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Electrical properties of ceramic coatings after heavy-ion irradiation and lithium implantation

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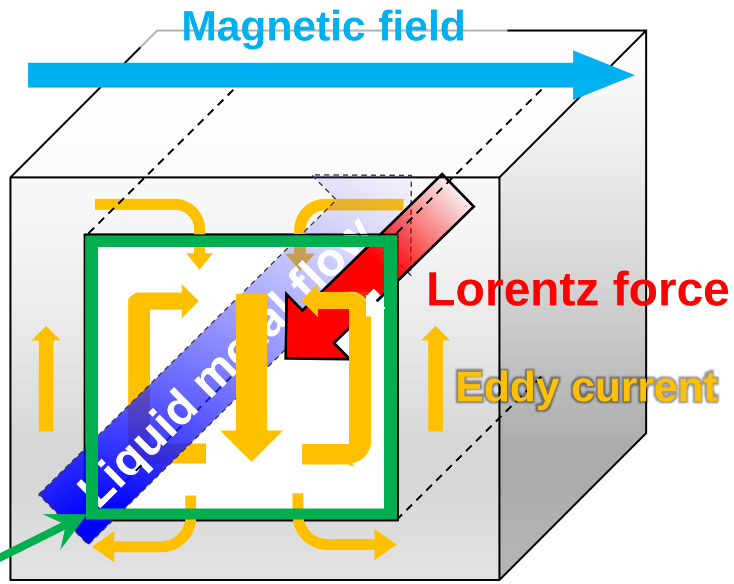
Contents

Introduction Research background

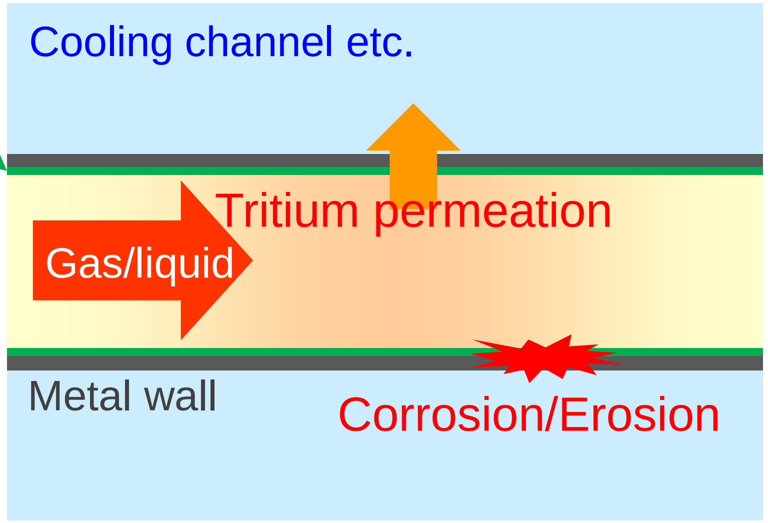
Liquid lithium-lead (Li-Pb) blanket concept

- High thermal efficiency by high-temperature operation.
- Continuous processing of liquid breeder.
- ✓ MHD pressure drop (Lorentz force against liquid metal flow generated by the interaction with a magnetic field).
- ✓ Tritium permeation due to a low tritium solubility in Li-Pb.
- ✓ Corrosion of structural materials by liquid Li-Pb flow.



Conceptual diagram of MHD pressure drop.

Functional coating



- Functional coating has been studied since the 1970s using mainly ceramics (oxides, carbides, and nitrides) due to their high electrical resistivity, low hydrogen isotope permeability, and chemical stability.
- Historically, electrical insulator and tritium permeation barrier were developed separately; however, both functions are required in Li-Pb blanket concepts.

Introduction Research background

Requirements for functional coating

1) Electrical conductivity

$< 10^{-2}$ S m^{-1} ($> 10^{2}$ Ω m) for 1 μm-thick coating [1,2]

2) Tritium permeation reduction

Permeation reduction factor (PRF)

PRF = $J_{uncoated} / J_{coated} > 10^2$–$10^3$

3) Compatibility with flowing Li-Pb

~550 ºC (on F82H), > 10000 h

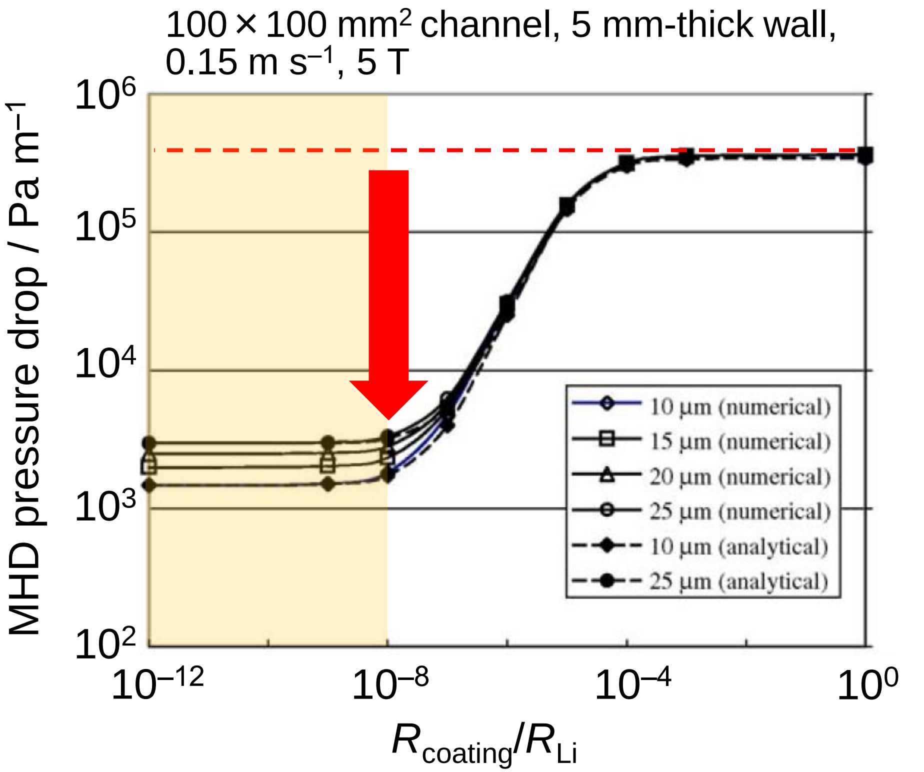
Flow rate: ~1.4 m s^{-1} [3], shear stress: > 1.2 MPa [4]

4) Irradiation tolerance (neutrons and gamma-rays)

2–3 kGy s^{-1} at first wall, ~100 dpa (≈ F82H) [3]

5) Others (activation, thermal conductivity, etc.)

Coating thickness should be < 10 μm?



Relationship between electrical insulation and MHD pressure drop [1].

Electrical conductivity at 500 ºC

Li: 3.0×10^{6} S m^{-1}

Li-Pb: 7.4×10^{5} S m^{-1}

F82H: 1.2×10^{6} S m^{-1}

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[1] H. Hashizume, *Fusion Eng. Des.* 81 (2006) 1431–1438.

[2] T. Tanaka *et al.*, *Fusion Eng. Des.* 88 (2013) 2569–2572.

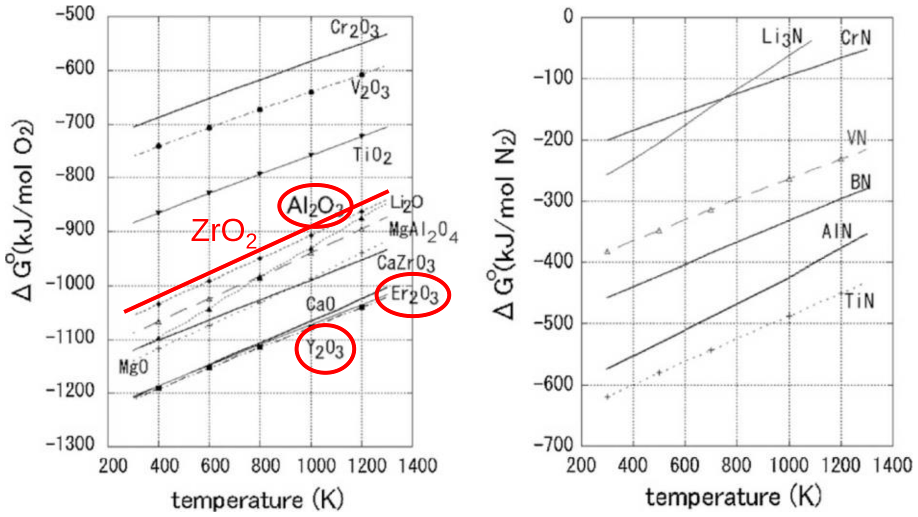
[3] T. Tanaka, *et al.*, *J. Nucl. Mater.* 569 (2022) 153917.

[4] R. K. Choudhary et al., *J. Nucl. Mater.* 466 (2015) 69–79.

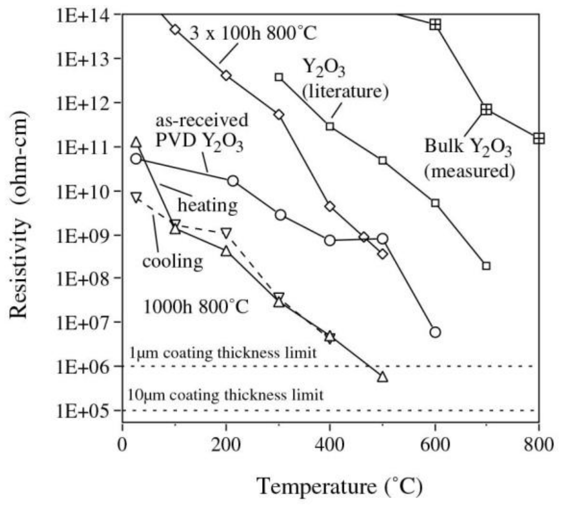
Introduction Progress on coating research

1) Electrical insulation

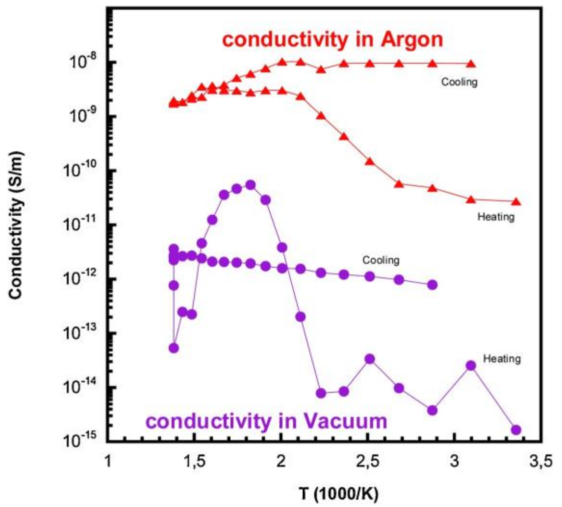
- Since the 1980s, ceramic materials have been considered and tested for an insulation material in self-cooled Li blankets [5].
- Y_2O_3 and Er_2O_3 were selected from the viewpoints of electrical insulation and Li compatibility.
- After starting consideration of Li-Pb as a promising liquid metal breeder (~1990s), ZrO_2 and Al_2O_3 were also considered due to the milder reducing condition than pure Li.
- These oxide coatings showed a high electrical resistivity (low conductivity) at high temperatures (600–750 ºC).



Free energies of oxide and nitride formation for selected ceramics [6].



Resistivity as a function of temperature for EB-PVD Y_2O_3 coatings before and after exposure to Li at 800 ºC [7].



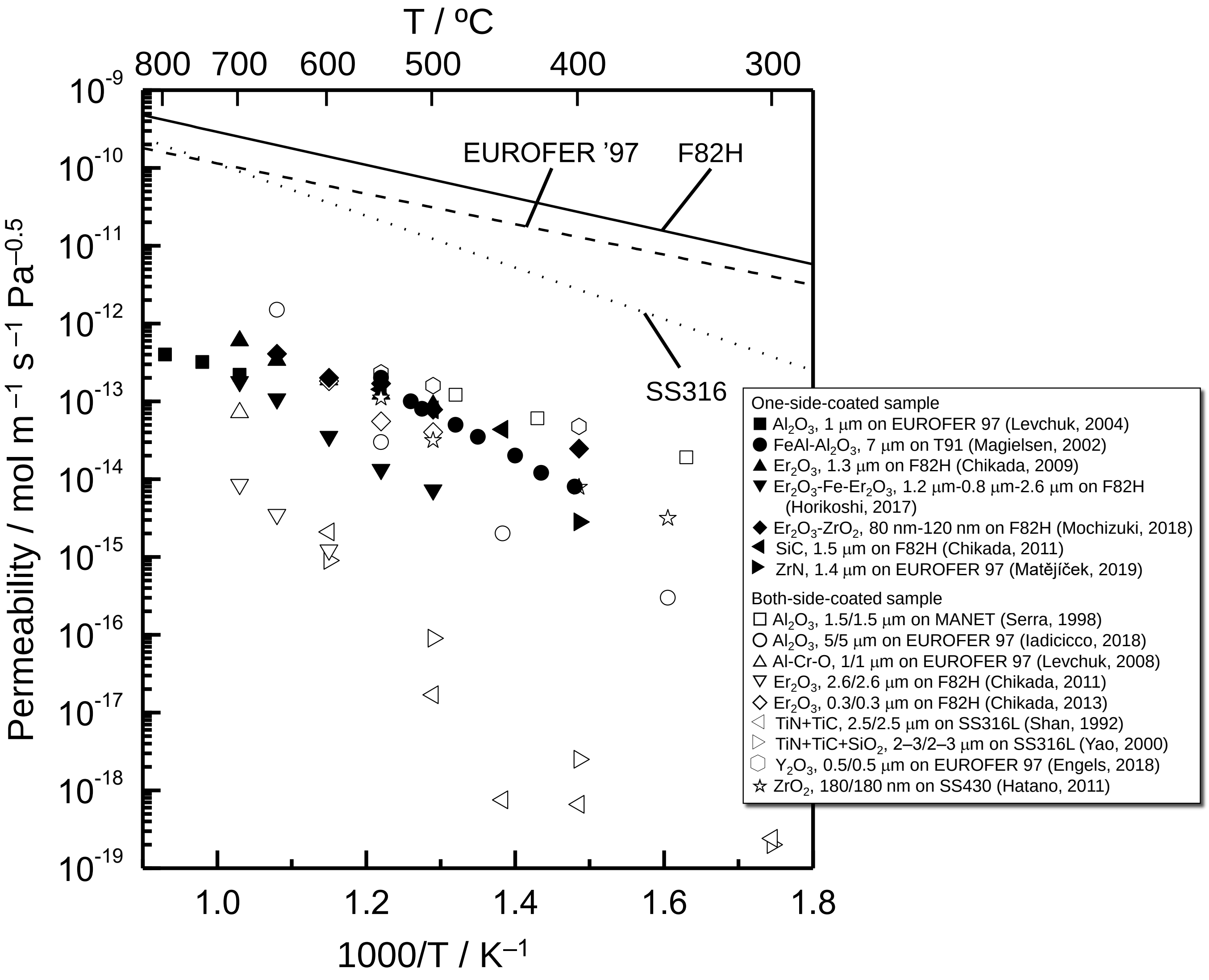
Electrical conductivity of PLD Al_2O_3 coating in argon and under vacuum [8].

[5] Y.Y. Liu *et al.*, *J. Nucl. Mater.* 141–143 (1986) 38–43.
[6] T. Muroga *et al.*, *Fusion Eng. Des.* 85 (2010) 1301–1304.
[7] B.A. Pint *et al.*, *J. Nucl. Mater.* 329–333 (2004) 119–124.
[8] M. Utili *et al.*, *Fusion Eng. Des.* 170 (2021) 112453.

Introduction Progress on coating research

2) Tritium permeation reduction

- Tritium permeation is a common issue in most blanket concepts (except for Li blanket).
- Although the permeation data differed by 4 orders of magnitude using the same coating material, the hydrogen permeation mechanism in the ceramic coating was experimentally and computationally elucidated in the 2010s [9].
- Not only single-layer coatings but also multilayer coatings have been developed and shown high permeation reduction performance.



Comparison of hydrogen isotope permeability for ceramic coatings with PRFs of > 1000 [9].

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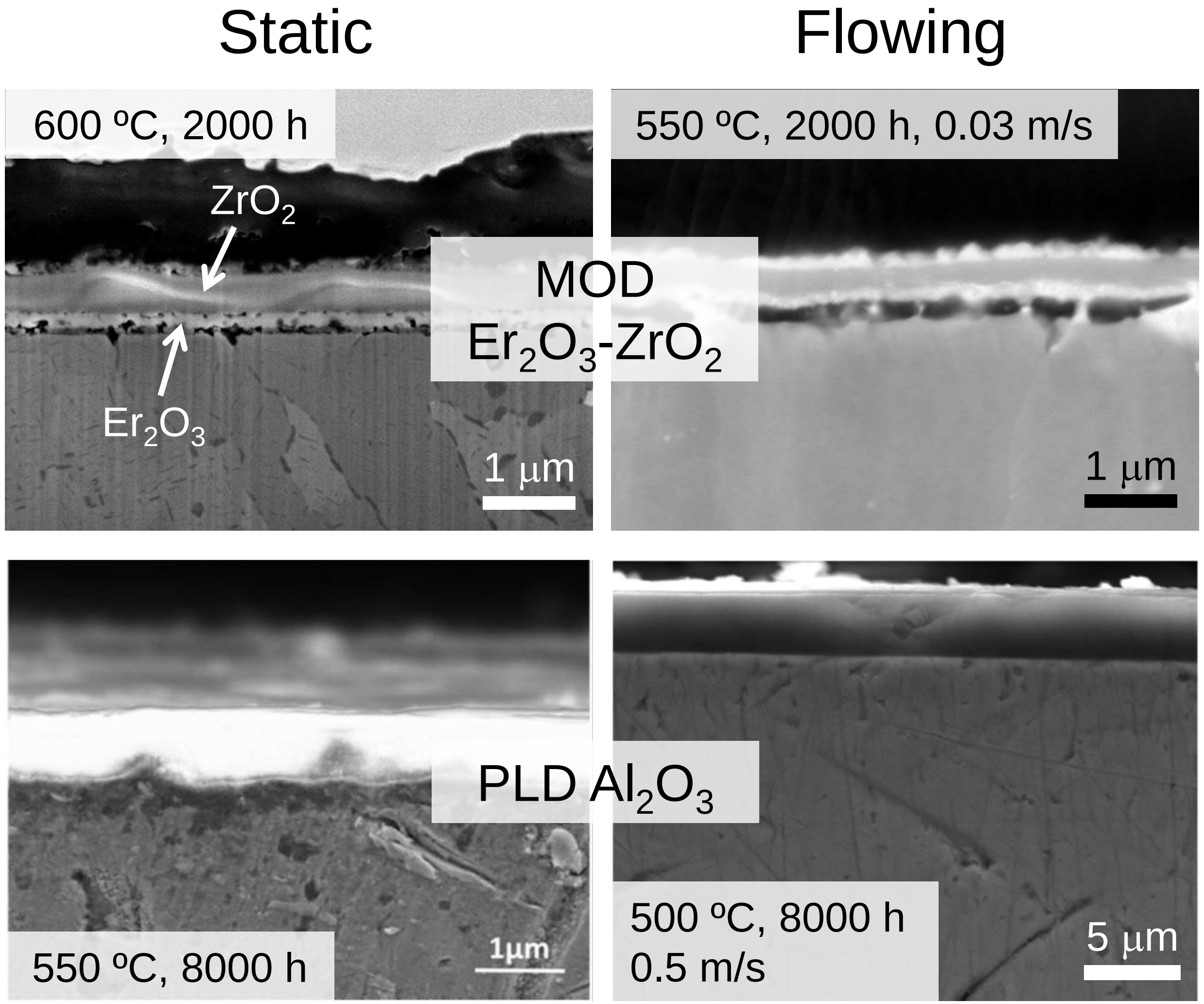
[9] T. Chikada, Ceramic Coatings for Fusion Reactors In: R. Konings and R. Stoller (eds.) Comprehensive Nuclear Materials 2nd edition, vol. 6 (2020) pp. 274–283, Oxford: Elsevier.

Introduction   Progress on coating research

3) Compatibility with flowing Li-Pb

- A number of static Li-Pb exposure tests were reported, while quite a few of flowing tests.
- Recently in EU, Al_2O_3 coatings fabricated by pulse-laser deposition (PLD) showed Li-Pb compatibility under flowing condition with a flow rate of 0.5 m s^{-1} [11].
- Recently in Japan, ceramic-metal joint coatings have been developed and shows promising results in Li-Pb exposure tests under flowing conditions. (Monday poster session PS1-28)



Cross-sectional SEM micrographs of MOD Er_2O_3-ZrO_2 coating and PLD Al_2O_3 coating after static and flowing Li-Pb exposure [10,11].

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[10] T. Chikada *et al.*, presented at SOFT2022.

[11] M. Utili *et al.*, *Fusion Eng. Des.* 170 (2021) 112453.

Introduction Progress on coating research

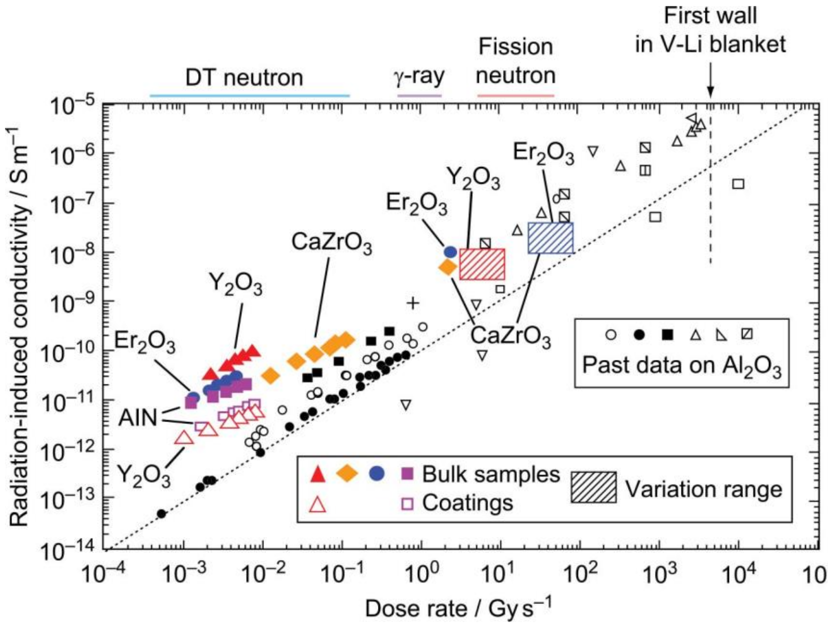
4) Irradiation tolerance

Radiation-induced conductivity (RIC)

Temporal increase in conductivity by excitation.

→ Brought by both neutron and gamma-ray.

- Basic data have been accumulated with a wide range of dose rate and various ceramics. [9]
- Coatings have not been tested in a reactor-level high dose rate.



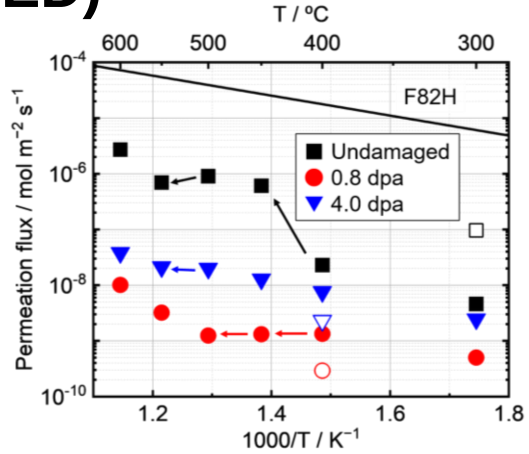
RIC as a function of dose rate measured by DT-neutron (FNS), fission neutron (JMTR), and γ-ray irradiations for bulk and coating of insulator coating candidate ceramics [9].

Radiation-induced electrical degradation (RIED)

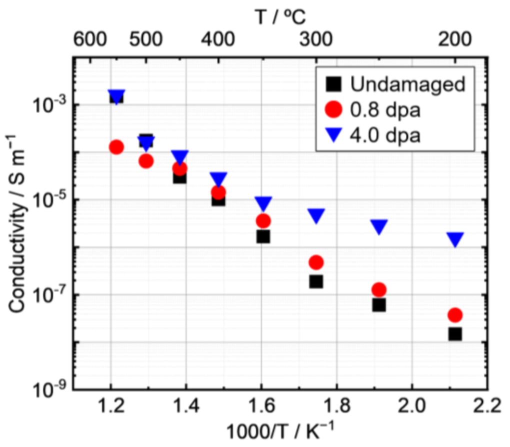
Insulation degradation by displacement.

→ Mainly brought by neutron irradiation.

- Recently irradiated data using heavy-ion and neutron have been reported including conductivity and permeation.
- No serious degradation has been reported.



Arrhenius plots of deuterium permeation flux for ZrO_2 coating with and without 6.0 MeV Ni^{2+} irradiation [12].



Arrhenius plots of electrical conductivity for ZrO_2 coating with and without 2.8 MeV Fe^{2+} irradiation [12].

[9] T. Chikada, Ceramic Coatings for Fusion Reactors In: R. Konings and R. Stoller (eds.) Comprehensive Nuclear Materials 2nd edition, vol. 6 (2020) pp. 274–283, Oxford: Elsevier.

[12] H. Fujiwara *et al.*, Fusion Eng. Des. 191 (2023) 113509.

Introduction Progress on coating research

5) Others

Activation

- Al, Zr, and Er are highly activated by neutron irradiation, while Si and Y are lower.
- In EU DEMO WCLL blanket, the target thickness of Al_2O_3 coating is < 10 μm in order to reduce the amount of activated products to 900 kg for all the BB modules [11].

Thermal conductivity

- Al_2O_3 has a thermal conductivity similar to RAFM steel (~30 W m^{-1} K^{-1}), while that of Y_2O_3 (~14) and ZrO_2 (~3) are lower.
- Our previous study showed that a ZrO_2-Fe joint coating satisfied the requirement of electrical resistivity but showed a slightly (~5 %) smaller thermal conductivity than that before joining due to an interface resistance [13].

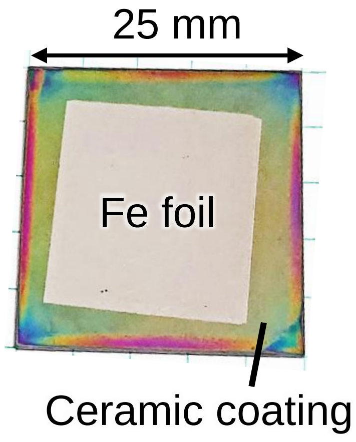
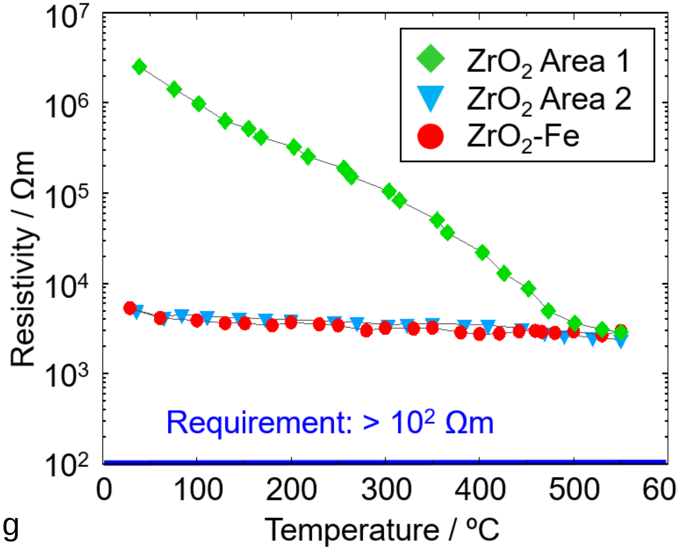
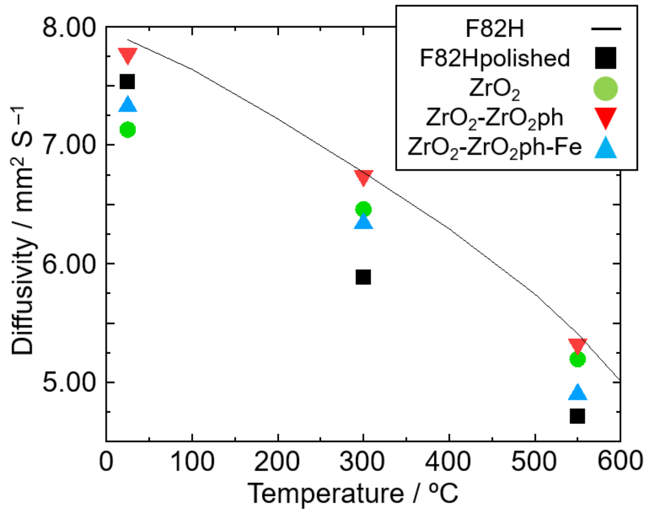


Photo of ZrO_2-Fe joint coating prepared by hot pressing.



Temperature dependence of electrical resistivity for ZrO_2 single-layer and ZrO_2-Fe joint coatings [13].



Thermal diffusivity of F82H and coated samples [13].

[11] M. Utili *et al., Fusion Eng. Des.* 170 (2021) 112453.
[13] R. Norizuki *et al., Fusion Eng. Des.* 168 (2021) 112438.

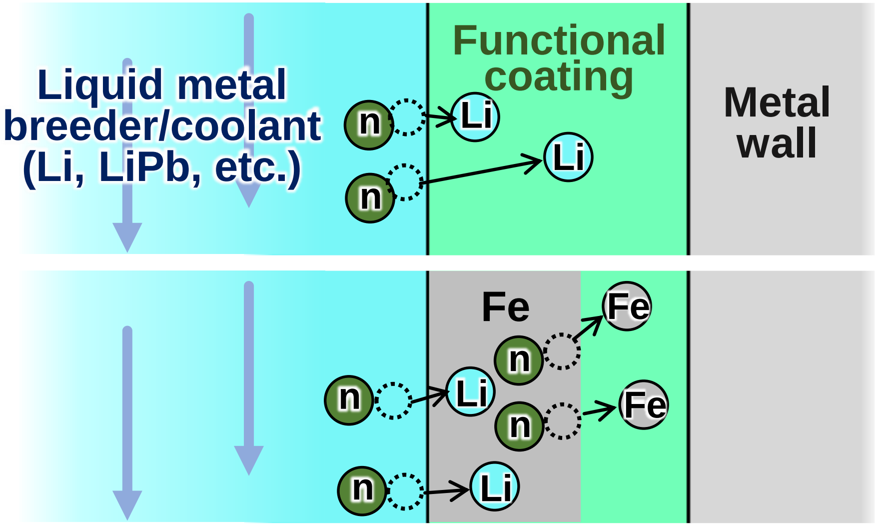
Introduction A new concern in irradiation effect

Effect of recoil atom implantation [3]

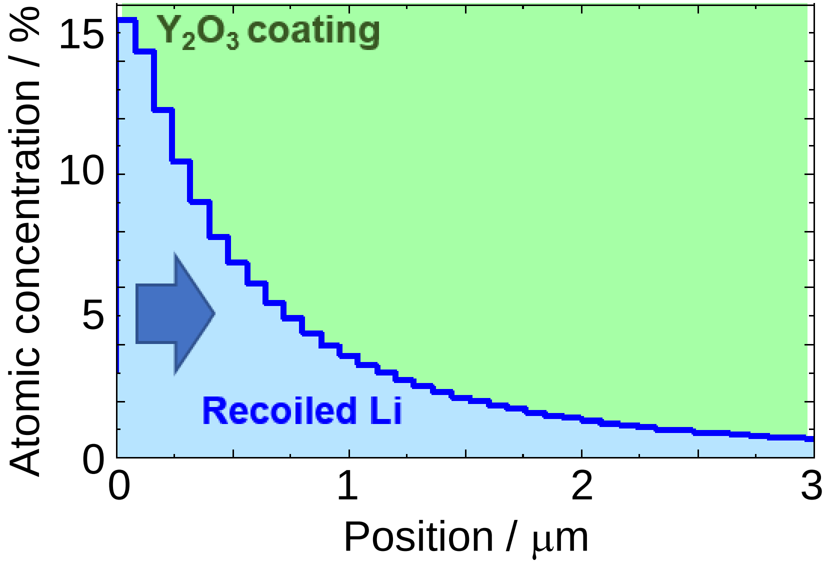
- ☐ 14 MeV neutrons undergo elastic collision with Li.
- ☐ The maximum recoil energy is 6.9 MeV, corresponding to the range of implanted Li of ~10 μm in the coating.
- ☐ Li concentration at the coating surface is ~1.8 at% after 7.5-year operation in Li-Pb blanket.
- ☐ In the case of ceramic-metal (Fe) joint coating, Li will be implanted in the metal layer and Fe will be implanted in the coating (range: ~0.25 μm).

→ **Change in performances of functional coating?**

In this study, we investigated the effect of Li and Fe implantation on electrical properties of functional coatings for the simulation of recoil atoms in Li-Pb blanket systems.



Conceptual diagram of implantation of recoil atoms from liquid metal breeder/coolant and ceramic-metal joint coating.

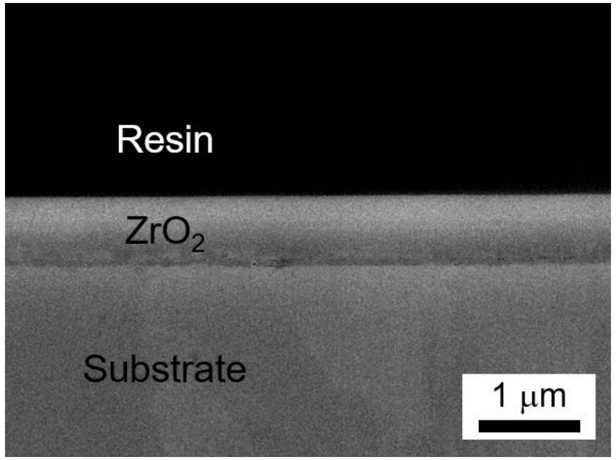


Calculated distribution of recoil Li atoms from Li breeder/coolant.

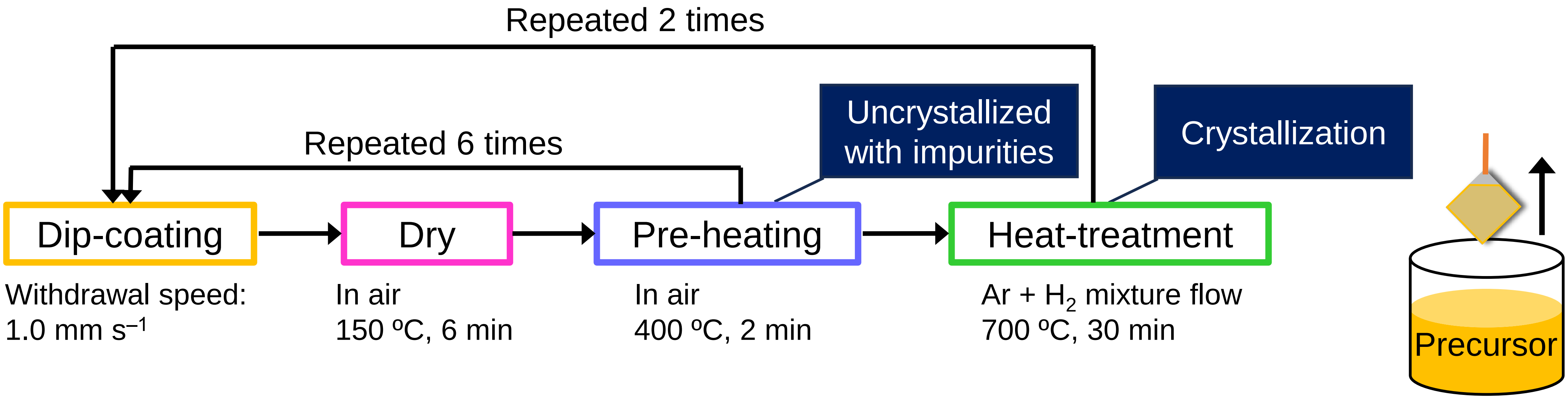
[3] T. Tanaka, *et al.*, *J. Nucl. Mater.* 569 (2022) 153917.

Experimental details Coating preparation

- Substrate: Reduced activation ferritic/martensitic steel
  F82H (Fe-8Cr-2W、BA-07heat)
- Size: $25\ \mathrm{mm}^{W} \times 25\ \mathrm{mm}^{L} \times 0.5\ \mathrm{mm}^{t}$
- Ceramic layer: ZrO_2 (SYM-ZR04®)
- Coating method: **Metal organic decomposition (MOD)** [12]
- Coating thickness: ~700 nm



Cross-sectional micrograph of ZrO_2 coating.


Repeated 2 times

Repeated 6 times

Uncrystallized with impurities

Crystallization

Dip-coating
Withdrawal speed:
1.0 mm s^{-1}

Dry
In air
150 ºC, 6 min

Pre-heating
In air
400 ºC, 2 min

Heat-treatment
Ar + H_2 mixture flow
700 ºC, 30 min

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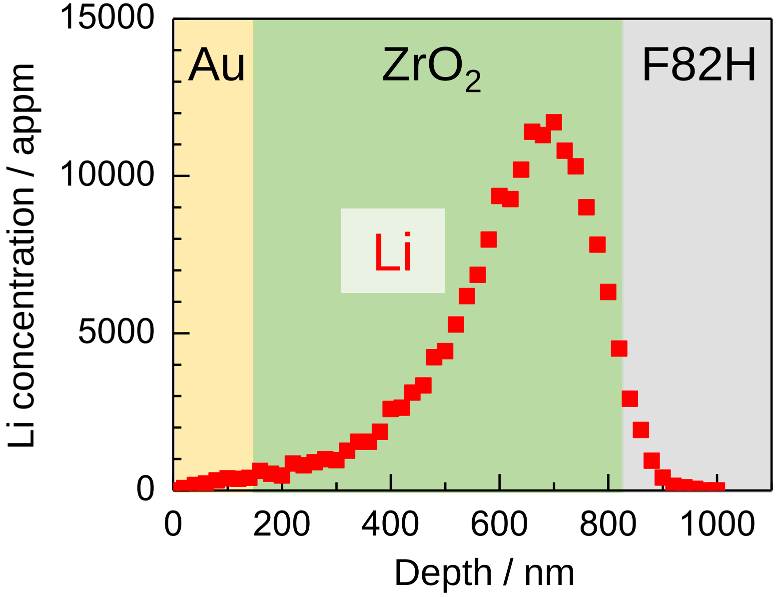
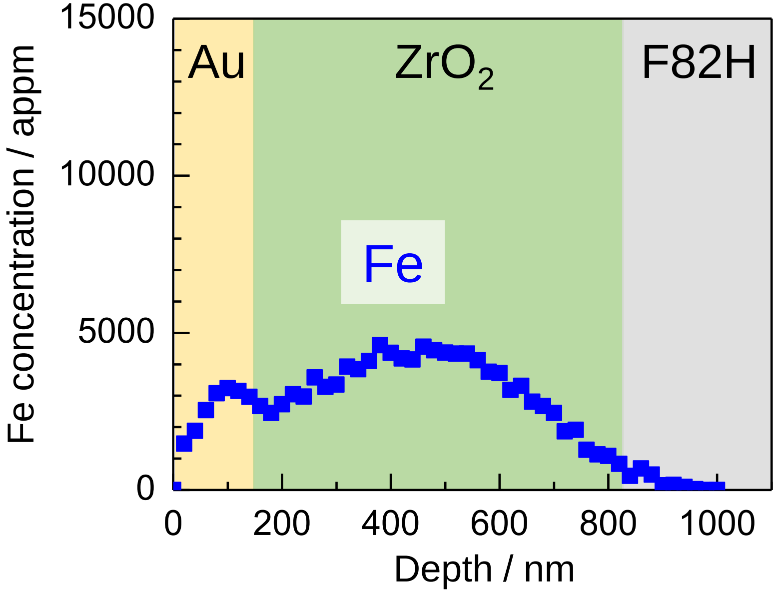
[12] H. Fujiwara *et al.*, Fusion Eng. Des. 191 (2023) 113509.

Experimental details Irradiation and implantation

- ☐ Accelerators: TIARA at QST
  HIT at The University of Tokyo
- ☐ Size: 25 mm^W × 25 mm^L × 0.5 mm^t
- ☐ Ion energy and species:
  6.0 MeV Ni^{2+} for damage introduction
  150–250 keV Li^+ for Li implantation
  1.0 MeV Fe^{2+} for Fe implantation
  (Comparison) 2.8 MeV Fe^{2+}
- ☐ Ion flux: 1–4 × 10^{16} m^{-2} s^{-1}
- ☐ Irradiation temperature: no heating (< 100 ºC)
- ☐ Damage/ion concentration:
  Ni^{2+} 1 dpa (displacement per atom)
  Li^+ 1200–12000 appm
  Fe^{2+} 100–5000 appm
- ☐ Simulation code: SRIM-2013



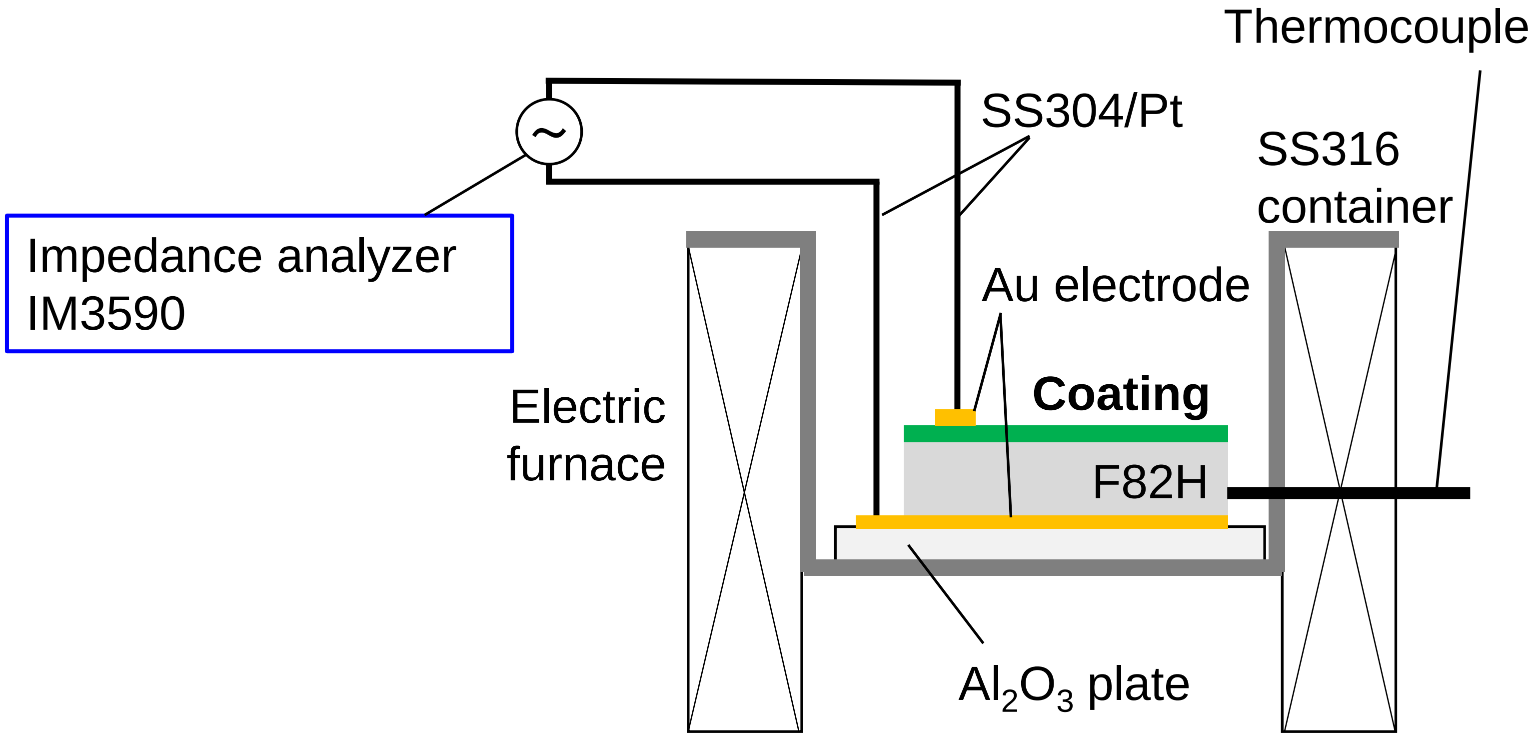
Li depth profile after 250 keV-Li implantation.



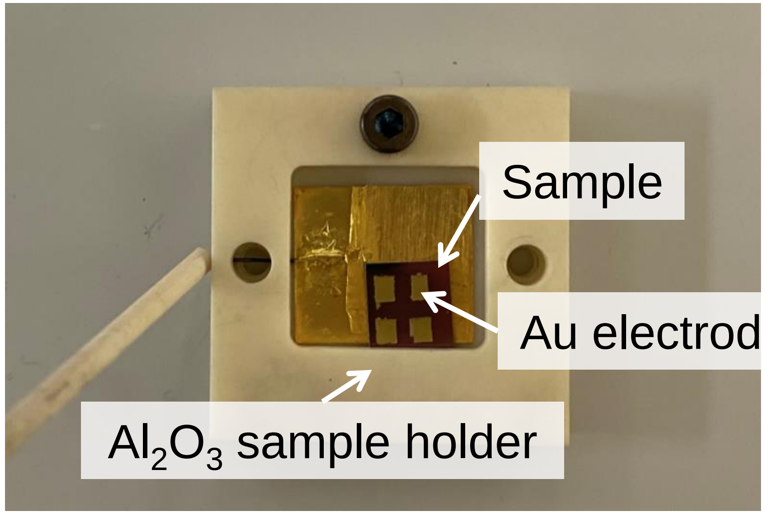
Fe depth profile after 1.0 MeV-Fe implantation.

Experimental details   Electrical conductivity measurement

- Measurement system: IM3590 (Hioki E.E. Corp.)
- Applied voltage: DC 0.5–2 V
- Test temperature before implantation: room temperature (R.T.)
  after implantation: R.T. (~25)–550 ºC
- Atmosphere: air

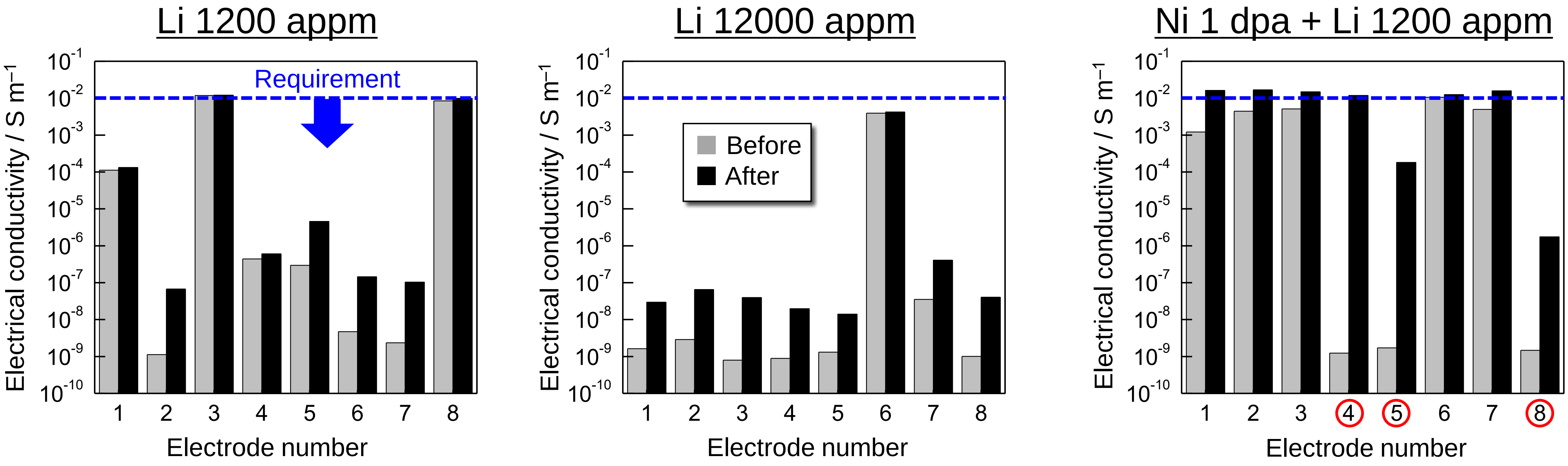


Setup of electrical conductivity measurement.



Photograph of sample part.

Results and discussion   Li implantation effect

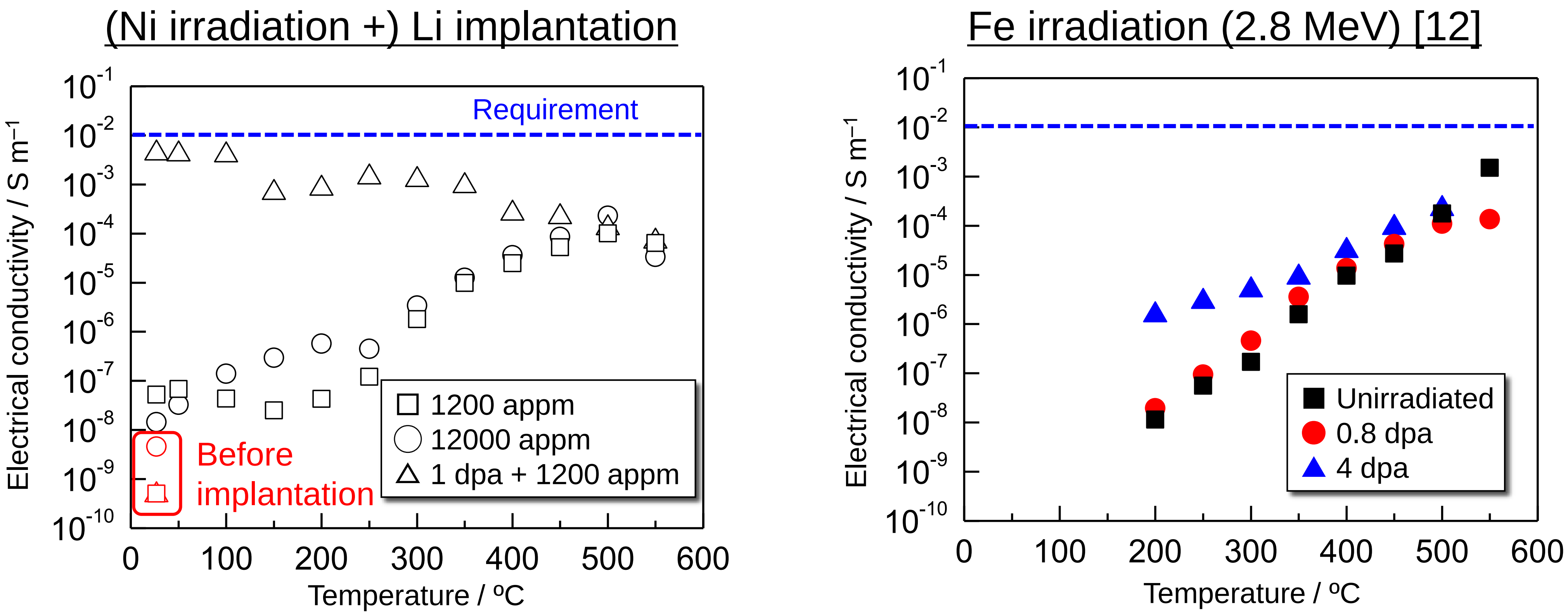


Electrical conductivity of ZrO_2-coated samples before and after Ni irradiation and Li implantation at R.T.

- Each sample showed increase in electrical conductivity after Li implantation with and without Ni irradiation, while Li dose dependence was not clear.
- Some areas exceeded the upper limit (10^{-2} S m^{-1}).
- The coated sample with irradiation damage and Li implantation showed 3–7 orders of magnitude higher conductivities after irradiation/implantation.

Recoil Li and irradiation damage increase electrical conductivity in ceramic coatings.

Results and discussion Li implantation effect

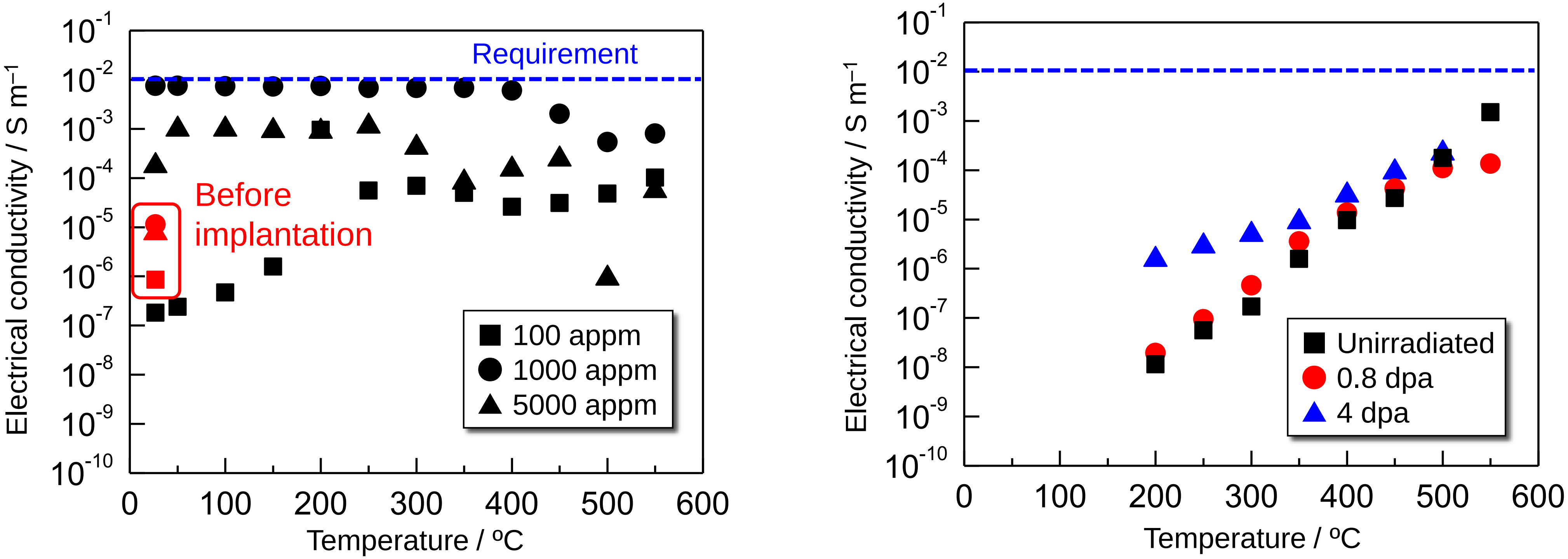


Electrical conductivity of ZrO_2-coated samples before and after Ni/Fe irradiation and Li implantation at R.T.

- Li implantation of up to 1.2 at% did not largely affect electrical conductivity, which shows less effect than a 4 dpa-damaged coating.
- Sequential irradiation and implantation drastically increased the electrical conductivity of the ZrO_2 coating, while the conductivity showed similar values at > 450 ºC probably due to damage recovery and ion diffusion.

[12] H. Fujiwara *et al.*, Fusion Eng. Des. 191 (2023) 113509.

Results and discussion Fe implantation effect



Fe implantation (1.0 MeV)

Fe irradiation (2.8 MeV) [12]

Electrical conductivity of ZrO_2-coated samples before and after Fe implantation/irradiation at R.T.

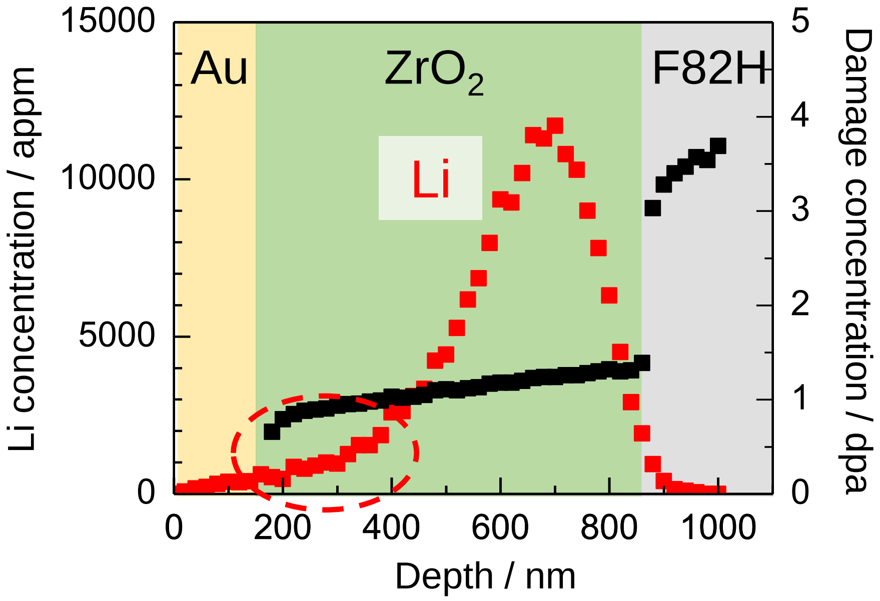
- The ZrO_2-coated samples with 1000 and 5000 appm Fe showed 1–3 orders of magnitude higher conductivity after implantation and became the values similar to unirradiated and irradiated samples at > 400 ºC probably due to ion diffusion.
- Fe implantation effect on electrical conductivity was higher than that of Li and Fe irradiation even lower implantation/irradiation doses.

[12] H. Fujiwara *et al.*, Fusion Eng. Des. 191 (2023) 113509.

Results and discussion Mechanism

Li implantation vs. Ni irradiation + Li implantation

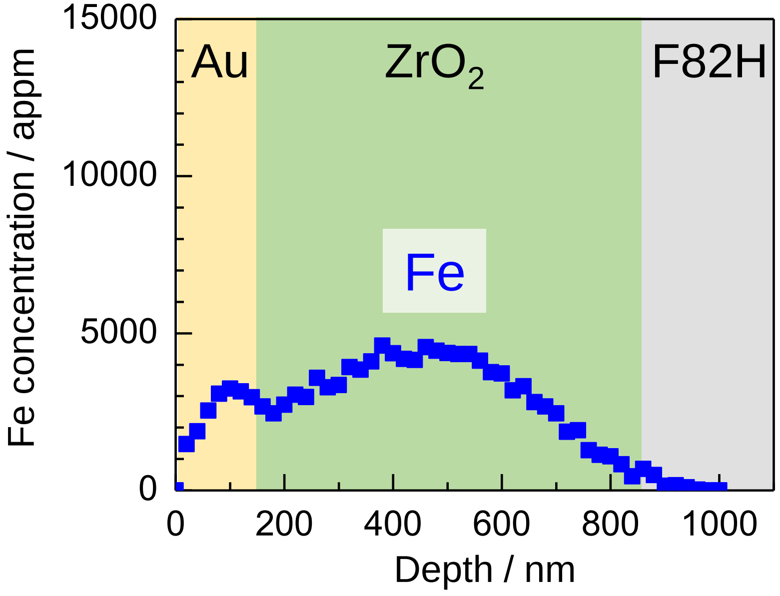
- ☐ In Li implantation, Li concentration near the surface is relatively low, resulting in fewer electron paths through the coating.
- ☐ The defect distribution was rather uniform through the sample irradiated using 6.0 MeV Ni, indicating that the irradiation damage helped creating channels for electron transport.



Li depth profile after 250 keV-Li implantation with damage distribution by 6.0 MeV-Ni irradiation.

Li implantation vs. Fe implantation

- ☐ 1.0 MeV-Fe implantation brought rather uniform ion distribution with displacement damage than that of Li-implanted sample, resulting in the increase in electrical conductivity because the channels would be connected through the coating.
- ☐ Note: since the range of recoil Fe in ZrO_2 is ~0.25 μm, the effect in the actual Li-Pb blanket will be different.



Fe depth profile after 1.0 MeV-Fe implantation.

Summary

Effects of recoil ions on electrical conductivity in ceramic coatings were investigated to understand possible changes in the performance of functional coating in Li-Pb blanket systems.

- ☐ Implanted Li and Fe increase electrical conductivity in ceramic coatings and increase more with heavy ion irradiation.
- ☐ The depth distributions of irradiation damage and implanted ions through the ceramic coatings affect magnitude of the increase in electrical conductivity.
- ☐ The effect of implanted ions and introduced irradiation damage decreases at high temperatures due to diffusion of implanted ions and damage recovery.

Future investigations

- ☐ Li-Pb exposure tests for ceramic-Fe joint coating after Li implantation to understand the Li effect on corrosion behavior.
- ☐ Hydrogen permeation measurements for Li/Fe implanted ceramic coatings.