Technical Report

Development of Sn-containing Stainless Steel, NSSC™ FW1&2

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Abstract

We summarized the corrosion resistance and the suppression mechanism of surface hot-shortness, which is the basic technology of Sn-containing stainless steel (NSSC FW1 & 2). The addition of a small amount of Sn promotes the suppression of active dissolution and passivation in an aqueous solution, and is effective in saving Cr content. The suppression of surface hot-shortness was explained in the suppression of the appearance of Sn enriched liquid metals due to the diffusion of Sn in the steel. FW1 & 2 have realized reduction of the Cr content in the commercial process, which could not be achieved by the conventional product, based on the corrosion resistance by the addition of a small amount of Sn and the mechanism of suppressing the surface hot-shortness. This steel has been highly evaluated by the market as new products that simultaneously achieved resource and environmental measures for stainless steels and raw material cost measures.

1. Introduction

The world production of stainless steel in 2018 in terms of crude steel exceeded 50 million tons (all the units herein are metric) according to statistical data of the International Stainless Steel Forum (ISSF).[1)] Stainless steel is roughly classified into two types: the austenitic (γ phase) type typically such as SUS304 (18Cr-8Ni) (Japanese industrial standard type 304 stainless steel) and the ferritic (α phase) type such as SUS430 (17Cr). The raw materials Cr and Ni are designated as rare metals in Japan, and after Lehman's fall in 2008, their saving and effective use have been requested by related industries as a social requirement.

As the Ni price rose,[2)] new resource-saving grades of stainless steel that could replace SUS304 were sought, and many development studies were promoted. The main trends of such development were: i) austenitic stainless steel of Cr-Mn-Ni composition in which Ni is partially replaced with Mn,[3)] ii) lean duplex stainless steel in which the Ni content is reduced by adding a large amount of N,[4)] and iii) high-purity ferritic stainless steel with reduced impurity elements such as C and N. The situation of these three types of steel in the world is as follows: i) is used in India and China at present as the 200 series steel; ii) Europe took the lead in the development and commercial use, and lately, Nippon Steel Stainless Steel Corporation has developed NSSC 2120™ with improved weldability,[5)] the application of which is expanding; and iii) has been developed mainly in Japan in appreciation of the economic efficiency of the raw materials. Its production is supported by the advanced refining and manufacturing technology of the country,[6)] and its application has expanded in other countries over the last few years.

Following the trend of high-purity ferritic stainless steel in the above context, Nippon Steel Stainless Steel has developed new grades of steel containing Sn, NSSC™ FW1 & 2,[*1] in which the amount of Cr is reduced by adding Sn in a small amount as the world's first approach on an industrial scale, and launched them onto the market for commercial use. This paper describes the course of the development of the Sn addition, its application to commercial production, basic technology that enabled the development of FW1, and its evolution into FW2. Finally, the development of FW1 & 2 is evaluated from the social viewpoint of saving rare metal resources.

2. Background of Development and Application of Developed Steel

The development of stainless steel containing Sn was driven largely by the social conditions from 2004, when Nippon Steel & Sumikin Stainless Steel Corporation was established, to the aftermath of Lehman's fall in 2008. **Figure 1** compares the change of stainless steel production (in terms of crude steel) of the world and Japan in the 10-year period from 2004.[1)] While the world production

[*1] The denomination "NSSC FW" is a registered trademark of Nippon Steel Stainless Steel Corporation.

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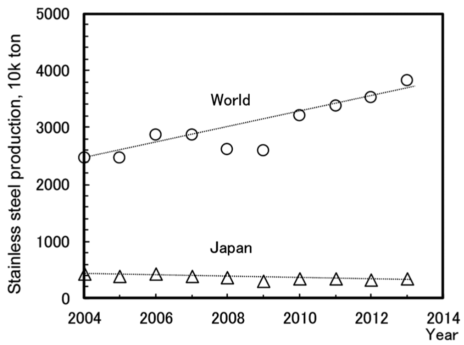

Fig. 1 Changes in stainless steel production in 10 years from 2004

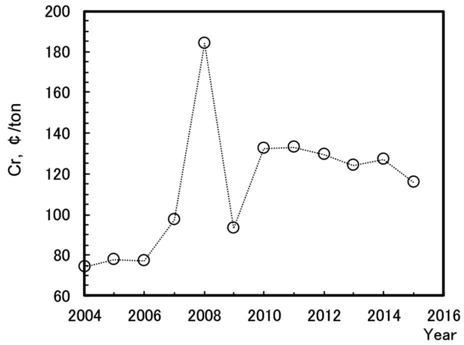

Fig. 2 Price change of Cr raw material

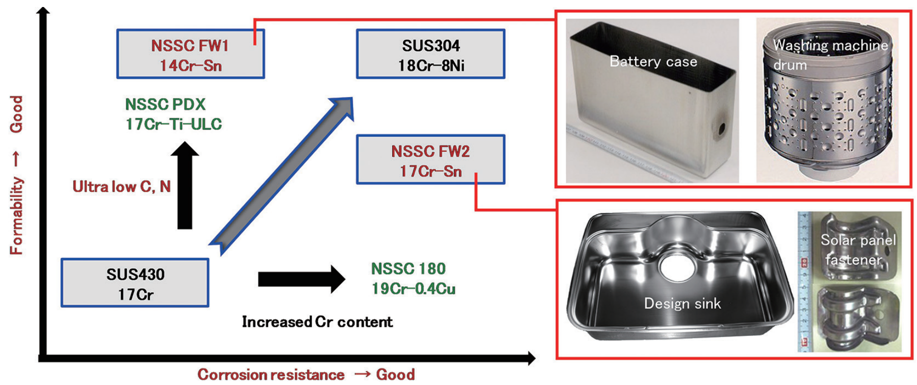

Fig. 3 Relative positions and applications of NSSC FW1 & 2

is on an upward trend driven by China at an annual rate of 5%, that of Japan is gradually declining from 3 million tons in 2004. This has resulted from nothing but the fall of Japan's competitiveness in stainless steel for general use such as SUS304 and SUS430 in the world market. **Figure 2** shows the price change of the raw material of Cr, the basic alloy element of stainless steel.[7] In the period from 2010 to 2015, the Cr price soared to 1.7 times that in 2004. Japan's general-purpose stainless steel lost its price competitiveness in the overseas market because of the increasing Cr price and the appreciation of the yen. To maintain competitiveness in the global market in a sustainable manner in the period after Lehman's fall, therefore, it was required as a matter of urgency to respond to the needs for development of new resource-saving products by measures free from the technical knowledge of the past.

High-purity ferritic stainless steel is a resource-saving product based on the advanced refining and manufacturing technology of Japan. Traditionally, corrosion resistance was enhanced following the alloy design concept of increasing the amount of Cr in consideration of the corrosiveness of the use environment; in other words, a higher Cr content was the practical solution in the pursuit of higher corrosion resistance. The idea and approach of decreasing the content of Cr, the most fundamental alloy element, for improving corrosion resistance was never considered nor attempted before 2010. **Figure 3** shows the positioning of Sn-containing stainless steels, NSSC FW1 and FW2, of high corrosion resistance with decreased Cr content, and examples of their application. Traditionally, NSSC PDX (17Cr-Ti)[6, 8] and NSSC 180 (19Cr-Nb-Cu)[9] have been used as alternatives to SUS304 and SUS430. As the microelements for these steel grades, Ti, Nb, etc. were used for stabilizing the metallographic structure, and Cu, etc. for improving corrosion resistance. On the other hand, Sn causes cracking of steel at hot working even when its content is as small as less than 0.1%.[10] The development of NSSC FW1 and FW2, however, has been achieved through alloy design combining the idea of utilizing Sn, a tramp element in conventional steel manufacture, contrary to the past knowledge, and the technology of high-purity steel refining in which Japan specializes. The Cr content of FW1 (14Cr-Sn) is reduced to an extreme, and its formability is among the best of this type of steel, and in appreciation of the fact, it is widely used for forming applications for indoor water-related facilities. FW2 (17Cr-Sn) has corrosion resistance equal to that of SUS304 (such as NSSC 180) in normal air environments and the same formability as that of high-purity ferritic stainless steel, and as such, is used for corrosion-resistant applications either indoors or outdoors.

3. Basic Technologies

The stainless steel containing Sn, NSSC FW1 and FW2, has been developed on the basis of two element technologies. One is corrosion resistance produced by the addition of Sn in a very small amount. Sn is, however, a tramp element that hinders the manufacturability of steel, and causes cracking at hot forming (surface hot shortness[10]). Therefore, the second is the technology to suppress surface hot shortness by the addition of Sn. These two element technologies are closely related to the development of FW1 (14Cr-Sn). The ideas, test results, and studies related to the two technologies are introduced in the following sub-sections.

3.1 Development of corrosion resistance with Sn addition in small amounts

The corrosion resistance in a natural environment can be described using electrical potential, an index of oxidizing and reducing properties of the material in question, and pH, an indicator of acidity and basicity, typically as in the Pourbaix pH/potential diagram. Ac-

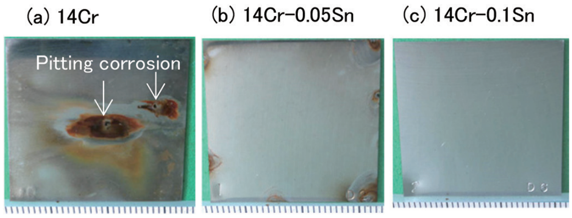

Fig. 4 Appearances of (a) 14Cr, (b) 14Cr-0.05Sn, and (c) 14Cr-0.1Sn steels (surfaces finished to #600) after immersion in aqueous solution of 0.5% NaCl at 80°C for 168 h [11]

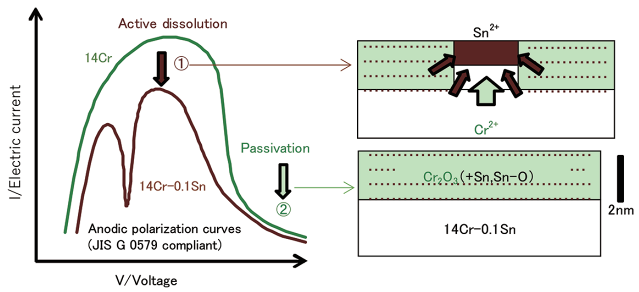

Fig. 5 Schematic illustration of passivation promoting mechanism of 14Cr-0.1Sn steel in aqueous solution

cording to this diagram, the passivity range of Sn, in which it is not corroded, is wider than that of Cr, the basic alloy element of stainless steel. This fact led us to consider that the addition of Sn may serve to improve the corrosion resistance of high-purity ferritic stainless steel.

Figure 4 [11] shows the result of the immersion test in an aqueous solution of 0.5% NaCl at 80°C for 168 h to evaluate the effect of Sn addition in small amounts on corrosion resistance. The photographs clearly show that the rusting or perforating corrosion of 14Cr steel was suppressed by Sn addition of 0.05 to 0.1%. No rusting of 14Cr-0.1Sn steel whatsoever in the test has clarified that Sn addition by approximately 0.1% creates corrosion resistant steel.

Figure 5 schematically illustrates the mechanism of accelerating passivation of 14Cr-0.1Sn steel in an aqueous solution; it was estimated from the polarization curve [11] in a 5% H_2SO_4 aqueous solution at 30°C (according to JIS G 0579). The anodic dissolution peak (I_{crit}) of 14Cr steel is significantly lowered by the addition of 0.1% Sn to follow the two-peak curve as shown with arrow ①, and the decrease was equal to or less than that of 17Cr steel. The significant decrease in active dissolution is presumably because a chemical species of Sn (considered to be Sn^{2+}) [12] is adsorbed to the steel surface in the aqueous solution, which suppresses the dissolution of the steel. Moreover, the polarization behavior in the passivation region (≥ 0 V) seems to accelerate the passivation as indicated by arrow ② as a result of the decrease in I_{crit}; that is, the passivation is considered to result from the regeneration of a passivation film in the process of suppressing the active dissolution.

Figure 6 [13] shows the analysis result of the chemical state of Sn in a very small amount in the passivation film (the specimen surface being finished to 2B according to JIS G 4305) by hard X-ray photoelectron spectroscopy (at 7939 eV) using the SPring-8; here, Sn 2p3/2 photoelectron spectra were detected at take-off angles (TOA) of 80 and 40°. Normally, the intensity of photoelectrons is greatly attenuated toward the low angle side, where the escape depth is small. In this case, however, the photoelectron intensity of Sn 2p3/2 did not decrease from TOA=80 to 40° but instead increased slightly,

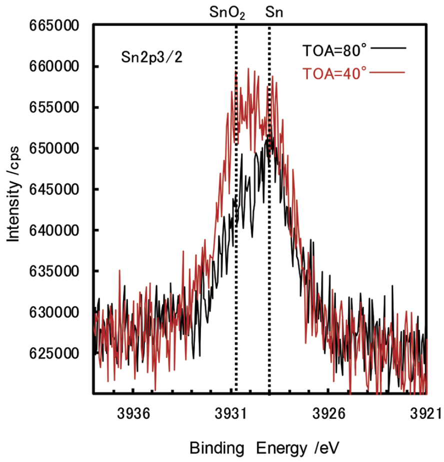

Fig. 6 Sn 2p3/2 photoelectron spectrum in the passive film by hard X-ray photoelectron spectroscopy (7939 eV) [13]

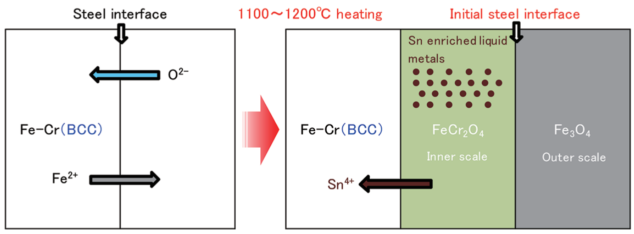

Fig. 7 Schematic illustration of the mechanism for suppressing surface hot-shortness in Sn-containing stainless steel

which means that Sn existed from the base metal surface to the passivation film with a high probability. The intensity of the photoelectron spectrum at TOA=40° was higher than that at 80° in the range from 3929 to 3931 eV, which indicates that Sn was in a chemical state of metal or oxide (most probably tetravalent in the form of SnO_2) from the steel surface to the passivation film. The corrosion resistance of the material in an aqueous solution is considered to result from the elution of Sn ions that existed from the surface layer to the passivation film.

The above result confirms that the Sn addition in small amounts suppresses the active dissolution of the steel, accelerates its passivation in an aqueous solution, and is effective at reducing the amount of Cr addition as a measure to develop corrosion resistance.

3.2 Mechanism of suppressing surface hot shortness

The main iron source in the manufacture of stainless steel is scrap iron melted in electric arc furnaces, and at this stage, Sn is a typical tramp element, like Cu. Ferritic stainless steel is far less prone to cracking at hot forming (surface hot shortness) due to Cu than ordinary steel. [14]

Figure 7 schematically illustrates the mechanism of suppressing surface hot shortness of Sn-containing stainless steel inspired by past study results. [14] The diagrams represent the interface between the base metal and the oxide layer forming during the heating for hot rolling. On a hot rolling line, slabs are heated for a long time to 1100 to 1200°C before the rolling, and with ferritic stainless steel, an outer scale layer of Fe_3O_4 forms as a result of the outward diffusion of Fe; in addition, an inner scale layer of $FeCr_2O_4$ forms at the base metal surface as a result of the inward diffusion of O. Sn, which is nobler than Fe, is considered not to be oxidized but to diffuse from the surface into the steel matrix in a BCC structure or re-

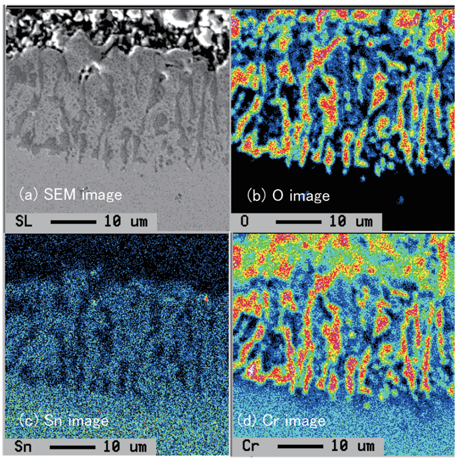

Fig. 8 SEM and EPMA images of the inner scale and scale/steel interface of 14Cr-0.1Sn steel at 1 100°C for 4 h[16]
(a) SEM image, (b) O distribution image, (c) Sn distribution image, (d) Cr distribution image

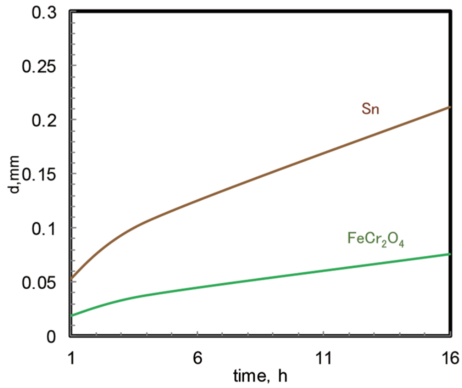

Fig. 9 Calculated distance of Sn diffusion in BCC and $FeCr_2O_4$ thickness at 1 100°C

main in the inner scale. Surface hot shortness occurs as a result of Sn in an amount exceeding the solid solution limit and depositing as a low-melting-point metal[15] at the base metal surface.[10] Because the diffusion coefficient of Sn in ferritic stainless steel (in BCC) is higher than that in carbon steel (in FCC) roughly by two orders of magnitude, it is considered to diffuse and be diluted more easily in ferritic stainless steel. Even when the low-melting-point metal of Sn forms, it is expected mostly to remain harmless in the inner scale layer.[14]

Figure 8[16] shows a sectional photomicrograph of the interface between the base metal of 14Cr-0.1Sn steel and the inner scale layer, which formed during holding at 1 100°C for 4 h, taken through a scanning electron microscope (SEM) and the mapping images of O, Sn, and Cr by an electron probe micro analyzer (EPMA). The areas in light green or red in the mapping images are the portions where the element in question is densely concentrated. The inner scale layer had a complicated mixed structure of oxide with high Cr concentration ($FeCr_2O_4$) and metal. In the EPMA mapping of Sn, areas in light green or red were not observed in the inner scale or near the interface with the base metal, which means that Sn did not concentrate or form alloy phases in those portions.

Figure 9 shows the calculated distance of the diffusion of Sn in the BCC structure of steel and the thickness of an inner scale layer of $FeCr_2O_4$, both at 1 100°C. Here, the diffusion coefficient D of Sn was calculated as 7.8×10^{-13} m^2/s,[17] its diffusion distance d as $(D\cdot t)^{1/2}$, the growth rate coefficient kp of $FeCr_2O_4$ as 10^{-14} m^2/s,[18] and its thickness as $(kp\cdot t)^{1/2}$, t being time (h). The graph shows that the diffusion distance of Sn at 1 100°C is sufficiently larger than the growth rate of $FeCr_2O_4$, and the difference between the two is more conspicuous in the temperature range above 1 100°C. In other words, the diffusion rate of Sn in steel is far greater than the growth rate of the inner scale layer, and it is presumed that Sn is prevented from concentrating at the base metal interface, and the low-melting-point metal from depositing.

Thus the surface hot shortness of stainless steel containing Sn is suppressed because the low-melting-point metal is prevented from depositing as a result of rapid diffusion and dilution of Sn in steel.

4. Application of Technologies of FW1 to FW2

NSSC FW2 (17Cr-Sn) realizes weather resistance equal to that of SUS304 (NSSC 180) and the ease of industrial manufacture (in refining and casting) thanks to the findings derived from the basic technologies of FW1 (14Cr-Sn). Those findings are explained below.

Figure 10 shows the effects of the addition of Sn, Ni, and Cu by 0.2 to 0.3% on the weather resistance of 17Cr steel as evaluated through the cyclic corrosion test (CCT)[19] using synthetic seawater. The extent of corrosion after 12 cycles of CCT is substantially equal to that after exposure in coastal areas in Okinawa for two years. The index of rusting RN of 17Cr-Sn steel was improved to a level comparable to NSSC 180 due to the combined addition of Ni and Cu, which confirmed that Sn addition by a small amount was effective at

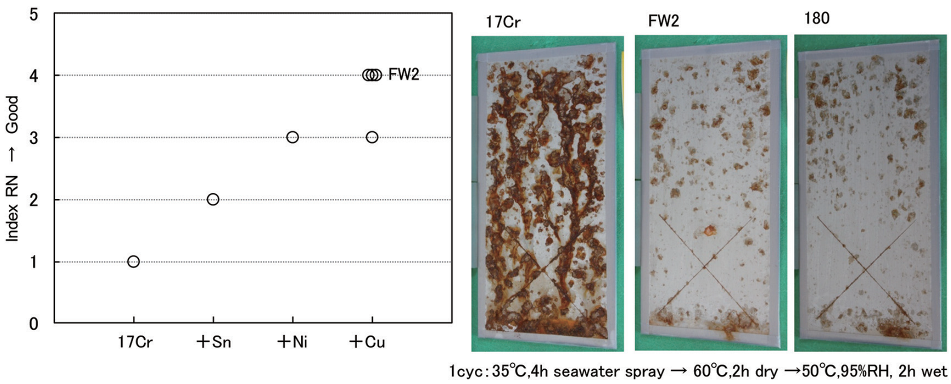

Fig. 10 Index RN and appearances of specimens (surfaces finished to #600) after 12 cycles of cyclic corrosion test with synthetic seawater

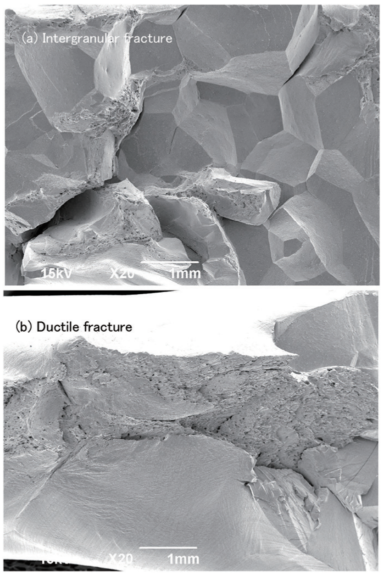

Fig. 11 Fracture surface of 17Cr-Sn steel slabs after 250°C Charpy impact test (JIS Z 2242 compliant)
(a) Intergranular fracture, (b) Ductile fracture

developing a weather resistance equal to that of SUS304 even with decreased addition of Cr.

Figure 11 shows photomicrographs of fracture surfaces of cast specimens of 17Cr-Sn steel at toughness evaluation by a Charpy impact test in a warm condition according to JIS Z 2242; here, V-notch sub-size test pieces were cut out from the thickness center of as-cast slabs 250 mm thick, and the test temperature was 250°C. Sn is a typical example of the elements that segregate at crystal grain boundaries; the toughness of commercially manufactured ingots may be markedly lowered when Sn is added by only a very small amount.[20] The smooth fracture surface in part (a) is that of a typical intergranular fracture (grain boundary embrittlement). It is caused mainly by Sn segregation at crystal grain boundaries, but segregates of Nb and other stabilizing elements at grain boundaries also lead to intergranular embrittlement.[21] The adverse effect of such segregates, however, can be attenuated by the refining technology of high-purity steel. In the fracture surface in part (b), the crystal grains are drawn more than in part (a), and dimples characteristic to brittle fracture are seen near the center of the image. The slab shown in part (b) exhibited good Charpy impact values exceeding 150 J/cm^2 in the warm condition. These slabs of 17Cr-Sn steel were manufactured applying the steel refining and casting technologies to avoid the grain boundary embrittlement by Sn.

Commercial production of FW2 (17Cr-Sn) has been made practicable thanks to the improvement of weather resistance by the combined addition of Ni and Cu in very small amounts and the steel refining and casting technologies to prevent the grain boundary embrittlement by Sn.

5. Evaluation in Social Aspects

NSSC FW1 was launched onto the market in July 2010, and FW2 in December the same year. Nippon Steel Stainless Steel received in 2012 the Prime Minister's prize of the 4th Monodzukuri Nippon Grand Award (in the categories of product and technical development)[22] for the development of NSSC FW1 and FW2; the word Monodzukuri means manufacture or production, and the award system is intended for wide acknowledgement of achievements in manufacturing, which has formed the basis of Japan's industrial culture, and its transmission to the future and development. Since its institution in 2005, the prizes have been awarded every other year.

FW1 & 2 have gained high market appreciation as epoch-making new products that save the use of rare metals, attaining excellence in resource saving, environmental measures, and the cost economy of raw materials simultaneously. The monthly sale of the two steel grades towards the end of the fiscal year 2012 (ending in March 2013) was as large as 2 500 t (30 000 t per year). In the global market of stainless steel, where the presence of Chinese makers has increased since Lehman's fall, the development of NSSC FW1 and FW2 is highly evaluated as an encouragement for the cultivation of domestic technology and activation of Japanese industry.

6. Conclusion

This paper presented the technologies to achieve corrosion resistance and suppress surface hot shortness, which constitute the basis of the development of new stainless steel products containing Sn, NSSC FW1, and FW2.

The studies have revealed that the addition of Sn by a very small amount is effective at suppressing active dissolution of steel in aqueous solutions, accelerating passivation of the material, and decreasing the addition amount of Cr for corrosion resistance. It has also been clarified that the surface hot shortness of stainless steel containing Sn can be suppressed by accelerating the diffusion and dilution of Sn in steel and thus preventing low-melting-point metal from depositing. With NSSC FW1 and FW2, thanks to the development of corrosion resistance by Sn addition in a very small amount and the measures to suppress surface hot shortness, which made the Sn addition viable, reducing the Cr content to below the lower limit by conventional practice has become commercially viable. The developed steels are highly appreciated in the market as epoch-making products that simultaneously attain saving of raw materials, higher environmental performance, and lower material costs. The technical concept of the developed steels is expected to be carried over to the development of yet other new products and technologies in the field of stainless steel, where increasingly tough competition continues with overseas makers.

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