



# Preparation of tritium permeation barrier consisting of titanium by the pack cementation method



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## ABSTRACT

In this work, tritium permeation barriers were prepared on the surface of super-clean reduced activation martensitic (SCRAM) steel by the pack cementation method. The pack cementation process was conducted by packing samples in a powder mixture consisting of titanium, ammonium chloride and alumina powder at 1000 °C for 30 min to form a titanized coating. Subsequently, the samples were nitrided in an ammonium atmosphere and then oxidized in air at 760 °C for 1 h to obtain a multilayered structure. The results showed that the as-prepared titanized coatings consisted of two layers. The exterior layer was made of TiN and the interior layer was a diffusion layer resulting from titanium atoms diffusing into the substrate. After being nitrided and then oxidized, the coatings were discovered to have transformed into a three-layered structure. The outer layer was rutile TiO<sub>2</sub>, the middle layer was Ti-N and the inner layer was Ti-C. Hydrogen permeation tests were performed on the coatings and pure matrix steels at room temperature. The results revealed that the three-layered structure coatings exhibited good barrier properties against hydrogen penetration. This three-layered structure coating may be a good material to increase the hydrogen permeation resistance of SCRAM steel.

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## 1. Introduction

Efficient tritium handling is an important issue for structural materials, such as steels, that have a high permeability to tritium in the operational temperature range of a deuterium–tritium fusion reactor. Many efforts for reducing the hydrogen permeation have been made, such as materials selection, microstructure control and surface modification. Among them, surface modification is an important technique for technical and economical reasons [1]. In general, a thin ceramic coating as a tritium permeation barrier (TPB) on metal structural materials is a promising way [2] to decrease tritium permeation to the air environment. The usual TPBs include TiO<sub>2</sub> [3], TiN [1] and TiN/TiC [4] etc., which have been studied for decades.

Tritium permeation barriers can be prepared by means of chemical vapor deposition (CVD), physical vapor deposition (PVD), pack cementation (PC), hot-dipping aluminization (HDA), electro-chemical deposition (ECD), plasma spraying (PS), and sol-gel, among others. However, large discrepancies in thermal coefficients between the ceramic barrier and the substrate [5,6] often lead to pore and crack formations at interfaces at high temperature, which may cause the failure of the coatings

[7–9]. Moreover, in fusion reactors, components with large dimensions and complex geometries have to be prepared with high-quality TPBs on both outer surfaces and inner walls [10]. In this case, many fabrication methods might not be suitable for mass production and complex geometries. Comparing the above mentioned approaches, pack cementation is a promising method that has several advantages including the feasibility of depositing coatings on complex shaped surfaces, reliable adhesion to substrates by sufficient diffusion, controllable procedures and simplicity of the device used for processing [11].

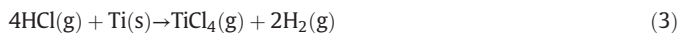
The barrier potentials of H atoms diffusing through surfaces and interfaces are higher compared with diffusion inside materials, so increasing the number of interfaces should improve the tritium permeation resistance of coatings. It has been suggested that more effective permeation suppression could be obtained by multi-interface film structures [12].

Therefore, in the present work, a new preparation process (titanizing and subsequent heat treatment) is suggested to fabricate multilayered coatings. The new method can be easily applied to prepare coatings for large surfaces and complex geometries in fusion reactors, on both the inner walls and outer surfaces, especially inside pipe walls. To avoid the influence of high temperature on the mechanical properties of steels, coatings were prepared simultaneously with the heat treatment of the matrix steels: tetanizing occurred while quenching the steel and nitriding and oxidizing of the coatings was performed while tempering the steel.

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During the pack cementation process, it is believed that the active Ti was created by the following chemical reactions [13]:



Several types of reactions could occur subsequently, when  $\text{TiCl}_4$  frees the diffusive Ti and the Ti diffuses into the substrate metal, A. These reactions can be represented schematically as follows [14]:

Substitution reaction:



Reducing reaction:



Thermal decomposition reaction:



To achieve a multilayered coating, a subsequent heat treatment of the deposited coatings was conducted in an ammonium atmosphere to enhance the crystallization of the TiN, and further annealing in air was performed to form  $\text{TiO}_2$  on the surface.

The microstructure, thickness and phase composition of the coatings were studied by scanning electron microscopy (SEM) with an X-ray energy dispersive spectrometer (EDS) and X-ray diffraction (XRD). Hydrogen permeation resistance was studied as well.

## 2. Experimental

### 2.1. Sample preparation

The chemical composition of SCRAM steel used as the substrates in this research is shown in Table 1. In our previous study, a twice-quenching process of SCRAM steel was developed that could refine its microstructure and thus decrease its ductile brittle transition temperature (DBTT) [15]. In the present study, steels were subjected to the following twice-quenching process: 1020 °C 0.5 h quenching/760 °C 2 h tempering + 1000 °C 0.5 h quenching/760 °C 2 h tempering. Coatings were prepared simultaneously with the second quenching treatment of the steels: titanizing occurred while quenching the steel and nitriding and oxidizing of the coatings was performed while tempering the steel. After the first quenching treatment, substrate specimens were cut into small disks of  $\Phi 20 \text{ mm} \times 5 \text{ mm}$ . Prior to the experiment, all the specimens were abraded with sandpaper to a 1000-grit finish, then degreased in acetone for 5 min and washed with deionized water for 5 min in an ultrasonic cleaning instrument.

### 2.2. Pack cementation

SCRAM steel was titanized by employing a halide-activated pack cementation process [14]. The pack powder mixtures consisted of the following ingredients: 99.5% commercial titanium powder with a 150- $\mu\text{m}$  particle size as raw material; 99.0% aluminum oxide with a 125- $\mu\text{m}$

**Table 1**  
Chemical composition of the SCRAM steel in wt.%

Composition wt.%	Si	P	Ti	V	Cr	Mn
	0.28	0.0061	0.021	0.097	9.26	0.43
	W	C	S	O/ppm	N/ppm	Fe
	2.3	0.073	0.005	31	150	Balance

**Table 2**  
Composition of the mixture powders and working conditions.

Powder mixture composition, wt.%			$T/^\circ\text{C}$	$t/\text{h}$
Ti	$\text{Al}_2\text{O}_3$	$\text{NH}_4\text{Cl}$		
57	40	3	1000	0.5

particle size as filler material; and ammonium chloride as an activator. The ammonium chloride was dehydrated and finely ground before preparation of the mixtures and 3 wt.%  $\text{NH}_4\text{Cl}$  was used in the experiments. The titanium and aluminum oxide powders were added with concentration of 57 wt.% and 40 wt.%, respectively. The mixture powders were homogeneously mixed by stirring. The composition of the mixture powders and working conditions of the pack cementation process are shown in Table 2.

The packs were prepared by filling the powder mixtures around the substrate in a cylindrical alumina crucible with a 36 mm diameter and 50 mm height. Only one sample, placed in the middle of the crucible, was treated each time. The crucible was then sealed with an alumina lid using high-temperature cements. The cement sealants were cured for 24 h at room temperature and further cured inside an oven with temperature of 100 °C for 1 h. The pack was then loaded into an electric muffle furnace. After reaction, the packs were removed from the furnace and cooled to room temperature in water. After that, the samples were removed from the crucibles and ultrasonically cleaned in ethanol. These coatings are referred to as the “as-prepared titanized coating”.

### 2.3. Nitridation and oxidation process

To obtain a multilayered coating, the as-prepared titanized coating was subsequently treated in an ammonium atmosphere and atmospheric air to obtain the TiN and  $\text{TiO}_2$  layers, respectively. The nitridation process was held at 760 °C for 1 h in the ammonia atmosphere and then cooled to room temperature. The subsequent oxidation process was conducted at 760 °C in atmospheric air for 1 h. A fourth treatment coating was prepared as well: the as-prepared titanized coating was oxidized directly at 760 °C in atmospheric air for 2 h. The abbreviations of coatings after different treatments are shown in Table 3.

### 2.4. Characterization techniques

Crystal structures of coatings were analyzed by X-ray diffraction (XRD) with  $\text{CuK}\alpha$  radiation at 40 kV. The surface morphology of the coatings was examined by scanning electron microscopy (SEM). To verify the multilayered structure, cross sections of the coatings were also observed using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer. Chemical analyses were also performed on the cross sections by EDS.

The hydrogen permeation was tested by an electrochemical technique using a Devanathan electrochemical cell. The electrochemical technique has a great potential for investigating hydrogen uptake and permeation in materials. This technique is well known for its many excellent advantages, such as simplicity, flexibility, and high sensitivity [1]. Hydrogen permeation via electrochemical measurement is driven by H atoms, whereas hydrogen permeation via gas-phase measurement is driven by hydrogen molecules. However, the diffusion forms for

**Table 3**  
Abbreviations of coatings after different treatment.

Treatment coating	As-prepared titanized coating	Nitrided coating	Nitrided and subsequently oxidized coating	Oxidized coating
Abbreviation	TC	NC	NOC	OC

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