KAWASAKI STEEL TECHNICAL REPORT

No.40 (May 1999)

Steinless Steel and Steel Platel

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Development of Ti-bearing High Performance Ferritic Stainless Steels R430XT and RSX-1*

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1 Introduction

Stainless steel is used widely in house wares, electrical equipment, various types of design material, industrial equipment, automotive parts, and construction materials because it does not rust in the ordinary living environment and offers a beautiful surface gloss. Among the stainless steels, austenitic SUS304 (18Cr-8Ni) has various excellent properties such as formability, corrosion resistance, and weldability, and is therefore used both in the largest number of applications and in the greatest quantity. On the other hand, SUS430, which is a representative type of ferritic stainless steel, is inferior to SUS304 in formability, ridging property (a stripe pattern originating in surface corrugations which occur during forming), corrosion resistance, and weldability. For this reason its applications are limited in spite of its economical price.

Efforts have been made to remedy these shortcomings of SUS430 since an early date, and include the development and practical application of steels such as SUS447J1 (30Cr-2Mo) and SUS444 (18Cr-2Mo) for improved corrosion resistance and SUS430LX (16Cr-Ti-Nb) for improved formability. However, because these steels were developed by further enhancing certain excellent properties or improving certain drawbacks, they continued to be inadequate in general applicability. In particular, high purification by reducing the content of C and N and stabilizing them with Nb and Ti, which was generally performed as a method of improving formability and corrosion resistance, caused the coarsening of the solidification structure of the slab and the growth of a banded structure due to reduction of the γ-phase during hot rolling, and thus had the negative effect of causing a remarkable increase in ridging.[1] Therefore, the development of a technology which would improve the r-value and elongation and at the same time solve the problem of ridging was desired.

In previous research, the authors isolated the respective effects of C and N in ferritic stainless steels[2,3] and compared the effects of Ti and Nb,[4,5] and thereby found a method of solving the above-mentioned problems of high purity ferritic stainless steels. As equipment for realizing this method in industrial production, Kawasaki Steel possesses a new steelmaking shop[6,7] which is capable of mass producing high purity stainless steel with controlled contents of C and N and a new hot strip mill[8] which makes it possible to improve material properties remarkably by controlled rolling.

With ferritic stainless steels which are intended to cover a wide range of applications, there are cases in

* Originally published in *Kawasaki Steel Giho*, **30**(1998)2, 93–98

which corrosion resistance becomes inadequate at the level of SUS430. Accordingly, in the steels developed in the present work, the most appropriate alloy composition was investigated[2,9] with the aims of improving corrosion resistance under an exposure in the field, which is the main service environment for stainless steel, and in addition, of improving the corrosion resistance of the weldment.

Based on the results of the study outlined above and the capabilities of the new facilities at Kawasaki Steel, the high performance ferritic stainless steels R430XT and RSX-1, which also have a high degree of general applicability, were developed. This paper describes the development of these steels and the features of the products.

2 Experimental Procedure

2.1 Test Specimens

The range of the chemical composition investigated is shown in **Table 1**. The main components studied were C, N, Cr, Ti, Nb, Mo, Cu, and Ni. Test specimens were prepared on a laboratory scale from 50 kg ingots which were melted in a high frequency induction vacuum melting furnace, hot rolled, annealed as hot band, and cold rolled and annealed, and finally provided for experiments in the form of annealed cold rolled sheets with a thickness of 0.7–1.0 mm. In addition, the preparation conditions were varied with each steel type as required by the purpose of the investigation[2,10].

2.2 Formability Tests

Tensile tests were performed at a cross-head speed of 10 mm/min using JIS13B test pieces. The r-value was measured at an elongation of 15%. The average r-value was calculated as $r = (r_{0°} + 2 \times r_{45°} + r_{90°})$. (The angle refers to the direction at which the test piece was taken relative to the rolling direction.) The evaluation of the ridging property was performed by applying a #600 polished finish to the surface of JIS5 tensile test pieces taken parallel to the rolling direction and visually comparing the degree of ridging which occurred under 25% tensile deformation with a standard sample. Ridging grades between 1 and 3 were given, with 1 indicating that absolutely no ridging could be detected, and the degree of ridging becoming more pronounced as the value increased.

Table 1 Chemical compositions of steels investigated

(mass%)

C	Si	Mn	P	S	Cr	Mo, Cu, Ni	N	Ti, Nb / (C + N)
0.000 5~0.030	0.1	0.2	0.03	0.005	16~22	0~1.5	0.004~0.015	0~15

2.3 Corrosion Tests

When the aim is to develop a stainless steel with high general applicability, corrosion resistance in a neutral chloride environment becomes the most important property. Therefore, the pitting potentials of test specimens which were mechanically polished through #600 SiC metallographic paper with water were measured in a 3.5% NaCl aqueous solution in accordance with JIS G 0577. In addition, in order to investigate corrosion resistance under cyclic corrosive conditions such as those in the atmospheric environment, the pitting potential of the same samples was measured periodically, and the changes in the pitting potential at the time of measurements were investigated.[2]

2.4 Corrosion Tests of Weldment

The objects of the newly developed steels also include welding applications. Because corrosion of the weldment frequently occurs at parts where a thin oxidation film has formed, the effect of a thin oxidation film, which corresponds to this welding scale, on corrosion resistance was investigated. As a method of simulating the rapid oxidation which occurs under a shielding gas during welding, a thin oxide film was formed by holding the test pieces at 400–1 150°C × 4 s under an atmosphere consisting of 99% Ar + 1% air. Corrosion resistance was then evaluated by measuring the pitting potential in a 3.5% NaCl aqueous solution.[9]

3 Experimental Results

3.1 Formability

Generally, the formability of ferritic stainless steels is improved by reducing the content of the interstitial elements C and N, but the ridging property deteriorates. **Figures 1** and **2** show the results of experiments in which the effects of C and N were investigated separately with the aim of satisfying both of these requirements. Although the r-value is improved by reducing C

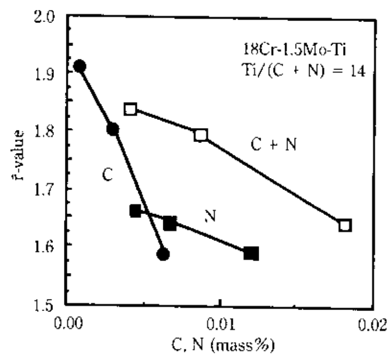


Fig. 1 Effects of C and N contents on the r-value of 18%Cr-1.5%Mo-Ti ferritic stainless steels

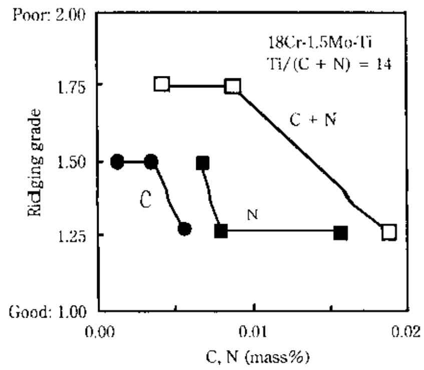


Fig. 2 Effects of C and N contents on the ridging grade of 18%Cr-1.5%Mo-Ti ferritic stainless steels

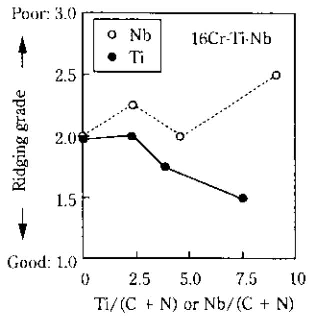


Fig. 3 Effects of Ti or Nb/(C + N) value on the ridging grade of 16%Cr-Ti · Nb ferritic stainless steels

and N, the degree of improvement is greater when C is reduced, and the *r*-value is comparatively insensitive to reductions in N. On the other hand, C and N have similar effects on the ridging property, which deteriorates as the contents of C and N decrease. Accordingly, in order to satisfy the requirements of both high *r*-value and the ridging property in Ti-bearing ferritic stainless steels, it is important to reduce the content of C as far as possible while keeping an appropriate level of N.

Figure 3 shows the results of experiments in which Ti and Nb were compared as stabilizing elements for C and N. In contrast to Ti-bearing steels, in which the ridging property improves as Ti/(C + N) increases, the ridging property deteriorates in Nb-bearing steels as Nb/(C + N) increases. As the reason why Ti addition is more effective than Nb addition in improving the ridging property, it is considered that, because the chemical affinity for N is stronger in Ti than in Nb, a small amount of TiN is precipitated in the continuous casting stage, resulting in a finer solidification structure, and because the TiN which precipitates is relatively coarse, recrystallization during hot rolling occurs more easily with Ti addition.[10]

For improving the formability of Ti-bearing stainless steels, simple adjustment of the content of alloying elements is inadequate; it is also necessary to optimize the production conditions. The authors made a detailed study of the production process, and also found conditions which will satisfy the requirements of both high *r*-value and the ridging property in the production conditions.[2,3] The critical point, which led the basis of that technology, lay on an elucidation of recrystallization behavior during hot rolling. It was found that recrystallization during hot rolling occurs easily in ferritic stainless steels under the appropriate rolling conditions, and colonies of grains with the same orientation, which originate in the solidification structure to be the main cause of ridging, are broken up and destroyed. **Figure 4** shows an example of the effect of hot rolling conditions on the *r*-value and ridging property. Optimizing the rough hot rolling condition and lowering the FDT are effective in improving the ridging property and *r*-value. Adequate recrystallization during annealing of the hot band is also effective in improving the ridging property, but because over-annealing invites coarsening of grains, and thus can cause orange peel after forming, it is essential to select appropriate conditions.

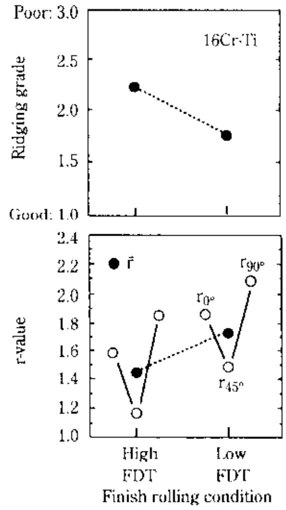


Fig. 4 Effect of hot rolling condition on the *r*-value and ridging grade of 16%Cr-Ti ferritic stainless steel

3.2 Corrosion Resistance

Because the corrosive conditions in atmospheric environments generally change cyclically, pits that have developed show behavior which is characterized by temporary repassivation, followed by activation, etc. However, the effect of alloying elements under conditions in which the corrosion environment changes in this manner had not been adequately investigated. **Figure 5** shows the change in the pitting potential which was measured cyclically in 18%Cr steel and 18%Cr steel with added Cu, Ni, and Mo. In all the steels, the pitting potential showed a tendency to increase as the number of cycles increased, but in comparison with the 18%Cr steel, the

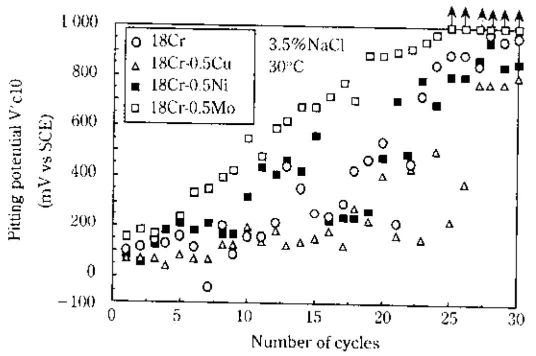


Fig. 5 Change in the pitting potential of ferritic stainless steels with the number of cyclic measurement

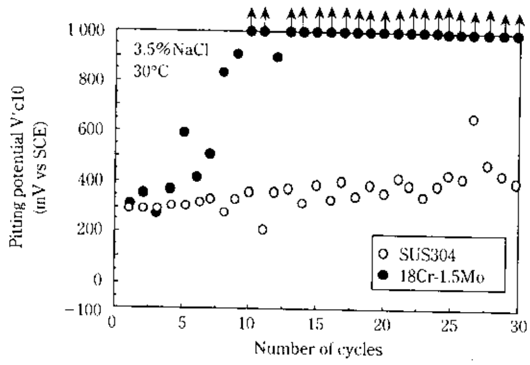


Fig. 7 Change in the pitting potential of SUS304 and 18%Cr-1.5%Mo ferritic stainless steel with the number of cyclic measurement

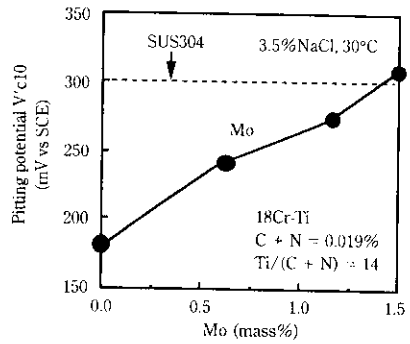


Fig. 6 Effect of Mo content on the pitting potential of 18%Cr-Ti ferritic stainless steels

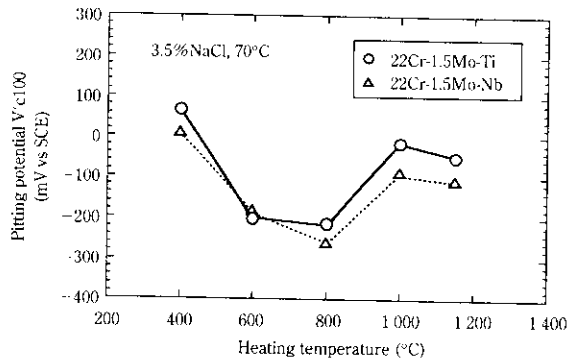


Fig. 8 Effect of heating temperature on the pitting potential of Ti and Nb stabilized 22%Cr-1.5%Mo ferritic stainless steels

degree of increase was small with 0.5% Cu addition and showed virtually no difference with 0.5% Ni addition. However, when 0.5% Mo was added, the degree of increase was large, and it can therefore be understood that Mo is particularly effective in improving corrosion resistance under cyclic corrosive conditions.

The level of corrosion resistance set in the newly developed steel should be decided depending on the application. The Mo content which is required to secure corrosion resistance equal to or better than that of general purpose stainless steel SUS304 is approximately 1.5%, as can be estimated from **Fig. 6**. **Figure 7** shows the pitting potential obtained by cyclic measurements of 18%Cr-1.5%Mo steel and SUS304. With SUS304, the increase in the pitting potential with the number of cycles is small, and new pits develop in each cycle, but in contrast, the pitting potental of the 18%Cr-1.5%Mo steel increases rapidly as the number of cycles increases. As a result, new pits do not develop in the latter steel after approximately 10 cycles. Because the pitting corrosion resistance of the 18%Cr-1.5%Mo steel improves remarkably with the number of cycles of the corrosion environment in this manner, the number of pits which develop is small in comparison with SUS304, and the material shows excellent corrosion resistance from the viewpoint of external appearance.

3.3 Corrosion Resistance of Weldments

Ferritic stainless steels have the outstanding property of not being susceptible to stress corrosion cracking. Apparatuses for hot water can be mentioned as an application in which this property is required. In the production process of these apparatuses welding is frequently used. A shielding-gas is indispensable when welding ferritic stainless steels, but even when a gas is used, a thin oxide film forms on the weldment. The mechanism of deterioration of corrosion resistance in areas where scale forms during welding differs depending on the temperature to which the area is heated. It is reported that the corrosion resistance of areas heated to high temperatures of over 1 000°C is affected by resistance of oxide film formed at such temperatures to Cl^- attack and the alloying elements which is related to the oxidation.[9] **Figure 8** shows the results of the corrosion resistance of areas where scales formed during welding when Ti or Nb was used as the stabilizing element. In a test which simulated rapid oxidation under shielding gas during welding, Ti-bearing steel and Nb-bearing steel showed no large dif-

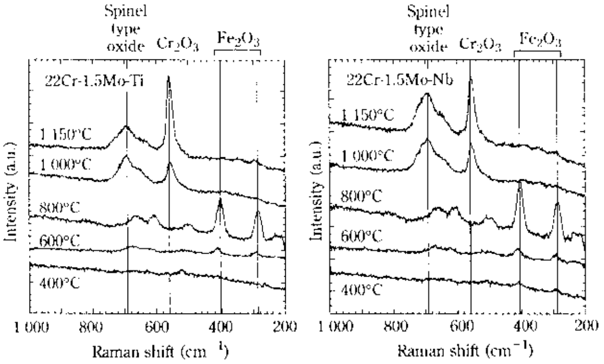


Fig. 9 Raman spectroscopic analysis of oxide films of Ti and Nb stabilized 22%Cr-1.5%Mo ferritic stainless steels

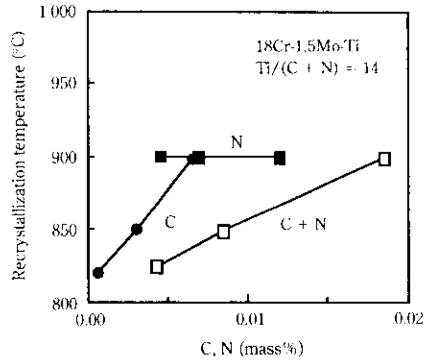


Fig. 10 Effects of C and N contents on the recrystallization temperature of 18%Cr-1.5%Mo-Ti ferritic stainless steels

ferences up to 800°C, but at high temperatures of 1 000°C and above, the Ti-bearing steel showed superior values. **Figure 9** shows the structures of the oxide films. The oxide films which formed at temperatures of 1 000°C and above were comprised of Cr_2O_3 and spinel type oxides. However, in comparison with the Nb-bearing steel, the film on the Ti-bearing steel contained fewer spinel type oxides and more Cr_2O_3. This fact is considered to be the reason why areas of Ti-bearing steels with welding scale show strong resistance to Cl^- attack. Accordingly, if use in applications which require corrosion resistance in the weldment is also considered, the adoption of Ti as the stabilizing element is appropriate.

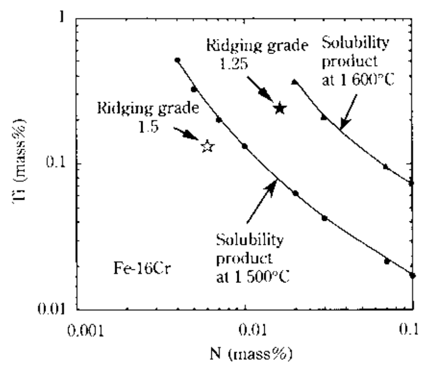


Fig. 11 Ridging property and solubility product of TiN in 16%Cr stainless steel

4 Study of Production Process

The experimental results showed that in order to produce a high performance ferritic stainless steel, it is important to reduce the C content to the lowest possible level and adjust the N content to keep a proper level, while also adding Ti. To produce a stainless steel with a higher level of general applicability, a study of manufacturability is also necessary.

Kawasaki Steel had already developed cold rolling by the tandem mill and a new pickling system in the CAL as a high efficiency production process. When general applicability is considered, it is important to be able to produce the newly developed steels with the CAL. To perform high speed annealing in the CAL, it is necessary to reduce the recrystallization temperature of the steels. This point was investigated because, even with Ti-bearing steel, which has a relatively low recrystallization temperature, the recrystallization temperature may exceed the annealing range of the CAL depending on the alloy composition. **Figure 10** shows the effect of C and N on the recrystallization temperature of Ti-bearing steel. The recrystallization temperature increases due to increases in the C content, but is insensitive to increases in N. Thus, from the viewpoint of manufacturability by the CAL, C should be reduced as low as possible.

The Ti addition was adopted in the newly developed steel. In this case, manufacturing-related problems with conventional Ti-bearing steels are TiN stringers, which cause surface defects in cold rolled products, and temper color during bright annealing. A composition design which keeps the proper amount of N for improvement of the ridging property has been adopted, but excessive N causes TiN stringers. **Figure 11** shows the evaluation results of the ridging property and the TiN solubility product curve in a 16%Cr steel. The ridging property is improved by increasing the content of Ti and N, but the content of Ti and N in the newly developed steels is controlled within the proper range because TiN clusters will develop, resulting in stringers, if the content greatly exceeds the solubility product during solidification in the continuous casting process.

Further, because Ti is an easily-oxidized element, temper color which is caused by the oxidation appears easily with the ordinary bright annealing finish. To solve this problem, the bright annealing line at Kawasaki Steel is equipped with a refiner for the atmosphere gas, which controls the dew point, and post treatment equipment, which eliminates a certain amount of temper color and

Table 2 Chemical compositions of R430XT and RSX-1

(mass%)

Steel	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	N
R430XT	0.005	0.10	0.20	0.031	0.003	16.3	0.10	—	Added	0.010
RSX-1	0.003	0.06	0.15	0.032	0.005	17.8	0.08	1.45	Added	0.007

Table 3 Mechanical properties of R430XT and RSX-1

Steel	0.2% proof strength (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Vickers hardness	$\bar{r}$-value	n-value	Erichsen value (mm)	Conical cup value (mm)	Ridging grade
R430XT	290	440	34	140	1.70	0.23	10.2	27.2	1.5
RSX-1	328	492	33	160	1.50	0.23	9.5	27.4	1.5
SUS304	265	660	58	160	1.00	0.48	13.0	27.2	1.0
SUS430	310	510	29	160	0.80	0.21	9.1	28.1	2.5

Sheet thickness: 0.7 mm

also improves corrosion resistance by modifying the oxide film. As a result, it is possible to obtain a bright annealed finish which has excellent corrosion resistance and is free of temper color, even in Ti-bearing steels.

5 Features of Newly Developed Steels

5.1 Chemical Composition and Mechanical Properties

The chemical compositions of the newly developed steels produced by the commercial process are shown in **Table 2**. These two types of steel are R430XT (ultra low C, low N-16%Cr-Ti-bearing steel), which is equivalent to SUS430 in its level of corrosion resistance, and RSX-1 (ultra low C, low N-18%Cr-1.5%Mo-Ti-bearing steel), which is equal or superior to SUS304 in corrosion resistance. As features of the chemical composition of both steels, the r-value and ridging property are satisfied simultaneously by adopting an ultra low C, low N composition, and formability, corrosion resistance, and weldability are obtaind by adding an appropriate amount of Ti for stabilizing C and N. Moreover, in the production process, as mentioned previously, the hot rolling conditions and cold rolling conditions have been optimized in order to realize further improvement in the r-value and ridging property.

Mechanical properties are shown with those of comparison steels in **Table 3**. Although the elongation values of R430XT and RSX-1 are low in comparison with SUS304, the r-values of the newly developed steels are excellent, and as a result, the new steels show virtually the same formability as SUS304 in the conical cup test. Moreover, as shown in **Photo 1**, the ridging which occurs during forming is substantially improved in comparison with SUS430. Thus, the newly developed steels offer formability on the same level as SUS304 in products which are processed mainly by draw forming.

Table 4 shows the results of Erichsen tests of TIG weldments in R430XT and SUS430 (sheet thickness, 1.2 mm; 2B finish). With R430XT, the deterioration of the ductility of the weldment in comparison with that of the base metal is negligible, and the formability of the weldment is markedly superior to that of SUS430.

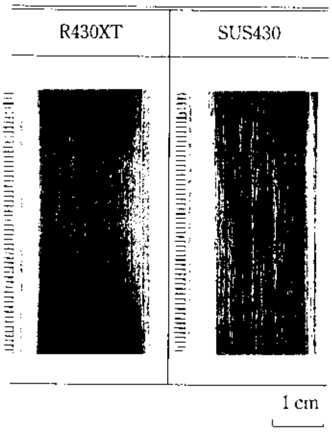


Photo 1 Appearance of 25% tensiled specimens

Table 4 Erichsen value of TIG-weldment of R430XT

Steel	TIG-weldment (mm)	Base metal (mm)
R430XT	10.4	11.2
SUS430	2.2	9.8

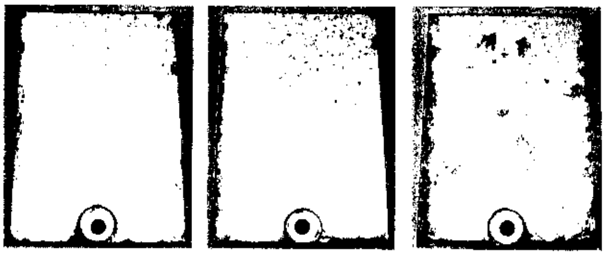
Sheet thickness: 1.2 mm

5.2 Corrosion Resistance

The pitting potential of R430XT and RSX-1 is shown in **Table 5** together with that of the comparison steels. R430XT shows corrosion resistance superior to that of SUS430, while RSX-1 is superior to SUS304. The results of a field exposure test for 3 months in a coastal area are shown in **Photo 2**. As mentioned previously, Mo-bearing RSX-1 is substantially superior to SUS304 in corrosion resistance because it shows particularly

Table 5 Pitting potential of R430XT and RSX-1 in 3.5%NaCl solution at 35°C

Steel	Pitting potential; V'c10 (mV vs SCE)
R430XT	110
RSX-1	320
SUS430	100
SUS304	300



(a) RSX-1 (b) SUS304 (c) SUS430 10 mm

Photo 2 Appearance of the steels after a field exposure test for 3 months in a coastal area

excellent corrosion resistance under the cyclic corrosive conditions.

5.3 Examples of Products

R430XT has been adopted in house wares, dewatering tanks of automatic washers, and other products due to its excellent formability and weldability. RSX-1 is used in external parts in which SUS304 has been used conventionally in applications which take advantage of its excellent corrosion resistance, and thus has naturally been adopted in the external parts of buildings, and also in the external members of small containers and similar parts. RSX-1 is also being used in the inner cases of electric pots (**Photo 3**) and other applications where excellent corrosion resistance is also required in weldments.

6 Conclusion

As a result of an investigation of the composition and production process of ferritic stainless steel, which was carried out in order to develop a high performance ferritic stainless steel with high general applicability, two new stainless steels which solve the problems of conventional high purity ferritic stainless steel were developed. These are R430XT (ultra low C, low N-16%Cr-Ti-bearing steel) and RSX-1 (ultra low C, low N-18%Cr-1.5Mo-Ti). The features of these steels are described below.

(1) By adopting a composition balance in which C is reduced as low as possible and an appropriate amount of N is retained, and optimizing hot rolling and cold rolling conditions, both the r-value and the ridging property can be satisfied, and excellent formability can be obtained.

(2) In cyclic corrosive environments, Mo is particularly effective in improving corrosion resistance. RSX-1, which contains 1.5% Mo, shows corrosion resistance superior to that of SUS304.

(3) Superior weldability and formability in areas of weldment can be obtained by Ti addition.

(4) Proper composition control makes possible various finishes, including not only annealing pickling finishes (2B, 2D), but also the bright annealing finish (BA), cold rolling by tandem mill-CAL finish, and others.

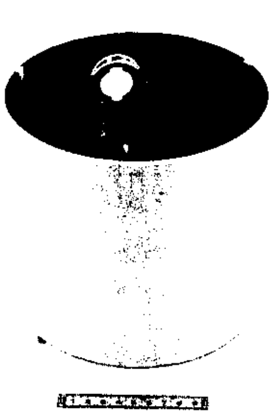


Photo 3 An example of the application of RSX-1 (inner case of an electric pot)

R430XT and RSX-1, are expected to be applied in a wide range of fields, including applications in which the ridging property is a problem with conventional ferritic stainless steels, applications requiring corrosion resistance and drawability, in which SUS304 has been used, and others.

References

1) Sutenresu Kyokai: "Sutenresukou Binran", (1995), 536, [Nikkan Kogyo Shinbunsha]
2) Y. Yazawa, T. Ujiro, S. Satoh, S. Kumazawa, M. Kobayashi, and S. Shiraishi: *CAMP-ISIJ*, **9**(1996)6, 1329
3) S. Kumazawa, M. Kobayashi, S. Shiraishi, Y. Yazawa, T. Ujiro, and S. Satoh: *CAMP-ISIJ*, **9**(1996)6, 1330
4) T. Yokota, T. Ujiro, S. Satoh, and T. Obara: *CAMP-ISIJ*, **9**(1996)6, 1326
5) M. Fujisawa, S. Ishikawa, Y. Kato, T. Ujiro, and S. Satoh: *Tetsu-to-Hagané*, **83**(1997)1, 66
6) Y. Nabeshima, S. Ogura, and S. Yamada: *Kawasaki Steel Giho*, **28**(1996)4, 206
7) Y. Kishimoto, K. Taoka, and S. Takeuchi: *Kawasaki Steel Giho*, **28**(1996)4, 213
8) T. Imae, N. Nomura, and S. Miyoshi: *Kawasaki Steel Giho*, **28**(1996)4, 219
9) S. Suzuki, Y. Usui, Y. Yazawa, T. Ujiro, and S. Satoh: *CAMP-ISIJ*, **10**(1997)3, 463
10) Y. Kato, Y. Yazawa, T. Ujiro, S. Satoh, and S. Kumazawa: *CAMP-ISIJ*, **10**(1997)6, 1201