Technical Report

Development of Stainless Steel Applications to ENE-FARM

Mitsuki SUGEOI* Masaharu HATANO
Atsutaka HAYASHI Hiroyuki MATSUYAMA

Abstract

We have summarized the suitability of the high Si stainless steel to fuel reformer and 22Cr-1.2Mo steel to interconnector. The reforming gas advanced the oxidation even by 650°C under low P_{O2} by H_2O, CO and CO_2 gas, and the oxide film of SUS310S became thicker than in air. High Si type NSSC™ 305B and NSSC FH11 formed a continuous Si oxide film directly under the Cr_2O_3 oxide film in the reformed gas, and exhibited better oxidation resistance than SUS310S. NSSC 220ECO has low thermal expansion and high-temperature strength that are equal to or higher than those of typical SOFC interconnect alloys, and has good oxidation resistance in air at 800°C.

1. Introduction

More than 300 thousand household fuel cell systems in total that employ hydrogen to generate electric power (ENE-FARM) have been installed since after the introduction of the solid polymer fuel cell to the market in May, 2009 for the first time in the world (as of November, 2019).[1] The "Basic Energy Plan" decided by cabinet in April, 2014 supports a target plan of spreading ENE-FARM to 1 400 thousand households in 2020 and 5 300 thousand households (10% of all households) in 2030.[2]

A schematic diagram of ENE-FARM is shown in **Fig. 1**. An ENE-FARM consists of a fuel cell stack that generates electric power with hydrogen and oxygen, a fuel reformer that produces hydrogen from city gas and a hot water storage tank for the hot water heated by waste heat. The stainless steel having heat and corrosion resistance as shown in **Table 1** is used as components of these units.

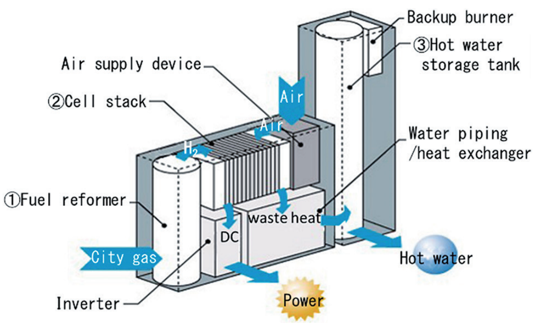

Fig. 1 Schematic diagram of household fuel cell system

The fuel reformer component is required to have oxidation resistance and high-temperature strength in a unique atmosphere that contains large amount of H_2 and H_2O and the balance of CO and CO_2 (hereinafter referred to as reformed gas), and SUS310S (25Cr-20Ni) (hereinafter referred to as 310S), a representative heat-resisting stainless steel, has been employed. For the fuel cell stack, either a polymer electrolyte fuel cell (hereinafter referred to as PEFC) or solid oxide fuel cell (hereinafter referred to as SOFC) is used. The interconnector of the former cell is required to have electric conductivity and corrosion resistance in a sulfuric-acid environment, and

Table 1 List of applicable materials for household fuel cell systems

Parts	Required features	Applicable materials
①Fuel reformer	Heat resistance of 300–800°C (oxidation resistance, strength)	310S: 25Cr-20Ni 305B: 19Cr-13Ni-3.5Si FH11: 18Cr-2.5Si-Nb
②Cell stack (for SOFC) /Interconnector	Heat resistance around 800°C (electrical conductivity, low thermal expansion coefficient, oxidation resistance)	220ECO: 22Cr-1.2Mo 445M2: 22Cr-1Mo
③Hot water storage tank	Crevice corrosion resistance	190: 19Cr-2Mo-Nb+Ti 220ECO: 22Cr-1.2Mo

* Researcher, Function Creation Research & Development Div., Research & Development Center, Nippon Steel Stainless Steel Corporation
3434 Ooaza-shimata, Hikari City, Yamaguchi Pref. 743-8550

therefore, carbon is employed.[3] The latter cell interconnector is required to have electric conductivity around 800°C and oxidation resistance in air, and stainless steel of the high Cr-system added with rare earth metals has been used.[4, 5] Since hot water storage tanks require crevice corrosion resistance, the high corrosion-resistant stainless steel of the high Cr-system containing Mo is used.

Recently, the ENE-FARM life has been prolonged and the sales price has lowered, and enhancement of the function and resource-saving of the component materials have become crucial. To replace 310S of the fuel reformer, Nippon Steel Stainless Steel Corporation has proposed and promoted the application of the following steels: NSSC 305B (19Cr-13Ni-3.5Si) (hereinafter referred to as 305B) and NSSC FH11 (18Cr-2.5Si-Nb) (hereinafter referred to as FH11) of the high Si system. The use of rare earth metals such as Ni and Cr is reduced or eliminated in the steel. Furthermore, for the SOFC interconnector, the application of SUS445J1 (22Cr-1.2Mo) that does not contain rare earth metals (hereinafter referred to as 445J1) has been promoted. This article describes the application of stainless steel to the fuel reformer and SOFC interconnector wherein the heat resistance property is considered crucial.

2. Study on Applicability to ENE-FARM

The applicability of the stainless steel was studied by calculating the thermodynamic characteristics in the operating environment and by the detailed analysis of the oxide film formed in the oxidation test conducted in the target environment. The practicability of the stainless steel selected through such analysis was evaluated by an endurance test of about 7000 h in the real environment.

The fuel reformer produces hydrogen by steam-reforming the fuel of the hydrocarbon system like city gas using a catalyzer. The operating temperature of the fuel reformer is around 650°C, and the reformed gas consists of large amount of H_2 and H_2O and the balance of CO and CO_2. The reformed gas has a unique atmosphere in which the oxidation-promoting agents such as H_2O, CO and CO_2[6] exist in the reductive H_2 gas.

Figure 2 shows the result of the thermodynamic calculation of the oxygen potentials (hereinafter referred to as P_{O2}) in the reformed gas and in air. P_{O2} at 650°C was obtained from the calculation by using the thermodynamic calculation software MALT (1st Version). From this, P_{O2} in the reformed gas is significantly lower than that in

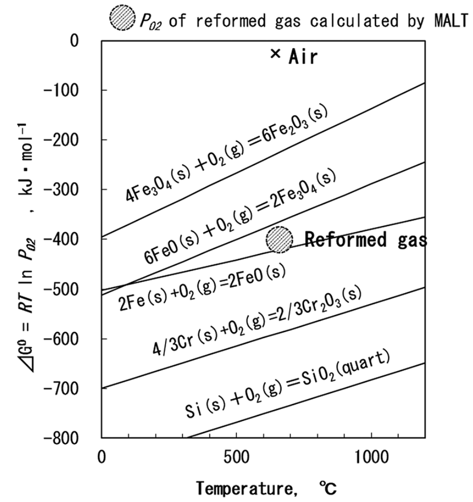

Fig. 2 Relationship between oxygen potential in reformed gas atmosphere and standard generation free energy of oxides

air, and smaller than the reducing pressure of Fe_3O_4. In addition, from the calculation viewpoint, the P_{O2} value doesn't change even if H_2 is replaced by N_2. From this P_{O2} value, in the reformed gas, progress in oxidation seems to be suppressed. However, since the reformed gas contains a large quantity of H_2O, promotion of oxidation by the steam oxidation mechanism[6] is also conceivable. Si is an effective element that forms a protective oxide film under low P_{O2},[7] and in addition, reveals oxidation resistance characteristics in the steam-oxidizing atmosphere.[8–10] Based on the P_{O2} calculation and already available expertise,[7–10] applying the stainless steel of the high Si system to the reform gas environment was considered and then developed.

The SOFC interconnector requires the component material to have a small difference in a thermal expansion coefficient from ceramics and to have sufficient tensile strength around 800°C, and furthermore, the oxidation resistance characteristic with respect to the air electrode becomes problematic. NSSC 220ECO (22Cr-1.2Mo) (hereinafter referred to as 220ECO) which is a general-use corrosion-resistant stainless steel[11] was designed to be an alternative replacement for the rare-earth-metal-containing SOFC interconnector alloys (Crofer).

3. Test Method

3.1 Oxidation test in reformed gas

Test pieces were taken from 310S that has already been applied to fuel reformers, 305B of the high Si system and FH11. The chemical compositions are shown in **Table 2**. The atmospheric gas of the oxidation test was composed of a mixture of H_2, or N_2-based H_2O, CO and CO_2. The surface finish of the test piece was #600 wet-polished or the same as that of the finished product. After the oxidation test, the measurement of the weight gain by oxidation (hereinafter referred to as ΔW) and the observation of the appearance were conducted. The oxide film was analyzed by glow discharge optical emission spectrometry (hereinafter referred to as GDS), X-ray diffractometry (CuK α ray) and an electron probe microanalyzer (hereinafter referred to as EPMA).

The practicability of 305B was evaluated by a 7000 h endurance test conducted in a real operating environment. After the endurance test, the thickness of the oxide film was measured by the observation of its cross-section with an optical microscope. The structure of the oxide film was examined by the analysis of the map obtained by scanning electron microscope/energy dispersive X-ray spectroscopy (hereinafter referred to as SEM/EDS).

3.2 Various evaluations of materials for interconnector usage

Test pieces were taken from Crofer 22APU8, a steel exclusively used for SOFC interconnector steel (hereinafter referred to as Crofer) and 220ECO. The chemical compositions are shown in **Table 3**. The linear expansion coefficient (hereinafter referred to as the thermal expansion coefficient) was measured by the horizontal difference detection method in the range from room temperature (20°C) taken as the base up to 800°C. With respect to the tensile strength,

Table 2 Chemical compositions of test pieces for oxidation test in reformed gas atmosphere

(mass%)

	C	Si	Mn	Cr	Ni	Al	Nb	N
310S	0.04	0.47	1.06	25.2	18.9	0.03	0.01	0.03
305B	0.05	3.28	0.76	19.1	13.9	0.01	0.01	0.01
FH11	0.01	2.57	0.28	17.9	0.1	0.02	0.27	0.01

Table 3 Chemical compositions of evaluation various test pieces for interconnectors

(mass%)

	C	Si	Mn	Cr	Mo	N	La
220ECO	0.007	0.15	0.14	22.2	1.2	0.014	–
Crofer 22APU	0.007	0.03	0.43	22.6	–	0.004	0.07

sheet test pieces having a 10 mm parallel section and a 35 mm gauge length were prepared, and measured at 20°C and in the range of 200°C to 800°C. The tension rate was 0.1 mm/min until 0.2% proof stress was reached, and 3 mm/min thereafter until fracture. The oxidation resistance was evaluated by a 1 000 h-continuous oxidizing test in air of 800°C. The oxide film formed in the oxidation test was examined by GDS and X-ray diffractometry (CuK α ray).

4. Result of Experiment and Consideration

4.1 Oxide film formed in reformed gas

ΔW obtained in the oxidation test of 100 h at 650°C in air and reformed gas is shown in **Fig. 3**. ΔW obtained in the reformed gas is 1.7 times larger than the one obtained in air, and the development of oxidation in reformed gas was confirmed. The appearance of the oxide film developed in air exhibited a grey tone while the one developed in the reformed gas was dark green, that is, color tone of oxide film was different.

In **Fig. 4**, the concentration profiles of Fe, Cr, Ni, Si, Mn and O from the surface of the oxide film obtained by GDS analysis are shown. The thickness of the oxide film was estimated by the half-value width of O where the intensity of the O concentration profile is reduced to half. The oxide film developed in air consists of Cr oxide with a thickness of below 0.2 μm, and Mn was concentrated in the outer layer of the oxide film, and Si was concentrated on the interfacial surface between the oxide film and the base metal. In the meantime, the oxide formed in the reformed gas consists of Cr oxide, and the thickness is about 0.3 μm, and larger than the one developed in air. Mn was concentrated in the inner layer of the oxide film, and Si was recognized in the entire region of the oxide film. The selective oxidation of Mn and Si is judged to have progressed in the reformed gas under low P_{O_2}. From the structural analysis of the oxide by X-ray diffractometry, the oxide film formed Cr_2O_3 in its outer layer, and $(Cr,Mn)_3O_4$ in its inner layer. This result corresponds to the change of the color tone to dark green in the reformed gas oxidation (color tone of Cr_2O_3).

The progress of the oxidation in the reformed gas is considered to be attributed to the deterioration of the protection of the oxide film due to the formation of $(Cr,Mn)_3O_4$ in the inner layer of the oxide film that has defect density higher than that of Cr_2O_3.[12)]

4.2 Influence of Si on oxide film

Figure 5 shows ΔW of 310S and 305B after 100 h and 1 000 h at 650°C. ΔW of 305B is 0.8 times that of 310S after 100 h, and 0.5 times that of 310S after 1 000 h, respectively. In 305B that contains Si, oxide film is thin, and the oxidation resistance in reformed gas was found to be higher than that of 310S.

The results of GDS analysis and X-ray diffractometry measurement of 305B after the 1 000 h test are shown in **Fig. 6**(a) and (b), respectively. Figure 6(a) shows that the oxide film thickness is about 0.7 μm, and the concentrations of Fe, Ni and Si in the outer layer are high. On the interfacial surface between the oxide film and the base metal, the concentration of Si in addition to the concentration of Cr is observed. In addition, considering the result of X-ray diffraction of oxide film, as shown in Fig. 6(b), it is interpreted that, in the oxide film, $(Fe,Cr)_3O_4$ and Fe_2SiO_4 are formed in the outer

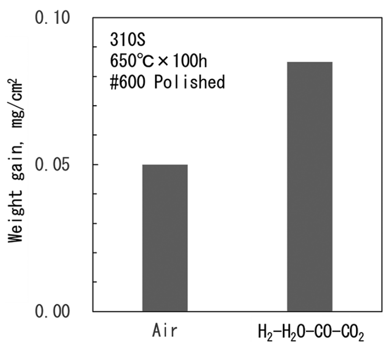

Fig. 3 Weight gain after oxidation test of 100 h at 650°C

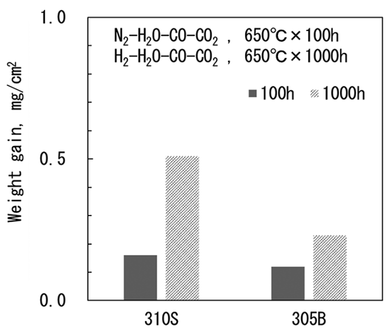

Fig. 5 Weight gain after oxidation test of 100 h and 1 000 h at 650°C

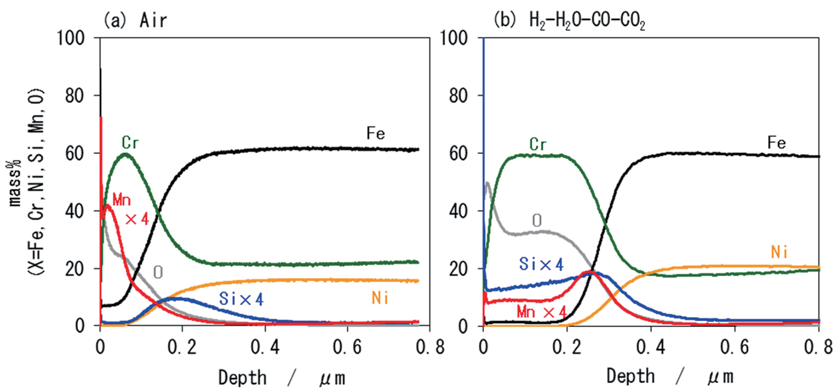

Fig. 4 Concentration profile of Fe, Cr, Ni, Si, Mn, O from surface of oxide film after oxidation test of 100 h at 650°C

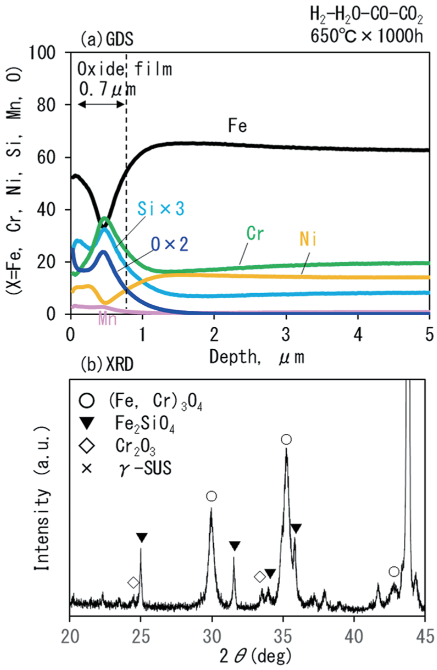

Fig. 6 Structural analysis of oxide film of 305B after 1 000 h oxidation test at 650°C

layer and Cr_2O_3 is formed in the inner layer. The concentration of Si on the interfacial surface detected by GDS may suggest the existence of a thin SiO_2 film that X-ray diffraction is unable to capture. In the meantime, the thickness of the 310S oxide is about 1.2 μm, in which the concentration of Si on the interfacial surface is not observed. The crystalline structure of the oxide detected by X-ray diffraction is scarcely different from that of 305B. From these results, the resistance to oxidation of 305B is improved by the formation of the Cr_2O_3 film, further characterized by the concentration of Si on the interfacial surface and the formation of Fe_2SiO_4 in the outer layer.

As a factor that made the 305B oxide film thinner than that of 310S, the following is considered. Si enriched on the interfacial surface suppressed the oxidation of Fe and the growth of Cr_2O_3 with the reduction of P_{O_2} on the interfacial surface with ferrite. These effects are also known as a mechanism for improving oxidation resistance of the stainless steel of the high Cr system under steam.[8] Fe_2SiO_4 is considered to be formed by the selective oxidation of Si in the reformed gas under low P_{O_2}. The ratio of Fe_2SiO_4 contained in the oxide film in the outer layer is about 0.1 according to the estimation based on the integration strength $(Fe_2SiO_4)/(Fe,Cr)_3O_4$ of X-ray diffraction, and therefore contribution to the improvement of oxidation resistance is considered to be small. From the above, the oxide film of 305B is considered to be made thinner by Si concentrated beneath Cr_2O_3.

Subsequently, a 100 h oxidation test at 650°C in the reformed gas was conducted for FH11 of ferritic (α) stainless steel. With respect to ΔW after the test, as compared with 0.17 mg/cm^2 of 310S, the value of FH11 was 0.03 mg/cm^2, and was greatly reduced. The result of the observation of the FH11 oxide film by EPMA is shown in **Fig. 7**. The oxide film is 0.4 μm thick, and mainly consists of Cr, and a continuous Si film is recognized on the interfacial surface between the oxide film and the base metal. From this, in FH11 of the α system, a thin continuous SiO_2 film is discovered on the interfacial surface between the 0.4 μm oxide film and the base metal, and the

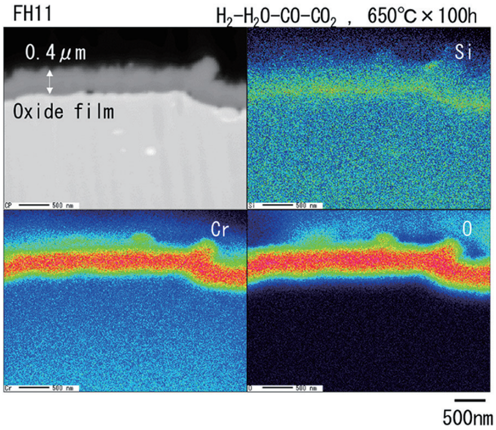

Fig. 7 EPMA analysis of oxidation film after oxidation test of 100 h at 650°C

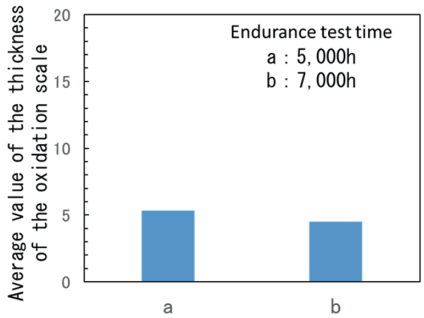

Fig. 8 Result of endurance test at real environment for 305B

enhancement of oxidation resistance by the addition of Si was remarkable as compared with the case of 305B of austenitic (γ) stainless steel. As a factor that enhanced oxidation resistance, the increase of the Si diffusion rate as a result of the change in crystal structure (from face-centered cubic (FCC) to body-centered cubic (BCC)) is considered. The diffusion rate coefficient of replacement type elements in BCC is 10 times higher than that of FCC.[13] The diffusion distance at 100 h at 650°C is calculated as about 2.5 μm in the α system, and estimated as less than 0.3 μm in the γ system. Owing to such difference in the crystal structure, it is considered that a continuous SiO_2 film is more readily formed in the α system.

4.3 Example of evaluation in real environment

In **Fig. 8**, the result of the endurance test for 305B in a real environment is shown. The oxidized scale thickness of test pieces a and b after tests of 5 000 h and 7 000 h was measured by the observation of the cross section. The average thickness of the oxidized scale of the test pieces a and b is about 5 μm. Judging from the growth rate of the oxide,[14] the oxidized scale is estimated to be the oxide of Cr_2O_3 to Fe_2CrO_4.

Figure 9 shows examples of the result of the observation of the oxidized scale section by SEM/EDS. The bright contrast area of Cr and O indicate the oxide films of Cr_2O_3 and $(Fe,Cr)_3O_4$ formed on the steel surface. Si is concentrated on the interface of the oxide and base metal, and the formation of a continuous Si film is revealed. Based on this, in 305B also, the effect of a continuous film of Si formed on the interface of oxide and base metal on enhancing oxidation resistance was recognized similarly to the case of FH11. Based on the endurance test result as above-stated, the stainless steel of the high Si system like 305B and so forth is installed on the fuel reformer of ENE-FARM (**Fig. 10**).

4.4 Applicability of 220ECO to interconnector

Figure 11 shows the result of the comparison of the thermal expansion coefficient of 220ECO in the temperature zone of 200°C to 800°C with that of Crofer. 220ECO shows smaller values compared with that of Crofer, and exhibits a thermal expansion coefficient equal to or below that of the alloy for the interconnector. In general, the thermal expansion coefficient of the stainless steel of the α system containing a high amount of Cr becomes smaller.[15] Since the amounts of Cr of Crofer and 220ECO hardly differ, in 220ECO, the addition of Mo of about 1% is considered to contribute to the decrease of the thermal expansion coefficient.

Figure 12 shows the high-temperature strength of 220ECO and Crofer in a range of 200°C to 800°C. The high-temperature strength of 220ECO is higher than that of Crofer, and in particular higher by about 150 MPa in the 600°C to 700°C range. Such high-temperature strength is comparable to that of Crofer 22H[5] that have high-temperature strength by addition of W and Nb. Thus, 220ECO achieved higher high-temperature strength by intensifying the solid-solution of Mo added to enhance corrosion resistance.

Subsequently, the long-term protection capability of oxidized film of 220ECO and Crofer was evaluated by a 1000 h continuous oxidation test at 800°C in air. **Figure 13** shows the concentration profiles of Fe, Cr, Mn and O from the surface obtained by analyzing the oxidized film by GDS. The thickness of the oxide film was estimated in the same manner as that introduced in Section 4.1. The oxide film of 220ECO is of the Cr oxide 1 μm thick, in which outer layer Mn is concentrated. On the other hand, the oxide film of Crofer is of the Cr-Mn oxide 2 μm thick, and Fe was also detected in the oxide film. Based on the structure analysis of the oxide by X-ray

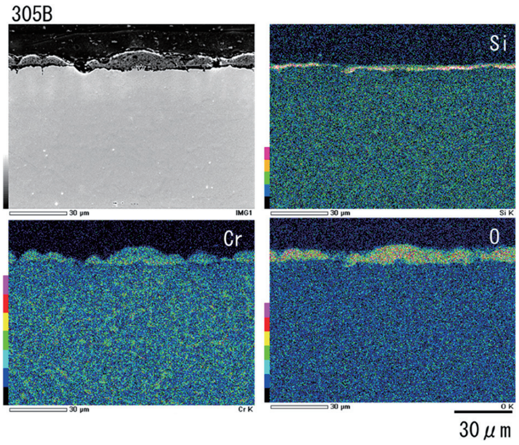

Fig. 9 Cross-sectional SEM/EDS analysis of oxidation scale formed on 305B in endurance test

Fig. 10 Panasonic ENE-FARM 2017 model

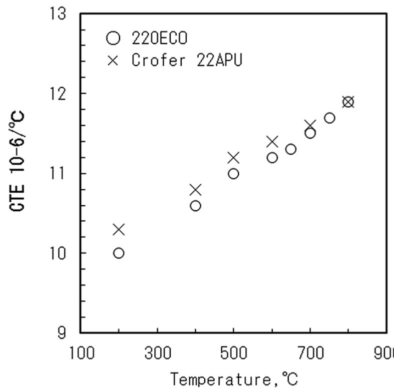

Fig. 11 Coefficient of thermal expansion from 200°C to 800°C

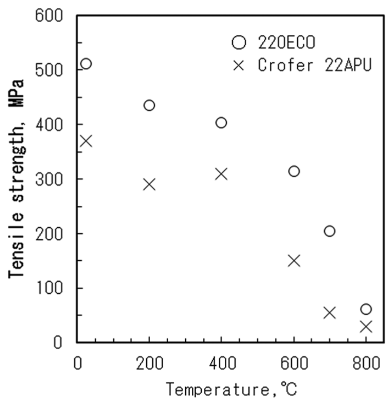

Fig. 12 Tensile strength from 20°C to 800°C

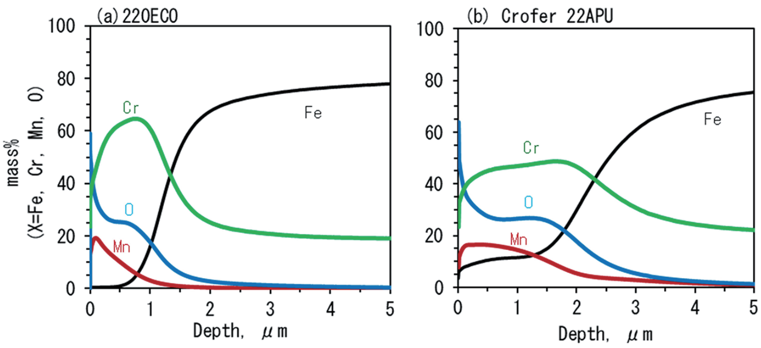

Fig. 13 Concentration profile of Fe, Cr, Mn, O from surface of oxide film after oxidation test of 1000 h at 800°C

diffractometry, Cr oxide is found as Cr_2O_3, and Cr-Mn oxide as $(Cr,Mn)_3O_4$. From this, the oxide film of 220ECO consists of Cr_2O_3, and the protection capability in air at 800°C is better than that of Crofer.

Thus, 220ECO is considered to be equipped with low thermal expansion and high-temperature strength equivalent to or superior to those of the representative interconnector alloy, and the oxidation resistance at 800°C in air is also comparable.

5. Conclusion

We have summarized the applicability of the stainless steel of the high Si system to the fuel reformer and of 22Cr-1.2Mo stainless steel to the interconnector.

In the reformed gas, oxidation of stainless steel is promoted at 650°C by H_2O, CO and CO_2 despite low P_{O_2}, and the thickness of the oxide film of 310S becomes larger than the one formed in air. In 305B and FH11 of the high Si system, a continuous Si film is formed beneath the Cr_2O_3 film in the reformed gas, and it expresses oxidation resistance higher than that of 310S. 220ECO is equipped with low thermal expansion and high-temperature strength equivalent to or superior to those of the representative SOFC interconnector usage alloy, and the oxidation resistance at 800°C in air is also excellent.

Today, stainless steel of the high Si system (305B, so forth) is applied to the ENE-FARM fuel reformer, and 445J1 (220ECO, so forth) is applied to the interconnector.

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Mitsuki SUGEOI
Researcher
Function Creation Research & Development Div.
Research & Development Center
Nippon Steel Stainless Steel Corporation
3434 Ooaza-shimata, Hikari City, Yamaguchi Pref.
743-8550


Atsutaka HAYASHI
Senior Researcher
Coil & Sheet Products, Automotive Products Research & Development Div.
Research & Development Center
Nippon Steel Stainless Steel Corporation


Masaharu HATANO
Chief Researcher, Dr. Eng.
Function Creation Research & Development Div.
Research & Development Center
Nippon Steel Stainless Steel Corporation


Hiroyuki MATSUYAMA
Senior Manager
Coil & Sheet Products Development Gr.
Products Development Div.
Nippon Steel Stainless Steel Corporation