§17. Hydrogen Permeability of Nitrided Stainless Steel

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Molten fluoride salts such as Flibe and Flinak have high potential for liquid blanket in nuclear fusion reactors. [1] The structural materials for the blanket require compatibility with fluoride salt high operation at temperature over 500°C. At the same time, inventory of the bred tritium inside the blanket system must be strictly controlled. Nitride has compatibility with fluoride salt.[2] And surface nitriding technique of metal surface based on electrochemistry in molten fluoride salt was applied.[3] Prior to tritium permeability measurement, hydrogen permeability was measured. This study presents hydrogen permeability of 316 stainless steel (316 SS) with nitride surface layer.[4]

For hydrogen permeability measurement, 316SS coin shape specimens (diameter = 12.0mm, thickness = 1.0mm) were treated by potentiostatic treatment at 600°C at 1.0V versus Li^+/Li. in LiF-KF-Li_3N (mixture ratio of 49mol% LiF, 49mol% KF and 2.0mol% Li_3N) for 240 min. Nitride layer with 70 μm of the thickness were formed at the surface. It consisted of CrN and α-$Fe_{x(x>8)}$N. Steady-state hydrogen permeability was evaluated by a build up method at a constant temperature in the range between 450 and 650°C. The specimen separates the system into high pressure side and low pressure side. After evacuating to 10^{-5} Pa in the both sides, hydrogen gas was filled at a constant pressure ranging from 1.0 to 40 kPa in the high pressure side. The hydrogen flux through the specimen was measured by quadrupole mass spectrometry.

Permeation flux of the nitrided 316 SS specimen was twice as much as that of the bare 316 SS specimen at low temperature around 450°C. When hydrogen pressure was applied to the specimens, permeation through the nitrided 316SS rose up more slowly to reach steady flux than that of bare 316SS. Nitriding could increase solubility and simultaneously limit diffusion. However, these differences between bare and nitrided 316SS specimens diminished with rising temperature. Using permeability P, hydrogen pressure introduced into the high pressure side p, and thickness of the specimen d, permeation flux J is defined,

$$J = \frac{Pp^n}{d}. \qquad (1)$$

The exponent n relates to permeation regime. Diffusion limits permeation when n = 0.5, following Sieverts' law, while surface recombination limits that when n = 1.[5] Activation energy of permeation E_P, gas constant R and absolute temperature T and assuming exponent n = 0.5, permeability is

$$P = \frac{Jd}{\sqrt{p}} = P_0 \exp\left(-\frac{E_P}{RT}\right). \qquad (2)$$

Figure 1(a) shows hydrogen permeability of bare 316SS and nitrided 316SS from 450°C to 650°C. Bare 316 SS specimen has permeation behavior consistent with result evaluated by T. Shiraishi et al.[6] The permeability of the nitrided 316 SS specimen seems to have linearity over 500°C. However, it was slightly larger than that of the bare 316SS specimen. The permeability increase was more remarkable under 500°C. The activation energy of the nitrided specimen in diffusion process was about 6.7 J/mol in the temperature range over 500°C. It is consistent with that of bare 316 SS. Figure 1(b) shows hydrogen pressure dependence of permeation flux in temperature range from 450°C to 650°C. Gradient of the lines corresponds to exponent n. It was 0.75 at 450°C and approached to 0.55 at elevated temperatures. Permeation flux looks to be proportional to the square root of pressure over 500°C. While permeability seems to be limited by diffusion process, i.e., ruled by Sieverts' law over 500°C, it apparently deviates from the law around 450°C.

While exponent n of the bare 316 SS was about 0.55, that of the nitrided 316 SS at 450°C was 0.70 and swerved from n = 0.5, i.e. Sieverts' law. This result suggests that the nitrided layer affects on permeation of nitrided 316 SS. Several reports have demonstrated nitrides as a hydrogen diffusion barrier.[7-11] The experimental results, however, was different from that. Instead of formation of CrN and α-$Fe_{x(x>8)}$N, the nitride layer enhanced permeability at the temperature below 500°C. When the specimen surface is electrochemically nitrided, various nitrides can be formed depending on temperature. These experimental results suggest that nitride composition exerts a strong influence on hydrogen permeability.

(a) (b)

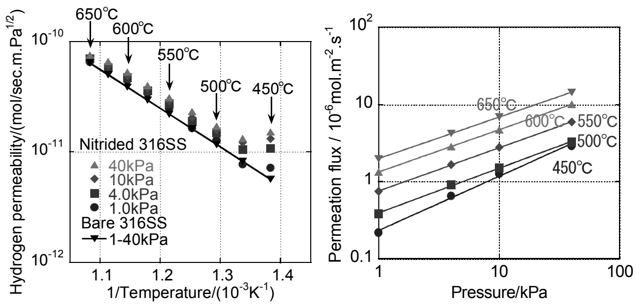

Fig.1. Temperature dependence of hydrogen permeability. (a) Hydrogen permeability and (b) permeation flux.

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