FR 9500 674

NITRIDE AND CARBIDE THIN FILMS AS HYDROGEN PERMEATION BARRIER ON MANET STEEL

G.BENAMATI[1], R.CHECCHETTO[2], M.BONELLI[2], L.M.GRATTON[2], L.GUZMAN[2], A.MIOTELLO[2], A.TERLAIN[3].

[1] ENEA Fusion Sector C.R.E. Brasimone, I-40032 Camugnano (BO), Italy
[2] Dipartimento di Fisica, Universita' di Trento, I-38050 Povo (TN), Italy
[3] CEA CEN, DTA/CEREM/DECM/SCECF/BP 6 92625 Fontenay Aux Roses Cedex, France

TiC / TiN bilayers, ~ 1.2 μm thick, were deposited on Manet II steel by the ion beam assisted deposition technique to investigate the possible use of this ceramic coating as hydrogen barrier. Hydrogen permeation experiments in the temperature range 470-570 K showed indeed that this coating is a very efficient barrier to the hydrogen permeation being able to reduce the hydrogen flux up to two order of magnitude with respect to the uncoated steel. Preliminary compatibility tests between coated Manet II and Pb-17Li showed no attack of Pb-17Li to the steel.

1. INTRODUCTION

The problem of tritium permeation into the blanket coolant circuits is very important because of its impact on both environmental and plant costs. In the case of future demonstration reactor (DEMO), in which the use of martensitic steel as structural material is envisaged, the problem of tritium permeation becomes particularly important (ref.1). One possible solution of this problem envisages the use of coating to limit the tritium leakage toward the coolant. Three main types of coating are presently under investigation: aluminised, titanium carbide and ternary oxides. However the adopted coating must be subjected to several requirements (ref.2); in particular the following characteristics must be met: good compatibility with the breeder (namely Pb-17Li), resistance to moderate thermal cycling, structural resistance against irradiation. Moreover the deposition process must not alter the structure of the martensitic steel and the deposition technique must be able to cover large components. The objective of the present work was to establish the possibility to use TiC and TiN as permeation barrier. Several studies have evidenced (ref.3-4) this possibility, but some problems (for example adhesion failure and porosity of the coating) remained unsolved with this coating.

In this work, thick coating was produced by Ion Beam Assisted Deposition (IBAD) technique and tests of permeation and compatibility with Pb-17Li have been performed.

2. EXPERIMENTAL

As substrate material we used some discs of 1.4914 martensitic steel, 0.5 mm thick with diameter of 18 mm, but because of the sealing gold "O"-rings the geometrical area for permeation was reduced to 2 cm^2.

TiC / TiN bilayer deposition was carried out by IBAD technique. Keeping the substrate temperature at 320 K, Ti atoms were evaporated from an e-gun crucible on the substrate and the N_2^+ beam was accelerated to 30 KeV: at the sample surface the ion current was 1.6 $\mu A\ cm^{-2}$. To form a nearly stoichiometric TiN compound, titanium was deposited at a rate of 0.2 nm sec^{-1}

in presence of nitrogen high purity gas at pressure of 10^{-3} Pa to favour N adsorption and diffusion in the growing film. By changing the reactive gas from nitrogen to acetylene at the same pressure, the TiC film was finally deposited on the nitride substrate. The thickness of the bilayer film used in this investigation was 0.25 μm TiC over 1 μm TiN. Hydrogen permeation rates through the samples were measured over the temperature range 470-570 K at an hydrogen inlet pressure of 2×10^{5} Pa. The experimental procedure chosen for the hydrogen permeation measurements is the membrane technique (ref.5): one side of the membrane is exposed to high purity gas at high pressure and the other side to the vacuum (usually the analysis chamber). Gas transport through the sample from the high pressure side to the vacuum causes in the chamber a pressure rise that can be monitored by appropriate pressure transducers. The experiments were carried out in a standard stainless steel UHV chamber evacuated by vacuum ion pump and provided by Quadrupole Mass Spectrometer and Ionization Gauge. Details concerning calibration procedure and permeation flux measurement are described in a previous work (ref.6). The samples was heated by a special resistance oven and the temperature, monitored by three independent thermocouples, was controlled by PID system: the thermal stability of the sample temperature was of the order of ±1 K.

3. SOME CONCEPTS ABOUT THE PERMEATION PROCESS THROUGH A SINGLE AND A BILAYER SYSTEM

Before illustrating the results obtained in our hydrogen permeation analysis, let us underline some concepts currently utilized in this kind of experiments. In a membrane of thickness d_a, where the rate limiting process for diatomic gas permeation is bulk diffusion rather than surface reactions, the steady state permeation flux is given by the Richardson law:

$$J_s = \frac{\Phi_a}{d_a}\sqrt{P}\ , \qquad (1)$$

where Φ_a is the permeability constant of the membrane and P the gas pressure in the high pressure side. The square root of P relationship is a result of the dissociative chemiesorption of the gas molecules at the solid surface (ref.7). For a bilayer system composed by a coating layer of thickness d_b and permeability Φ_b deposited on the membrane, the steady state permeation flux is given by:

$$J_c = \frac{1}{d_a/\Phi_a + d_b/\Phi_b}\sqrt{P}\ . \qquad (2)$$

By defining an effective permeability (ref.3)

$$\Phi_{eff} = \frac{d_a + d_b}{d_a/\Phi_a + d_b/\Phi_b}\ , \qquad (3)$$

the permeation flux through the bilayer system can be written as:

$$J_c = \frac{\Phi_{eff}}{d_a + d_b}\sqrt{P}\ . \qquad (4)$$

If the deposited layer is an efficient permeation barrier, then

$$\frac{J_c}{J_s} = \frac{1}{1 + (d_b/d_a)\times(\Phi_a/\Phi_b)} << 1 \qquad (5)$$

$$d_b/\Phi_b >> d_a/\Phi_a.$$

With the condition $d_b << d_a$, the effective permeability may be approximated by:

$$\Phi_{eff} = \Phi_b\frac{d_a}{d_b}\ , \qquad (6)$$

and its measure gives the value of the barrier permeability.

4. EXPERIMENTAL RESULTS

In Figure 1 is reported the Arrhenius plot of the measured hydrogen permeability as defined in (1) for uncoated 1.4914 martensitic steel compared with previous measurements by Forcey (ref.8). The obtained permeability values are a factor three greater than those of Forcey: this is probably connected to the fact that the effective area involved in the permeation of the sample is wider than the geometrical one: in fact DEKTAK analysis of the uncoated steel showed some surface roughness of the order of 5μm.

Data interpolation by least-square fit gives the following Arrhenius expression for the hydrogen permeability:

$$\Phi(T)=2.19\times10^{-10}\exp(-36100/KT)$$
$$(\text{mol cm}^{-1}\ \text{sec}^{-1}\ \text{Pa}^{-1/2}).$$

In Figure 2 is reported the time transient of the hydrogen permeation at the intermediate temperature of 530 K for the bare and the coated steel: the fluxes are normalized with respect to the steady state flux detected with the bare steel at the same temperature, but the signal pertinent to the coated sample is multiplied by 10 in order to obtain a visual comparison in the figure.
The effectiveness of the TiC / TiN coating as hydrogen barrier is shown in Table 1 where the strong reduction of the steady state permeation flux at each examined temperature is reported.

The effective permeability of the coated steel as defined in (3) is also reported in Figure 1 and compared with the permeability of the uncoated substrate. By equation (6) we can estimate an intrinsic permeability of the TiC / TiN ceramic coating 10^4 times lower than the permeability of the martensitic steel.

These results can be compared with some recent measurements on hydrogen isotopes permeation through similar barrier coating.

Forcey et al. (ref.3) for example, showed that the bilayer system TiN on TiC (3μm total thickness) deposited by chemical vapour deposition (CVD) on 316L stainless steel is three orders of magnitude less permeable to deuterium than the substrate.

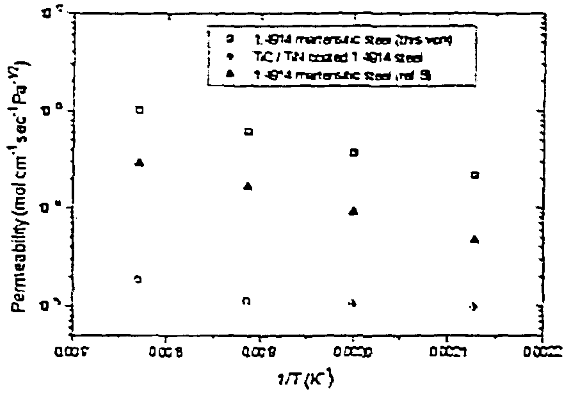

Fig.1 Arrhenius plot of the hydrogen permeability for uncoated and TiC / TiN coated 1.4914 steel compared to published data.

Shan et al. (ref.4) examining films of TiN+TiC (2.5 μm total thickness) deposited by CVD on 316L stainless steel surface found a reduction of five - six orders of magnitude in the tritium permeability of the barrier with respect to the substrate in the temperature range 470-770 K. This qualitative agreement between results from different experimental groups gives strong indications about the effectiveness of the TiC / TiN bilayer system as hydrogen isotopes permeation barrier suggesting these materials as good candidate for fusion reactor technology applications. Moreover the IBAD technique for coating deposition assures high adhesion of the coating itself with a reduced level of elastic energy into the film where also porosity is strongly reduced. All these properties warrant high resistence of the coating against thermal cycling.

Before concluding notice that we have performed preliminary compatibility tests between Manet II and Pb-17Li. The tests were carried out in static conditions at 450° C . Cylindrical specimens of about 10 mm on dia. and 15 mm on height were used with coatings prepared as in planar systems. Little detachment of these coatings were detected, but no attack of

TABLE I STEADY STATE HYDROGEN PERMEATION FLUX FOR UNCOATED AND TiC / TiN COATED STEEL.

T (K)	J_s (mol cm^{-2} sec^{-1})	J_c (mol cm-2 sec-1)
470	$(1.9\pm0.3)\times10^{-10}$	$(8.9\pm1.2)\times10^{-12}$
500	$(3.3\pm0.5)\times10^{-10}$	$(9.5\pm1.2)\times10^{-12}$
530	$(5.4\pm0.8)\times10^{-10}$	$(1.0\pm0.1)\times10^{-11}$
565	$(9.1\pm1.3)\times10^{-10}$	$(1.7\pm0.2)\times10^{-11}$

Pb-17Li to the steel was found. It is reasonable to think that the compatibility of TiC with Pb-17Li is good and the detaching were caused by mechanical problem. Thicker coating would be not affected by this problem.

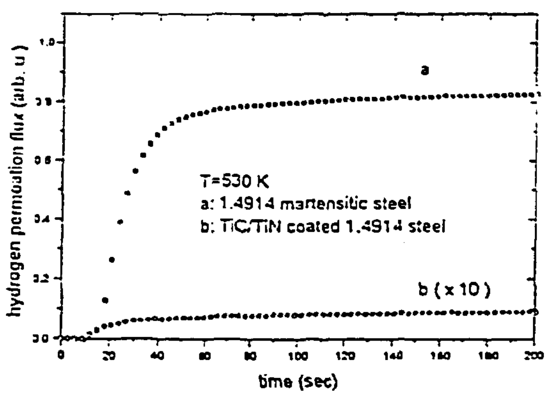

Fig. 2 Hydrogen permeation fluxes through different samples at 530 K:
a : uncoated 1.4914 steel
b : TiC / TiN coated 1.4914 steel (signal multiplied by 10)

5. CONCLUSIONS

We have shown that TiC / TiN bilayers 1.2 µm thick deposited on Manet II steel by the IBAD technique strongly reduce the hydrogen permeation in the temperature range from 470 K to 570 K. The reduction of the hydrogen permeation is an increasing function of the temperature and at the maximum investigated temperature the hydrogen flux resulted two order of magnitude lower with respect to the uncoated steel. Preliminary compatibility tests between Manet II and Pb-17Li showed no attack of the Pb-17Li to the steel.

6. REFERENCES

[1] E. Proust, L. Anzidei, G. Casini, M. dalle Donne, L. Giancarli, S. Malang, Fus. Eng. and Des. 22 (1993) 19.
[2] A. Terlain, G. Beneamati, H. U. Borgstedt, DEMO Blanket Selection Methodology and Data Comparison, CEA Report, FAR N 14728 (1993).
[3] K. S. Forcey, A. Perujo, F. Reiter and P. L. Lolli-Ceroni, J. Nucl. Mater. 200 (1993) 417.
[4] C. Shan, A. Wu, Y. Li, Z. Zhao, Q. Chen, Q. Huang and S. Shi, J. Nucl. Mater 191-194 (1992) 221.
[5] W. G. Perkins, J. Vac. Sci. Technol. 10, 4 (1973) 543.
[6] R. Checchetto, L. M. Gratton and A. Miotello, to be published in J. of Phys. D: Appl. Phys.
[7] P. L. Andrew, A. A. Haasz, J. Appl. Phys. 72, 7 (1992) 2749
[8] K. S. Forcey, D. K. Ross and J. C. B. Simpson, J. Nucl. Mater. 160 (1988) 117.