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Ultra-low C and N High Chromium Ferritic Stainless Steel

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Ultra-low C and N high chromium ferritic stainless steels, SR 26-1, S 30-2 and SR 26-4, have been produced by cost-saving steel making process called the "SS-VOD process". The chemical compositions of the steels are characterized by reducing C and N contents to extremely low levels to improve toughness and corrosion resistance, and by the addition of Nb to prevent intergranular corrosion of weldments. Being free of stress corrosion cracking and superior in corrosion resistance, the steels have been used as materials for heat exchangers and various chemical plants. Especially, S 30-2 and SR 26-4 steels having 2-4% Mo exhibit excellent corrosion resistance on the same level as those of AL-6X and Hastelloy C, and have been applied to heat exchangers for caustic soda plants and rectification towers for acetic acid plants. To obtain weldments having good properties as mentioned above, however, some appropriate measures in welding is necessary.

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1 Introduction

Being generally excellent in formability and corrosion resistance, austenitic stainless steels, represented by SUS304 and 316L, are used as materials for applications such as chemical plant parts and heat exchanger tube in hot-water environments. However, these stainless steels are very sensitive to stress corrosion cracking, which is often a serious problem when they are used in severe corrosive environments containing Cl^- ions.

On the other hand, ferritic stainless steels do not show any sensitivity to stress corrosion cracking, and their pitting corrosion resistance and crevice corrosion resist-

Synopsis:

Ultra-low C and N high chromium ferritic stainless steels, SR 26-1, S 30-2 and SR 26-4, have been produced by cost-saving steel making process called the "SS-VOD process". The chemical compositions of the steels are characterized by reducing C and N contents to extremely low levels to improve toughness and corrosion resistance, and by the addition of Nb to prevent intergranular corrosion of weldments. Being free of stress corrosion cracking and superior in corrosion resistance, the steels have been used as materials for heat exchangers and various chemical plants. Especially, S 30-2 and SR 26-4 steels having 2-4% Mo exhibit excellent corrosion resistance on the same level as those of AL-6X and Hastelloy C, and have been applied to heat exchangers for caustic soda plants and rectification towers for acetic acid plants. To obtain weldments having good properties as mentioned above, however, some appropriate measures in welding is necessary.

ance improve with increasing chromium or molybdenum content. In this sense, therefore, high chromium ferritic stainless steels may be said to be suitable for the above-mentioned applications. However, the use of conventional ferritic stainless steels has been limited because their ductility and toughness of welded joints are much inferior to those of general austenitic stainless steels.

It was made clear by Binder et al.¹⁾ that the ductility and toughness of ferritic stainless steels generally depend greatly on chromium content. Ductility and toughness decrease with increasing chromium content, but an extreme reduction of the carbon and nitrogen contents of steel is very effective in improving these properties. Based on these findings, E-Brite 26-1 (26Cr-1Mo) with low carbon and nitrogen contents was developed by Airco Inc. of U.S.A. using a combination of a vacuum-induction furnace (VIF) and an electron beam refining furnace.²⁾ However, the manufacturing cost of this steel is high, greatly limiting its application.

In recent years, there has been remarkable progress in the stainless steel manufacturing process, and it has

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become possible to reduce the carbon and nitrogen in steel at low cost by the VOD process or AOD process. Nevertheless, levels of reduction thus attained are not sufficient, and a steelmaking process for reducing carbon and nitrogen in steel to extremely low levels at low cost has been awaited.

Kawasaki Steel has long made strenuous efforts to develop the above-mentioned process and succeeded in developing the SS-VOD process, a revolutionary steelmaking technology. The company has undertaken technical cooperation with Showa Denko K.K., which has a record of producing high-chromium molybdenum-containing steels, for contracted production of SHOMAC **30-2**(S30-2) and for the joint development and production of SHOMAC RIVER 26-1(SR26-1) and SHOMAC **RIVER 26-4**(SR26-4). These steels have found such applications as materials for power-plant condenser tubes, flue-gas desulfurization units, parts for the diaphragm process for caustic soda, and organic acid plants.

The SS-VOD process has already been reported in detail by Iwaoka et al.³⁾ Therefore, this paper presents results of experimental examinations of the ductility and toughness of high chromium steels and the features of SR26-1, S30-2 and SR26-4 produced by the SS-VOD process.

2 Effects of Reducing Carbon and Nitrogen Contents

2.1 Toughness

Figure 1 shows the effects of the carbon and nitrogen



Fig. 1 Effect of (C+N) content on Charpy impact toughness of TIG weld metals



Fig. 2 Charpy absorbed energy vs. test temperature plots of specimens cooled at various cooling rate from 1 200°C to 700°C, followed by water quenching (4 mm thick, 2 mm V-notch)



Fig. 3 Charpy absorbed energy vs. test temperature plots of specimens reheated after solution treatment at 1 200°C (4 mm thick, 2 mm V-notch)

contents on the Charpy impact behavior of TIG weld metals of 30Cr-2Mo steel.⁴⁾ Charpy impact behavior is greatly influenced by carbon and nitrogen contents; the brittle transition temperature decreases and toughness increases as carbon and nitrogen contents decrease.

Figure 2 shows the effect of cooling rates from 1 200°C to 700°C after heat treatment (1 200°C × 10 min) on the toughness of 4-mm thick plates of 26Cr-1Mo and 30Cr-2Mo steels, both containing 30 ppm of carbon and 60 ppm of nitrogen.⁵⁾ Water-quenched plates show the best toughness, but toughness decreases with decreasing cooling rate. Figure 3 shows the results of the Charpy impact test on specimens subjected to heat treatment in the temperature range of 700 to 900°C for 60 min after water quenching from 1 200°C.⁵⁾ Toughness decreases due to heat treatment after water quenching. As clarified by the authors,⁵⁾ the reason for

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this decrease in toughness with a decrease in the cooling rate from high temperatures or heat treatment after quenching seems to be that the above-mentioned thermal history causes chromium carbides and nitrides to precipitate at grain boundaries and that these chromium carbides and nitrides become crack initiation sites. In general in high chromium ferritic stainless steels, chromium carbide and nitrides precipitate easily at grain boundaries during cooling from high temperatures, causing a decrease in toughness. Therefore, it is necessary to reduce the (C + N) content to about 100 ppm, in consideration of the toughness of welded joint.

In ferritic stainless steels, carbide- and nitrideformers, such as Ti and Nb, are often added to stabilize carbon and nitrogen to prevent intergranular corrosion of welded joint. Figure 4 shows the effects of these stabilizing elements on the toughness of TIG weld metals of 25Cr-3Mo steels containing about 180 ppm of (C + N).³⁾ The steel without stabilizing elements exhibits the best toughness. Toughness decreases with the addition of 0.3% Ti or Nb, and this is especially remarkable in the Ti-added steel. In Ti- or Nb-added steel, carbides and nitrides of these elements precipitate more readily than chromium carbides and nitrides on cooling during welding. In titanium-containing steel, in particular, coarse TiN particles precipitate, and these tend to become crack initiation site. This is considered to explain the above-mentioned decrease in toughness. Therefore, addition of excessive amounts of stabilizing elements is undesirable from the view point of the toughness of ultra-pure chromium ferritic stainless steels. However, from the standpoint of prevention of sensitization at welded joints described in Sec. 2.2 below, addition of these elements is necessary. The addition of niobium, moreover, is more desirable than that of titanium for the improvement of toughness.



Fig. 4 Charpy energy vs. temperature curves for TIG weld metals of 2 mm thick sheet of 25% Cr-3% Mo steels containing 0.018% (C+N) and Nb or Ti (welding was carried out with Ar gas shielding on both surfaces)





Fig. 5 Effects of notch sharpness and grain size on Charpy impact toughness of the 4 mm-thick plate of 26 Cr-1 Mo steel solution-treated at 1 000°C

Figure 5 shows effects of the grain size and notch sharpness on toughness of the 4 mm-thick plate of 26Cr-1Mo steel quenched after solution-treatment at 1 000°C for 10 min, where the grain size of the specimens was changed by heating at various temperatures between 1 000 and 1 200°C for 10 min prior to the solution-treatment.5) In the Charpy impact test on specimens with a blunt notch, toughness decreases with increasing grain size. On the other hand, in the impact test on specimens having brittle weld cracks, made by electron beam welding after setting a thin Ti and mild steel sheet on the test pieces, toughness is not influenced by grain size, the energy transition temperature is almost constant at about 30°C, and the toughness is low. Considering these results, it may be considered that crack initiation is influenced by the grain size, while crack propagation is not.

Therefore, grain refinement is very effective in improving notch toughness, and from this viewpoint, long heating periods at high temperatures are undesirable. Furthermore, notch toughness is low even in ultralow C and N ferritic stainless steels if there are acute defects such as incomplete penetration of butt welds. In this case, therefore, attention to welding procedures is necessary, as described in Sec. 3.4.

2.2 Corrosion Resistance

Figure 6 shows the effect of the (C + N) content on the intergranular corrosion sensitivity of TIG welded joints. (C + N) content more than 150 ppm leads to intergranular corrosion. However, the intergranular corrosion sensitivity does not exist at lower (C + N) contents, even without the addition of stabilizing elements.

Table 1 shows effects of (C + N) content on pitting corrosion resistance in TIG welded joints for various high chromium steels. At (C + N) contents of 150 ppm or more, pitting corrosion occurs and the corrosion



Fig. 6 Results of Strauß test on TIG welded joints of 2 mm thick sheets of high Cr-Mo steels containing various amounts of C and N (welding was carried out with Ar gas shielding on both surfaces)

Table 1	Immersion test results in 5% FeCl ₃ aq. solu-
	tion (FeCl ₃ · $6H_2O$ 50g/l + HCl 1.83 g/l) at
	50°C for 24 h

	(C+N)content (%)	Stabilizing element (%)	Corrosion rate (g/m²·h)
25Cr-3Mo	0.020		2.09
	0.025		14.5
	0.025	0.28Ti	0.02
	0.025	0.33Nb	0.02
	0.012		0.02
29Cr-4Mo-2Ni	0.026		1.31

Table 2 Strauß test results on 26 Cr-1 Mo steels

Steel	Air-cooled from 1 200°C after 5 min heating	Senstized at 650°C for 30 mm after air cooling from 1 200°C	
26Cr-1Mo	Pass	Fail	
26Cr-1Mo-0.2Nb	Pass	Pass	

weight loss increases. However, pitting corrosion is prevented by adding stabilizing elements such as Nb or Ti, even at high (C + N) contents.

The Strauß test was conducted on a 26Cr-1Mo steel and a 26Cr-1Mo-0.2Nb steel, both containing 100 ppm of (C + N), which were subjected to heat treatment at 1 200°C for 5 min followed by air cooling or to sensitization at 650°C for 30 min after air cooling. As shown in Table 2, neither of the two steel grades shows intergranular corrosion sensitivity when air-cooled, while the steel without the stabilizing element Nb is sensitive to intergranular corrosion after sensitizing heat treatment. Therefore, even in ultra-low C and N high chromium ferritic stainless steels, it is necessary to add stabilizing elements in order to prevent sensitization when these steels are subjected to heat cycles, as in multi-pass welding. Even when multi-pass welding is not conducted, the addition of stabilizing elements is necessary because of the pickup of carbon and nitrogen at weld metals from the welding atmosphere as described later.

Figure 7 shows the pitting corrosion behavior of steels in a 20% NaCl aqueous solution containing $1\% Na_2Cr_2O_7$ ·2H₂O, as determined by electro-chemical measurement of pitting potentials.⁶⁾ The critical pitting temperature is higher in 29Cr-2Mo steel and Nb-stabilized 29Cr-2Mo steel than in SUS 304 or SUS 316. Further, in the former steels pitting corrosion does not grow even if it occurs. The addition of Ni in 29Cr-2Mo steel lowers the critical pitting temperature, but it tends to



Fig. 7 Temperature dependency of pitting behaviour of steels in $(20\% \text{ NaCl}+1\% \text{ Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O})$ solution

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Table 3 Stress corrosion test results of 29 Cr-2 Mo steels in boiling 42% MgCl₂ and 20% NaCl solution containing 1% Na₂Cr₂O₇·2H₂O (Ubent specimens)

Steel	Boiling 42% MgCl ₂ solution	Boiling (20% NaCl +1% Na2Cr2O7. 2H2O) Solution
29Cr-2Mo	Pass	Pass
29Cr-2Mo-0.5Ni	Fail	Pass
29Cr-2Mo-1Ni	Fail	Pass
29Cr-2Mo-2Ni	Fail	Fail

promote pitting growth. **Table 3** shows the effect of Ni content on the stress corrosion cracking sensitivity of 29Cr-2Mo steels investigated by the U-bend test in various boiling solutions. Sensitivity to stress corrosion cracking increases with increasing Ni content. Cracking occurs at Ni contents of 0.5% or more in a boiling 42% MgCl₂ solution and at Ni contents of 2% or more in a 20% NaCl solution containing 1% Na₂Cr₂O₇·H₂O. The reason for this increase in sensitivity to stress corrosion cracking with increasing nickel content seems to be related to the fact that, as shown in Figure 7, "pitting to grow" tends to occur due to the addition of nickel; that is, steel is liable to undergo active dissolution in an acidic aqueous solution of chlorides.

For this reason, it is necessary to reduce the nickel content of high chromium ferritic stainless steels to the lowest levels possible, from the standpoint of resistance to pitting corrosion and stress corrosion cracking.

3 Ultra-low C and N High Chromium Ferritic Stainless Steels

Based on the above experimental results, Kawasaki Steel produces three types of ultra-low C and N high chromium ferritic stainless steel, SR26-1, S30-2, and SR26-4, in consideration of applicability to various corrosive environments and economy. The characteristics of these three steel grades are described in the following.

3.1 Chemical Compositions and Manufacturing Process

The chemical compositions of SR26-1, S30-3 and SR26-4 are given in **Table 4**. In all these steels, the carbon and nitrogen contents are reduced to extremely low levels of 20 to 30 ppm and 50 to 70 ppm respectively, by the SS-VOD process, to improve formability, toughness, and corrosion resistance of base metals and welds. Furthermore, the steels are stabilized by the addition of niobium, and the nickel contents are low. These ultralow C and N high chromium ferritic stainless steels are continuously cast into slabs after the SS-VOD refining, then hot-rolled, cold-rolled, annealed, and pickled to produced cold-rolled steel sheets and plates.

3.2 Physical and Mechanical Properties

Tables 5 and 6 show the physical and mechanical properties of the ultra-low C and N high chromium ferritic stainless steels, respectively. As C and N levels are extremely low, movement of magnetic domain walls is easy; therefore, these steels show excellent magnetic properties. Mechanically, in spite of their high chromium and molybdenum contents, these steels are relatively ductile because of their ultra-low carbon and nitrogen contents.

Figure 8 shows results of the Charpy impact test on 3mm thick sheets of SR26-1, S30-2 and SR26-1. All three steel grades show ductile-brittle transition temperatures of -50° C or below, indicating excellent toughness. In general, the Charpy impact properties of ferritic stainless steels, however, are greatly affected by plate thickness, as shown in Fig. 9, with toughness decreasing remarkably as plate thickness increases. Therefore, it is necessary to give attention to plate thickness even with ultra-low C and N high chromium ferritic stainless steels. Although maximum plate thickness varies with place of application and service temperature, it is desirable to use clad plates when thicknesses of 6 mm or

Table 4 Chemical compositions of SR26-1, S30-2, and SR26-4 stainless steel

	Steel	С	Si	Mn	Р	S	Cr	Ni	Cu	Mo	N	Nb
6-1	Specification	<u>≤</u> 0.010	≤0.40	≤0.40	≤0.03	≤0.02	25.0~27.5	≤0.6		1.21~1.5	<u> </u> 	15×(%C+%N) ~0.8
SR2	An example	0.002	0.34	0.09	0.019	0.003	26.0	0.17	0.02	1.3	0.005	0.15
-2	Specification	≤0.010	≤0.40	≤0.04	≤0.03	≤0.02	28.5~32.0	≤0.6		1.5~2.5		15×(%C+%N) ~0.8
S3C	An example	0.003	0.15	0.04	0.015	0.004	30.0	0.18	0.01	2.0	0.007	0.15
6-4	Specification	≤0.010	≤0.40	≤0.04	≤0.03	≤0.02	25.0~27.5	≤0.6		3.5~4.5		$15 \times (\%C + \%N)$ ~0.8
SR26	An example	0.003	0.09	0.09	0.004	0.002	25.5	0.26	0.01	3.97	0.006	0.15

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(%)

Table 5 Physical properties of SR26-1, S30-2, and SR26-4 in comparison with those of commercial grade stainless steels

	SR26-1	S30-2	SR26-4	Type 316L	Туре 430
Density (g/cm ²)	7.67	7.64	7.72	8.0	7.7
Specific heat ^{*1)} $(cal/g \cdot C)$	0.12	0.12	0.12	0.12	0.11
Thermal conductivity*2) (cal/cm·s·C)	0.045	0.045	0.045	0.039	0.062
Coeff. of expansion ^{$*3$} (C ^{-1})	11.0×10 ⁻⁶	9.8×10 ⁻⁶	1.1×10^{-6}	16.0×10^{-6}	10.4×10^{-6}
Electrical resistivity (Ω/cm)	64×10^{-6}	64×10-6	64×10^{-6}	74×10^{-6}	60×10^{-6}
Young's modulus (kgf/mm ²)	2.1×10^{4}	2.3×10^{4}	2.1×10^{4}	2.0×10^4	2.0×10^{4}
Magnetic property	Ferro-magnetic	Ferro-magnetic	Ferro-magnetic	Non-magnetic	Ferro-magnet

*1 0~300°C

*² 20°C

*****⁸ 0∼300°C

Table 6Mechanical properties of 0.7 mm thick sheets
of SR26-1, S30-2, and SR26-4 in comparison
with those of type 316L and Type 430

Steel	0.2% proof strength (kgf/mm ²)	Tensile strength (kgf/mm²)	Elongation (%)	Hardness HV (5kg)
SR26-1	41	53	32	165
S30-2	43	60	30	190
SR26-4	45	61	26	190
Type 430	35	53	30	167
Type 316L	28	63	50	170



Fig. 8 Charpy impact properties of 3 mm thick plate

more are required.

3.3 Corrosion Resistance in Various Corrosive Environments

 Table 7 shows results of measurements of pitting potential of ultra-low C and N high chromium ferritic



Fig. 9 Relation between ductile-brittle transition temperature and thickness of TIG weldments (Charpy impact test)

stainless steels in a 3.5% NaCl aqueous solution at various temperatures. In general, pitting potential increases with increasing chromium and molybdenum contents and decreases with increasing test temperature. All three steels show higher pitting potentials than SUS 316L.

Figure 10 shows results of an immersion test with a 10% FeCl₃·6H₂O aqueous solution. SR26-4 shows the

			(mV vs. SCE)
	Te	est temperature,	°C
Steel	80°C	70°C	60°C
SR26-1	271	304	452
S30-2	413	621	0
SR26-4	547	716	0
SUS 316L	96		174

O: Pitting potential was not observed.

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Fig. 10 Corrosion rate in 10% FeCl₃·6H₂O solution (48 h test)

best pitting corrosion resistance, followed by S30-2 and then by SR26-1. All the ultra-low C and N high chromium ferritic stainless steels, however, provide better pitting corrosion resistance than SUS 316L. Figure 11 shows results of the crevice corrosion test in a



Fig. 11 Corrosion rate in 10% FeCl₃.6H₂O solution for 45 h (the specimens were tied with glass rods by rubber bands)

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10% FeCl₃· $6H_2O$ aqueous solution, where specimens were tied with glass rods using rubber bands. SR26-4 shows the best crevice corrosion resistance; S30-2 also provides better crevice corrosion resistance than SUS 316L.

In recent years, the steel AL6X (20Cr-25Ni-6Mo) has been used in a portion of the heat exchanger tubes and condenser tubes used in power plants in the United States. **Figure 12** shows a comparison of the corrosion rate between AL6X and ultra-low C and N high chromium ferritic steels in an immersion test in 10% FeCl₃·6H₂O aqueous solution containing 1/20 N HCl, where specimens were fastened with teflon nuts and bolts to make a crevice. Both SR26-4 and S30-2 show smaller corrosion weight losses than AL6X. Furthermore, the temperature at which crevice corrosion occurs is high with the ultra-low C and N high chromium ferritic stainless steels, meaning their crevice corrosion resistance is excellent.

Being excellent in pitting corrosion resistance and crevice corrosion resistance, the three ultra-low C and N high chromium ferritic stainless steels, especially S30-2 and SR26-4, can be applied to condenser tubes with result comparable to AL6X. At the Ichihara Steam Power Station of Showa Electric Power Co., 0.5 to 0.7 mm thick TIG welded tubes installed in condensers



Fig. 12 Corrosion rate in $(10\% \text{ FeCl}_3 \cdot 6\text{H}_2\text{O} + 1/20 \text{ N} \text{ HCl})$ solution for 48 h (the specimens were fastened by teflon bolt and nut)



Fig. 13 Resistance to stress corrosion cracking of stainless steels uniaxially stressed in boiling 42% MgCl₂ solution

have been used for the past five years, with no leakage and scarcely any corrosion.

Figure 13 shows results of a stress corrosion cracking test in a boiling 42% $MgCl_2$ aqueous solution. The ultralow C and N high chromium ferritic stainless steels are not susceptible to stress corrosion cracking because of their low nickel contents.

Figures 14 and 15 show the results of immersion tests in boiling HCl aqueous solution and boiling H_2SO_4 aqueous solution, respectively. All three ultra-low C and N high chromium ferritic stainless steels are inferior to SUS 304 and SUS 316L in sulfuric acid resistance and



Fig. 14 Immersion test results in boiling HCl solution for 48 h



Fig. 15 Immersion test results in boiling H₂SO₄ solution for 48 h

hydrochloric acid resistance at concentrations exceeding 5% and 1%, respectively, but on the contrary, much superior at lower concentrations.

Table 8 gives the nitric acid resistance and caustic soda resistance of the ultra-low C and N high chromium ferritic stainless steels. Due to their extremely low C and N contents, all the steels show small corrosion weight losses in nitric acid and no susceptibility to intergranular corrosion. The caustic soda resistance results shown in this table are based on immersion tests conducted to estimate corrosion resistance for the concentration

Table 8	Immersion test results in 65% HNO ₃ and
	$(50\% \text{ NaOH} + 5\% \text{ NaCl} + 0.05\% \text{ NaClO}_3)$
	boiling solutions, and in (30% NaOH +
	10% NaCl + 0.05% NaClO ₃) solution at 90°C
	(g/m²-h)

Steel	65% HNO3, boiling	50%NaOH+ 5%NaCl+ 0.05%NaClO ₃ , boiling*	30%NaOH+ 10%NaCl+ 0.05%NaClO ₃ , 90° **
SR26-1	0.104	0.13	0.016
S30-2	0.005	0.019	0.007
SR26-4	0.004		-
SUS 316L	0.028	3.2	0.13
SUS 304L	0.144	2.0	0.095
Nickel		0.023	

* Corrosive environment in first effect evaporator of heat exchanger for caustic soda

** Corrosive environment in second effect evaporator of heat exchanger for caustic soda

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Steel	80% CH₃COOH B.P.	50%HCOOH B.P.	10% (COOH) ₂ B.P.
SR26-1	0	0.09	0.14
S 30-2	0	0.04	0.14
SR26-4	0	0.02	0.12
SUS 316L	0.26	0.45	0.86
SUS 304L	0.29	1.48	_

Table 9 Corrosion rates after immersion in boiling organic acid solutions for 48 h $(g/m^2 \cdot h)$

process of a diaphragm-type caustic soda plant. All the ultra-low C and N high chromium ferritic stainless steels are excellent in caustic soda resistance and show lower corrosion rates than SUS 316L, which has conventionally been used in Japan in the first and second effect evaporators in the concentration process. Furthermore, the corrosion resistance of S30-2 is equal to that of pure nickel conventionally used in the first effect evaporator.

Table 9 gives results of corrosion tests in various organic acids. The ultra-low C and N high chromium ferritic stainless steels show excellent resistance to CH_3COOH , HCOOH and COOH. Figure 16 shows

results of a test in a H_2O -CH₃COOH-COOH-type mixed acid solution conducted to estimate corrosion resistance in the rectification process of an acetic acid plant using the acetaldehyde process. All these ultra-low C and N high chromium ferritic stainless steels have wider composition ranges with corrosion rates of 0.1 mm/year or less than does SUS 316L, or even Hastelloy C and Ti, thus providing outstanding corrosion resistance.

3.4 Weldability

As described in Sec. 2.1, toughness and corrosion resistance of weld metal are substantially influenced by its carbon and nitrogen contents. Even the properties of ultra-low carbon and nitrogen steel sheet and plate will deteriorate if pickup of carbon and nitrogen occurs during welding, making it important to select proper welding procedures.

Figure 17 shows the relation between the degree of nitrogen and oxygen pickup in TIG weld metals and contamination of the torch-side-shielding argon gas by air.⁴⁾ Nitrogen and oxygen contents of weld metal increase considerably on contamination with even a small quantity of air. **Figure 18** shows the effect of back-shielding gas on the toughness of TIG weld metals of 2-mm thick SR26-1 sheet.³⁾ When back-shielding gas is



Fig. 16 Corrosion rate in boiling (CH₃COOH + HCOOH) solution

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Fig. 17 N and O pickup of TIG weld metals due to the contamination of air in torch-side shielding Ar gas



Fig. 18 Charpy energy vs. temperature curves for TIG weld metals of SR26-1 steel (TIG welding was performed with or without backup Ar gas)

not used, weld metal toughness decreases remarkably, the weld metal becoming susceptible to intergranular corrosion due to pickup of nitrogen from the welding atmosphere. During welding, therefore, not only torchside-shielding but back-shielding should be adequate, and it is also desirable that these be used in conjunction with after-shielding. Further, if steel sheets are contaminated with oil, pickup of carbon at the weld metal may result during welding, causing a decrease in toughness and corrosion resistance. Therefore, it is necessary to ensure removal of oil with an organic solvent.

In general welding, preheating and post heating are sometimes used. As described in Sec. 2.1, however, the heat treatment at 600 to 800°C causes chromium carbides and nitrides to precipitate, lowering toughness. Therefore, preheating and postheating should not be used.

In addition, it is necessary to prevent weld defects. As described in Sec. 2.1, notch sensitivity is high even in ultra-low C and N chromium ferritic stainless steels; weld defects, such as lack of fusion, undercuts, pinholes, and microfissures, act as notches and lower toughness.

Table 10 Typical welding conditions

Welding conditions	2 mm	4 mm	6 mm	
Dia. of filler metal	2.0 mmø	2.0 & 2.4 mmø	2.0 & 2.4 mmø	
Tungsten electrode (2%ThO2)	1.6 mmø	2.4 mmø	2.4 mmø	
Current	70~100 A	100~140 A	140~180 A	
Travelling speed	100~150 mm/min	100~150 mm/min	100~150 mm/min	
Torch-shielding gas	8~16 l/min	10~20 l/min	10~20 1/min	
Back-shielding gas	about 10 l/min	about 10 l/min	about 101	
After-shielding gas	20~30 l/min	20~30 1/min		
Dia. of torch nozzle	16 mmø	19 mmø	19 mmø	
Joint symmetry	I batt	60°V groove	60°V & 60° × groove	
Number of pass	1	2	3-4	

Therefore, it is necessary to take appropriate measures to avoid these weld defects. Among the details of welding procedure to which attention may be given, for example, are tabs attached for the shifting of welding starting and end points from the root position. Moreover, TIG welding is most suitable for use with high chromium ferritic stainless steels, while MIG welding and plasma welding are undesirable because the attendant pickup of oxygen or hydrogen in weld metal with these methods impairs toughness.

Table 10 shows examples of optimum welding conditions for ultra-low C and N high chromium ferritic stainless steels. **Table 11** shows the mechanical properties of TIG welds of S30-2 steel under the optimum welding conditions. Welding performed under the optimum conditions makes use of the characteristics of ultralow C and N high chromium ferritic stainless steels, yielding welded joints with excellent performance while maintaining the outstanding corrosion resistance of these steels.

When TIG welding requires the use of filler metals, those of the same material as the base metal should, as a rule, be used in view of resistance to stress corrosion cracking. However, filler metals of austenitic stainless steel such as Y-316L may sometimes used, except in surfaces directly exposed to the corrosive environment. In such cases, welding should be performed so as to prevent pickup of carbon and nitrogen by the exposed surface from the interior layers of the weld metal.

3.5 Examples of Applications

Based on the above-mentioned properties, as well as results of wide-ranging field tests and records of pur-

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Table 11 Mechanical pro	operties of	S30-2	steel
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	Tensile properties					Bendability		Charpy impact properties	
	0.2% proof strength (kgf/mm²)	Tensile strength (kgf/mm²)	Elongation (%)	Reduction of area (%)	Rupture pattern	r=2t	r =0	DBTT (°C)	Shelf energy (kgf • m/cm ²)
Mother metal 6 mm thick	43	57	32	72	Ductile	Good	Good	-20	25~30
Welded joint 6 mm thick	44	59	_	-	Ductile	Good	Good	-20~0	25~30
Weld metal 12 mm thick	51	60	25	71	Ductile	_		-	

chases, it is considered that these ultra-low C and N high chromium ferritic stainless steels find their principal application in the following fields:

- (1) Plants producing organic acids such as acetic acid, lactic acid, and their derivatives
- (2) Environments containing Cl⁻ ions, which cause stress corrosion cracking, pitting corrosion, and



Photo 1 Heat exchanger for the caustic soda first effect evaporator made of S30-2 stainless steel



Photo 2 Rectification tower for acetic acid plant made of \$30-2 stainless steel

crevice corrosion in austenitic stainless steels such as SUS 316L

- (3) Diaphragm process of caustic soda production
- (4) Pollution control equipment, such as flue-gas desulfurization units
- (5) Petroleum refineries
- (6) Food processing plants
- (7) Applications that require both corrosion resistance and magnetic properties, for example, solenoid valve core material, which utilizes soft ferromagnetic properties

Photos 1 and **2** show examples of application of S30-2, a heat exchanger for a caustic soda plant first effect evaporator and a rectification tower for an acetic acid plant.

4 Conclusions

The ultra-low C and N high chromium ferritic stainless steels, SR26-1, S30-2, and SR26-4, produced by the SS-VOD steelmaking process for lowering the carbon and nitrogen contents to extremely low levels not only do not have the susceptibility to stress corrosion cracking observed in austenitic stainless steels, but provide excellent corrosion resistance in various corrosive environments and are also excellent in the ductility and toughness of base metal and weld metal. However, if welding conditions, such as degreasing of steel sheets to be welded and gas shielding, are improper, the pickup of carbon and nitrogen by weld metal occurs and material properties deteriorate. Therefore, attention should be paid to this point.

Recent progress in welding techniques, however, has led to the application of the ultra-low C and N high chromium ferritic stainless steels to various fields, such as parts in seawater environments and various types of chemical plants, and it is expected that applications of these ultra-low C and N high chromium ferritic stainless steels will further increase in the future.

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