

Wet-Chemical Methods for Fabrication of Tritium Permeation Barrier Coatings

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We thank to Dr. T. Chikada and Prof. T. Terai of U. Tokyo for fruitful discussion.

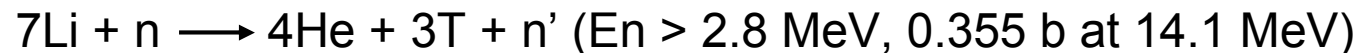
1. Why we need permeation barrier?

If we need 3 GW fusion power,

we have to consume 600 g T (200 PBq) per day

breed 700 g T (250 PBq) per day

handle 12 kg (4 EBq) per day (5% burning in plasma)



Natural Isotope Ratio ${}^6\text{Li}$ (7.6 %), ${}^7\text{Li}$ (92.4%)

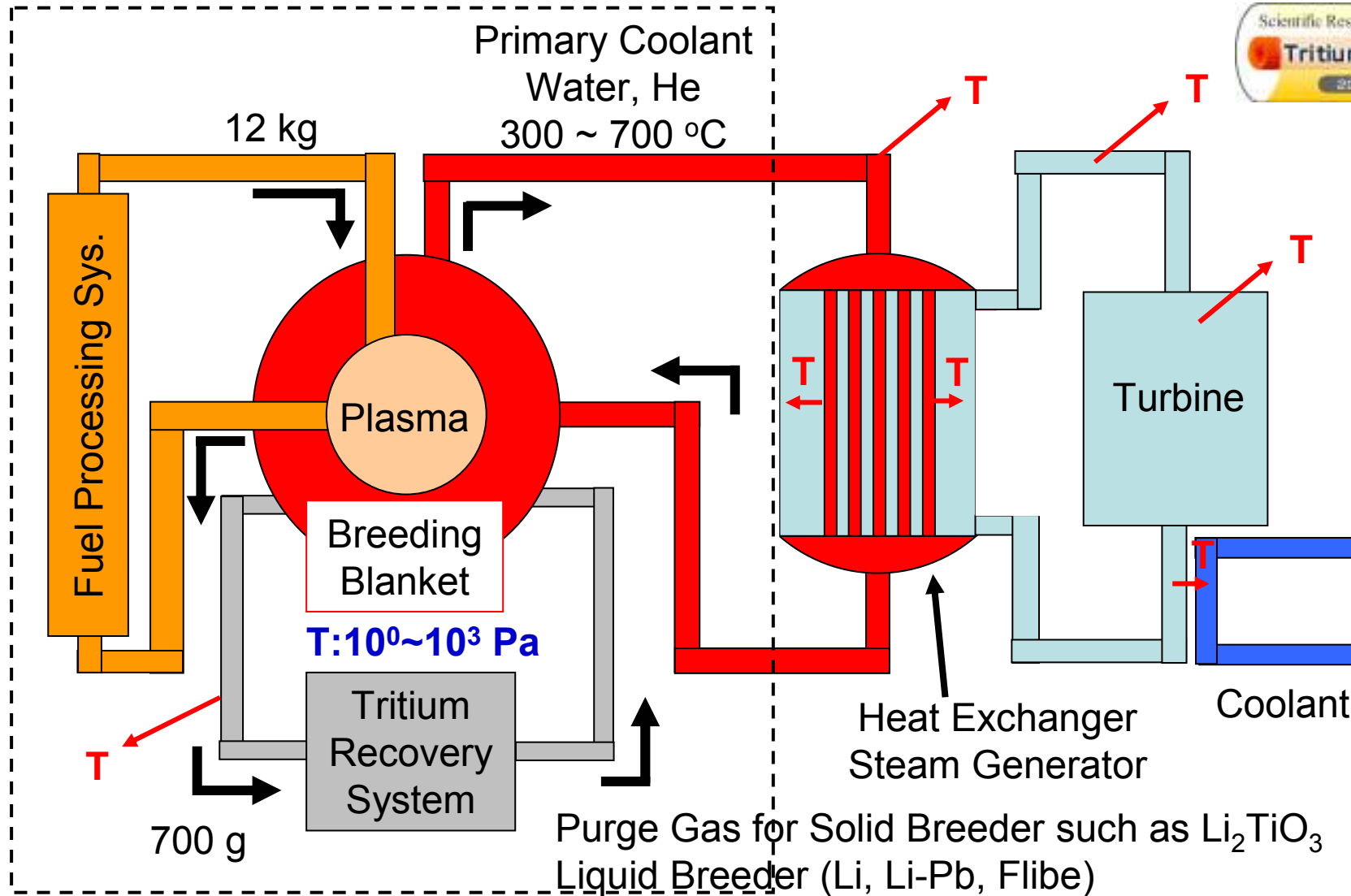
Tritium release from reprocessing plant for spent nuclear fuels

20 PBq per year = 55 TBq/day (0.15 g)

If we hope to have tritium emission comparable with or less than that of reprocessing plant, we can be allowed to release only 10 ppm of daily handling.

Of course, we are willing to have much safer system.....

In addition, achievement of tritium breeding ratio larger than unity is must issue!



Tritium travels a lot. In addition, many parts of fusion system are hot. Thus permeation could be serious issue.

We need to reduce T release from hot parts, joints and turbine system for sustainable fuel supply and acceptable impact to the environment.

Partial pressure of tritium in blanket could be in order of $10^0 - 10^3$ Pa.

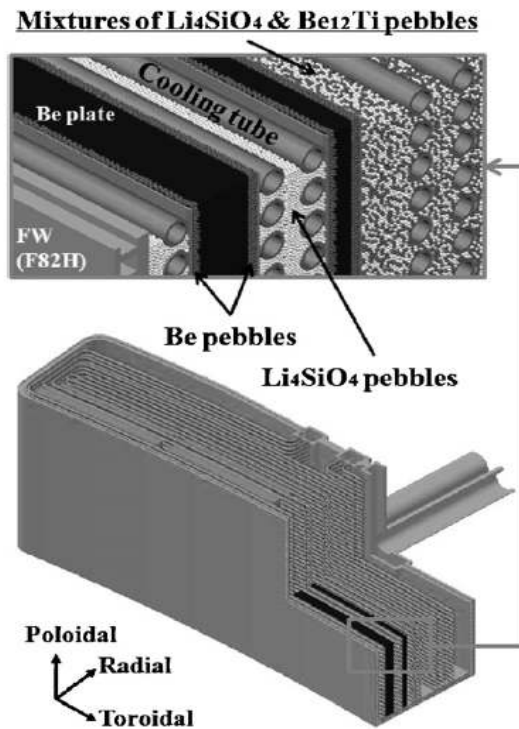


Fig. 2. Replaceable blanket for SlimCS.

Example of blanket design
Y. Someya et al. FED, 2011.

In blankets, tritium breeder and coolant are separated from each other by mm-thick RAFS pips or sheets in most cases.

RAFS: Reduced Activation Ferritic Steel

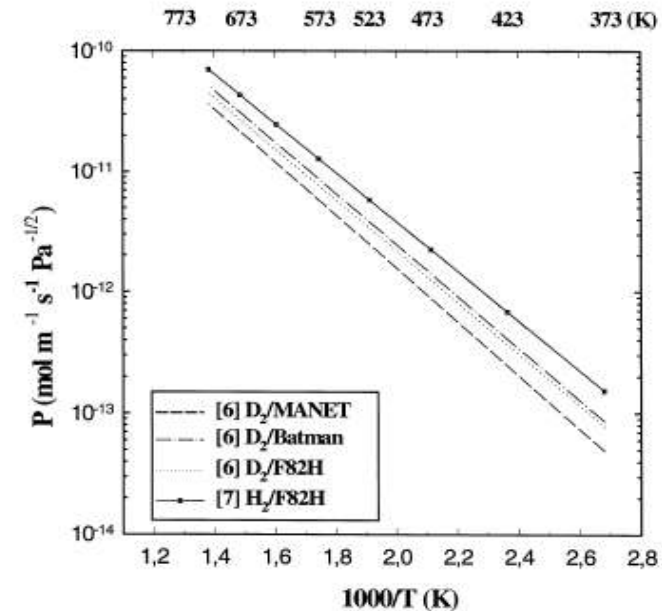


Fig. 6. Arrhenius plot of hydrogen and deuterium permeabilities for MANET, F82H and Batman steel [6,7].

Permeability of hydrogen isotopes through RAFS

E. Serra et al., JNM, 1998.

At driving pressure of 1 Pa, RAFS with 1mm thick permeates 20 TBq $\text{m}^{-2} \text{day}^{-1}$ of tritium at 500 °C.

T. Yamanishi et al., FED 81(2006)797
W. Farabolini et al., FED 81(2006)753
H. Nakamura et al., FED 81(2006)1339
Y. Song et al., FED 84(2009)1779
etc.

Results of numerical evaluation have shown that we need to reduce tritium permeation to $1/50 \sim 1/100$ (= PRF 50 ~100).

Permeation Reduction Factor (PRF)

= Steady State Permeation Rate w/o Barrier / Permeation Rate with Barrier

2. Requirements for Permeation Barriers

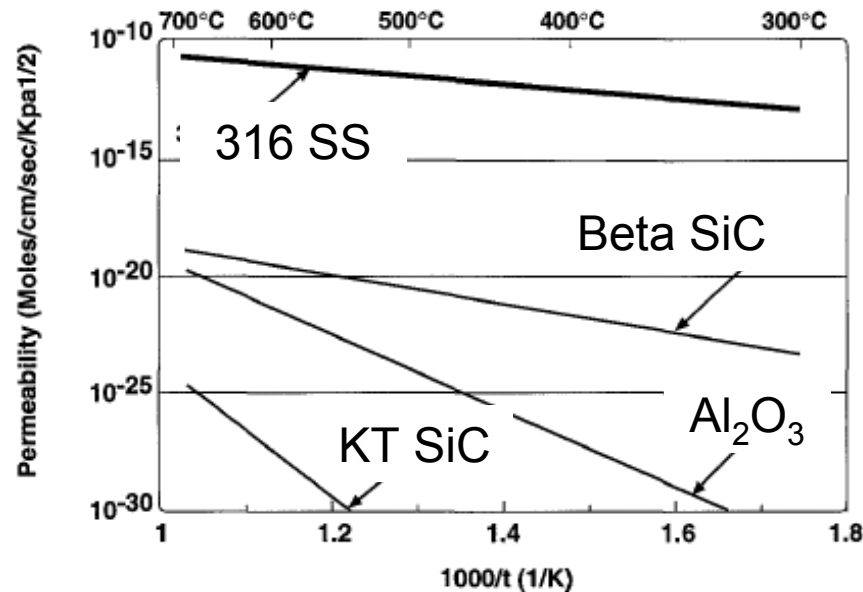


Fig. 2. Comparison of the permeability of SS316 with those of Al₂O₃ and SiC.

Comparison of permeability of metals and ceramics

G.W. Hollenberg et al., FED 28 (1995) 190.

Tritium permeation can be mitigated by preparing layers of low permeability materials (e.g. ceramics).

Requires for Barrier Coatings

- ✓ Low hydrogen permeability
- ✓ Low crack density
- ✓ Comparable thermal expansion coefficient with substrate
- ✓ Durable under irradiation and given chemical environment
- ✓ High thermal conductivity (or thin)
- ✓ Low activation

Requires for Fabrication Techniques

- ✓ Applicable for large and complicated structures
- ✓ Heat treatments in fabrication process does not influence microstructure and mechanical properties of substrate materials
- ✓ Applicable for various elements

Current status of permeation barrier studies

- ✓ Aluminizing has been widely investigated, but Al is not low-activation.
- ✓ Excellent barriers have been obtained by plasma processes (for example, Chikada et al., PRF ~ 100,000 with Er_2O_3 prepared by arc-plasma deposition, Proc. 23rd IAEA Fusion Energy Conf.), but this type of fabrication techniques cannot be applied to large and complicated structures.

Influence of barrier materials on neutron-induced activation
(after 300 years cooling)

E. T. Cheng, FED 48(2000)455.

Mater.	Hands on Recycling* (mass ppm)	Near Surf. Disposal (mass ppm)	Equivalent Thickness on 1 mm RAFS (μm) **
Al (Al_2O_3)	13 - 79	660 - 3920	8.4
Er (Er_2O_3)	0.82 - 7.3	36 - 319	0.15
Ti (TiN)	9.3 - No limit	No limit	No limit
Zr (ZrO_2)	660 - 8800	2.9 - 38%	250

* 10 $\mu\text{Sv/h}$

** for near surf. disposal
(average)

Hands on recycling would be unrealistic with Al and Er.

Our opinion

- ✓ We need PRF more than 100 but not 100,000. A target value with laboratory-scale experiment could be 1,000.
- ✓ Barrier coatings should consist of low activation elements if they are fabricated on low activation structural materials.
- ✓ Fabrication method should be applicable for large and complicated structures.

We have chosen wet-chemical methods to fabricate ZrO_2 coatings as permeation barrier.

ZrO_2

- ✓ **Comparable thermal expansion coefficient with steels.**
- ✓ **Low activation**
- ✓ **ZrO_2 is already nuclear material (oxide film on fuel cladding tubes of fission reactors) and many studies on hydrogen isotope behavior, irradiation effects, thermal conductivity etc.**

3. Wet-chemical methods

3-(1) Procedures of coating fabrication and analysis

Specimen: Disk of type ferritic steel (SS430)

$t = 0.5 \text{ mm}$

Step 1 Sol-Gel Method (SG) (Step 1)

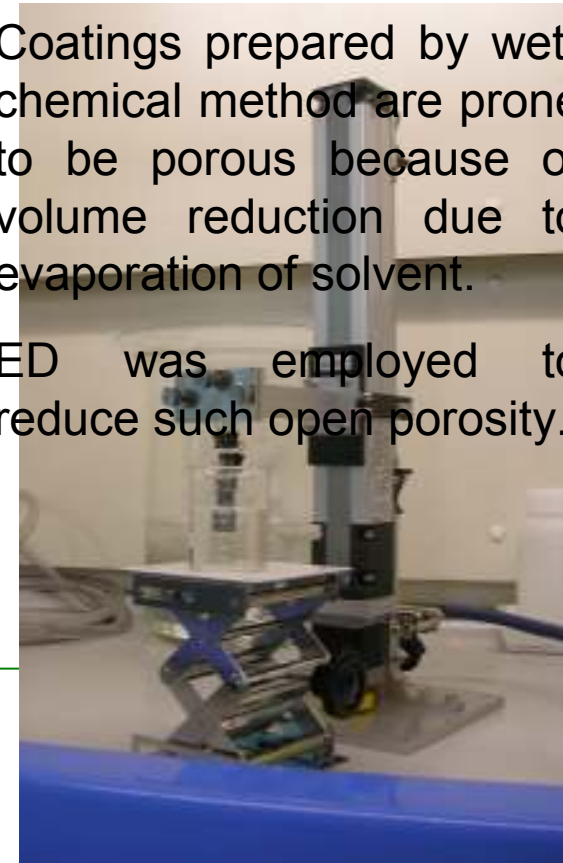
- 20
- (i) Dip Coating
 zirconium 1-propoxide, 1-proponal, acetyl acetone (AcAc), water
 - (ii) Drying in Air at 120 °C
 - (iii) Heating in Air at 550 °C for 2h

Step 2 Electrochemical Deposition (ED) (Step 2)

- 8
- (i) Anodic Polarization in $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ethanol solution results in deposition of $\text{Zr}(\text{OH})_4$.
 - (ii) Drying in Air at 150 °C
 - (iii) Heating in Air at 550 °C for 1 h to convert $\text{Zr}(\text{OH})_4$ to ZrO_2 .

Coatings prepared by wet-chemical method are prone to be porous because of volume reduction due to evaporation of solvent.

ED was employed to reduce such open porosity.

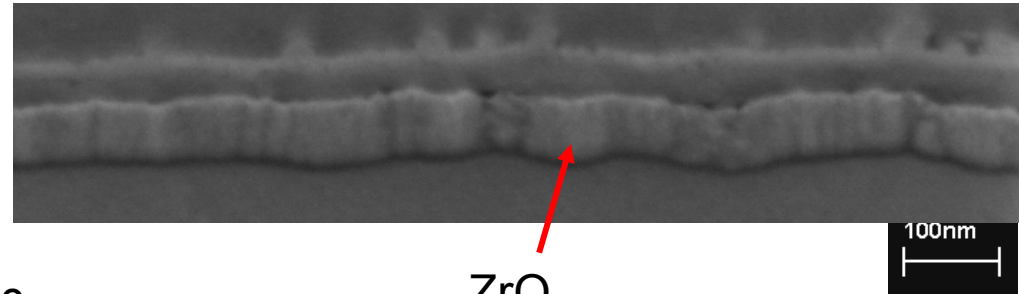


For details, K. Zhang & Y. Hatano, JNM, in press (Proc. ICFRM-14) (thinner coatings).

Uniform layers of tetragonal ZrO_2 in columnar structure were formed on both sides of specimens.

Two different films were prepared:

- (i) ZrO_2 (SG) (Step 1) only: 80 nm
- (ii) ZrO_2 (SG)+ ZrO_2 (ED) (Step 2) = 180 nm

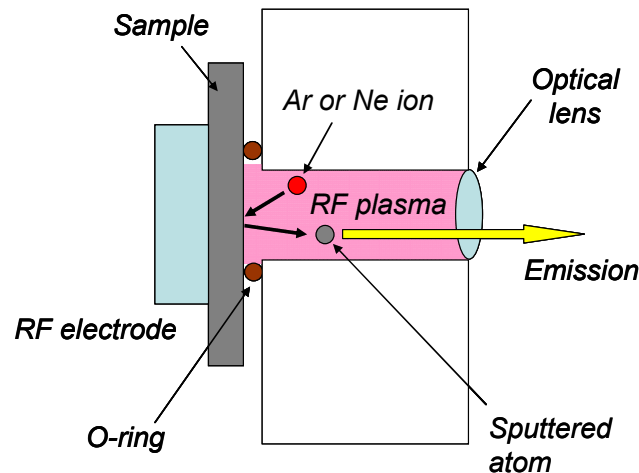


ZrO_2

Cross Section of Step 2 (ED) Coating [1]

[1] K. Zhang & Y. Hatano, JNM, in press (Proc. ICFRM-14).

Depth Profile Measurements (Glow Discharge Optical Emission Spectroscopy)



Glow-discharge optical emission spectroscopy (GDOES) is a technique to measure depth profiles of constituent elements in a solid sample by (1) sputtering with rf-glow discharge plasma, and (2) detecting optical emissions from atoms accommodated in plasma.

Permeation Experiments

A conventional vacuum device evacuated by a turbomolecular pump to 10^{-6} Pa and separated into upstream and downstream chambers by specimen

300 ~ 550 °C, 0.1 MPa driving pressure of H_2 or D_2

Tritium Retention Measurements

An ultra-high vacuum device evacuated by an ion pump to 10^{-7} Pa.

$T / (D + T) = 0.17$ gas from ZrNi alloy getter.

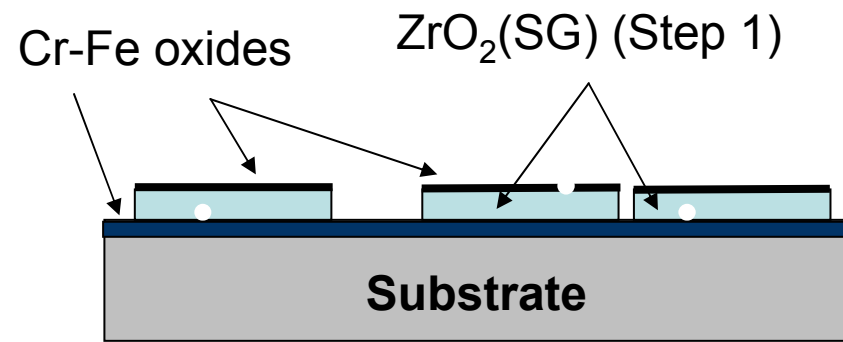
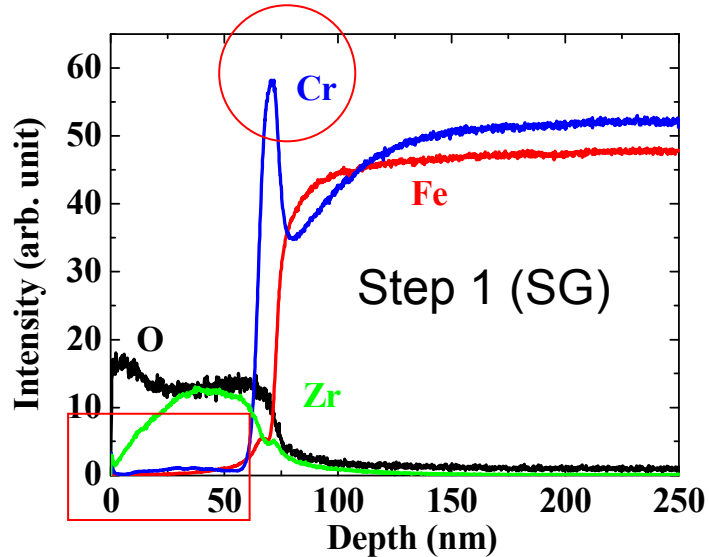
Coating specimens were exposed to DT gas at 300 °C and 1 kPa total pressure for 12 h.

Tritium concentration was measured with imaging plate (IP) technique and β -ray induced X-ray spectroscopy (BIXS).

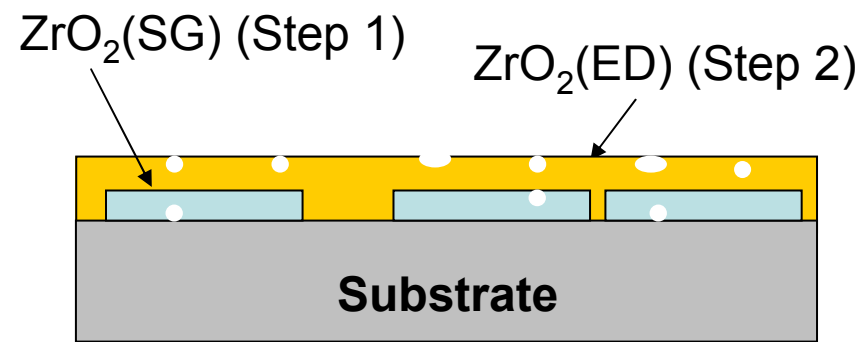
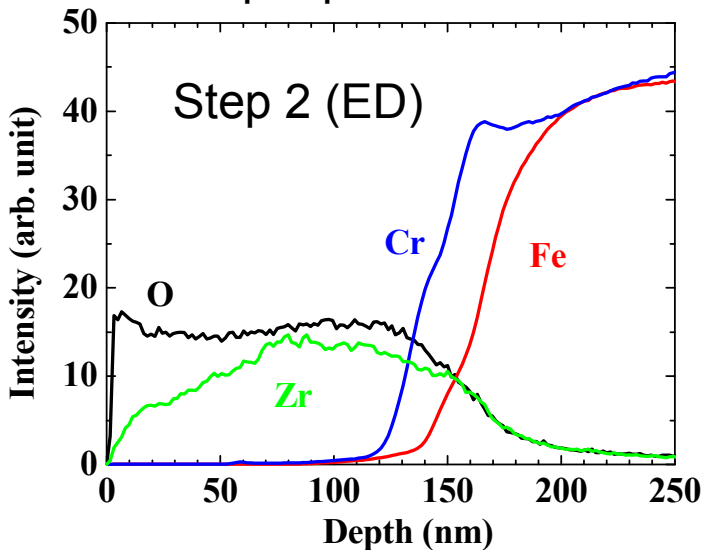
Dense bulk ZrO_2 specimens (single and polycrystal) were also examined for comparison.

Note that ZrO_2 layer prepared by wet-chemical method was compatible with vacuum at elevated temperature and no significant contamination of DT gas.

3-(2) Depth profiles of constituent elements in coatings



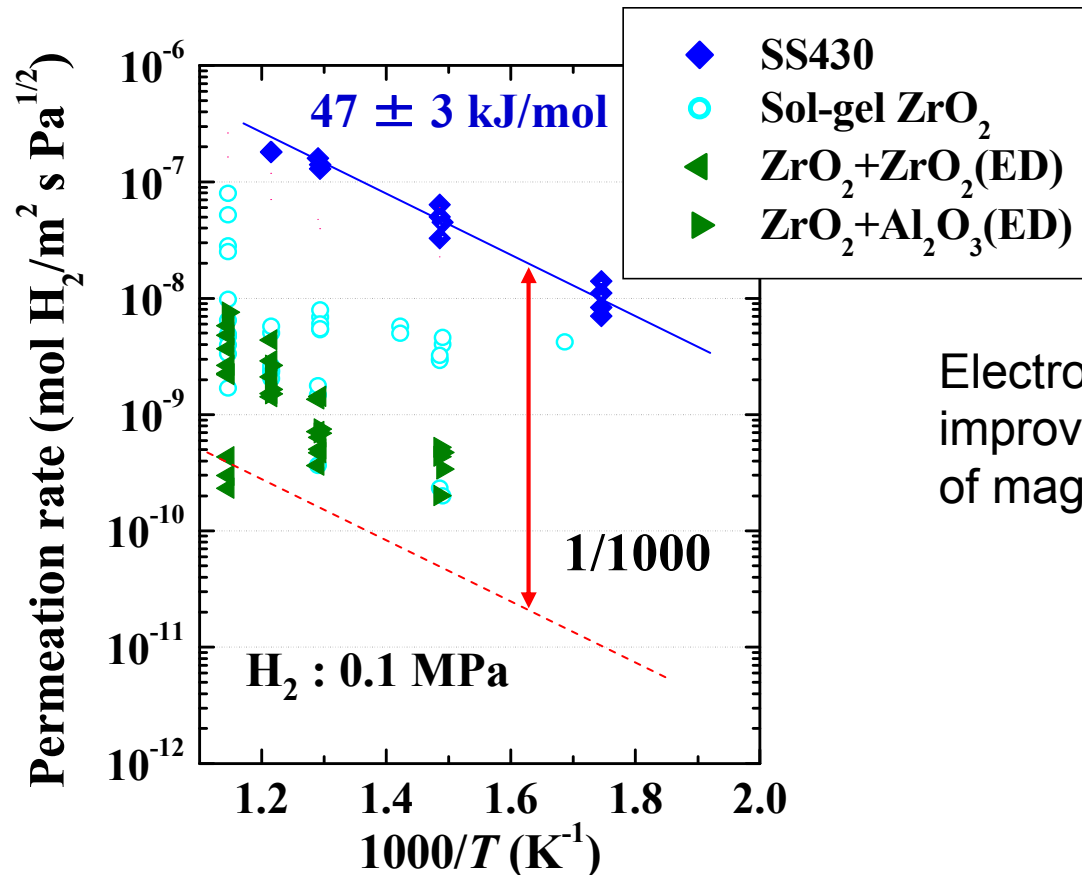
Depth profiles measured by



Depth profiles in Step 2 coating

3-(3) Results of permeation tests

- (i) Thinner coatings examined in the previous study [1]
50 nm (SG) + 50 nm (ED) = 100 nm



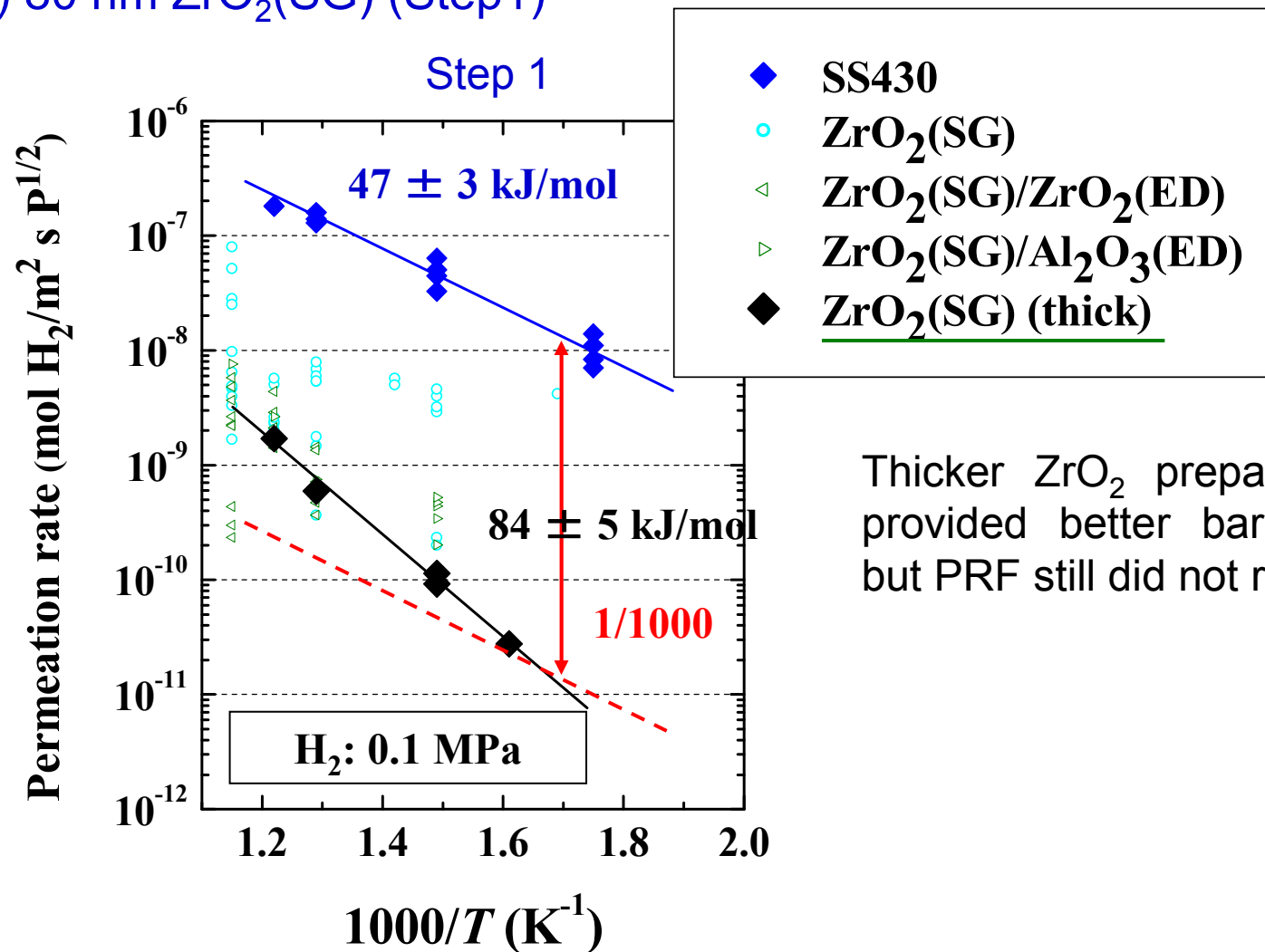
Electrochemical deposition (Step 2) improved barrier effects by an order of magnitude, but still insufficient.

Hydrogen permeation rate through SS430 with or without ZrO₂ coating

[1] K. Zhang & Y. Hatano, JNM, in press (Proc. ICFRM-14).

3-(2) Results of permeation tests

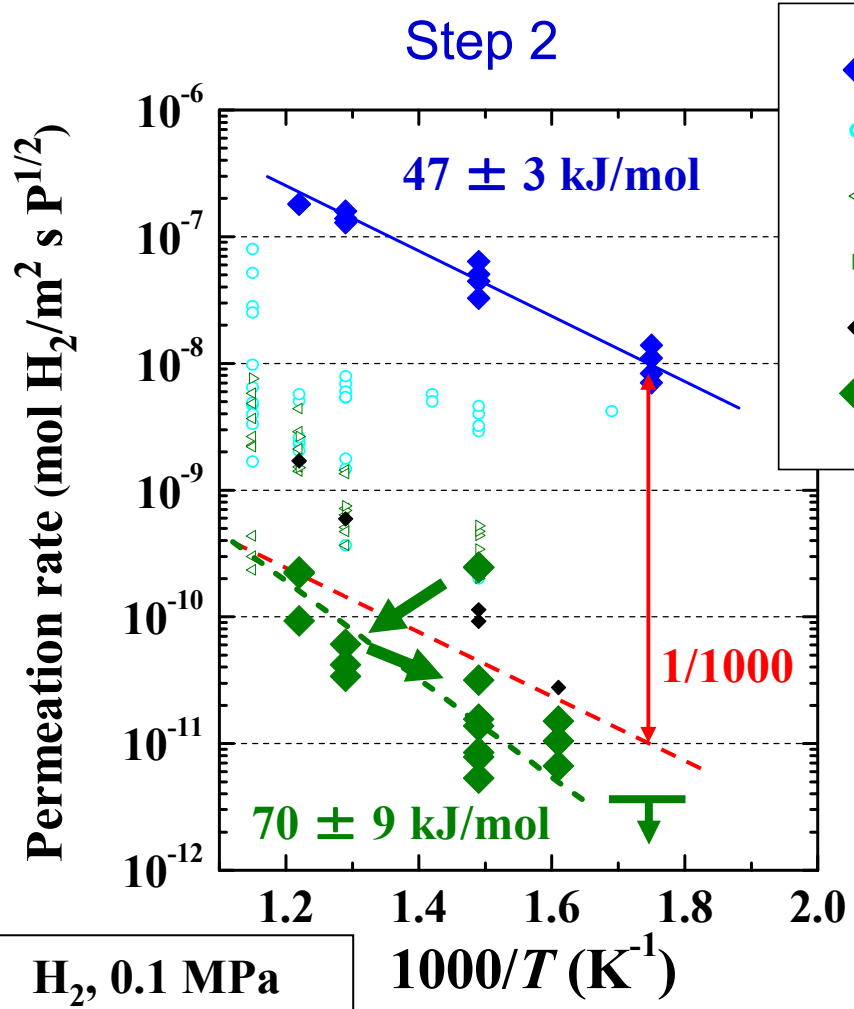
(ii) 80 nm ZrO₂(SG) (Step1)



Thicker ZrO₂ prepared by SG provided better barrier effects, but PRF still did not reach 1000.

Barrier effects of thicker sol-gel ZrO₂ (80 nm)

(iii) 80 nm (SG) + 100 nm (ED) = 180 nm (Step 2)



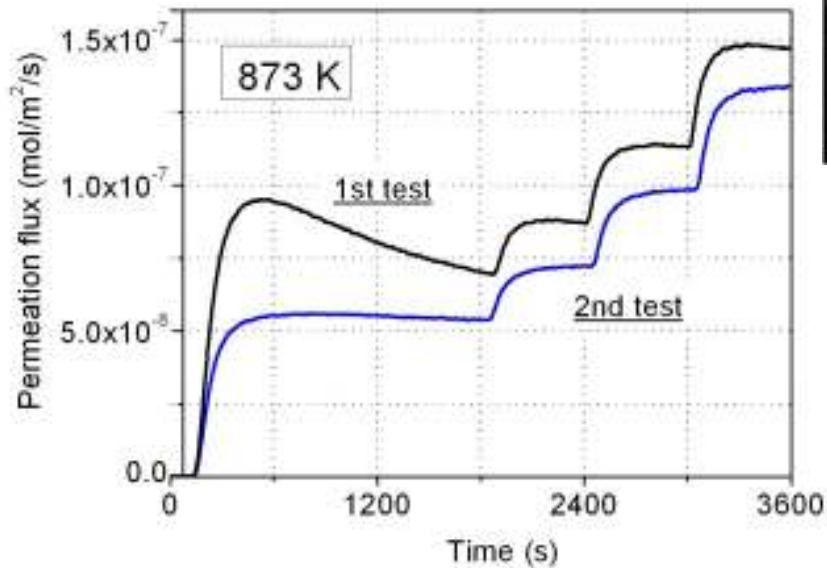
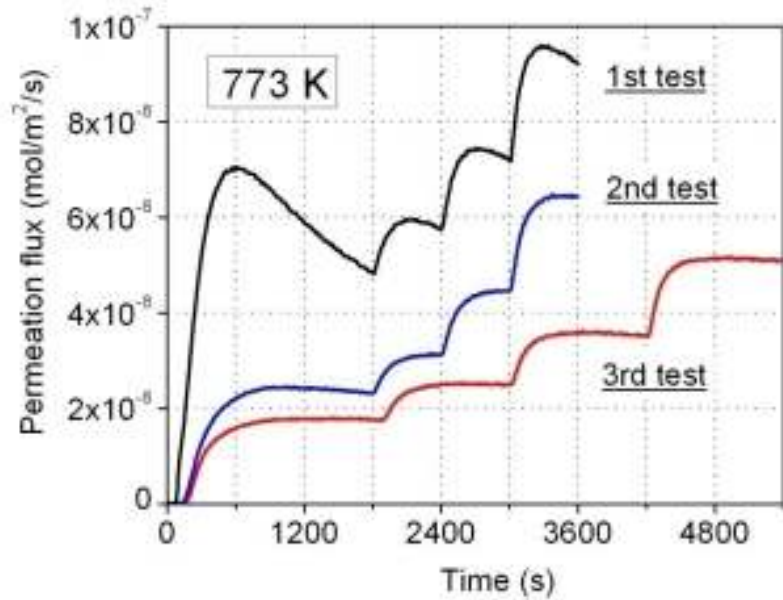
- ◆ SS430
- ZrO₂(SG)
- △ ZrO₂(SG)/ZrO₂(ED)
- ▽ ZrO₂(SG)/Al₂O₃(ED)
- ◆ ZrO₂(SG) (thick)
- ◆ ZrO₂(SG)+ZrO₂(ED) (thick)

Barrier effects of thicker ZrO₂ prepared by ED were poor in beginning but gradually improved with time.

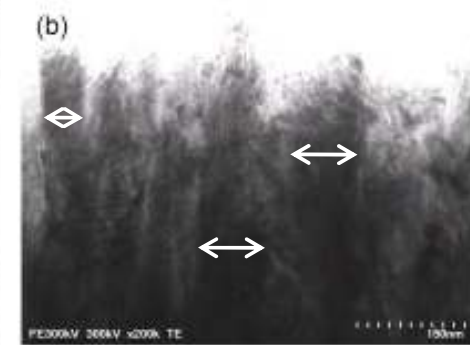
This coating provided PRF ≥ 1000 at 300 – 550 °C (expected temp. of ferritic steels in blanket).

Barrier effects of thicker electrochemically deposited ZrO₂ (180 nm)

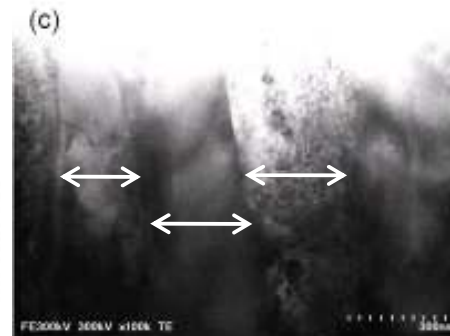
Similar improvement in PRF with time has been reported by Chikada et al., JNM in press.



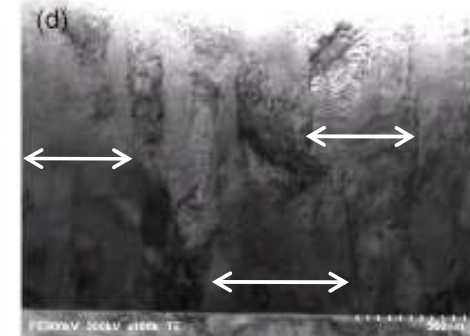
As deposited



After permeation measurements at 500°C



After permeation measurements at 600°C



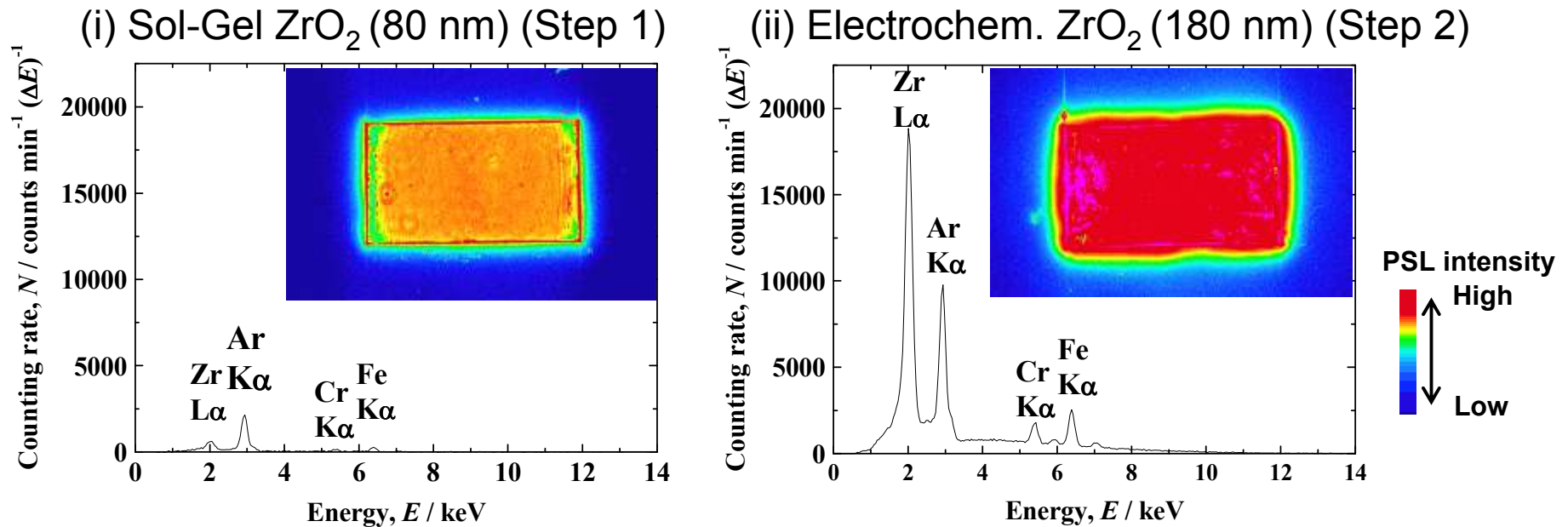
After permeation measurements at 700°C

Correlation between permeation rate and grain size in Er_2O_3 .

T. Chikada et al., JNM, in press.

Grain boundary (GB) diffusion dominates permeation rate.

3-(4) Results of Tritium Retention Measurements



IP image and b-ray induced X-ray spectrum after exposure to tritium gas (1 kPa, $T/(D+T) = 0.17$) at 300 °C for 12 h.

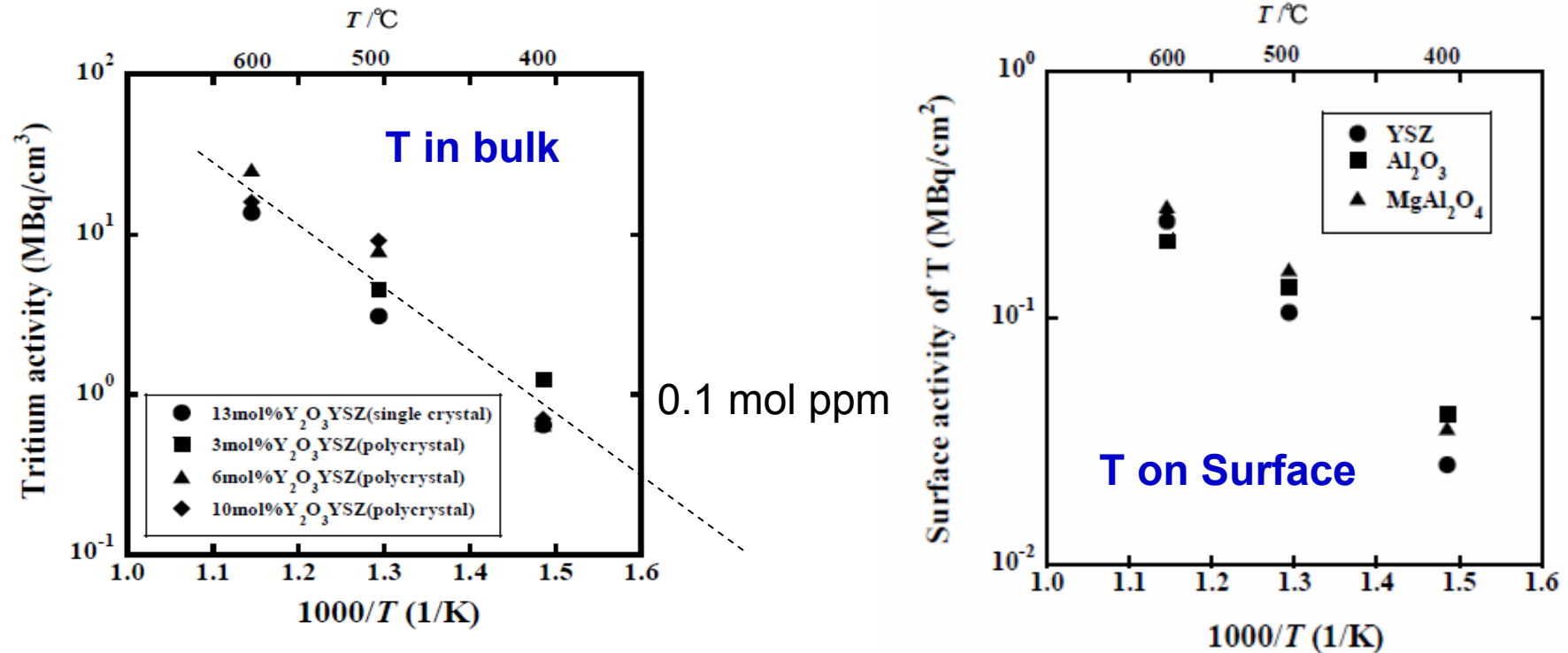
Tritium concentration in coatings

Sol-Gel ZrO_2 (80 nm)(Step 1): T 50 mol ppm, D+T 300 mol ppm

Electrochem. ZrO_2 (180 nm))(Step 2): T 150 mol ppm, D+T 1000 mol ppm

Tritium concentration in ZrO_2 (ED) was significantly higher than that in ZrO_2 (SG) in spite of much lower permeability...

Tritium retention by *dense bulk* ZrO₂ (yttria stabilized cubic zirconia, YSZ)



Tritium retention on surface and in bulk of dense yttria-stabilized zirconia (YSZ) (single and polycrystal specimens) (cubic structure).

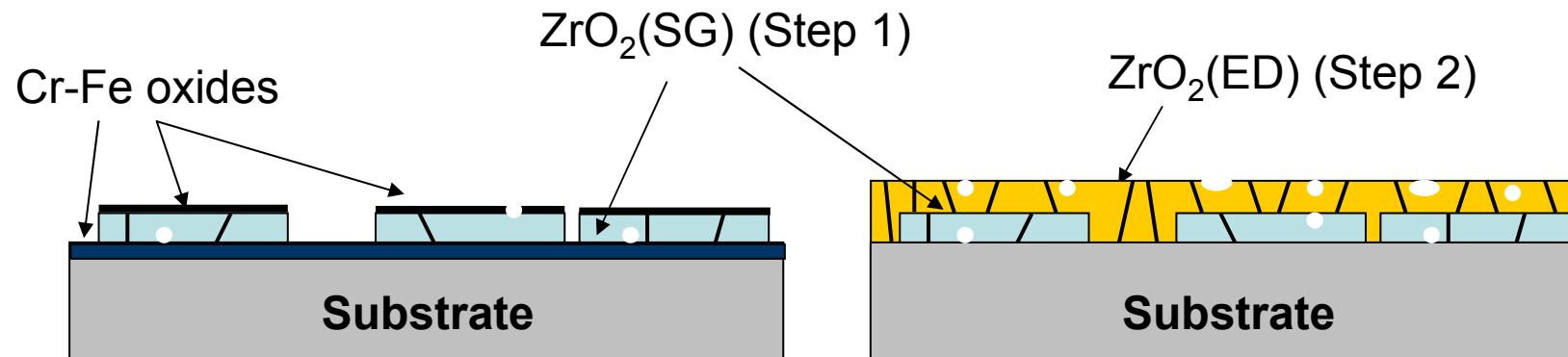
Tritium solubility in the bulk of dense ZrO₂ is very low.

Polycrystal specimens showed higher T concentration than single crystal.

Surface T concentration is relatively high (several % of oxygen atoms on the surface trapped hydrogen isotopes).

Tritium in coatings seems to be trapped in GBs and pores.

3-(5) Discussion on Permeation Mechanism

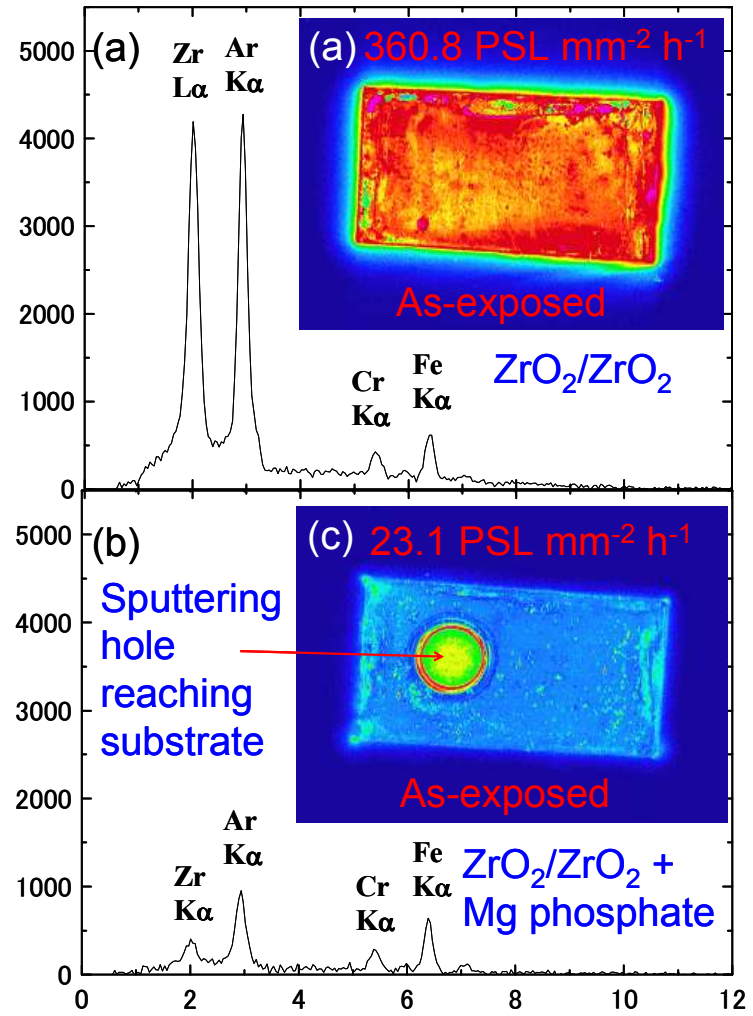


- ✓ ZrO₂(SG) ... Higher permeability, lower tritium retention.
(Step 1) Coating should be relatively dense but coverage should be small.
- ✓ ZrO₂(ED) ... Lower permeability, higher tritium retention.
(Step 2) Coating should be relatively porous but coverage should be large.

Diffusion process through or dissociative sticking process on GBs seems to control permeation rate. Reduction in permeability observed with ZrO₂(ED) (Step 2) at high temperature is considered to be due to grain growth and reduction in GB density.

Improved barrier effects by electrochemical deposition was due to improved coverage by ZrO₂.

Preparation of Mg phosphate layer



Energy, E / keV
 BIXS spectra and IP images of
 (a) ZrO_2/ZrO_2 ,
 (b) $ZrO_2/ZrO_2 + Mg$ phosphate

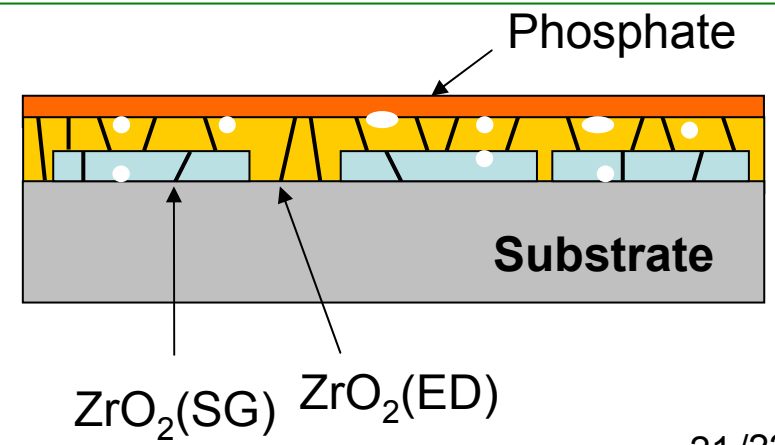
PSL intensity
 High
 Low

In order to reduce tritium retention in $ZrO_2(ED)$ (Step 2), amorphous Mg phosphate over layer was prepared by dip coating technique. (Step 3)

$ZrO_2(ED)$ T: 150 mol ppm, D: 1000 mol ppm

With Mg phosphate T: 5 mol ppm, D: 30 mol ppm

Preparation of amorphous phosphate layer significantly reduced tritium retention in coating!
 Permeation tests is in preparation.



4. Summary

- ✓ ZrO₂ coating (180 nm) was successfully prepared by wet-chemical methods (dip coating + electrochemical deposition) on ferritic steel.
- ✓ The ZrO₂ coating provided PRF ≥ 1000 at 300 ~ 550 °C.
- ✓ The permeation rate was initially high and gradually reduced with time by keeping the specimens at high temperatures.
- ✓ Tritium retention in the ZrO₂ coatings was significantly higher than that in dense YSZ. Polycrystal YSZ showed higher T retention than single crystal.
- ✓ Diffusion process of hydrogen isotopes through GBs or dissociative sticking process on GBs seems to dominate permeation rate. Further improvement may be possible by controlling microstructure.
- ✓ Preparation of amorphous Mg phosphate over layer significantly reduced tritium retention; permeation test is in progress.