KAWASAKI STEEL TECHNICAL REPORT

No.41 (October 1999)

Advances in Iron and Steel Technologies,

Commemorating the 30th Anniversary of

Technical Research Laboratories

Recent Activities in Research of Stainless Steels

Susumu Satoh, Takumi Ujiro, Kazuhide Ishii

Synopsis :

The demand and requirements for advanced properties of stainless steels for automotive exhaust systems, buildings, and electrical products are increasing. High performance ferritic stainless steels for automotive exhaust manifolds (R429EX: 15Cr-0.9Si-0.45Nb), catalytic converters (R20-5USR: 20Cr-5Al-La-Zr), and mufflers (R436LT: 18Cr-1.2Mo-Ti, R432LTM: 18Cr-0.5Mo-Ti) were developed on the basis of the studies of thermal fatigue, high temperature oxidation, and condensate corrosion. High purity ferritic stainless steels (R30-2: 30Cr-2Mo, R24-2: 24Cr-2Mo, R445MT: 22Cr-1.5Mo, RSX-1: 18Cr-1.5Mo) for buildings were also developed on the basis of the study of atmospheric corrosion. Investigations into ridging mechanism led to the improvement of the formability of ferritic stainless steels (R430UD: 17Cr, RSX-1). Kawasaki Steel produces these excellent ferritic stainless steels by using newly installed production facilities in Chiba Works.

The body can be viewed from the next page.

Recent Activities in Research of Stainless Steels*

Susumu Satoh
Dr. Eng.,
General Manager,
Stainless Steel Lab.,
Techinical Res. Labs

Takumi Ujiro
Senior Researcher,
Stainless Steel Lab.,
Techinical Res. Labs

Kazuhide Ishii
Senior Researcher,
Coating Lab.,
Technical Res. Labs

Synopsis:

The demand and requirements for advanced properties of stainless steels for automotive exhaust systems, buildings, and electrical products are increasing. High performance ferritic stainless steels for automotive exhaust manifolds (R429EX: 15Cr-0.9Si-0.45Nb), catalytic converters (R20-5USR: 20Cr-5Al-La-Zr), and mufflers (R436LT: 18Cr-1.2Mo-Ti, R432LTM: 18Cr-0.5Mo-Ti) were developed on the basis of the studies of thermal fatigue, high temperature oxidation, and condensate corrosion. High purity ferritic stainless steels (R30-2: 30Cr-2Mo, R24-2: 24Cr-2Mo, R445MT: 22Cr-1.5Mo, RSX-1: 18Cr-1.5Mo) for buildings were also developed on the basis of the study of atmospheric corrosion. Investigations into ridging mechanism led to the improvement of the formability of ferritic stainless steels (R430UD: 17Cr, RSX-1). Kawasaki Steel produces these excellent ferritic stainless steels by using newly installed production facilities in Chiba Works.

1 Introduction

Kawasaki Steel began the full-scale production of stainless steels around 1960. In the 1980s, the company introduced advanced equipment for stainless steels at Chiba Works with the aim of realizing higher levels of quality and productivity. In particular, the construction of No. 4 steelmaking shop, No. 3 hot strip mill, and the new cold rolling and annealing plant had been completed and operation of these facilities had been started by 1995. At No. 4 steelmaking shop, the company established a technology for low cost production of high quality stainless steel[1,2] by developing a smelting reduction method for Cr ore and the SS-VOD (strongly stirred-vacuum oxygen decarburization) method, which is capable of refining high purity stainless steels in large quantity (180 t). The notable technologies developed at No. 3 hot strip mill were a technology for rolling wide coil from mild steel to high alloy stainless steels using a high capacity mill and the world's first technology for continuous hot rolling by joining sheet bars.[3] Technologies established for cold rolling and annealing processes included a high speed cold rolling and annealing technology using a new cluster mill and new annealing and pickling line, and a technology for realizing high productivity using the tandem mill and a continuous annealing and pickling line which is used jointly for stainless steels and carbon steels.[4]

The applications of stainless steels have grown greatly in the last ten years, and fields where further growth is expected in the future include automotive exhaust systems, building materials, and electrical products. The success of stainless steels in these fields is attributable to the fact that the durability of stainless steels satisfies the increased marketplace needs for longer life and maintenance free performance. In the stainless steel research laboratory, new products which meet the requirements of these growth fields have been developed utilizing the advanced equipment mentioned adove. This report will present an outline of these new products.

2 Development of Stainless Steels for Automotive Applications

In order to respond to the strengthening of automotive emission regulations, higher engine performance, and longer guarantee periods, stainless steels are increasingly being adopted in automotive exhaust systems. In the exhaust system, because the features which are required vary greatly depending on the part, research and development have been conducted as required by the specific application. The products which have been developed as a result include R429EX, which is excellent in resistance to thermal fatigue and formability, as a

* Originally published in *Kawasaki Steel Giho*, 31(1999)1, 28–33

Table 1 Chemical compositions of stainless steels for automotive exhaust system

(mass%)

Steels	C	Si	Mn	Cr	Mo	Ti	Nb	Others
R429EX	0.01	0.9	0.4	14.8	—	—	0.45	
R20-5USR	0.01	0.2	0.1	20.1	—	—	—	Al/5.8 La/0.08 Zr/0.03
R436LT	0.01	0.1	0.2	17.8	1.2	0.3	—	
R432LTM	0.01	0.1	0.2	17.5	0.5	0.3	—	
SUH409L	0.01	0.3	0.3	11.2	—	0.3	—	
SUS436J1L	0.01	0.3	0.3	17.5	0.5	—	0.38	
SUS430J1L	0.01	0.5	0.2	19.3	—	—	0.45	Cu/0.5
R434LN2	0.005	0.3	0.2	19.0	1.9	—	0.25	

material for exhaust manifolds; R20-5USR, which possesses excellent resistance to high temperature oxidation, for catalytic converters; and R436LT and R432LTM, which have superior corrosion resistance, for mufflers. The representative chemical compositions of these newly developed steels are shown in **Table 1**.

2.1 Stainless Steel for Exhaust Manifolds

Because the exhaust manifold is heated to a high temperature in a condition which is restricted by surrounding parts, resistance to thermal fatigue and resistance to oxidation are required in the exhaust manifold material. Due to the higher performance of engines in recent years, a material which is capable of withstanding higher service temperatures than in conventional use had been required. At the same time, because the shapes of exhaust manifolds have become increasingly complex, improved formability had been required. Therefore, the effect of alloying elements such as Cr, Mo, Cu, Si, and others and the factors which influence resistance to thermal fatigue were investigated, and a study was carried out with the aim of obtaining both formability and resistance to oxidation. In addition, the fact that the effect of high temperature strength and elongation on fatigue properties differs depending on the restraint ratio was clarified.[5] Based on these results, R429EX (15Cr-0.9Si-0.45Nb) was developed. This new product has resistance to thermal fatigue better than that of Type 436J1L (17.5Cr-0.4Nb-0.5Mo) and Type 430J1L (19Cr-0.4Nb-0.5Cu), which had been used conventionally, and an even higher level of formability.

2.2 Stainless Steel for Metal Honeycomb

In order to purify exhaust gas, automobiles which are powered by gasoline engines are equipped with a catalytic converter in which a noble metal catalyst is supported by a honeycomb substrate. Ceramic substrates have mainly been used in this substrate, but recent years have seen increasing use of metal substrates, which are assembled from stainless steel foil, in response to stricter emission regulations. This change is attributable to various advantages of metal substrates, which include the fact that the wall thickness is thinner, and consequently, the resistance to the exhaust gas flow is lower, and heating up is easier when the engine is started due to the small heat capacity of the metal, and as a result, the start-up property of the catalytic reaction is good.

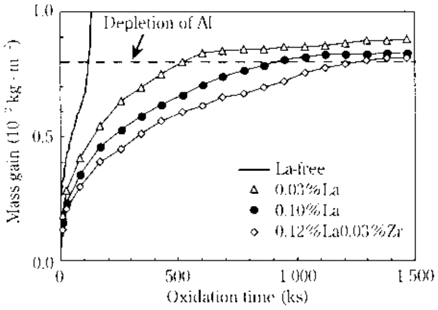

Fig. 1 Oxidation behavior of 50 μm thick foil samples without addition of La and with addition of La, La-Zr to 20Cr-5Al steels at 1 373 K in air

Because the substrate is heated to 900°C or higher by the high temperature exhaust gas and the catalytic reaction, 20Cr-5Al stainless steel foil, which has excellent resistance to oxidation, is used as the substrate material. When this steel is oxidized, a protective film of Al_2O_3 forms on the surface, giving the material excellent resistace to oxidation. However, foils of this material have the problem of Al depletion because their volume is small as compared with their large surface area, and consequently, it is important to reduce the oxidation rate. Although various elements, including the rare earth elements and others, had been studied in the past mainly from the viewpoint of improving the adhesiveness of the oxide film, in this work, the effect of these elements on the oxidation rate was studied in detail. It was found that La is effective in reducing the oxidation rate,[6] and that a compound addition of Zr, together with La, further reduces the oxidation rate,[7] leading to the development of R20-5USR (20Cr-5Al-La-Zr). **Figure 1** shows the change in mass with time in the oxidation of foils with compositions of 0.03% and 0.10% La and 0.12% La-0.03% Zr at a temperature of 1 373 K. It can be understood that the oxidation rate decreases as the amount of La addition increases, and the oxidation rate is further reduced by a compound addition of La and Zr. The Al_2O_3 film grows due to the fact that oxygen ions diffuse through the grain boundary of the film and reach the

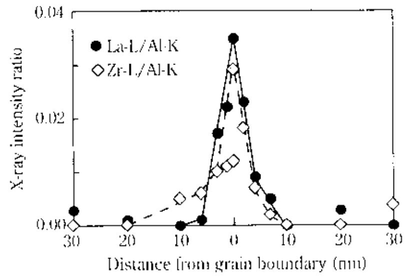

Fig. 2 X ray intensity ratios of La-L, Zr-L to Al-K in EDX spectrum across grain boundaries in Al_2O_3 layer formed on foils containing 0.12%La-0.03%Zr after oxidation at 1 473 K for 72 ks

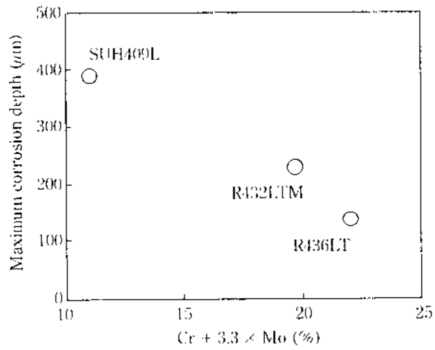

Fig. 3 Effect of Cr and Mo contents on the maximum corrosion depth in the synthetic condensate corrosion test

film/steel interface, resulting in the formation of new Al_2O_3. It is considered that the addition of La and Zr reduces the oxidation rate by suppressing this diffusion of oxygen. **Figure 2** shows the results of a TEM-EDX analysis of the grain boundary of the Al_2O_3 film which formed on the 0.12%La-0.03%Zr foil. It is assumed that enrichment of La and Zr occurred at the grain boundaries, and this suppressed the diffusion of oxygen through the grain boundaries.[8]

R20-5USR has earned an high evaluation for its excellent oxidation resistance, and is widely used in catalytic converters in both Japan and other countries.

2.3 Stainless Steel for Mufflers

Mufflers are required to possess high corrosion resistance (resistance to wet corrosion), because the condensate of exhaust gas causes inner corrosion of the muffler. In particular, steel types with higher corrosion resistance than the conventionally used Al-plated steel, Type 409L, and Type 410L, have become necessary as the guarantee period on automotive parts has been extended in recent years.

As a result of Kawasaki Steel's efforts to clarify the mechanism of condensate corrosion, the company has developed a test method which reproduces this phenomenon.[9] **Figure 3** shows the results of a synthetic condensate corrosion test of stainless steels used in mufflers. It can be understood that the maximum corrosion depth, which is related to perforation of the muffler, decreases in proportion to Cr(%) + 3.3 × Mo(%), and therefore Cr and Mo are effective in improving condensate corrosion resistance. Further, the results of an estimation of material life obtained by applying the method of extreme value analysis to the maximum corrosion depth data showed that the life of Type 409L is 3.3 times as that of Al-plated steel, and the life of R436LT (18Cr-1.2Mo-0.3Ti) is 1.7 times as that of Type 409L.[10]

Based on this knowledge, R436LT and R432LTM (18Cr-0.5Mo-0.3Ti) containing 18%Cr and Mo were developed as high corrosion resistance muffler materials. These steels are manufactured using high productivity, low cost production equipment for carbon steel (cold rolling by the tandem mill, annealing and pickling by a continuous annealing line for carbon steel), and are widely used as muffler materials.

3 Development of Stainless Steels for Buildings

In the stainless steel market, building applications have shown large growth in recent years. When stainless steels are used as interior materials, corrosion resistance on the level of Type 304 is adequate, but in exterior materials and roofs, a higher level of corrosion resistance is required.

Kawasaki Steel has six sites for field exposure tests in various parts of Japan, namely, at the company's Chiba Works and Chita Works, and at Igaueno, Shionomisaki, Kagoshima, and Okinawa, and has clarified the mechanism of atmospheric corrosion, the effect of the alloy composition, environment, etc., and the methods of selecting the optimum base material by carrying out a wide range of research on the atmospheric corrosion resistance of stainless steels in various environments, including industrial areas, rural areas, volcanic areas, coastal areas, and others.

3.1 Factors Influencing Resistance to Atmospheric Corrosion in Stainless Steels and Selection of Base Materials

When various types of stainless steel were subjected to field exposure tests, the ratio of the rusted area decreased and resistance to atmospheric corrosion increased in both ferritic steels and austenitic steels as the pitting index increased (P.I. = Cr + 3.3 × Mo: ferritic type; P.I. = Cr + 3.3 × Mo + 16 × N: austenitic type). However, even with the same P.I., the ferritic type showed a higher resistance to atmospheric corrosion than either the austenitic type or dual phase type due to the smaller number of pitting points, which is a result of higher purity,[11,12] and strong repassivation capacity,

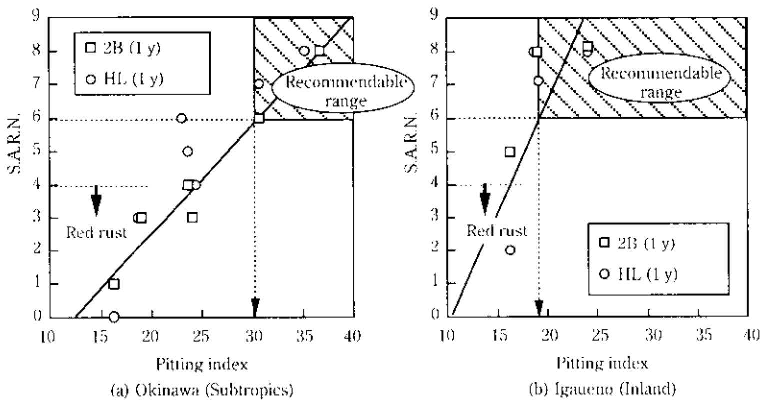

Fig. 4 Relation between pitting index and rusting evaluation of S.A.R.N. after 1y exposure in various environment

Table 2 Chemical compositions of the stainless steels for architectual materials

(mass%)

Steels	C	Si	Mn	Cr	Ni	Mo	Others	P.I.*	Application
R30-2	0.003	0.2	0.1	30.0	0.2	2.0	Nb	36.6	Kansai International Airport
R24-2	0.004	0.2	0.1	24.0	0.2	2.0		30.6	Niigata Airport
R445MT	0.004	0.1	0.15	22.0	0.2	1.5	Ti, Nb	27.0	Makuhari Messe
RSX-1	0.004	0.1	0.15	18.0	0.1	1.5	Ti	23.0	Osaka City Dome
SUS304	0.05	0.5	1.0	18.2	8.5	—		18.7	
SUS316	0.06	0.5	1.3	16.5	10.5	2.0		23.6	

*P.I. = Cr + 3.3 × Mo: Ferritic stainless steels, P.I. = Cr + 3.3 × Mo + 16 × N: Austenitic stainless steels

which is a result of Mo addition.[13]

Resistance to atmospheric corrosion of stainless steels can be evaluated roughly by P.I. values.[14] A P.I. value with a rating No. (S.A.R.N.) of 6 or higher, in which atmospheric corrosion shows slight stain rust but is not a problem from either the viewpoint of appearance or perforation, is decided according to the environment in which the material will be used.[15] **Figure 4** shows the results of field exposure tests which were conducted in Okinawa and Igaueno. In Igaueno, which is a rural area, it is possible to use even Type 304 class, which has a P.I. value of 18, but in Okinawa, a P.I. value of at least 30 is necessary. If this relationship is investigated in each region, it becomes possible select the most appropriate stainless steel for buildings.

As a first principle, corrosiveness in various regions can be evaluated by the amount of chloride in the atomospheric dust. However, the atmospheric corrosion resistance of stainless steel is affected not only by the local environment, but also by the part of the building. In particular, the atmospheric corrosion of the eaves is extremely severe.[16] With R30-2 (Type 447J1: 30Cr-2Mo steel), virtually no atmospheric corrosion occurs in areas near the coast, even in eaves.

3.2 Kawasaki Steel's Stainless Steels for Architectural Materials

Kawasaki Steel's stainless steels for architectural materials are shown in **Table 2**. High purity ferritic stainless steels such as R30-2 for use in various building materials was developed to meet environmental applications. For interior and exterior materials in inland areas, the optimum material is RSX-1, which shows resistance to atmospheric corrosion equal to or better than that of Type 304. For coastal regions, R445MT and R24-2 are suitable. Moreover, R30-2 shows excellent resistance to atmospheric corrosion even when applied to eaves in coastal zones.

Based on the above research and development, R30-2 was adopted as the roofing material for the terminal building of the New Kansai International Airport (**Photo 1**).[17] In this stainless steel roof, which covers an area as large as 90 000 m^2, R30-2 demonstrates both excellent resistance to atmospheric corrosion and the unique design qualities of stainless steels.

4 Improvement of Ridging Property of Ferritic Stainless Steels

When press formed, the ferritic stainless steels, represented by Type 430, develop a pattern of concave/convex surface irregularities extending in the rolling direction, which is called ridging, and invites an increase in the load in the subsequent process of product grinding.

Because colonies of grains exist in stainless steel sheets near orientations which have been elongated in

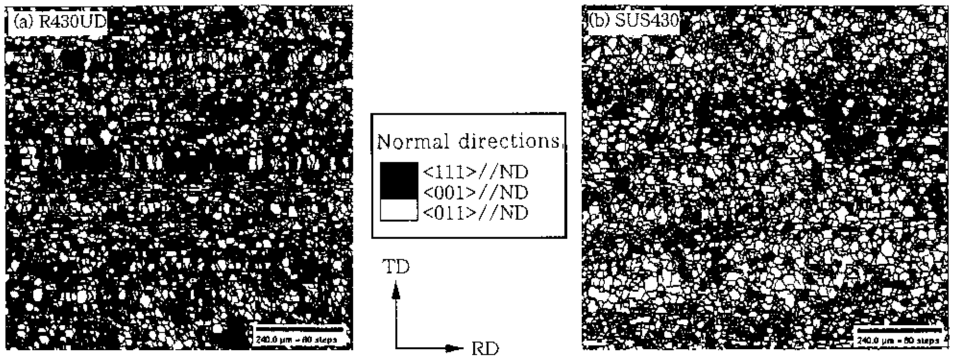

Fig. 5 Texture maps for normal direction, tolerance angle = 15°, of the 1/4 thickness ND plane of samples (a) R430UD and (b) SUS430

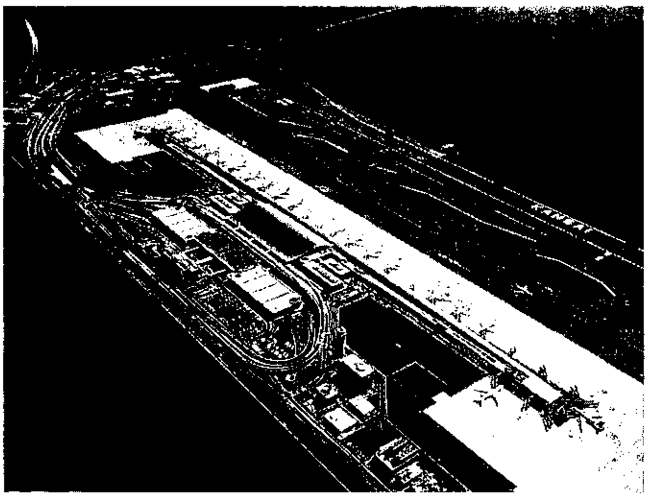

Photo 1 Passenger terminal building of Kansai International Airport

the rolling direction, it is considered that ridging occurs as a result of differences in the plastic deformation behavior of respective colonies.[18,23]

Kawasaki Steel developed R430UD (composition identical to Type 430), which has an extremely small amount of ridging, by destroying these colonies. This is accomplished by optimizing hot rolling conditions using Chiba Works No. 3 hot strip mill, which is the world's most modern facility. **Figure 5** shows the results of an EBSD (electron back scattering diffraction) measurement of the orientation distribution of Type 430 and R430UD (in both cases, at the 1/4 thickness plane of product sheets with a thickness of 0.7 mm). In the case of Type 430, colonies exist with the <110>, <111>, and <100>//ND orientations extending in the rolling the direction. In contrast, distinct colonies do not exist in the R430UD, but rather, the <111>//ND orientation is present in large quantity.

Further, by applying the same hot rolling technology, RSX-1 was developed as a ferritic stainless steel that has an excellent ridging property and corrosion resistance on the same level as Type 304.

5 Conclusion

The following ferritic stainless steels were developed as new products making use of the advanced facilities for stainless steels which were introduced at Chiba Works.

(1) Ferritic Stainless Steels for Automobiles

As a product for exhaust manifolds, R429EX (15Cr-0.9Si-0.45Nb) was developed by devising a composition design which satisfies the requirements of both resistance to thermal fatigue and formability. For use in the metal substrate of catalytic converters, it was found that the oxidation rate can be reduced by a compound addition of La and Zr, resulting in the development of R20-5USR (20Cr-5Al-La-Zr) with excellent resistance to high temperature oxidation. As muffler materials, R436LT (18Cr-1.2Mo-Ti) and R432LTM (18Cr-0.5Mo-Ti) were developed by clarifying the mechanism of condensate corrosion.

(2) Ferritic Stainless Steels Buildings

Research on the mechanism of the atmospheric corrosion of stainless steels revealed that ferritic stainless steels showed higher resistance to atmospheric corrosion than austenitic stainless steels, and further, clarified the effect of material factors and environmental factors on resistance to atmospheric corrosion. As a result, high purity ferritic stainless steels R30-2 (30Cr-2Mo), R24-2 (24Cr-2Mo), R445MT (22Cr-1.5Mo), and RSX-1 (18Cr-1.5Mo) were developed as building materials with excellent resistance to atmospheric corrosion.

(3) High Formability Ferritic Stainless Steels

Colonies in ferritic stainless steel, which are an origin of ridging, were characterized by the EBSD method. Hot rolling conditions for destroying these colonies were studied in the laboratory. By applying the results at Chiba Works No. 3 hot strip mill, high formability ferritic stainless steels R430UD (17Cr) and RSX-1 (18Cr-1.5Mo), which have excellent ridging properties, were developed.

References

1) Y. Nabeshima, S. Ogura, and S. Yamada: *Kawasaki Steel Giho*, **28**(1996)4, 206–212
2) Y. Kishimoto, K. Taoka, and S. Takeuchi: *Kawasaki Steel Giho*, **28**(1996)4, 213–218
3) H. Nikaido, S. Isoyama, N. Nomura, K. Hayashi, K. Morimoto, and H. Sakamoto: *Kawasaki Steel Giho*, **28**(1996)4, 224–230
4) M. Kobayashi, T. Kawasaki, Y. Mihara, H. Satoh, M. Takada, and A. Yanagishima: *Kawasaki Steel Giho*, **20**(1988)1, 20–26
5) A. Miyazaki, A. Tada, and S. Satoh: *CAMP-ISIJ*, **7**(1994)6, 1683
6) K. Ishii and T. Kawasaki: *J. of the Jpn. Ins. of Metals*, **56**(1992)7, 854–862
7) H. Shimizu, M. Kohno, and K. Yoshioka: *Kawasaki Steel Giho*, **25**(1993)2, 119–123
8) K. Ishii, M. Kohno, and S. Satoh: *Kawasaki Steel Giho*, **30**(1998)2, 104–108
9) T. Ujiro, M. Kitazawa, and F. Togashi: *Materials Performance*, **33**(1994)12, 49–53
10) T. Ujiro, M. Kitazawa, and S. Satoh: *J. of the Soc. of Materials Sci. Jpn.*, **45**(1996)11, 1192–1197
11) T. Ujiro, Y. Yazawa, M. Tochihara, M. Fujisawa, and S. Satoh: Proc. of 42th Joint Symp. on Corrosion Science and Technology, (1995)C-102
12) M. Fujisawa, S. Ishikawa, Y. Katoh, T. Ujiro, and S. Satoh: *Tetsu-to-Hagané*, **83**(1997)1, 66–71
13) Y. Yazawa, T. Ujiro, S. Satoh, S. Kumazawa, M. Kobayashi, and S. Shiraishi: *CAMP-ISIJ*, **9**(1996), 1329
14) Y. Yazawa, T. Ujiro, S. Satoh, and K. Yoshioka: *Zairyo-to-Kankyo*, **44**(1995)12, 654–660
15) Technical Report of Kawasaki Steel: "Atmospheric Corrosion Resistance of the Stainless Steels for Buildings"
16) M. Tochihara, T. Ujiro, Y. Yazawa, and S. Satoh: *Zairyo-to-Kankyo*, **46**(1997)9, 572–579
17) S. Satoh: *Kagaku-to-Kogyo*, **68**(1994), 551
18) H. C. Chao: *Trans. Am. Soc. Met.*, **60**(1967), 37
19) H. Takechi, H. Kato, T. Sunami, and T. Kayama: *Trans. Jpn. Inst. Met.*, **8**(1967), 233
20) R. N. Wright: *Metall. Trans.*, **3**(1972), 83
21) K. Bethke, M. Hoscher, and K. Luke: Mater. Sci. Forum, 157–162(1994), 1137
22) M. Fujikura: *Denki Seiko*, **40**(1969), 147
23) J. Harase, K. Ohota, R. Shimizu, and T. Takeshita: *Tetsu-to-Hagané*, **76**(1990), 118