Nitriding Treatment of Reduced Activation Ferritic Steel as Functional Layer for Liquid Breeder Blanket[*]

Masatoshi KONDO, Takashi WATANABE[1], Teruya TANAKA[2], Dongxun ZHANG[1] and Akio SAGARA[2]

Tokai university, 4-1-1 Kitakaname, Hiratuka 259-1292, Japan
[1]*The graduate university for advanced studies, 322-6 Oroshi-cho, Toki 509-5292, Japan*
[2]*National Institute for Fusion Science, 322-6 Oroshi-cho, Toki 509-5292, Japan*

The development of functional layers such as a tritium permeation barrier and an anti-corrosion layer is the essential technology for the development of a molten salt type self cooled fusion blanket. In the present study, the characteristics of a nitriding treatment on a reduced activation ferritic steel, JLF-1 (Fe-9Cr-2W-0.1C) as the functional layer were investigated. The steel surface was nitrided by an ion nitriding treatment or a radical nitriding treatment. The nitridation characteristic of the steel surface was made clear based on the thermodynamic stability. The thermal diffusivity, the hydrogen permeability and the chemical stability in the molten salt Flinak were investigated. The results indicated that the nitriding treatment can improve the compatibility in the Flinak without the decrease of the thermal diffusivity, though there was little improvement as the hydrogen permeation barrier.

1. Introduction

The functional layers such as a tritium permeation barrier and an anti-corrosion layer coated on structural materials are the essential technology for a molten salt type self cooled fusion blanket [1]. The candidates are the stable oxides or nitrides, such as Er_2O_3, Y_2O_3 and AlN [2]. Then, the coating method of these materials has been developed [3,4]. Nitriding is a known process to improve the mechanical property of a steel surface. However, the information of the nitriding treatment as the functional layer was limited so far. In the present study, the nitriding treatment of a reduced activation ferritic steel was performed by an ion nitriding treatment and a radical nitriding treatment. The nitridation characteristic of the surface was discussed based on the thermodynamic stability. The thermal diffusivity and the hydrogen permeability were experimentally investigated. The chemical stability in molten salt LiF-NaF-KF (Flinak) [5], which is the simulant fluid of LiF-BeF$_2$ (Flibe), was investigated.

2. Nitriding Treatment

The test material used for the nitriding treatment is a reduced activation ferritic steel, JLF-1 (JOYO-HEAT), and the chemical composition is 9Cr-1.98W-0.49Mn-0.2V-0.09C-0.015N-Fe balanced (wt%). The specimens
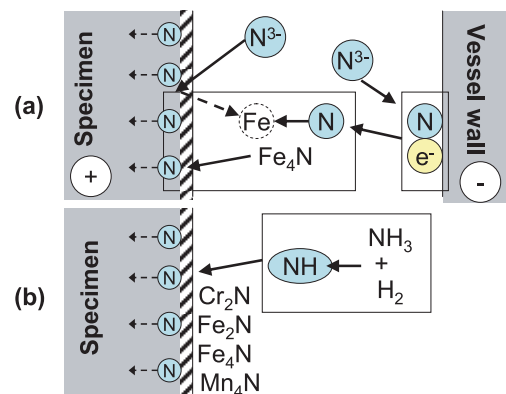

Fig. 1 Schematic mechanism of (a) ion nitriding treatment and (b) radical nitriding treatment.

were heat-treated at 1050°C/3.6 ks/air cooled (normalizing) and 780°C/3.6 ks/air cooled (tempering). The size was 15 mm × 10 mm × 1 mm, and the surface was finely polished. The specimen nitrided in an ion nitriding treatment process (IN/JLF-1) was prepared by an ion sputtering and nitrides deposition in glow discharge condition. The specimen nitrided in a radical nitriding treatment (RN/JLF-1) was chemically nitrided by reactive NH radical, which was made by glow discharge in the gas mixture of hydrogen and ammonia [6]. Figure 1 shows the schematic mechanism of the ion nitriding treatment and the radical nitriding treatment. Table 1 shows the treatment conditions.

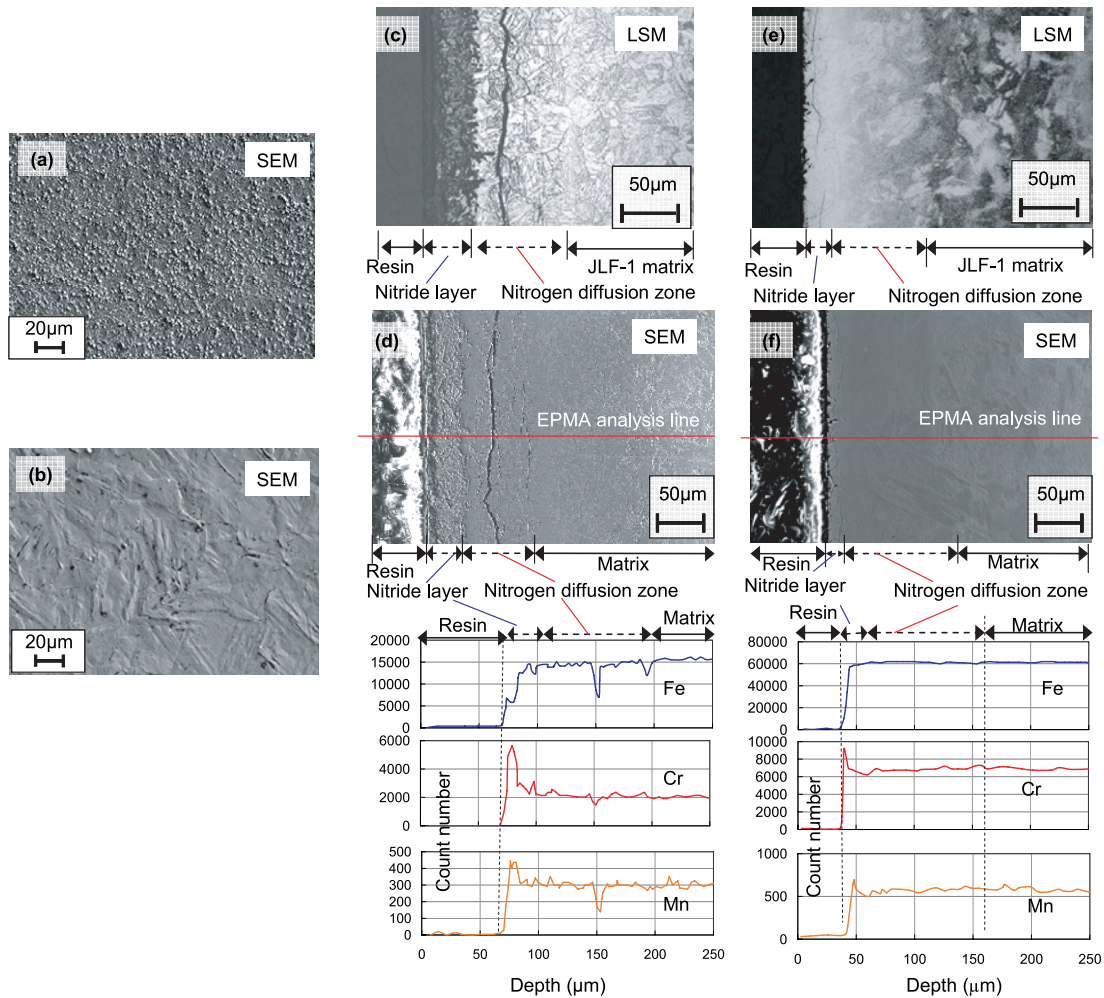Figures 2 (a) and (b) show scanning electron micro-

Fig. 2 Analysis on surface and cross section of specimens by LSM and SEM/EPMA, (a) Surface SEM image of IN/JLF-1 specimen, (b) Surface SEM image of RN/JLF-1 specimen, (c and d) surface cross sectional analysis on IN/JLF-1 and (e and f) surface cross sectional analysis on RN/JLF-1.

Table 1 Conditions of nitriding treatment.

	Ion Nitridation (IN/JLF-1)	Radical nitridation (RN/JLF-1)
Temp.	560 °C	450 °C
Time	5 hour	5 hour
Gas	N_2:H_2:Mix gas = 2:1:1 (Mix gas: N_2 and CO)	H_2:NH_3 = 8:2 (130 Pa)

scope (SEM) images of the specimens' surfaces after the ion nitriding and the radical nitriding process, respectively. The analysis results by electron probe micro analyzer (EPMA) indicated as the nitrogen concentration on the surface was 4.6 wt% (13.4 at%) for IN/JLF-1 and 1 wt% (4 at%) for RN/JLF-1. The surface with the deposited nitrides was observed after the ion nitriding treatment. The surface might be deformed because of the expansion of the specimen by the radical nitriding treatment.

Figures 2 (c-f) show the cross sectional images of the specimen surface analyzed by laser scanning microscope (LSM) and SEM/EPMA after the etching procedure in NaOH solution. In the IN/JLF-1 specimen, a porous nitride layer observed (Figs. 2 (c and d)). In the RN/JLF-1 specimen, there was the nitrided layer in white color consists of thin nitride layer and thick nitrogen diffused layer (Figs. 2 (e and f)). It was found that the layer was uniformly formed though the matrix had complicate microstructure due to the martensite lath structure.

The results of the EPMA analysis for the surfaces showed that Cr and Mn were enriched at the edge of the surface in both specimens (Figs. 2 (d and f)). This layer can be Cr and Mn rich Fe-Cr-Mn nitride layer according to the thermodynamic stability as indicated in Fig. 3. The nitride of Cr or Mn was more stable than that of Fe in the thermodynamic evaluation. Cr and Mn were enriched on the surface for the formation of the stable nitrides. In this process, nitrogen was released from the nitride on the specimen surface when the nitrides changed into more stable state, and diffused into the matrix of the steel.
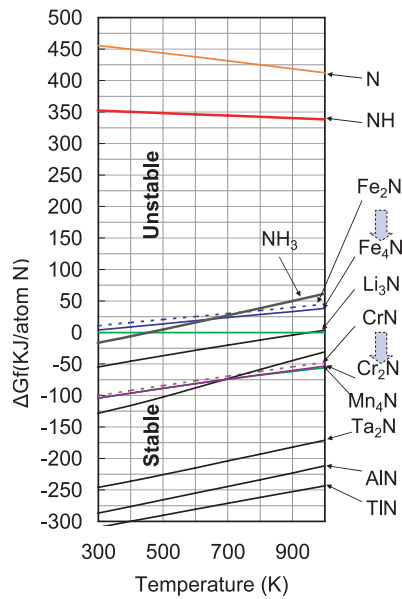
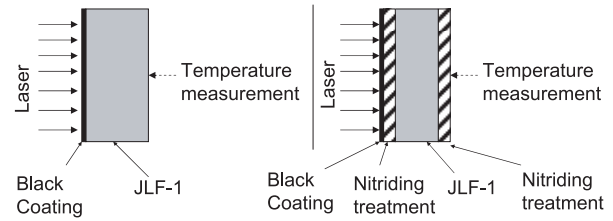Fig. 3   Gibbs standard free energy for formation of nitrides.

Fig. 4   Measurement of thermal diffusivity by laser flash method (a) JLF-1 (b) RN/JLF-1 and IN/JLF-1.

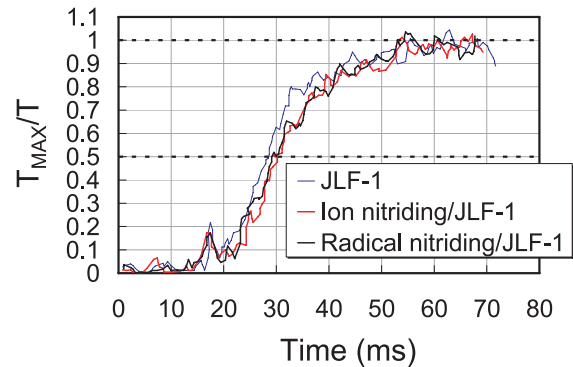
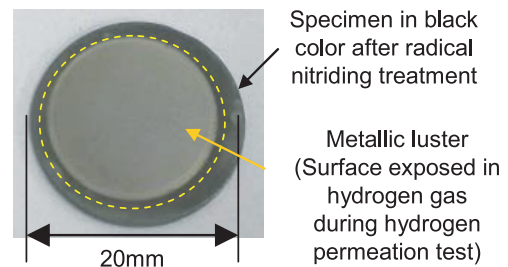Fig. 5   Temperature transient of specimen in laser flash experiment.

Fig. 6   RN/JLF-1 specimen after hydrogen permeation test.

The thickness of the nitride layer was evaluated by the depth of Cr enrichment in EPMA analysis results, and that was approximately 20 μm in the IN/JLF-1 specimen and 5 μm in RN/JLF-1 specimen. The layer formed by the radical nitriding treatment was thinner and more compact than that by the ion nitriding treatment.

3. Thermal Diffusivity of Treated Material

The influence of the nitriding treatment on the thermal diffusivity was investigated by means of laser flash method (Fig. 4). The thermal diffusivity of the treated specimen was estimated by so-called half-time method [7]. The initial temperature of the specimen was 31.40 °C. The output of the laser was 1 J. The laser irradiated area was 19.63 mm². The specimen surface was covered by black coating. The specimen thickness of JLF-1, IN/JLF-1 and RN/JLF-1 was 0.92 mm, 0.99 mm and 0.97 mm respectively. The experiment was carried out 5 times for each specimen. Figure 5 shows the one example of the temperature transient after the laser was irradiated to the specimen. The difference by the treatment was not detected. The averaged thermal diffusivity of JLF-1, IN/JLF-1 and RN/JLF-1 was 8.295×10^{-2} cm²/s, 8.498×10^{-2} cm²/s, and 8.188×10^{-2} cm²/s, respectively. The mean deviation of the value for each sample was approximately 5 %. This indicated that the treatment can not decrease the thermal diffusivity probably because the layer was much thinner than the steel matrix.

4. Hydrogen Permeability

The hydrogen permeability of the nitrided sample was investigated using the hydrogen permeation apparatus, which was reported in detail in ref. [8]. In this test, RN/JLF-1 specimen was selected since the layer on the specimen was more compact than that on the IN/JLF-1 specimen. The sample size was 20 mm in diameter and the thickness was 0.9 mm. The both sides of the specimen were nitrided. The permeation test was performed at 400 °C. The partial pressure for one side compartment was 40 kPa, and that for the other side was evacuating condition. Then, the transient of the hydrogen partial pressure was measured. The test results indicated that the hydrogen permeability of the RN/JLF-1 was 2.66×10^{-11} mol/m/s/Pa$^{0.5}$ and this was the same to that without the treatment [8]. The specimen after the test had metallic luster though the initial specimen was color in black (Fig. 6). This was because the Fe-Cr nitride layer was unstable in the atmosphere at high hydrogen concentration, and the layer was removed during the test. The possible chemical reaction between Cr_2N and hydrogen is
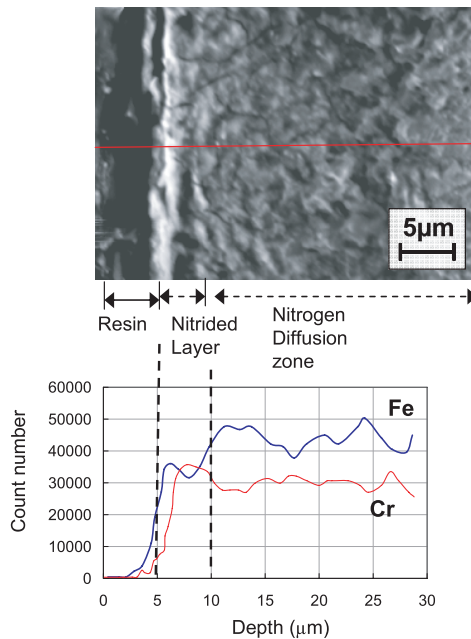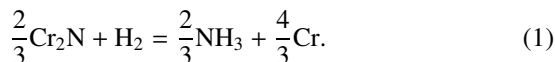
Fig. 7 Cross sectional SEM/EPMA analysis of RN/JLF-1 specimen after exposure to Flinak.

expressed as

$$\frac{2}{3}Cr_2N + H_2 = \frac{2}{3}NH_3 + \frac{4}{3}Cr. \tag{1}$$

The reaction energy was 60.2 kJ/mol, and the value indicated that Cr_2N was possibly reduced to Cr metal. Furthermore, Fe-Cr-Mn nitride might be more unstable for hydrogen.

5. Chemical Stability in Molten Salt Flinak

Molten salt Flibe was proposed to be used as liquid breeder in FFHR [1]. Flinak (LiF–KF–NaF) has similar chemical and thermal characteristics and can be used to the simulant fluid of Flibe (LiF–BeF$_2$). Flinak also has the potential to be a candidate for the tritium breeder in a self-cooled fusion blanket or as a secondary heat-transfer fluid of a blanket system. Then, Chemical stability of the RN/JLF-1 specimen in the Flinak was investigated by means of a static corrosion test. The specimen was immersed into the molten salt Flinak at a static condition at the temperature of 600 °C for 2216 hr. The crucible was made of JLF-1. The Flinak purified by an electro refining method [5] was used. The quantity of the Flinak was 3 cc. The impurity was Fe: 52.6 wppm, Cr: 2.6 wppm and H$_2$O

42.6 wppm. After the exposure, the specimen was picked up and rinsed in LiCl-KCl. Figure 7 shows the results of cross sectional analysis after the exposure.

The surface indicated that the chemical composition of the nitrided layer was the same to that before the exposure (Fig. 2 (f)). It was already made clear that the specimen without the nitriding treatment was corroded by an electrochemical corrosion at the boundary of the micro structure of the surface, due to the local difference of the chemical composition by the lath structure [5]. The electrochemical corrosion was not detected on the surface in the present work. The weight loss of the specimen was 0.08 g/m^2, and this was much lower than that obtained by the exposure of a naked JLF-1 specimen for 1000 hr (1.85 g/m^2). The nitriding layer uniformly covered on the complicated martensite lath structure decreased the local difference of the electro potential on the surface. Then, the electrochemical corrosion was suppressed.

6. Conclusion

The nitridation characteristics of JLF-1 by the ion nitriding treatment and the radical nitriding treatment were investigated. It was found that the Cr and Mn rich Fe-Cr-Mn nitrides were formed on the surface. The nitriding treatment can improve the compatibility in the Flinak, because the nitrogen diffusion layer uniformly covered on the surface decreased the local difference of the electro potential for the electrochemical corrosion. The nitridation did not decrease the thermal diffusivity. There was little improvement as the hydrogen permeation barrier possibly because the Fe-Cr-Mn nitride was not stable in the atmosphere at high hydrogen concentration.

[1] A. Sagara et al., Fus. Sci. and Tech. 47, 524 (2005).
[2] T. Watanabe et al., J. Plasma Fusion Res. SERIES 9, 342 (2010).
[3] H. Hishinuma et al., J. Nucl. Mater., in press (2011).
[4] D. Zhang et al., Fus. Eng. and Design, in press (2011).
[5] M. Kondo et al., Fus. Eng. and Design 85, 1430 (2010).
[6] K. Fukada, Journal of the JSTP, vol.40, 13 (1999).
[7] W.J. Parker, R.J. Jenkins, C.P. Butler and G.L. Abbot, Journal of applied physics 32, 1679 (1961).
[8] D. Zhang, T. Tanaka and T. Muroga, J. Nucl. Mater., in press (2011).