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Technical Report

Development of New Lean Duplex Stainless Steel Series NSSC 2120™, NSSC™ 2351

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Abstract

For lean duplex stainless steels, high heat input welding significantly reduces their corrosion resistance due to the precipitation of chromium nitride in the heat affected zone. To address this problem, we developed original duplex stainless steels named NSSC 2120 and NSSC 2351 that can replace SUS304 and SUS316L respectively, using a composite design from two viewpoints, which are to reduce the precipitation driving force for chromium nitrides by lowering the Cr_2N precipitation start temperature which is an index required for phase diagram calculation, and to maintain the amount of austenite in the welds by reducing the ferrite amount of the base metal. Utilizing the features of high strength, light weight, and resource saving, they are being applied to a wide range of fields including structural materials for infrastructure such as dam facilities and water gates.

1. Introduction

Duplex stainless steel consists of two metallurgical microstructures of the austenite phase and ferrite phase at an ordinary temperature, and exhibits properties different from that of austenitic stainless steel and ferritic stainless steel that cover most stainless steels. The duplex stainless steel has the advantage of higher strength with a smaller Ni content as compared with austenitic stainless steel, and is attracting attention from the viewpoint of resource saving.

The conventional duplex stainless steels (SUS329J3L: 22%Cr-5%Ni-3%Mo-0.15%N, SUS329J4L: 25%Cr-6%Ni-3%Mo-0.15%N) have pitting corrosion resistance higher than that of the high corrosion-resistant general-use austenitic stainless steel SUS316L. However, since the steel needs a high content of costly Mo, and the alloying metal cost has increased accordingly, the steel has been used limitedly such as the tank material of a chemical tanker that specifically requires high corrosion resistance. On the other hand, alloy-metal-saving type duplex stainless steel (lean duplex stainless steel) intended to replace the general-use austenitic stainless steels SUS304 or SUS316L has been developed, and is applied to diversified applications.

Nippon Steel Stainless Steel Corporation has developed the lean duplex stainless steel series of NSSC 2120 (21%Cr-2%Ni-3%Mn-1%Cu-0.17%N) and NSSC 2351 (23%Cr-5%Ni-1%Mo-0.17%N) that is able to substitute SUS304 and SUS316L, respectively. The composition of either steel is designed so as to minimize to the extent possible the deterioration of the corrosion resistance at the weld heat affected zone, a problem of duplex stainless steel, in particular lean duplex stainless steel, and to improve the pitting corrosion resistance above the SUS304 and SUS316L levels respectively including welds.

In addition, by taking advantage of such excellent properties as high corrosion resistance, high strength, and resource saving of the duplex stainless steel, the steel has been successfully applied to construction materials in the civil engineering field. Presently, the steel is widely applied in various fields such as water-related infrastructure part materials like dam and water gates, and solar panel mounts, thus creating a new market for stainless steel.

This article describes the outline, properties, and application examples in the new market of the lean duplex stainless steels of NSSC 2120 and NSSC 2351.

2. Outline of Lean Duplex Stainless Steel and Problem of Conventional Lean Duplex Stainless Steel

2.1 Outline of lean duplex stainless steel

In duplex stainless steel, the austenite phase and ferrite phase compatibly exist at an ordinary temperature to increase ferrite-stabi-

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lizing compositions such as Cr and Mo and decrease austenite-stabilizing compositions such as Ni and N from that of austenitic stainless steel.

The pitting resistance equivalent number (PREN: Cr+3.3Mo+16N), a composition index that shows the pitting corrosion resistance, of the conventional duplex stainless steels of SUS329J3L and SUS329J4L, is about 35 and 38 respectively, significantly higher than that of about 25 of SUS316L, and they are steels having high corrosion resistance with high alloying metal costs. To solve the problem, lean duplex stainless steel was developed in Europe and the U.S from the mid 1980s to the 2000s. The lean duplex stainless steel is a low cost alloying metal steel wherein the costly Ni and Mo are replaced with Cr, Mn, and N while keeping the corrosion resistance down at the levels of SUS304 and SUS316L. For example, UNS S32304 specified in ASTM (JIS SUS323L: 23Cr-4Ni-0.1N)[1] corresponds to SUS316L, and UNS S32101 (21Cr-1.5Ni-5Mn-0.22N)[2] corresponds to SUS304 likewise. Particularly around 2004 when the alloying metal price soared, such lean duplex stainless steels became relatively reasonable with a low content of Ni and Mo as compared with austenitic stainless steel, and encouraged by this move, stainless steel producers in the world developed diversified types of stainless steel. However, about the SUS304-substituting stainless steel in particular among the lean duplex stainless steels, the deterioration of corrosion resistance of the weld heat affected zone, a coherent problem of duplex stainless steel, became significant particularly in large heat input welding. In addition, since production was difficult, and the production cost rose, the merit of the reduction of alloying metal cost was negated. So and the practical application remained stagnant.

2.2 Deterioration mechanism of weld heat affected zone properties in duplex stainless steel

In duplex stainless steel, N is an important element that is used extensively for the enhancement of PREN, stabilization of the austenite phase, and improvement of strength. In particular, N is very effective in maintaining the austenite phase of welds, and is currently added to almost all steels. Furthermore, since N is of low cost, the element is added extensively in lean duplex stainless steel to replace a part of Mo and Ni, and in many of the SUS304-substituting steels, more than 0.20% is added. In the meantime, the element deteriorates weld properties as described below.

The deterioration of the weld properties of duplex stainless steel occurs due to the mechanism as shown below.[3] N dissolves in a large quantity in the austenite phase. However, at an ordinary temperature, it dissolves in the ferrite phase only in a small quantity. In the base metal of duplex stainless steel, N is mostly distributed in the austenite phase. In duplex stainless steel, however, the austenite phase disappears at a high temperature near the melting point, and the steel becomes the ferrite single phase. Therefore, when welding is conducted, in the heat affected zone nearest to the fusion line, the austenite phase disappears or is reduced, and accordingly, N dissolves into the ferrite phase in a large quantity. The austenite phase is reprecipitated, however, not to the extent before welding as cooling progresses rapidly after welding. Therefore, N remains in the ferrite phase in the state of oversaturation, and is precipitated in the form of Cr nitride below about 900°C at which temperature the solid solution limit of N begins to fall. Deterioration of toughness and/or corrosion resistance is thus caused.

2.3 Problem of conventional lean duplex stainless steel

The past measure taken to solve this problem is to add more N which seems counterproductive. The reason for this is to expediate the reprecipitation of the austenite phase so that the austenite phase absorbs N, the oversaturated N in the ferrite phase is decreased, and the precipitation of nitride is suppressed thereby.[4] Since N has an overwhelmingly high diffusion rate as an austenite-stabilizing element as compared with other elements, even under a rapid-cooling condition, N alone can migrate and form the austenite phase.

This method was effective in conventional duplex stainless steel like SUS329J3L, and the deterioration of the corrosion resistance of welds was not large. However, in the case of S32101, a substitute of SUS304, due to more N being added than that of the conventional duplex stainless steel and the solid-solution limit of N deteriorating to save Ni, so Cr nitride becomes more readily precipitated. As a result, the upper limit of proper welding thermal input is set at about 1.5–2 MJ/m (15–20 kJ/cm)[5] which is lower than that of 2.5–3.5 MJ/m (25–35 kJ/cm) of SUS329J3L. For structural use materials with a thickness of several millimeters up to several tens of millimeters are welded at many locations, and the low welding thermal input linked to the increase in the welding pass impairs working efficiency.

3. Development of Lean Duplex Stainless Steel NSSC 2120 Having Excellent Properties as Structural Material

3.1 Composition design

To solve the abovementioned problem, two new concepts were applied in NSSC 2120, and a new type, lean duplex stainless steel that can significantly enhance the upper limit of the weld thermal input was realized. The first is: as a means of reducing the Cr nitride in the heat affected zone, instead of promoting reprecipitation of austenite by increasing N as described above, two methods are implemented in parallel: one is to maintain the amount of reprecipitation of austenite and the other is to suppress the precipitation driving force of Cr nitride. The second is the employment of Cr_2N precipitation start temperature obtained from the phase diagram calculation based on steel compositions as an index of the Cr nitride precipitation driving force.

Figure 1[6] shows the result of the observation of the locations of pitting corrosion of the weld of S32101 that occurred after immersion in the ferric chloride solution. In SUS329J3L and the like, in the case of the welding by using a filler material, corrosion resistance deteriorates most significantly in the neighborhood of the fusion line in the heat affected zone. At this position, the steel is heated once up to the temperature immediately below the melting point of the steel wherein only the ferrite single phase exists and the entire N dissolves into the ferrite phase. Furthermore, as the amount of austenite reprecipitation reaches its lowest level, Cr nitride is precipitated mostly therein. On the other hand, in S32101, pitting corrosion occurred in the region outside the ferrite single phase region preferentially. To clarify the mechanism, the sample was heated with varying maximum heating temperatures, was etched with oxalic acid, and the microstructure observed; and furthermore, the precipitates extracted by the replica method were observed by transmission electron microscopy (TEM). The results of these observations are shown in **Fig. 2**.[7] In the sample heated up to 1360°C that is the ferrite single phase temperature, the ferrite/ferrite grain boundary scarcely exists, and the precipitates mainly consist of Cr_2N and CrN precipitated intragranularly. On the other hand, in the sample heated up to 1250°C and therefore not within the ferrite single phase (hereinafter referred to as the dual phase temperature), groove type corrosion is witnessed in the ferrite/ferrite grain boundaries that exist in abundance, and at the said locations, precipitation of film type Cr_2N was

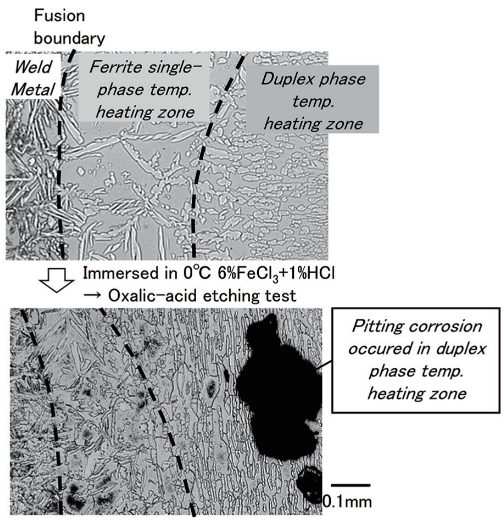

Fig. 1 Characteristics about position of pitting corrosion of lean duplex stainless steel weld (S32101)[6)]

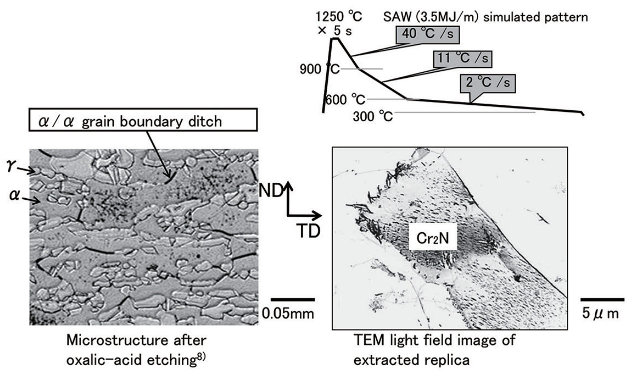

Fig. 2 Microstructure & TEM image of extracted replica of HAZ simulated heat cycle tested sample of lean duplex stainless steel (S32101)[7)]

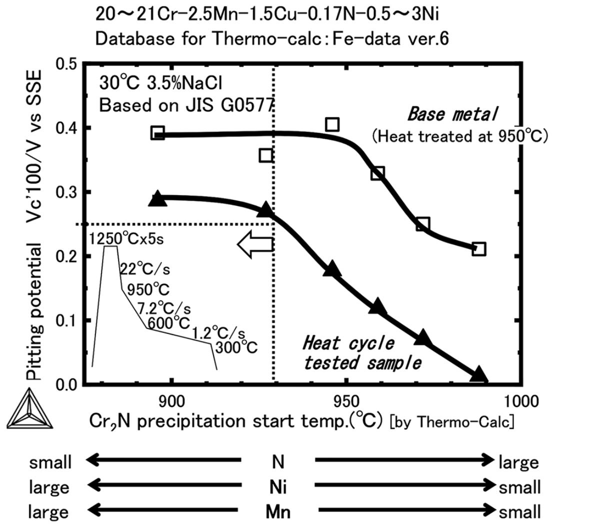

Fig. 3 Effect of Cr_2N precipitation start temp. on pitting potential of base metal & heat cycle tested sample[7)]

observed.

This is explained as follows. In the case of heating up to the ferrite single phase temperature, since the austenite phase reprecipitation starts at the ferrite grain boundaries during cooling, most of the ferrite grain boundaries become ferrite/austenite grain boundaries, and the scarcity of N in ferrite means the precipitation of austenite cannot be produced. Therefore, Cr nitride is not precipitated in grain boundaries but finely precipitated in the ferrite phase intragranularly. On the other hand, in the case of heating up to the dual phase temperature, Cr nitride is precipitated in a film-like manner in the then existing ferrite/ferrite grain boundaries, and as a result thereof, the size of the Cr-scarce layer increases, and this phenomenon is considered to have influenced the result. In the case of heating up to the dual phase temperature, the austenite phase in the base metal remains, so the promotion of the reprecipitation of austenite by the addition of N does not work. To suppress the precipitation of Cr nitride in this region, suppression of the precipitation driving force is required.

To reduce the precipitation driving force of Cr nitride, the reduction of N is effective. However, as described above, N is a crucial element in the reprecipitation of austenite. Therefore, elimination of the addition of N is not a practical option. Furthermore, the nitride precipitation driving force is also influenced by the interaction with other elements and the austenite phase ratio. Therefore, in this development, we utilized the phase diagram calculation by thermodynamic calculation software Thermo-Calc®, and culclated the limit Cr_2N precipitation starting temperature, at which temperature Cr nitride will be precipitated in equilibrium, and employed it as an index. We decided to decrease this temperature. **Figure 3**[7)] shows the effect of the Cr_2N precipitation starting temperature on the pitting potential of the base metal and the simulated heat cycle tested sample. It was found that the lower the temperature, the more effectively the deterioration of corrosion is suppressed. On the other hand, regarding the amount of reprecipitation of austenite, it was confirmed that the amount of austenite at welds is sufficiently maintained even when the amount of N is controlled at a somewhat lower level by adjusting the components of austenite stabilizing elements other than N such as Ni, Mn, and Cu, and thereby reducing the amount of ferrite in the base metal (target: not more than 50%). By the introduction of the concept of Cr_2N precipitation starting temperature, the multidimensional optimization of compositions not only the Cr nitride precipitation driving force and the austenite reprecipitation characteristics, but also productivity and alloying metal cost have become possible, leading to the establishment of NSSC 2120.

3.2 Result of evaluation of properties

Table 1 shows an example of compositions of NSSC 2120. Additionally, **Fig. 4** shows the result of the tensile strength test. The 0.2% proof stress of NSSC 2120 is about two times higher than that of SUS304. Furthermore, in **Fig. 5**, the pitting potential of the NSSC 2120 base metal, the MAG weld joint using a flux wire (FCAW), and the submerged arc weld joint (SAW) with a heat input of 35 kJ/cm above the upper limit of the recommended value of S32101 are compared with that of S32101 and SUS304.[6)] The base metal and the welds of NSSC 2120 exhibit corrosion resistance higher than that of SUS304.

Thus, it has been clarified that NSSC 2120 has corrosion resistance higher than that of SUS304 including the welds, and is a high strength material.

Table 1 Example of chemical composition of steels

(mass%)

Steel		C	Mn	Cr	Ni	Mo	Cu	N	PREN	Estimated ferrite amount (%)	Cr_2N precipitation start temp. (°C)*
Developed steel	NSSC 2120	0.03	3.2	20.9	2.3	0.5	1.1	0.17	25	46	910
	NSSC 2351	0.02	1.3	23.6	5.2	1.3	0.3	0.17	30	53	923
Duplex stainless steel (Comparative)	S32101	0.02	5.0	21.6	1.6	0.3	0.3	0.21	26	55	929
	SUS323L	0.02	1.6	23.6	4.0	0.3	0.2	0.14	27	63	912
	SUS329J1	0.01	0.3	24.4	4.6	1.8	0.1	0.12	32	78	951
	SUS329J3L	0.01	1.8	22.6	5.8	3.1	0.2	0.16	35	54	963
Austenitic stainless steel (Comparative)	SUS304	0.05	0.9	18.1	8.1	0.2	0.3	0.05	20	−	−
	SUS316L	0.01	0.9	17.6	12.2	2.1	0.2	0.03	25	−	−

PREN: Pitting Resistance Equivalent Number Cr + 3.3Mo + 16N * Calcurated by Thermo-calc / Fe-Data ver.6

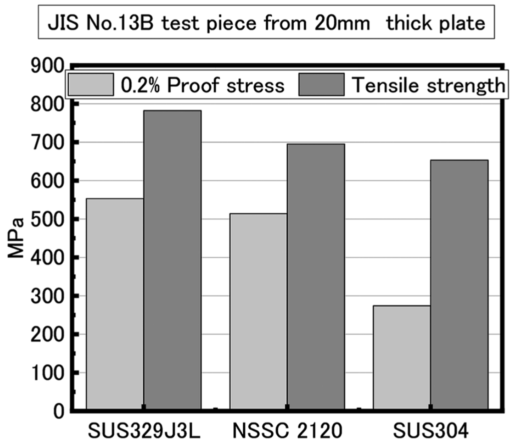

Fig. 4 Example of tensile strength of NSSC 2120 and other stainless steel plates

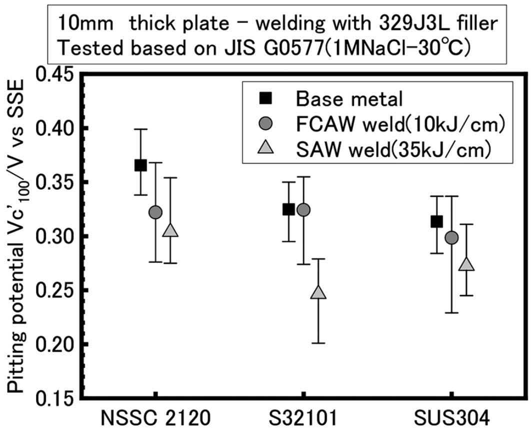

Fig. 5 Pitting potential of base metal & weldings of NSSC 2120 and other steels[6)]

4. Development of New Stainless Steel Market with NSSC 2120

NSSC 2120 contains less Ni than SUS304, and reduction of thickness is possible because of its high strength, and therefore, it is an excellent material that is doubly resource-saving and enables weight reduction. In recent years in Japan, various natural disasters have occurred, and to cope with them, strengthening of social infrastructure is required. This steel was considered to be highly appropriate for structural materials of social infrastructure.

Table 2 Estimation of construction cost and life cycle cost of a water gate

7 × 7.8 m 54.6 m²	Carbon steel (SM490)	SUS304	NSSC 2120
Thickness/mm	12–16	14	9–12
Construction cost	1 (Standard)	1.2	1.02
Life cycle cost	1.14	1.2	1.02

However, although stainless steel is superior from the viewpoint of life cycle cost because of the maintenance cost minimization, initial investment is considered large, and therefore, stainless steel is rarely employed for such usage. Furthermore, since social infrastructure is a field that requires high municipality, JIS-specified steels are used basically, and employment of new steel has been considered difficult.

To improve the situation, the following two actions were taken. The first is the first case of stainless steel registration to the New Technology Information System (NETIS), an information service system provided by the Ministry of Land, Infrastructure, Transport and Tourism for the purpose of publicizing new technologies and promoting the practical use thereof. The second is the concrete presentation of the superiority in using NSSC 2120 based on the structural calculation conducted by the steel manufacturer itself. **Table 2** shows the virtual cost of a water gate calculated on the assumption that it is constructed by using NSSC 2120, and compared with the cases of using carbon steel and SUS304.[9)] As compared with the case of carbon steel, NSSC 2120 is superior in life cycle cost, the sheet thickness can be reduced, and therefore the construction cost does not differ greatly from the case of carbon steel. Furthermore, by reducing the weight of the gate, load to gate-operating motors is alleviated.

As a result of these efforts, the duplex stainless steel represented by NSSC 2120 is now recognized as a competitive material to carbon steel or Al alloy, and a move to employ it in infrastructure facilities nationwide is growing. Furthermore, the application to bridges and structures for the preservation of cultural assets has started. Application examples of NSSC 2120 are shown in **Fig. 6**.

NSSC 2120 was registered to JIS as SUS821L1 in 2015. In ad-

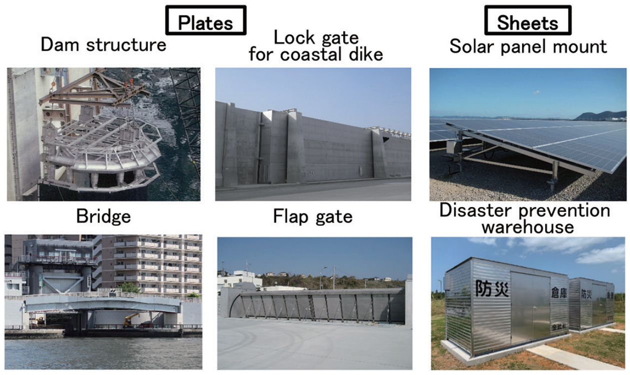

Fig. 6 Application examples of NSSC 2120

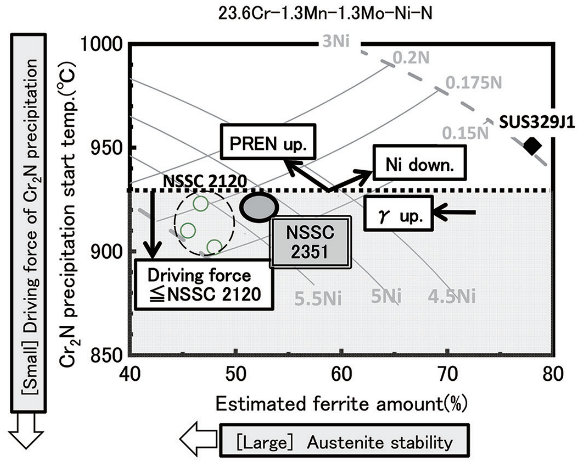

Fig. 7 Derivation of appropriate component of NSSC 2351 by equivalent line map of estimated ferrite amount and Cr_2N precipitation start temperature

dition, this development received the METI Minister Award of the 6th Monodzukuri Nippon Grand Award of fiscal 2015 and the 39th Japan Institute of Metals and Materials Technical Development Award in 2016.

5. Development of Duplex Stainless Steel NSSC 2351 Applicable to Brackish Water and Other Environments

5.1 Problem of substitute duplex stainless steel of SUS316L and the concept of new steel

NSSC 2120 is a substitute steel of SUS304, and used for facilities in fresh water and/or a lock gate that does not go under water normally. For usage such as a water gate under brackish water conditions that requires high pitting corrosion resistance, SUS323L stainless steel that was developed in the mid 1980s as a substitute duplex stainless steel for SUS316L is applied. However, under stringent conditions whereby a high level of chlorides almost equal to the level of sea water is contained, the corrosion resistance of welds of SUS323L occasionally goes below that of SUS316L. In the meantime, the higher ranking steel SUS329J3L is a steel of high alloying metal cost. Therefore, development was started aiming at a duplex stainless steel that is equipped with corrosion resistance inclusive of welds equal to or higher than that of SUS316L and an alloying metal cost lower than that of SUS329J3L and SUS316L.

One of the JIS-specified duplex stainless steels is SUS329J1 (23–28%Cr, 3–6%Ni, 1–3%Mo, ≤1.5%Mn). The PREN of the said JIS standard steel exceeds that of SUS323L, and the alloying metal cost is lower than that of SUS329J3L. It has a composition system satisfying that of the target steel of this report. However, the steel is considered to be one that has inferior weldability, and therefore, is exclusively used for forged products with no welding. Therefore, the development of new SUS329J1 was launched to solve the welding performance problem based on the SUS329J1 composition system.

5.2 Composition design

N is not specified in the compositions of SUS329J1, and the problem of inferior weldability is attributed to the small amount of austenite reprecipitation at weld heat affected zone due to low N. Therefore, based on the addition of N as a premise, we further decided to incorporate the following concepts which are similar to those used in designing the NSSC 2120 composition: ① to control the precipitation driving force of Cr nitride with the Cr_2N precipitation starting temperature, ② to maintain the amount of austenite reprecipitation at welds by reducing the amount of ferrite in the base metal. First, a 23.6Cr-1.3Mn-1.3Mo composition system was established according to the composition range of the standard of SUS329J1, and Cr and Mo were set near the lowest limit and Mn was set near the upper limit. To find the optimum values of Ni and N, an equivalent line map of the ferrite amount estimated by calculation from compositions (X-axis) and the Cr_2N precipitation start temperature (Y-axis) was then devised (**Fig. 7**). From this, Ni and N that satisfy the following conditions were considered as optimum: a) the Cr_2N precipitation start temperature to be equal to or below that of NSSC 2120, b) PREN amount to be the highest, c) amount of Ni to be the smallest, and d) the austenite amount to be the largest. As a result, a composition system of 23.6%Cr-5.2%Ni-1.3%Mo-0.17%N was derived. Furthermore, microalloying technology was introduced, suppression technology of Cr nitride precipitation in welding was further conducted, and the composition system was finally decided.

5.3 Comparison of properties with those of existing SUS329J1 and SUS316L, SUS323L

Table 1 shows examples of compositions of NSSC 2351 and that of existing SUS329J1 for comparison. In NSSC 2351, PREN is higher than 30, the base metal pitting corrosion resistance is higher than that of SUS316L, and the alloying metal cost does not exceed that of SUS316L. A 2 mm-thick cold-rolled and annealed steel sheet of this steel and that of the existing SUS329J1 were both TIG bead on welded without using a welding rod under the welding condition of 225A-10V-50cm/min (heat input 3 kJ/cm). The microstructure of the section with the weld line portion included was observed after oxalic-acid etching. **Figure 8** shows the microstructures around the welding metal center. In the existing SUS329J1 steel, most of the weld metal is of the coarse ferrite phase, and the austenite phase is precipitated at the ferrite grain boundaries very thinly; while in NSSC 2351, a large amount of the fine austenite phase is precipitated intragranularly.

Next, 12 mm-thick hot-rolled and annealed steel sheets of NSSC 2351, SUS323L, SUS329J3L, and SUS316L were FCAW-welded (three passes) under the welding condition of 200A-30V-35cm/min (heat input 10 kJ/cm), and SAW-welded (two passes) under the welding condition of 550A-32V-30cm/min (heat input 35 kJ/cm) using the welding rod of SUS329J3L. A plurality of test samples were taken from the surface layer and immersed in 6%$FeCl_3$ +1%HCl for testing, and the lowest temperature where pitting cor-

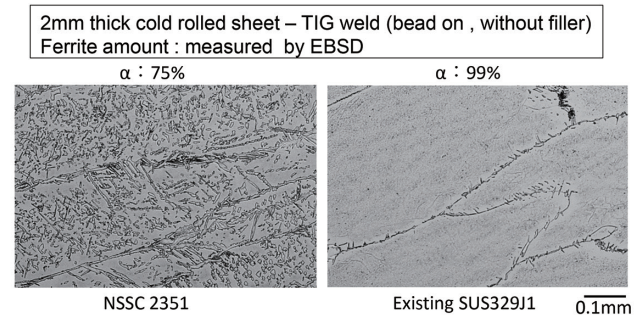

Fig. 8 Comparison microstructure of TIG weld metal without filler (3 kJ/cm)

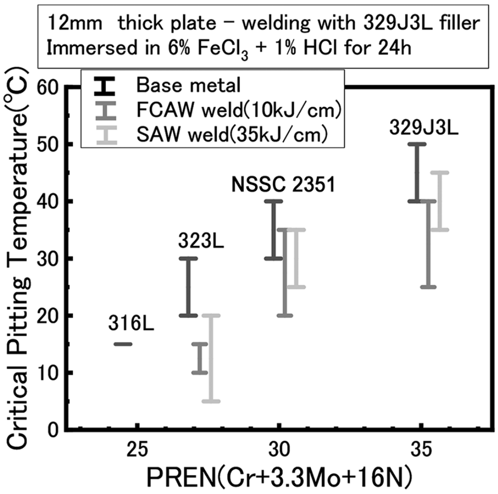

Fig. 9 Critical pitting temperature of base metals & weldings by ferric chloride immersion test[10]

rosion starts to occur (critical pitting temperature: CPT) was pursued. **Figure 9**[10] shows the relationships between PREN and the measured CPT results of the base metal and welds of various steels. The corrosion resistance of welds of SUS323L is below that of the base metal of SUS316L. On the other hand, in NSSC 2351, the corrosion resistance of the base metal and the welds is higher than that of the base metal of SUS316L.

Thus, NSSC 2351 is a duplex stainless steel that is applicable to infrastructure facilities such as water gates in coastal areas, food, and chemical tanks, etc., where SUS316L has been conventionally used, and has features of high strength and resource saving.

6. Conclusion

We developed the distinctive lean duplex stainless steel series NSSC 2120 and NSSC 2351 capable of substituting SUS304 and SUS316L. We created this strategic merchandise having high added values of high strength and resource saving, and furthermore, through the expansion of sales with high level problem-solution using these steels, we are creating a new big stainless steel market. Regarding manufacturing cost and productivity issues, we have realized a high productivity compatible with that of general use stainless steel production by timely equipment investment and steady intangible improvements.

This report mainly described the application to the usage of heavy plate structural material. However, also regarding the usage of thin sheets, this steel is widely used as a substitute material of SUS304 and SUS316L by taking advantage of the meritorious characteristics of high strength, weight saving, and resource saving, and greater expansion of usage is expected.

References

1) Berhardsson, S.: Duplex Stainless Steels ’91, 1991, p. 137
2) Johansson, P. et al.: 4th European Stainless Steel Science and Market Congress, Vol. 2, 2002, p. 153
3) Miyuki, H. et al.: Sumitomo Metals. 42, 272 (1990)
4) Blom, K.J.: Proc. Int. Conf. Stainless Steels ’87, 1987, York
5) Holmberg, B. et al.: Duplex 2007 International Conference & Expo., 2007, Grado
6) Oikawa, Y. et al.: Materia Japan. 55, 70 (2016)
7) Oikawa, Y. et al.: Journal of the Japan Welding Society. 82, 435 (2013)
8) Oikawa, Y. et al.: CAMP-ISIJ. 25, 1183 (2012)
9) Endo, Y. et al.: Electric Power Civil Engineering. 385, 14 (2016)
10) Oikawa, Y. et al.: CAMP-ISIJ. 33, 227 (2020)

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