

Development of Welding Consumables for High-Corrosion-Resistant Stainless Steel NSSC[®]260A for Chemical Cargo Tankers

Hiroshige INOUE*¹
Yutaka TADOKORO*²
Takeshi HASHIMOTO*²
Hajime NAGASAKI*³

Ryo MATSUHASHI*¹
Shigeo FUKUMOTO*²
Manabu MIZUMOTO*³

Abstract

A highly corrosion-resistant stainless steel, NSSC260A, for application to chemical cargo tankers and welding consumables for the steel were developed. The stainless steel and welding consumables were designed to exhibit good resistance to corrosion by sulfuric acid, crude phosphoric acid and salt water. The developed welding consumables, flux-cored wire NITTETSU FC-317LNCU for CO₂ welding and NITTETSU BF-317LNCU (flux) × NITTETSU Y-316C (solid wire) for submerged arc welding, proved that it is possible to attain weld joints that satisfy required corrosion resistance and mechanical properties, and their actual use for construction of chemical cargo tankers began in June 2004.

1. Introduction

Since the middle of the 1970s, stainless steels such as Type 304 and Type 316L have come to be used for the cargo tanks of chemical tankers as the main material in place of ordinary carbon steels with paint coating. Chemical tankers carry a wide variety of cargoes such as chemicals, petroleum products and food materials, and the corrosion of tanks by the cargo has always been a major problem. The principal corrosion problems of stainless steel tanks caused by the cargoes and operation of chemical tankers are, especially, (a) general corrosion by sulfuric acid solution forming through dilution of crude sulfuric acid, (b) blackening corrosion by gaseous crude phosphoric acid and (c) local corrosion such as pitting and crevice corrosion by residual salt from sea water or brackish water used for washing cargo tanks.

In consideration of the above, and to improve transportation efficiency by greatly reducing vessel maintenance work and decreasing environmental loads, the authors started the development

of a stainless steel and welding consumables for the steel having significantly improved corrosion resistance for application to chemical cargo tankers, and in 2003, launched a new stainless steel, NSSC260A¹⁾, and welding consumables, NITTETSU FC-317LNCU and NITTETSU BF-317LNCU × NITTETSU Y-316C, to the market. This paper reports the development of the welding consumables specially designed for the new stainless steel.

2. Guidelines for Development of New Stainless Steel and Welding Consumables for Chemical Cargo Tankers

Fig. 1 shows the target corrosion resistance set out for the development of NSSC260A. The principal mode of corrosion of chemical tanks in environments containing sulfuric or phosphoric acid is general corrosion. To enhance the resistance of stainless steel to general corrosion, it is necessary to increase the value of the general corrosion resistance index ($GI = -Cr + 3.6Ni + 4.7Mo + 11.5Cu$)²⁾. Furthermore, since stainless steel for chemical tanker applications

*¹ Steel Research Laboratories

*² Nippon Steel & Sumikin Stainless Steel Corporation

*³ Nippon Steel & Sumikin Welding Co., Ltd.

Table 1 Chemical compositions and mechanical properties of NSSC260A

Steel grade	Chemical composition (mass%) and PI, GI value							Mechanical properties			
	Cr	Ni	Mo	Cu	N	PI	GI	0.2% YS (MPa)	TS (MPa)	EI (%)	Hardness (HB)
NSSC260A	22.3	16.8	3.2	1.7	0.18	35.7	72.8	340	680	50	170

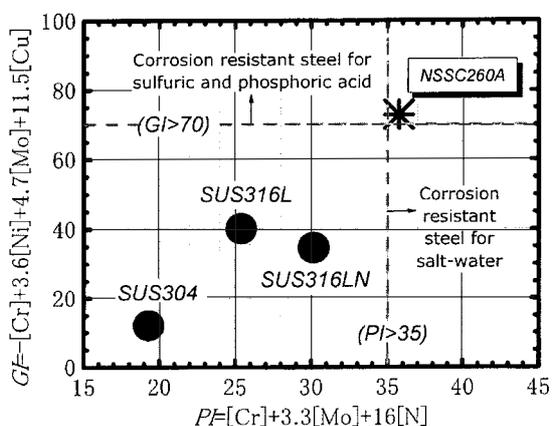


Fig. 1 Position in Figure PI-GI of the new corrosion resistant steel: NSSC260A

must also have good resistance to pitting corrosion in environments containing chloride ions from washing water such as sea water, it is necessary to increase the value of the pitting corrosion resistance index (PI = Cr + 3.3Mo + 16N)³⁾. In view of the above and in consideration of the costs and efficiency in production, the chemical composition of the new stainless steel, NSSC260A, was set so that the values of the GI and PI were 70 or more and 35 or more, respectively. **Table 1** shows the main component elements and mechanical properties of the developed steel.

As for the welding methods, on the other hand, CO₂-gas-shielded arc welding using flux-cored wire (hereinafter written as FCAW) and submerged arc welding (hereinafter written as SAW) are widely employed for constructing chemical tankers. For this reason, welding consumables for FCAW and SAW for the new stainless steel were developed. Since the properties of welds must be the same as those of base metal, the quality targets of weld metal were set as specified below.

- (1) Strength: A 0.2% proof stress of 315 MPa or more
- (2) Ductility: An elongation of 30% or more (to secure ductility for corrugation)
- (3) Toughness: A vE at - 20 of 27 J or more (to meet the requirement for Class NK accreditation)
- (4) Corrosion resistance
 - Resistance to pitting corrosion: same as base metal (a pitting potential of 1000 mV vs. Ag/AgCl or more in a 3.5% solution of NaCl at 30)
 - Resistance to general corrosion: same as base metal (a corrosion rate of 1 mm/y or less in a 50% solution of sulfuric acid at 40)

3. Design of Chemistry of Welding Consumables

3.1 Development of welding wire for FCAW

The chemistry of the welding wire for FCAW of NSSC260A was

designed to match the base metal. The authors studied the corrosion resistance and mechanical properties of weld metal based on the chemical composition of the NSSC260A base metal and changing the contents of the main alloying elements of Cr, Ni, Mo and Cu. The base metal also contains N, which is well known to enhance strength and resistance to pitting corrosion, as a main component element, but to prevent blowholes at CO₂ welding, its content was set at 0.05%.

Fig. 2 shows the relation between the value of PI and the pitting potential (in a 3.5% solution of NaCl at 30) of weld metal measured according to JIS G 0577, and **Fig. 3** that between the value of GI and the corrosion rate (in a 50% solution of sulfuric acid at 40) of weld metal. A pitting potential of 1000 mV vs. Ag/AgCl or more is realized with a PI of 30 or more, and a corrosion rate of 1 mm/y or less with a GI of 55 or more. Different from base metal, weld metal has a

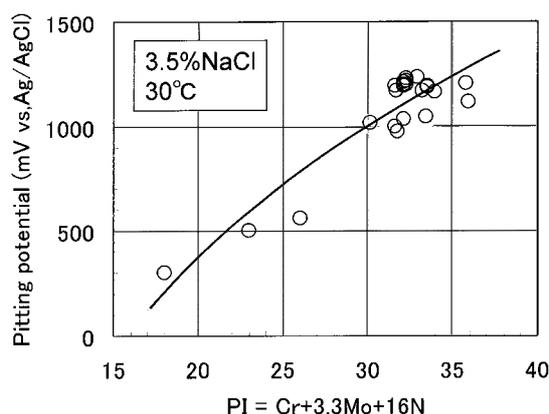


Fig. 2 Relation between pitting potential of weld metal and PI value

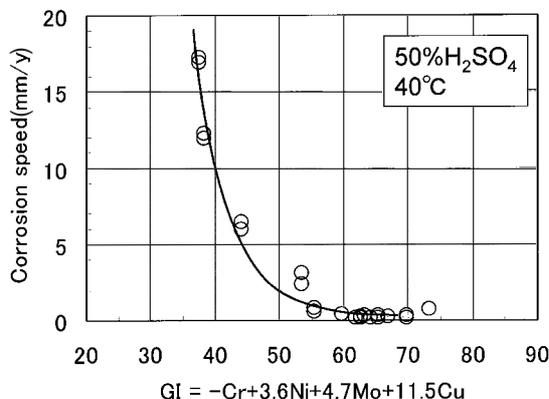


Fig. 3 Relation between corrosion rate in 50% sulfuric acid of weld metal and GI value

heterogeneous, dual-phase microstructure consisting of ferrite and austenite, and it is known that its corrosion resistance is usually inferior to that of base metal owing to solidification segregation, uneven elementary distribution between the phases and precipitation of carbides and the like. Despite the above, the authors found that when the values of PI and GI calculated from the chemical composition of weld metal were equal to or larger than the respective lower limits, the weld metal would have corrosion resistance equal to that of base metal, and confirmed that these indices were effective as guidelines for the chemistry design of the welding wire.

Fig. 4 shows the effects of Mo and Cu on the toughness of weld metal; it is clear from the graphs that an increase in the amount of either Mo or Cu decreases the Charpy absorbed energy at -20 °C,

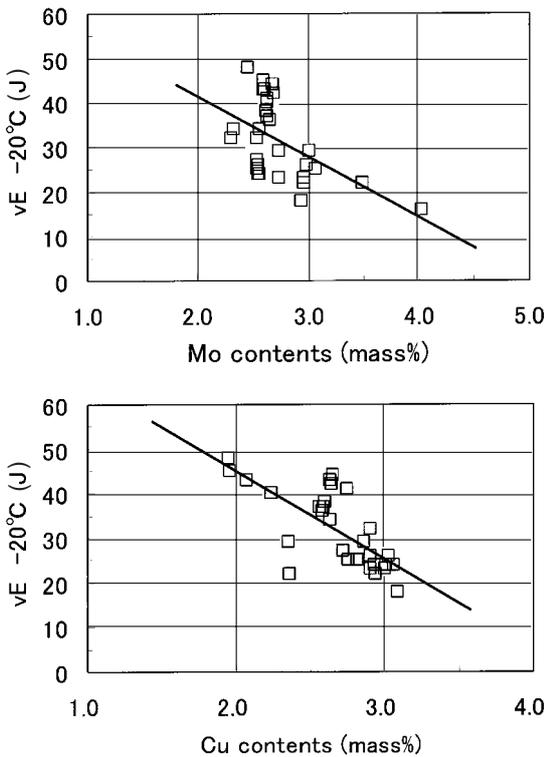


Fig. 4 Effect of Mo and Cu contents on toughness of deposited metals

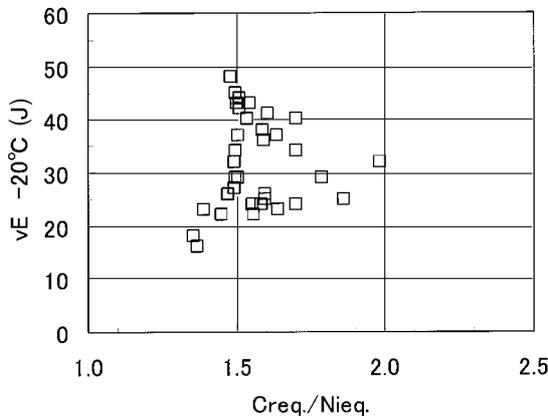


Fig. 5 Effect of Cr eq./Ni eq. ratio on toughness of deposited metals

and thus, to secure a good toughness it is effective to decrease the contents of these elements. On the other hand, both these elements increase the values of PI and GI to enhance corrosion resistance. For this reason, it is important in the design of the weld metal chemistry to find optimum amounts of Mo and Cu that minimize the decrease in toughness while satisfying both PI ≥ 30 and GI ≥ 55.

Another well-known factor that influences the toughness of weld metal is the amount of ferrite⁴⁾; Fig. 5 shows the effect of the ratio between a Cr equivalent (Creq) and a Ni equivalent (Nieq), an index of the amount of ferrite, on the toughness (Charpy absorbed energy at -20 °C) of weld metal. Note that, since the developed stainless steel and welding wire contain Cu, the Cr and Ni equivalents were calculated according to Hammar's equivalent equations⁵⁾ given below.

$$Creq = Cr + 1.37Mo + 1.5Si + 2Nb + 3Ti$$

$$Nieq = Ni + 0.31Mn + 22C + 14.2N + Cu$$

Although the value of Charpy absorbed energy fluctuates with respect to the Creq/Nieq ratio, it has a peak near Creq/Nieq = 1.5. On the other hand, structural observations showed that in the Creq/Nieq range from 1.4 to 1.6, ferrite existed in the form of either vermicular or lacy ferrite, evidencing solidification in the FA mode⁶⁾, and when the ratio was 1.7 or more, it existed in the form of acicular ferrite, evidencing solidification in the F mode⁷⁾. Generally speaking, toughness is higher in FA mode solidification (less amount of ferrite) than in F mode⁸⁾, but some alloy systems in Fig. 5 showed low toughness even in the Creq/Nieq range of FA mode solidification (Creq/Nieq < 1.6). This is because the graph of Fig. 5 includes many alloy systems shown in Fig. 4 having the same value of the Creq/Nieq ratio but different contents of Mo and Cu; this indicates that toughness cannot be discussed in terms solely of the Creq/Nieq ratio.

In consideration of the above, the authors examined Charpy absorbed energy, 0.2% proof stress and elongation by multiple regression analysis using the Creq/Nieq ratio and the amounts of Mo and Cu as parameters. Fig. 6 shows the results; the analysis objects showed good correlations with their respective indices composed of the parameters. These graphs indicate that it is possible to design a chemical composition that satisfies the quality targets (a toughness, or Charpy absorbed energy of 27 J or more, a 0.2% proof stress of 315 MPa or more and an elongation of 30% or more).

Based on these analysis results, the authors set out guidelines for the chemistry design of the welding wire for FCAW to satisfy the quality targets, and following the guidelines, developed the FCAW welding wire (NITTETSU FC-317LNCU) for NSSC260A. The solid circles in Fig. 6 indicate the chemical composition finally selected, and Table 2 shows an example of the chemical composition of the weld metal obtained using the developed wire.

3.2 Development of welding consumables for SAW

In developing the welding consumables (wire and flux) for SAW of NSSC260A, the authors used as a basis the alloy system of 23Cr-13Ni-2.5Mo-2Cu-0.05N satisfying the quality targets and defined through the development study for the FCAW welding wire (NITTETSU FC-317LNCU). However, in consideration of heat input and welding conditions peculiar to SAW, they additionally studied the aspects described below.

The authors confirmed that, when a weld metal by SAW had the same chemical composition as that of another by FCAW, the weld joint by SAW would fail at side bending test at the center of weld metal. Fig. 7 shows an SEM micrograph of a side-bend fracture surface; what looks like a brittle phase with low ductility is found in dimples. Fig. 8 shows the microstructure of weld metal by multi-pass SAW and the amount of ferrite measured with a ferrite scope.

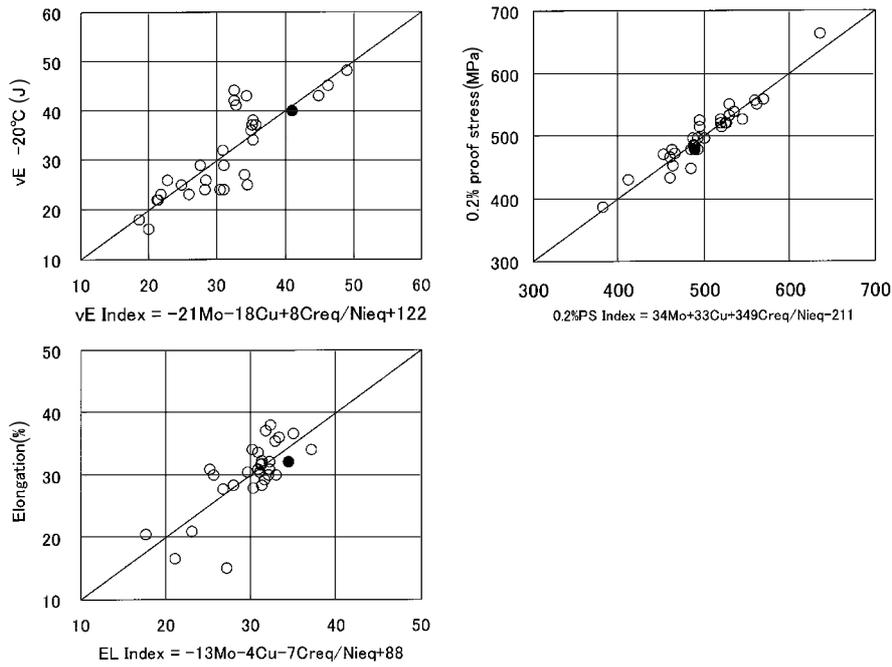


Fig. 6 Effect of Mo, Cu contents and Cr eq./Ni eq. ratio on toughness, 0.2% proof stress and elongation of deposited metals

Table 2 Chemical compositions of FCAW deposited metal

	Chemical composition of FCAW deposite metal										Cr eq./ Ni eq.	PI	GI
	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N			
FCAW	0.03	0.34	1.48	0.017	0.005	13.2	22.7	2.6	2.2	0.06	1.5	32	63

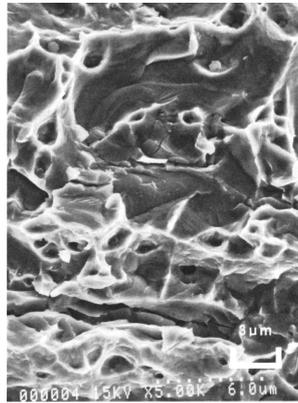


Fig. 7 Fracture surface of side bending test specimen

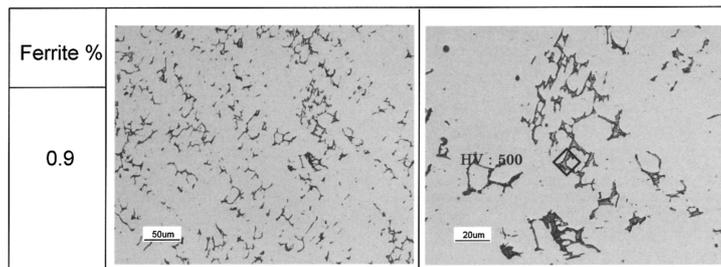


Fig. 8 Microstructures of 1st pass weld metal in SAW multi-pass welds

Although the amount of ferrite in the first-pass weld metal measured magnetically with a ferrite scope was as low as 0.9%, the actual microstructure exhibited networks of vermicular ferrite at microscope observation; the volume fraction of ferrite was several times higher than that measured with the ferrite scope. Hardness measurement of this ferrite phase revealed that its hardness was as high as 500 Hv.

The above indicates that the low ferrite amount of a first-pass layer measured with the ferrite scope was due to the transformation of ferrite in the first-pass layer into a phase under the heat cycles of subsequent passes, and the precipitation of the phase led to the failure of weld metal at side bend test.

Such an embrittlement due to the phase is not observed with FCAW but is peculiar to SAW; this is presumably because the cooling rate in the temperature range of phase precipitation decreases under the large heat input of SAW, making the precipitation of the phase easier. In this relation, since Mo is known to have significant effects on the precipitation of the phase⁹⁾, the authors investigated the effects of heat input and Mo content on the phase precipitation. Fig. 9 shows the influences of heat input and the Mo content in weld metal on side bend properties; the side bend properties improved as the Mo content or heat input decreased, evidencing that the decrease in the Mo content or heat input suppressed the precipitation of the phase. However, in the field welding practice in the construction of chemical tankers, the upper limit of heat input is usually set at approximately 50 kJ/cm in consideration of work efficiency. The above and Fig. 9 lead to a conclusion that an optimum content of Mo

for SAW weld metal is 2% or less, lower than that for the FCAW welding wire. Furthermore, since the base metal, NSSC260A, contains Mo by more than 3% and the dilution of welding wire with base metal is larger by SAW than FCAW, it is necessary to design the chemical compositions of welding consumables (wire and flux) for SAW taking the pick-up of Mo from base metal into consideration.

Another aspect peculiar to SAW is that the chemical composition of weld metal is determined by those of welding wire and flux, and in most cases, trace elements are supplied to weld metal from flux. In the case of the welding consumables for NSSC260A, however, Cu is indispensable, but if it is fed from the flux, many small cracks about 0.5 mm deep form in the base metal near the fusion boundary at a bead toe. Fig. 10 shows a result of element mapping at a crack; Cu was found to concentrate in the crack, evidencing that the crack resulted from liquid-metal embrittlement by Cu. This indicates that, when Cu is supplied from flux in SAW, the Cu in the flux melts under heat radiation from the arc or conduction through the base metal, and the molten Cu penetrates from the surface of base metal into its austenitic grain boundaries near a fusion boundary to form cracks. Note that the cracking due to liquid-metal embrittlement does not occur in FCAW, because a metal shell wraps flux that contains Cu. This suggests that for the supply of Cu in SAW it is important that the welding wire contain Cu.

Based on the results of the studies described above, guidelines for the chemistry design of the welding consumables (wire and flux) for SAW to satisfy quality targets were set out using the chemical composition of the FCAW welding wire as a basis and in consideration of the formation of the brittle phase and the cracking due to the liquid-metal embrittlement by Cu. More specifically, the design guidelines were as follows: (1) decreasing Mo content to suppress the precipitation of the phase and increasing Cr content to secure a desired value of the PI, (2) in view of the large dilution with base metal in SAW and consequent large Ni pick-up from the base metal, decreasing Ni content to prevent hot cracking, (3) increasing Cu content to secure a desired value of the GI with the decreased Mo content and supplying Cu not from the flux but from the wire to prevent the cracking due to the liquid-metal embrittlement by Cu (Here, it has to be noted that, since the toughness of SAW weld metal tends to be higher than that of FCAW weld metal, a higher content of Cu is permissible.), and (4) increasing N content because blowholes occur less in SAW than in FCAW. A welding wire, NITTETSU Y-316C, and flux, NITTETSU BF-317LNCU, for SAW of NSSC260A were developed in accordance with these guidelines. Table 3 shows

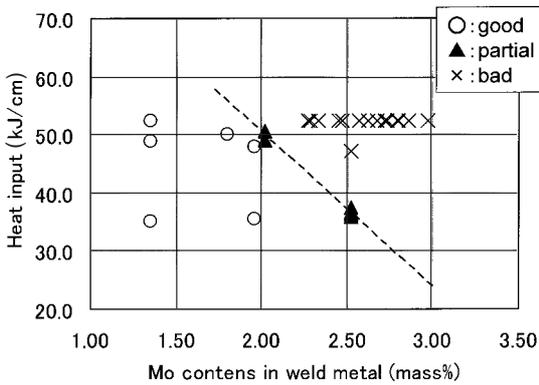


Fig. 9 Effect of Mo contents and weld heat input on side bend properties of SAW weld joints

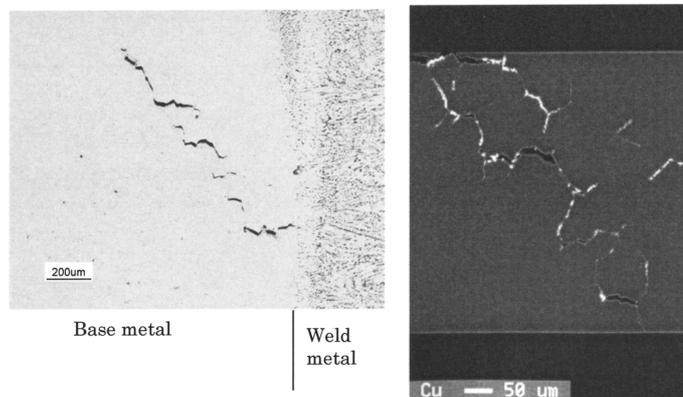


Fig. 10 Cu profile at cracks in HAZ near fusion boundary of SAW welds

Table 3 Chemical compositions of SAW deposited metal

	Chemical composition (mass%)										Cr eq./	PI	GI
	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N	Ni eq.		
SAW	0.04	0.56	0.76	0.030	0.004	10.6	25.3	1.7	2.6	0.09	1.8	32	51

Table 4 Mechanical properties of weld joints

	Tensile test		Impact test	Bend test		
	Tensile strength (MPa)	Fracture position	\sqrt{E} -20°C (J)	R = 2t		
				Face bend	Root bend	Side bend
FCAW	696	Weld metal	44	No defect	No defect	No defect
SAW	708	Base metal	103	No defect	No defect	No defect

Table 5 Results of corrosion tests of weld joints

	Pitting corrosion	General corrosion	
	Pitting potential mV vs. Ag/AgCl	Corrosion rate (mm/y)	
		50% H ₂ SO ₄	96% H ₂ SO ₄
FCAW	Over 1000	0.20	0.10
SAW	Over 1000	0.39	0.14

an example of the chemical composition of the weld metal obtained using the developed welding consumables.

4. Application to Chemical Tankers and Future Prospects

Tables 4 and 5 show the mechanical properties and corrosion test results, respectively, of joints of the NSSC260A stainless steel welded using the newly developed welding consumables. The weld joints by either FCAW or SAW satisfied the quality targets, and welding workability in terms of such as arc stability and slag removability was satisfactory.

The newly developed NSSC260A stainless steel plates and the welding consumables for the steel described herein were actually used for construction of a chemical cargo tanker in June 2004 and their good weldability was confirmed. It is expected that, while their actual use for chemical tankers will increase in view of the need for

higher transportation efficiency and economy, their use will expand to cover new applications such as smoke stacks, gas ducts, exhaust-gas desulfurization equipment and sulfuric-acid tanks by virtue of the excellent resistance to sulfuric acid corrosion.

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