supplying global energy needs. Therefore, entirely new source of energy is required, in an ideal case fulfilling the following criteria

- sufficient fuel supplies
- no harmful emissions
- no major operational hazards

Thermonuclear fusion expected to be harnessed in the first generation of power plants exhibits promising results regarding all the criteria. Energy production will be based on the following equations



Abundance of deuterium and lithium is sufficient for thousands of years, tritium will be produced in-situ. Emissions consist only of harmless helium, operational hazards do not involve risk of uncontrolled chain reaction or major radiation leaks. However, enormous complexity and demands (technological, as well as

economical) on the fusion facilities have delayed the harnessing of thermonuclear fusion. Joint international effort resulted in the construction of International Thermonuclear Experimental Reactor (ITER) that should demonstrate the feasibility of fusion and test the necessary systems for future fusion power plants. Permeation barriers are one of the most important parts of fusion facility concerning radiological safety and economical issues. These are typically thin coatings that lower the permeation and retention of hydrogen isotopes (mainly tritium) in the reactor structures. Selected materials have to withstand harsh reactor conditions, including

- strong thermal gradients and elevated temperatures
- presence of significant neutron and secondary charged particle irradiation
- potential contact with high temperature PbLi (corrosion issues) - depending on the reactor design (further information to be found in [1])

Excessive tritium permeation could result in

- degradation of the reactor material properties
- radiological hazard during operation and decommissioning
- lowering of the reaction probability and economical losses

Therefore, the presence of a permeation barrier is envisaged by numerous studies [2–4] to meet the safety

requirements of maximum allowable tritium losses (1g per year) and maximum tritium inventory (200g) [1]. Permeation barriers are also essential for early and safe decommissioning of fusion facilities after their shutdown. Besides reducing the permeation through metallic structures, typically easily permeable by hydrogen isotopes, other material and deposition properties of the permeation barriers have to be taken into account:

- stability and reliability of the coating (regarding the abovementioned conditions)
- compatibility with the substrate material
- capability to form dense and defect-free layers on complex surfaces

Regarding the coating stability in corrosive environment, some studies show that, depending on the coolant and tritium breeder choice, fusion facility components can be subjected to corrosion attack up to 700 μm per year, equal to 4 kg of dissolved material per year and square meter [5–7]. That would pose a significant risk to the structural integrity and operational reliability of the facility. Parts subjected to the corrosion attack are in most cases also threatened by tritium permeation, therefore the prospective coating ought to suppress both phenomena to a high extent. As candidate materials for the permeation barriers, commonly oxidic ceramics [2, 8] or nitrides [9, 10] are being studied. This study is focused on diffusion-based nitride layers, whose advantage lies in the applicability on large complex surfaces, including for example the inside of coolant tubes [11, 12]. Such nitride layers are qualitatively compared to thin coatings prepared by physical vapour deposition (PVD), which is an established technology for the production of thin and dense coatings. On an industrial scale, large surface areas can be coated, including curved surfaces, but still it is primarily a line-of-sight coating technology.

Nitriding is a thermochemical treatment that consists of the introduction of nitrogen into metallic material. According to the method of nitrogen introduction, several nitriding techniques are being distinguished:

- gas nitriding
- plasma/ion nitriding
- solid/liquid nitriding

Gas nitriding [13] is conducted at elevated temperature, submitting the samples to nitrogen-containing atmosphere, commonly ammonia or various nitrogen mixtures, e.g. H_2 and N_2 ; N_2 , NH_3 and CO_2 etc. Ion/plasma [14] nitriding uses a glow discharge to introduce nitrogen into the material; nitrogen ions are accelerated and impinge the surface. During solid nitriding [15], granulate containing nitrogen compound is used e.g. Fe_4KCN . The samples are surrounded by granulate and placed into heating oven for enhancing the diffusion.

Gas and plasma nitriding are well established and widely used and researched techniques, however the required facility is complicated. During gas nitriding, the process temperature may affect the hardness of the nitrated material. Plasma nitriding is faster than conventional gas nitriding and provides for a better control of the treatment parameters. This allows the control of the nitrated layer microstructure and also enables higher reproducibility of the results. Solid nitriding is a low-cost process in comparison to gas and plasma nitriding, when the only required facility is the furnace providing the heating. The heating generates atomic nitrogen that is able to diffuse into the material.

Nitriding promotes higher hardness of the specimen, increases wear resistance, fatigue resistance, corrosion resistance and, as it was observed, some nitrated materials have favourable permeation properties. Regardless of the used technique, surface cleaning of the samples is vital, because the contaminants can form a barrier preventing nitrogen from diffusing into the material. During the deposition, different layers are produced - diffusion and compound layer. Diffusion zone is a region characterized by solid solution in the original core microstructure with hardening precipitations. Compound layer typically consists of mixture of iron nitrides, in case of steel nitriding. With plasma nitriding, by controlling the process parameters, it is possible to determine the composition or even avoid the formation of the compound layer [16]. In this study, three types of diffusion-nitrated layers were prepared and characterized for their morphology, phase and elemental composition and thermal stability. A brief comparison with several nitride coatings prepared by the PVD technique is made.

2. EXPERIMENT

As a substrate, ferritic-martensitic steel P92 was used, whose characteristic composition is provided in [17]. It is very similar to EUROFER97 steel, developed as a reference structural material for the DEMO tokamak [18]. Such material is also commonly used in permeation measurements [19], so a direct comparison with untreated substrate could be made. The substrates were prepared in a disk shape with 0.5 mm thickness and 25 mm diameter, by electrical discharge machining [20], grinding with sand paper and metallographic polishing. The following types of diffusion-based nitride layers were prepared:

- plasma nitridation (430 °C, 24h), at Technical University of Liberec
- carbonitridation (560 °C, 10h) at Bodycote HT, s.r.o.
- salt nitridation (530 °C) at Katring Plus s.r.o.

Presence of the nitride layer and its elemental composition was investigated by Energy-dispersive X-ray Spectroscopy (EDS) in an EVO MA15 scanning electron

microscope (Carl Zeiss SMA, Germany) equipped with a Quantax system and X-Flash 5010 detector (Bruker, Germany). Phase composition was analyzed by X-ray diffraction (XRD) using a D8 Discover diffractometer (Bruker, Germany). For the XRD measurements, Rietveld method was used to determine the composition. To assess thermal stability of the coatings, the samples were annealed in a vacuum furnace for 1 hour at 550 °C, which is the foreseen temperature in the future reactor application, also used in the permeation measurements. After the annealing, the layer composition was verified again.

Additionally, six types of nitrides were deposited by PVD: WN, CrN and Cr₂N by magnetron sputtering at the Department of Materials Engineering (Faculty of Mechanical Engineering, Czech Technical University in Prague) and CrWN, CrAlN and ZrN by cathodic arc plasma deposition at IonBond Czechia s.r.o. Similar, but more comprehensive characterization was performed, including the permeation measurements at the facility of Jozef Stefan Institute in Ljubljana, Slovenia [21, 22]. The details of the PVD coating preparation and characterization will be provided in a dedicated paper [23].

3. RESULTS

3.1. DIFFUSION-NITRIDED LAYERS

Surface morphology of the three layers is shown in Figure 1. A semi-granular structure consisting of very fine grains can be observed; in case of ion nitridation, these seem to be more concentrated along substrate grain boundaries. This appearance is typical and has been observed in previous studies [13, 24]. No cracks were observed, which would be detrimental for the permeation barrier performance. Thickness of the diffusion nitrided coatings, provided by the manufacturer, reached approximately 100nm. EDS and XRD measurements confirmed presence of the nitride layer. Elemental composition, as determined by EDS, is shown in Table 1. Phase composition, as determined by XRD, is shown in Table 2. Due to the low thickness of the nitride layer, the substrate is detected by both methods. Before additional characterizations, the samples were annealed to assess their thermal stability. However, XRD measurements after the annealing showed that the nitride layer was significantly decomposed. This can be seen in Figures 2 and 3 for the plasma-nitrided samples. Similar situation was observed for the carbonitrided and salt-nitrided samples. Therefore, permeation measurements of these coatings were not performed. In the plasma nitrided sample, a change in surface morphology was observed as well, including the formation of occasional cracks. This can be seen in Figure 4. For the carbonitrided and salt-nitrided samples, the morphology remained very similar.

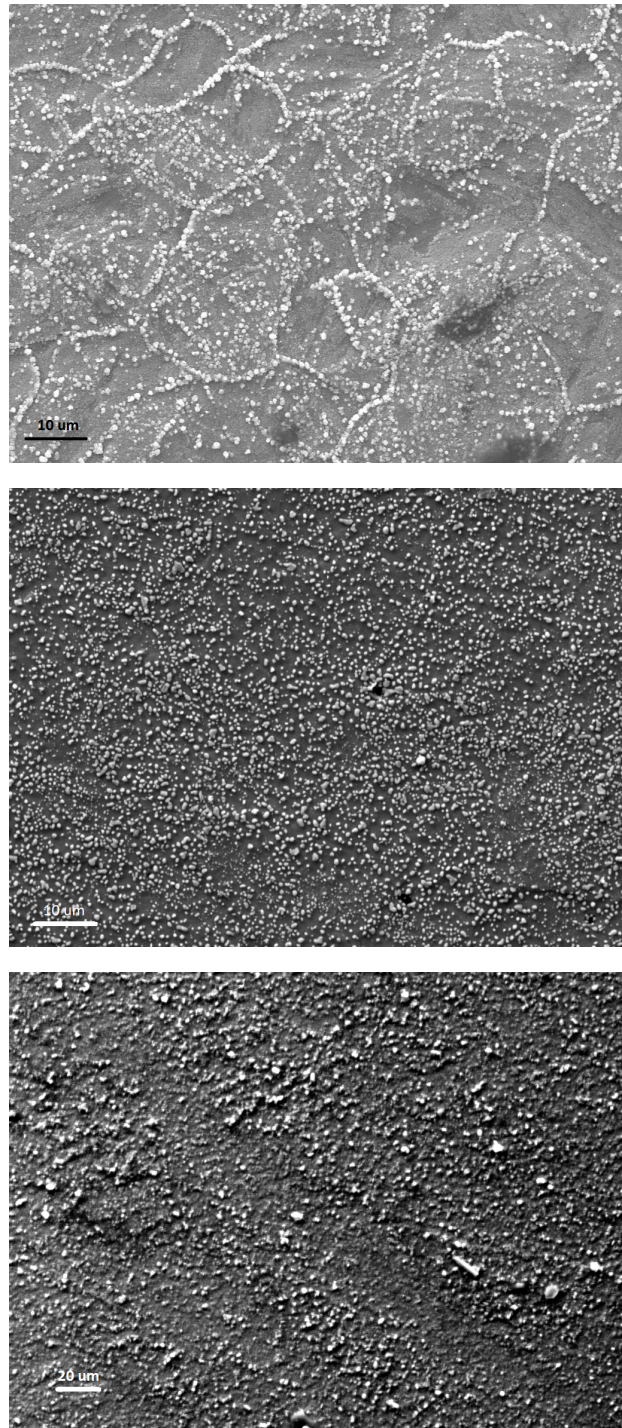


FIGURE 1. Surface morphologies of nitrided layers: plasma nitridation (top), carbonitridation (middle), salt nitridation (bottom).

3.2. PVD COATINGS

Successful deposition of the PVD coatings was confirmed by EDS and XRD measurements. Smooth and crack-free coatings were obtained, with thicknesses between 1.5 and 4.5 µm. Representative surface morphologies are shown in Figures 5 and 6. Scratch test showed good adhesion of the coatings. XRD measurements indicated all the PVD coatings to contain compressive stress, which is favorable as it suppresses

Fabrication method	N	O	Na	Mg	Al	Cr	Fe	W	C	Si
Plasma nitridation	6.3	0.9				9.6	81.9	1.3		
Carbonitridation	0.9	3.6			0.6	8.6	83.4	0.1	2.5	0.3
Salt nitridation	0.1	21.2	1.0	0.2	0.8	6.2	70.1	0.4		

TABLE 1. Composition of the nitride layers measured by EDS, wt. %.

Fabrication method	Fe ₂ N	Fe ₃ N	Fe ₄ N	Magnetite
Plasma nitridation	14.96	18.27	4.88	0.00
Carbonitridation	16.95	0.00	0.00	0.56
Salt nitridation	27.20	4.09	0.00	17.79

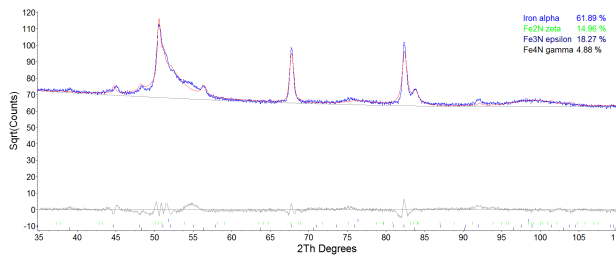
TABLE 2. Phase composition of the nitride layers measured by XRD, wt. % balance α -Fe.

FIGURE 2. XRD spectrum of the plasma nitrided sample.

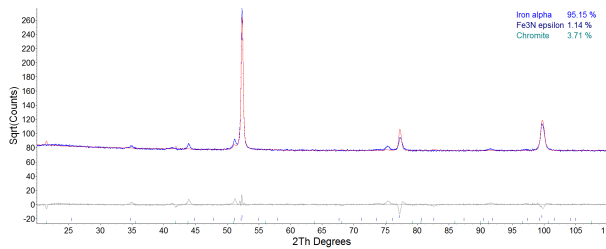


FIGURE 3. XRD spectrum of the plasma nitrided sample after thermal annealing.

crack propagation. All the PVD coatings showed potential for permeation barriers with permeation reduction factor (PRF) > 100 , in case of ZrN even > 10000 . Phase stability after the permeation test was verified again by XRD.

4. CONCLUSIONS

Thin nitride layers on P92 ferritic-martensitic steel were prepared by plasma nitridation, carbonitridation and salt nitridation. Formation of the nitride layer and its composition was determined by quantitative Rietveld analysis of diffraction patterns. SEM observations indicated the absence of surface cracking. However, after annealing at 550 °C, the layers were significantly decomposed. Therefore, hydrogen permeation was not measured. PVD coatings of selected nitrides were also deposited on EUROFER97 ferritic-martensitic steel, a reference material for DEMO construction. The composition, thickness and adhesion of the coatings were measured and permeation measure-

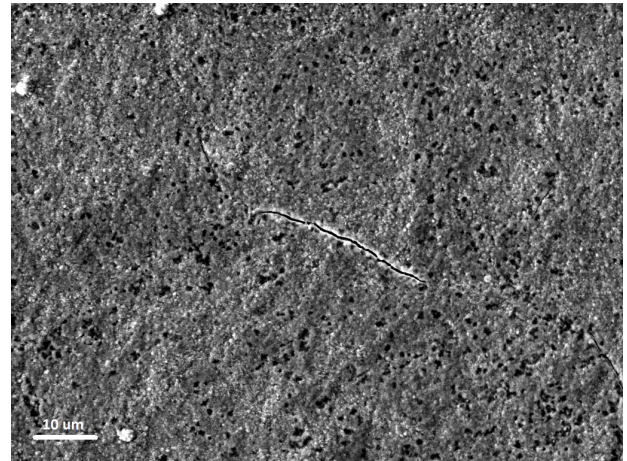


FIGURE 4. Surface morphology of plasma nitrided layer after thermal annealing.

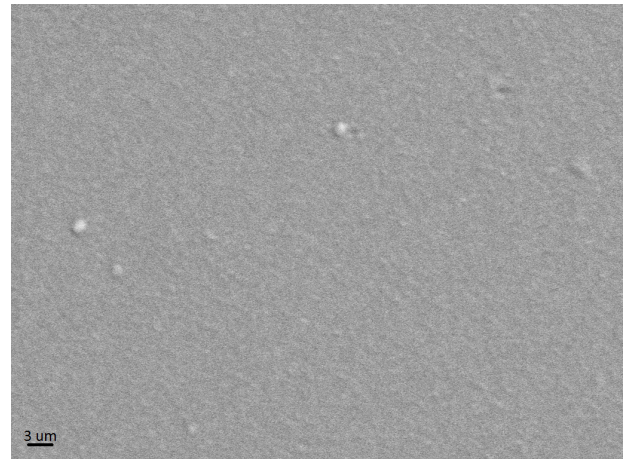


FIGURE 5. Surface morphology of magnetron sputtered CrN coating.

ments were performed. Thickness of the coatings was several μm , all coatings showed the desired composition and good adhesion. Permeation measurements confirmed suitability of selected nitrides as permeation barriers. Best result was achieved by ZrN - permeation reduction by three orders of magnitude. These coatings also demonstrated thermal stability at the test temperature. From these results, it can

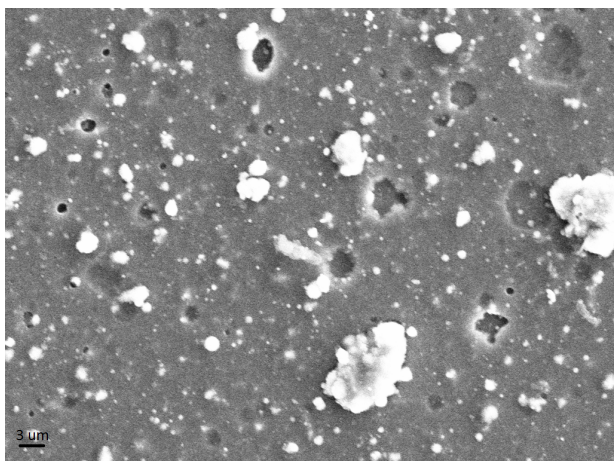


FIGURE 6. Surface morphology of cathodic arc plasma deposited CrAlN coating.

be concluded that the investigated diffusion-based nitride layers are not suitable for the application as permeation barriers at elevated temperature, due to the lack of thermal stability. From this point of view, as well as promising PRF values, PVD coatings seem more suitable. However, it should be noted that only a limited number of materials and techniques were examined and various other modifications exist, including technological parameter variations as well as different layer compositions.

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