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Technical Report

Development of Heat-resistant Stainless Steel, NSSC™NCA-F

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Abstract

As high heat resistance and Cr vaporization resistance are required for materials used in solid oxide fuel cell (SOFC) parts, Al-containing ferritic stainless steels are often used. Since Al reduces the processability and ductility while improving the heat resistance, a material with improved processability and ductility is required. As a method of reducing Al while maintaining the heat resistance, the effectiveness of adding Ti or Nb was examined. As a result, Nb-added ferritic stainless steel could reduce the Al content to 1.5 mass% while maintaining the heat resistance, and a new steel grade NSSC NCA-F (18Cr-1.5Al-Nb-B) was developed. Since NSSC NCA-F consists of excellent heat resistance, processability, and ductility, it is already being used as a material for SOFC fuel reformers.

1. Introduction

For reduced emission of CO_2, the application of fuel cells has expanded over the last few years to stationary power generation systems, fuel cell vehicles (FCVs), etc. Of the various types of fuel cells available, polymer electrolyte fuel cells (PEFCs) and solid oxide fuel cells (SOFCs) have been put into practical use for households in appreciation of high efficiency of power generation.

Because the inside of a hot module, the power generation unit of a SOFC, can reach temperatures of up to 800°C at a maximum and is highly humid, the materials used for its components are required to have excellent resistance to oxidation at high temperature and Cr vaporization. A Cr-based oxide film forms on the surface of stainless steel for general use, but because Cr oxide has a certain vapor pressure in a high temperature environment, it scatters inside the cell stack of the hot module and is adsorbed in the metal oxides of its components, and the cell performance deteriorates as a result.[1, 2] As a countermeasure, Al-containing ferritic stainless steel typically such as NSSC NCA-1 (18Cr-3Al-Ti) has been used for the components of SOFC hot modules, since a dense Al_2O_3 film forms on the steel surface in a high-temperature environment, which secures good resistance to high-temperature oxidation and prevents Cr vaporization.

However, the formability of such ferritic stainless steel of high Al content is poor, as is the toughness of weld joints and formed portions. A fuel reformer, a component of the SOFC hot module, is responsible for reforming the fuel gas using a catalyst provided in its inside, it is kept at high temperature, and Al-containing ferritic stainless steel excellent in heat resistance is suitable as its material. Since its manufacture involves complicated sheet forming and intensive welding work, however, the manufacturing yield tends to be low with conventional grades of Al-containing ferritic stainless steel.

In view of the situation and aiming at expanding the use of Al-containing ferritic stainless steel for SOFC components, we studied the metallurgy of a new steel grade that would offer a heat resistance comparable to that of NSSC NCA-1, good formability, and improved toughness of weld joints and formed portions, and as a result, succeeded in developing a new steel grade NSSC NCA-F (18Cr-1.5Al-Nb-B).

2. Alloy Design Concept

When added to ferritic stainless steel, Al improves the resistance to oxidation at high temperature by forming a dense Al_2O_3 film on the surface, but at the same time it deteriorates formability and the toughness of weld joints and formed portions.[3] In the present development study, therefore, to reduce the Al addition amount while maintaining good heat resistance, we studied the effects of other alloy elements, Ti and Nb. In addition, based on the finding to the effect that the toughness of formed portions of 17Cr-0.5Ti steel is improved by B addition, chemical compositions of a new steel was studied with B-containing steel in mind.[4]

3. Test Methods

3.1 Specimens

Table 1 shows the chemical compositions of two specimen

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Table 1 Chemical compositions of specimens

(mass%)

C	Si	Mn	Cr	Al	Nb	Ti	B
0.01	0.3–1.0	0.2	18	1.0–3.0	–	0.2	–
0.01	0.5–1.0	0.2	18	1.0–1.5	0.2	–	0.0015

steels. Cold-rolled sheets of these steels, 1.5, 1.0, and 0.6 mm in thickness, were prepared as the specimens for the tests described below by melting 30 kg of steel in a vacuum melting furnace, hot-rolling, annealing, dry honing, cold-rolling, and annealing and pickling.

3.2 Resistance to oxidation at high temperature

Test pieces 25 mm × 35 mm in size were cut out from the 1.0 mm-thick cold-rolled sheets, the entire surface was dry polished to #400, and subjected to a high-temperature oxidation test in accordance with JIS Z 2282 under the following two conditions: (1) heating to 1 100°C in normal atmosphere at a heating rate of 3°C/s, holding there for 24 h, and then cooling; and (2) heating to 600 and 900°C in normal atmosphere at the same heating rate, and then cooling without soaking. After the test, the mass gain by oxidation was measured, and the oxide scale was observed at cross sections using a scanning electron microscope (SEM) and a transmission electron microscope (TEM).

3.3 Toughness

To evaluate the toughness of weld joints, 1.5 mm-thick specimen sheets were welded by tungsten inert gas (TIG) welding at a current of 10 A and a welding speed of 300 mm/min, and then V-notch test pieces were prepared according to JIS Z 2202 so that the tip of the notch was positioned at the weld center and the impact direction was parallel to the welding direction. A Charpy impact test was conducted in accordance with JIS Z 2242 at room temperature (23°C) using three test pieces for each type of steel.

For the toughness evaluation of formed portions, test pieces were prepared by cutting out round test pieces 40 mm in diameter from the 0.6 mm-thick specimen sheets, drawing them at a drawing ratio of 2.25 as a primary forming, and then removing the flanges. The test pieces were subjected to a drop weight test at −40 to 0°C as a secondary forming, whereby a weight of 3.05 kg was dropped from a height of 100 mm to apply an energy of 3 J, and the occurrence or otherwise of cracks in each of them was examined. There were three test pieces used for each lot of steel and test temperature.

3.4 Formability

Formability was evaluated by a tensile test according to JIS Z 2241. Number 13B test pieces according to JIS Z 2201 were cut out from the 1.0 mm-thick specimen sheets so that the tensile direction was parallel to the rolling direction. Vickers hardness was measured at sheet section surfaces under a load of 5 kg.

3.5 Resistance to Cr vaporization

Specimen sheets were subjected to heat treatment at 800°C for 20 to 100 h in a tubular furnace into which air of 50 volume% humidity (hereinafter air-50%H_2O in short) was blown in.[5] The steam coming from inside the furnace was cooled, condensation water was collected, and its Cr content was measured by inductively-coupled plasma mass spectrometry (ICP-MS) to determine Cr vaporization per unit surface area of each specimen. They then underwent measurement of oxidation mass gain and glow discharge optical emission spectrometry (GDS).

3.6 Strength at high temperature

High-temperature strength was evaluated by a tensile test. Test pieces according to JIS Z 2201 were cut out from the 1.5 mm-thick specimen sheets so that the tensile direction was parallel to the rolling direction, and the test was conducted in accordance with JIS G 0567.

4. Tests Results and Discussion

4.1 Resistance to oxidation at high temperature

Figure 1 shows the effect of Al on oxidation mass gain after the high-temperature oxidation test at 1 100°C for 24 h. With both Ti-containing and Nb-containing steels, the mass gain tended to decrease as the Al content increased, but whereas with the former steel a marked decrease in the mass gain was observed with an Al content of 2.0 mass%, the latter showed high resistance to high-temperature oxidation with an Al content of 1.5 mass%. **Figure 2** shows sectional SEM photographs of the oxide scales of the two steels, both containing 1.5 mass% Al, after a heat treatment at 1 100°C for 24 h. Whereas with the Nb-containing steel, a uniform oxide scale approximately 3 μm in thickness and consisting mainly of Al oxide was observed, with the Ti-containing steel, a two-layered oxide scale 50 μm in total thickness was observed, an outer layer consisting mainly of Fe oxide and containing Cr and Ti by small amounts, and an inner layer consisting mainly of Cr oxide and containing Fe and Al by small amounts. This led to a very interesting finding that, with the same contents of Cr and Si, an Al_2O_3 film formed more stably with the Nb-containing steel with a smaller Al content than with the other.

In order to clarify the factors that caused the difference in the formation of the Al_2O_3 film between the two steels despite the same Al content, attention was focused on the oxide scale formation behavior at the initial stage of oxidation, that is, during the temperature rise. **Figure 3** shows sectional TEM photographs of the oxide scales after the heat treatments at 600 and 900°C at a heating rate of 3°C/s without soaking. At 600°C, a uniform oxide scale roughly 3 nm in thickness containing mainly Cr was found to have formed with both the steels. At 900°C, on the other hand, a uniform oxide scale ap-

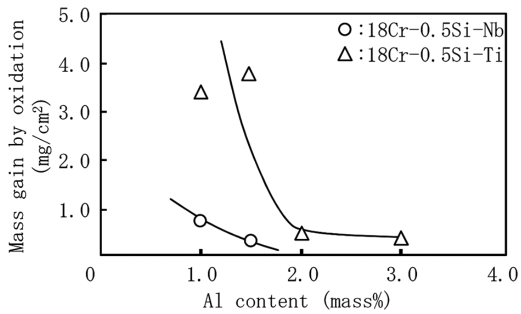

Fig. 1 Effect of Al on oxidation mass gain after oxidation test at 1 100°C for 24 h

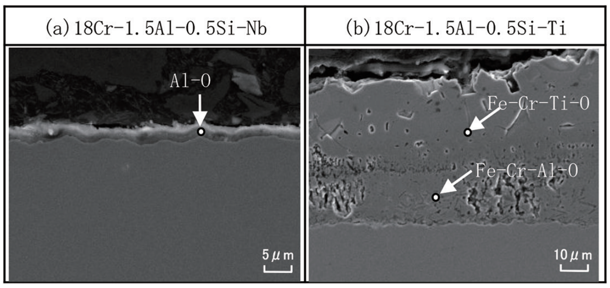

Fig. 2 Sectional SEM photomicrographs of specimens after oxidation test at 1 100°C for 24 h

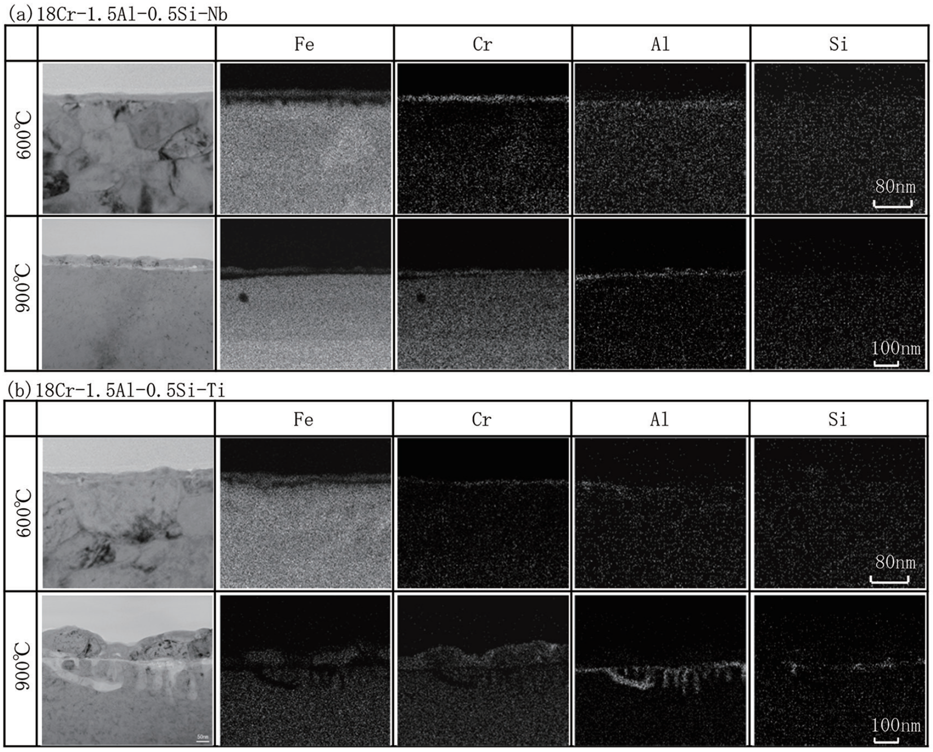

Fig. 3 Sectional TEM photomicrographs of specimens after oxidation test at 600 and 900°C without soaking

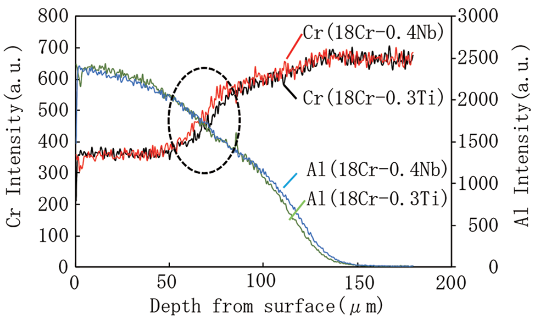

Fig. 4 EPMA profiles of Al-plated 18Cr steel after heat treatment at 1 100°C for 5 min

proximately 50 nm in thickness containing mainly Al was observed with the Nb-containing steel, and in contrast, with the Ti-containing steel, an oxide scale, approximately 70 to 120 nm in thickness and containing mainly Fe and Cr, and internal oxides of Al and Si were found.

In addition, to clarify the effects of alloy elements on the diffusion rate of the component elements in steel, the following test was conducted: sheets of Ti-containing (18Cr-0.3Ti) and Nb-containing (18Cr-0.4Nb) steels 1.0 mm in thickness were hot-dip plated with Al to a thickness roughly of 30 μm, heat-treated at 1 100°C for 5 min in normal atmosphere, the layer of surface oxide scale was removed to a depth of 20 μm, and then subjected to analysis using an electron probe micro analyzer (EPMA). **Figure 4** shows the intensity profiles of Al and Cr. Al was found to have diffused to a depth approximately of 150 μm, and the Al peak intensity of the Ti-containing steel at different depths was substantially the same as that of the Nb-containing steel. On the other hand, the Cr intensity of the Nb-containing steel was higher than that of the other in the depth range from 50 to 100 μm, approximately, from which it is presumed that the rate of Cr diffusion is higher in Nb-containing steel than in the other.

The above result points to the following: with Nb-containing steel, Cr diffuses rapidly, a dense oxide scale of a Cr_2O_3 system forms in an early stage of oxidation, the partial pressure of O_2 in the surface layer of the base metal falls, oxidation of Al is accelerated, and as a result, an Al_2O_3 film forms; and with Ti-containing steel, in contrast, Cr diffuses more slowly, the dense scale of the Cr_2O_3 system fails to form, the partial pressure of O_2 in the surface layer does not decrease, and as a result, an oxide scale of Fe and Cr systems grows without the formation of an Al_2O_3 film during a heat treatment, for example, at 1 100°C for 24 h as shown in Fig. 2. By adding Nb, it is therefore possible to decrease Al addition to 1.5 mass% and still maintain good oxidation resistance.

4.2 Toughness of weld joints

Figure 5 shows the effects of Al and Si on the Charpy impact value. Whereas the value of 18Cr-2.9Al-0.3Si-Ti steel equivalent to existing NSSC NCA-1 was 18 J/cm^2, an 18Cr-0.5Si system containing Nb demonstrated excellent impact values of 40 J/cm^2 or higher with Al addition by either 1.0 or 1.5 mass%. With 18Cr-1.5Al steel, the impact value decreased with the increase in Si content; it was as low as 19 J/cm^2 when Si content was 1.0 mass%.

The above indicates that decreasing the contents of Al and Si is effective at improving the toughness of weld joints, but as stated earlier, a minimum Al content of 1.5 mass% is required for good resistance to high-temperature oxidation. As a conclusion, an alloy composition of 18Cr-1.5Al-0.5Si-0.2Nb has been selected aiming at securing high toughness by lowering the content of Si.

4.3 Resistance to embrittlement at secondary forming

Figure 6 shows the temperature at which cracks occurred in each test piece at the drop weight test. The test pieces for the developed steel were prepared using the 18Cr-1.5Al-0.5Si-Nb steel with

B addition (the bottom line of Table 1) in consideration of the resistance to high-temperature oxidation and the toughness of weld joints as mentioned earlier. While the test pieces of the steel equivalent to NSSC NCA-1 cracked at −20°C, no cracks occurred in those of the above B-containing steel even at −40°C, which evidenced an extremely high resistance to embrittlement at secondary forming unseen with conventional ferritic stainless steel containing Al. The factors of this improvement are presumably the decrease in Al content, addition of B, and that of Nb instead of Ti.[6)]

Based on the above test results, to obtain excellent toughness of weld joints and formed portions while ensuring an oxidation resistance equivalent to that of NSSC NCA-1, the alloy composition of 18Cr-1.5Al-0.5Si-Nb-B was selected for NSSC NCA-F.

5. Characteristics of Developed NSSC NCA-F

5.1 Mechanical properties

Table 2 shows a typical chemical compositions of NSSC NCA-F. All the figures are of cold rolled and annealed sheets 1 mm in thickness after surface finishing to No.4 according to JIS G 4305. **Table 3** shows its mechanical properties. The 0.2% proof stress, tensile strength, and hardness of NSSC NCA-F are lower than those of NSSC NCA-1, and its elongation is 30.1%, higher than that of the latter, 28.0%, which shows that the developed steel is excellent in formability thanks to its material softness and high elongation.

5.2 Resistance to Cr vaporization

Figure 7 shows the amounts of Cr vaporization of NSSC NCA-F, NSSC NCA-1, and JIS SUS445J1 after the steam oxidation test at 800°C for 100 h. In contrast to 24.5 μg/cm^2 of JIS SUS445J1, the Cr vaporization amounts of NSSC NCA-F and NSSC NCA-1 were far lower, less than 0.5 μg/cm^2. **Figure 8** shows the GDS analysis results of the specimen surfaces after the measurement of Cr vaporization. While SUS445J1 had an oxide film containing mainly Mn in the outer layer and Cr in the inner, both NSSC NCA-F and NSSC NCA-1 had an oxide film containing mainly Al. This shows that an Al_2O_3 film forms on the surface of NSSC NCA-F in the air-50%H_2O atmosphere at high temperature to develop good resistance to oxidation and Cr vaporization equivalent to that of NSSC NCA-1.

5.3 Estimated service life in terms of resistance to high-temperature oxidation

Based on the above results, **Fig. 9** shows the change over time in the oxidation mass gain during the steam oxidation at 800°C. The service life in terms of the resistance to oxidation at high temperature was estimated under the following assumptions: all the oxides formed are Al_2O_3; and the chronological change in the mass gain due to oxidation follows the parabolic law expressed as in Equation (1) below.[7)] It was also assumed here that the diffusion rate of Al in steel was sufficiently high, and that the service life would be the period up to the time when all Al in steel was exhausted by oxidation and a new Al_2O_3 film would no longer form, namely the depletion time of Al in steel.

$$\Delta W = K \cdot \Delta t^{1/2}, \qquad (1)$$

where W is mass gain by oxidation, t is time (s), and K is a constant.

The service life in terms of the resistance to high-temperature oxidation of steel sheets of NSSC NCA-1, 1.0 mm in thickness, in a steam oxidation atmosphere at 800°C is estimated at 2.3 million

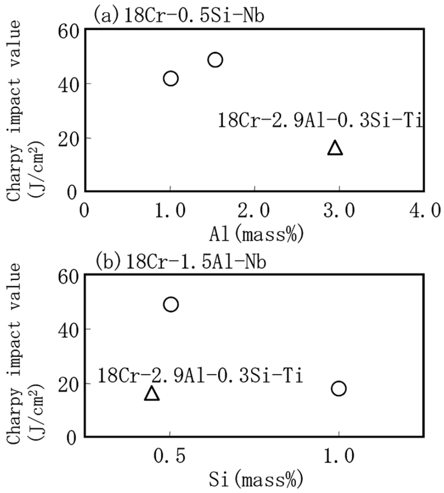

Fig. 5 Effects of Al and Si on toughness of weld joints

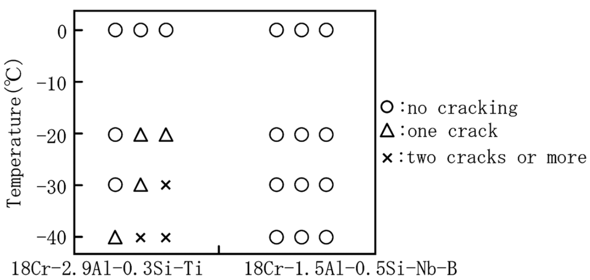

Fig. 6 Cracking at drop weight test at different temperatures

Table 3 Mechanical properties of NSSC NCA-F

	0.2%PS (N/mm^2)	TS (N/mm^2)	EL (%)	Hardness (HV)
NSSC NCA-F	372	540	30.1	177
NSSC NCA-1	425	580	28.0	192

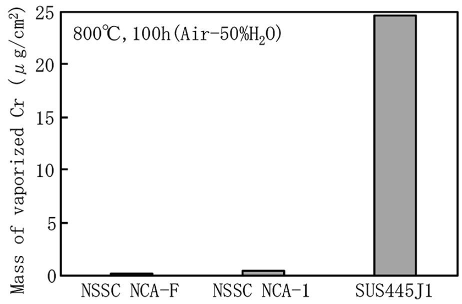

Fig. 7 Cr vaporization during steam oxidation test at 800°C for 100 h

Table 2 Typical chemical compositions of NSSC NCA-F

(mass%)

Steel	C	Si	Mn	Cr	Al	Nb	Ti	B
NSSC NCA-F	0.01	0.54	0.31	18.1	1.5	0.20	–	0.0024
NSSC NCA-1	0.01	0.34	0.23	18.0	3.1	–	0.16	–
SUS445J1	0.01	0.19	0.16	22.0	0.1	0.20	0.20	–

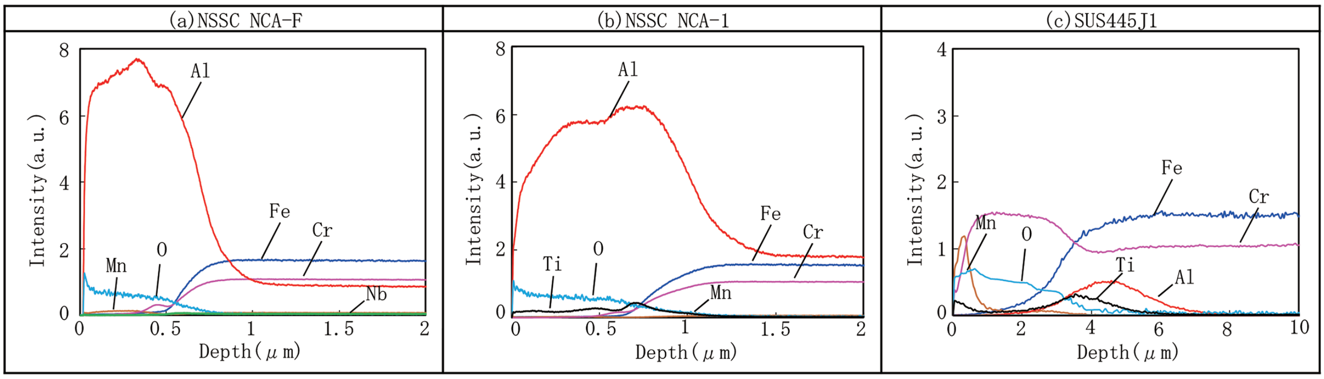

Fig. 8 GDS profiles after steam oxidation test at 800°C for 100 h

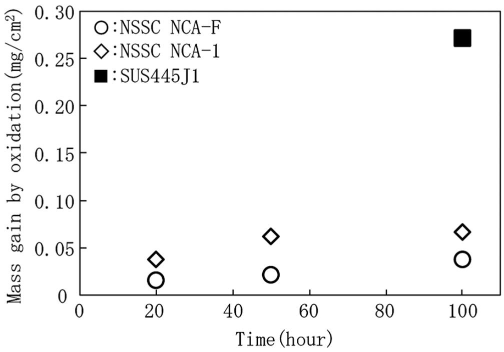

Fig. 9 Mass gain by oxidation during steam oxidation test at 800°C

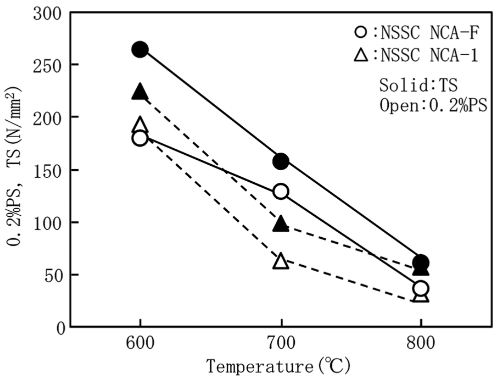

Fig. 10 High temperature strength of NSSC NCA-F

hours, and that of NSSC NCA-F at 0.57 million hours. Thus, in spite of the Al content lowered to 1.5 mass%, NSSC NCA-F is considered to have a sufficiently long service life in a high-temperature oxidation environment.

5.4 Strength at high temperature

Figure 10 shows tensile strength and 0.2% proof stress in a tensile test at different temperatures. NSSC NCA-F exhibited tensile strength higher than that of NSSC NCA-1 at any temperature from 600 to 800°C, and the difference was large especially at 700°C. The difference in the 0.2% proof stress at 700°C between the two was also large; this is presumably due to solid solution strengthening by Nb added to NSSC NCA-F.[8, 9]

The above test results corroborate the superiority of the developed NSSC NCA-F to conventional Al-added ferritic stainless steels in terms of formability, toughness, and high-temperature strength, in addition to its high heat resistance. Taking advantage of these excellent properties, it has been commercially used as the material for the fuel reformers of SOFCs.

6. Conclusion

An optimum alloy composition of a new steel grade having the same resistance to high-temperature oxidation as that of NSSC NCA-1, improved formability, and high toughness of weld joints and formed portions was sought in the present studies, and as a result, NSSC NCA-F (18Cr-1.5Al-Nb-B) has been developed. The results of the development studies are as follows.

(1) The addition amount of Al effective for decreasing the oxidation mass gain was studied using specimens of 18%Cr-0.5%Si steels. Whereas with Ti addition, an Al content of 2.0 mass% or more was necessary, with Nb addition, an Al content of 1.5 mass% proved sufficient.

(2) With Al addition by 1.0 and 1.5 mass%, the toughness of weld joints of 18%Cr-0.5%Si-Nb steel did not change; in either case, the Charpy impact value was higher than that of NSSC NCA-1. The Charpy impact value of 18%Cr-1.5%Al-Nb steel was improved when the Si content was decreased from 1.0 to 0.5 mass%.

(3) In the evaluation of the toughness of formed portions by a drop weight test, cracks occurred in NSSC NCA-1 at −20°C, but in contrast, no cracks occurred in NSSC NCA-F even at −40°C.

(4) In terms of mechanical properties, commercially manufactured NSSC NCA-F proved to be softer than NSSC NCA-1, and exhibited elongation equal to or higher than that of the latter. With the developed steel, an Al_2O_3 film formed in an air-50%H_2O atmosphere at 800°C. In addition, it exhibited a resistance to Cr vaporization equal to that of NSSC NCA-1, and higher tensile strength and 0.2% proof stress at 700°C.

References

1) Hotta, T., Yamaji, K., Kishimoto, H., Shimonozono, T., Brito, M.E., Yokokawa, H.: Hydrogen Energy System. 37 (2), 107 (2012)
2) Sakai, N., Yamaji, K., Hotta, T., Brito, M.E., Yokokawa, H.: Materia Japan. 44 (3), 207 (2005)
3) Inoue, N., Amafuji, M., Tagami, T., Takahashi, N.: Materia Japan. 45 (2), 147 (2006)
4) Fudanoki, F., Sumitomo, H.: Tetsu-to-Hagané. 84 (11), 42 (1998)
5) Fujimura, Y., Kumano, N., Imakawa, K.: Nisshin Steel Tech. Rep. (97), 25 (2016)
6) Miyakusu, K., Uematsu, Y., Hoshino, K.: Tetsu-to-Hagané. 72 (5), 189 (1986)
7) Taniguchi, S.: Bull. Iron Steel Inst. Jpn. 12 (11), 15 (2007)
8) Ohmura, K., Fujita, N., Kikuchi, M., Suzuki, T., Hiroshige, I.: CAMP-ISIJ. 4, 1796 (1991)
9) Kikuchi, M.: CAMP-ISIJ. 14, 689 (2001)


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