Ni-Base Alloy Clad Steel Plates for Flue Gas Desulfurization (FGD) Systems

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—Synopsis—

Abstract: In order to protect the environment from air pollution, flue gas desulfurization (FGD) systems are being constructed at a growing number of power plants where sulfur-containing coal is burned. These systems require highly corrosion-resistant Ni-base alloys since they operate in a very aggressive atmosphere containing acidic chlorides. This paper describes the characteristics and weldability of Ni-Cr-Mo alloy clad steel plates, which have emerged as a major structural material for FGD systems.

1. Introduction

As environmental problems such as acid rain, destruction of the ozone layer and global warming become aggravated, there has been a significant worldwide movement toward protection of the environment. In the U.S. and Europe, damage due to acid rain resulting from air pollution became evident in the late 1960's, and the U.S., Germany and other industrialized nations have established laws requiring the installation of flue gas desulfurization (FGD) systems in thermal power plants which burn coal with high sulfur content. In the U.S., following institution of the Clean Air Act of 1967, regulations governing air pollution have been gradually tightened, and many FGD systems are now in operation, with many new systems now under construction. Air pollution problems are not limited to the countries where contaminants are emitted and the effects transcend national borders. Thus, the need for global measures to prevent air pollution has been recognized. Of late FGD systems have been installed in many countries other than those mentioned above, including a number in Asia.

Early FGD systems used carbon steel with resin or rubber lining, or 300-series stainless steels, as corrosion-resistant materials. But premature failures due to corrosion were often experienced, and it became clear that the corrosive environment of the FGD systems was considerably severer than had been anticipated. In recent years, it has become accepted that the use of highly corrosion-resistant alloys is preferable considering the life cycle cost, even though initial costs are higher[1-3]. On the other hand, FGD system costs are enormous, and various methods have been proposed in order to lower construction costs; at present, sheet lining method and clad steel plates are primarily used[3-5], being economical compared with the use of solid alloy. Sheet lining method is mainly applied to the replacement of the lining of existing systems, whereas clad steel plates tend to be adopted for use in new FGD systems[5].

In this article, we discuss the mechanical properties and corrosion resistance of the Ni-Cr-Mo alloys C-276 (UNS-N10276) and C-22 (UNS-N06022) clad steel plates which are widely adopted in FGD systems, as well as the welding conditions and corrosion resistance of the welded joints of these materials.

2. FGD Systems and their Operating Environments

At present, some different types of FGD systems are in operation, and new systems are also in development. Of these, the systems based on the wet lime/limestone process is most common, and is expected to continue to be the most important type of FGD system hereafter as well[1]. In this process, the SO_2 contained in exhaust gases is reacted with CaO (lime) or with $CaCO_3$ (limestone) in the presence of water, to remove it in the form $CaSO_4$ (gypsum). H_2SO_4 is then produced as a byproduct, and at the same time the chlorides and fluorides contained in the fuel become HCl and HF respectively. Hence, the interior of the FGD equipment is exposed to a severe acidic chloride environment which corrodes materials, although the extent is different depending on the coal burned. In addition, when the water for cooling or producing a slurry of CaO or $CaCO_3$ is

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circulated in a closed loop, the corrosivity is further intensified due to the concentration of ions. In such cases, chloride ion concentrations can reach 10,000 ppm and above. The main modes of corrosion in such an environment are pitting and crevice corrosion, but uniform corrosion, èrosion/corrosion, and stress-corrosion cracking (SCC) also occur[6].

Figure 1, Table 1 and **Table 2** show the construction, the environment in each area, and classification of environments of the FGD systems in general use in the U.S.[1,7]. The main environmental factors are the chemical factor, the mechanical factor, and the temperature. The chemical factor and temperature are mainly related to corrosion, while the mechanical factor is related to abrasion. In Table 2, only the pH and the H_2SO_4 concentration are shown as chemical environment factors, but in actual practice the chloride ion and fluoride ion concentrations should be also included[6]. The harshest corrosive environments occur at [E], [F] and [G] in Fig. 1; in these areas, Ni-Cr-Mo alloys C-276 or C-22 are used. However, damage due to corrosion was experienced even when using these alloys, and the use of new alloys with still better corrosion resistance is being studied[3,6].

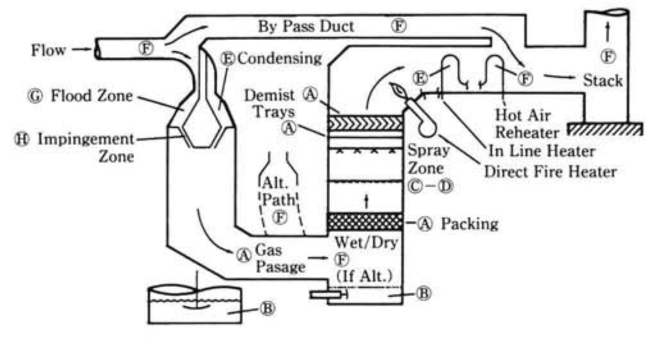


Fig. 1 Construction of a typical FGD system and environments in various parts[1,7]

Table 1 Environments in different parts of a typical FGD system (codes refer to locations in Fig. 1)[1,7]

CODE	CHEMISTRY	MECHANICAL ENVIRONMENT	TEMPERATURE
Ⓐ	MILDCORROSIVE(VAPOR)	MILD	MILD
Ⓑ	MODERATE(IMMERSION)	MILD	MILD
Ⓒ	MODERATE	MODERATE	MILD
Ⓓ	MODERATE	SEVERE	MILD
Ⓔ	SEVERE	MILD	MODERATE
Ⓕ	SEVERE	MILD	SEVERE
Ⓖ	SEVERE	SEVERE	SEVERE
Ⓗ	MODERATE	SEVERE	MODERATE

Table 2 Definition of environments in a typical FGD system[1,7]

	CHEMISTRY	MECH.ENVIRONMENT (ABRASIONLEVEL)	TEMPERATURE
MILD	pH 3-8 H_2SO_4	AGITATEDTK.,WALLS. DUCTS,THICKENER	AMBIENT TO 150°F
MODERATE	pH 0.1-3 8-13.9 H_2SO_4 15%	SPRAY ZONE TANK BOTTOMS	AMBIENT TO 200°F
SEVERE	pH$<$0.1 $>$13.9 H_2SO_4 15%	HI ENERGY VENTURI IMPINGEMENT-TURNING VANES,TARGETS	AMBIENT TO 360°F

3. Advantages of the Use of Clad Steel Plate in FGD Systems

In general, clad steel plates offer the greatest economic advantage when the cladding material is extremely expensive, and when the total thickness is large and the fractional thickness of the cladding material (the cladding ratio) is small. The plates used in FGD systems are thin, ranging between 6 and 20mm in thickness. There is, therefore, little advantage for clad steel plate when relatively inexpensive cladding material such as 300 series stainless steels is used, but the advantage is considerable when using high- grade stainless steel containing 6% or more Mo and Ni-base alloys as a cladding material. However, the use of clad steel plates in FGD equipment offers various benefits as described below, compared with the use of solid alloys and sheet lining method.

(1) Clad steel plate is economical compared with the correspondent high-alloy solid material.
(2) Clad steel plate longer and wider than high-alloy sheet can be supplied, reducing the number of welding seams in comparison with sheet lining method.
(3) Whereas sheet lining method is a two stage process where the interior is lined following the container fabrication, the use of clad steel plates offers single stage process, requiring less fabrication time.
(4) Because the clad steel plates are metallurgically bonded over the entire area, there is little danger of leaks at seal welds which is often experienced in sheet lining method. In addition, the leak tests required for the sheet lining method are unnecessary.
(5) In sheet lining method, steps are formed at seal welded areas, but clad steel plates can be butt-welded, resulting in a relatively smooth surface. As a result, cleaning and detection of damage are made easier. There are also few deposits which

might cause crevice corrosion.

(6) Spot-welding or plug welding required in sheet lining method is unnecessary because the entire area is metallurgically bonded.

4. Mechanical Properties and Corrosion Resistance of Ni-Base Alloy Clad Steel Plates

In the most corrosive areas of an FGD system, the materials used should not only be acid-resistant, but also be resistant to pitting corrosion and crevice corrosion; consequently Ni-base alloys with high Cr and Mo contents are used. We here discuss Ni-Cr-Mo alloys C-276 and C-22 clad steel plates, which are widely used in FGD systems.

The production process of clad steel plates at The Japan Steel Works is hot-rolling method. By this means the entire clad steel plate is metallurgically bonded over the entire area, and wider and longer plate can be manufactured, leading to the various advantages already mentioned.

Tables 3 and **4** show the typical chemical composition and mechanical properties of C-276 and C-22 clad steel plates which were produced for use in FGD systems. Tensile strength, ductility and shear strength fully satisfy the specifications for Ni-base alloy clad steel (JIS-G3602 and ASTM-A265). The impact energy at 0 ℃, however, is somewhat low

Fig. 2 Cross-sectional microstructure of C-276 alloy clad steel plate

Table 3 Typical chemical compositions of C-276 and C-22 alloy clad steel plates

Material		Chemical Composition (wt.%)												
		C	Si	Mn	P	S	Ni	Cr	Cu	Mo	Al	Fe	W	Co
C-276 CladPlate (1.6+4.8)mmt	Cladding	0.006	0.02	0.40	0.009	0.001	Bal.	15.38	0.14	15.39	0.18	6.79	3.67	0.30
	Base	0.14	0.23	0.91	0.014	0.004	0.02	0.01	0.01	0.01	0.01	Bal.	-	-
C-22 CladPlate (2+10)mmt	Cladding	0.003	0.01	0.10	<0.01	<0.01	Bal.	21.20	-	13.20	-	3.30	3.10	0.10
	Base	0.13	0.30	1.00	0.009	0.007	-	-	-	-	-	Bal.	-	-

Table 4 Typical mechanical properties of C-276 and C-22 alloy clad steel plates

Material	TensileProperties[1]			CharpyImpact	Bonding Properties		Face
	0.2%Y.S. (MPa)	T.S. (MPa)	EL. (%)	Energyat 0℃ (J)[2]	Shear Strength (MPa)	RamTensile Strength(MPa)	Bend Test[3]
C-276 CladPlate (1.6+4.8)mmt	303	516	49.4	44,48,43	366	-	Good
	294	516	48.6	56,55,51	392	-	Good
C-22 CladPlate (2+10)mmt	294	497	37.5	62,62,67	381	491	Good
	309	516	36.6		387	516	Good

1) Full thickness specimen
2) Half size specimen for C-276 clad plate and full size specimen for C-22 clad plate
3) R=1.0t for C-276 clad plate and R=1.5t for C-22 clad plate

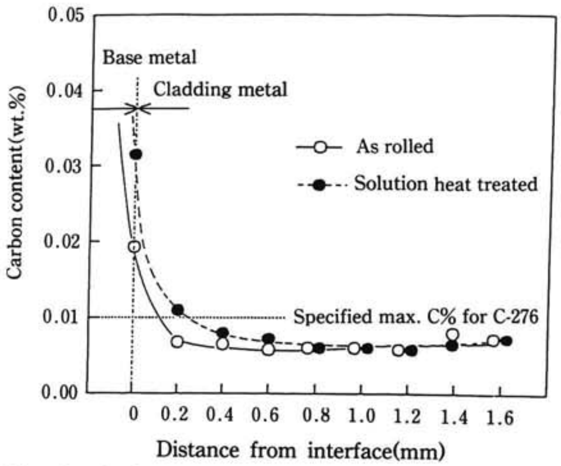


Fig. 3 Carbon distribution near the bonding interface in C-276 alloy clad steel plate

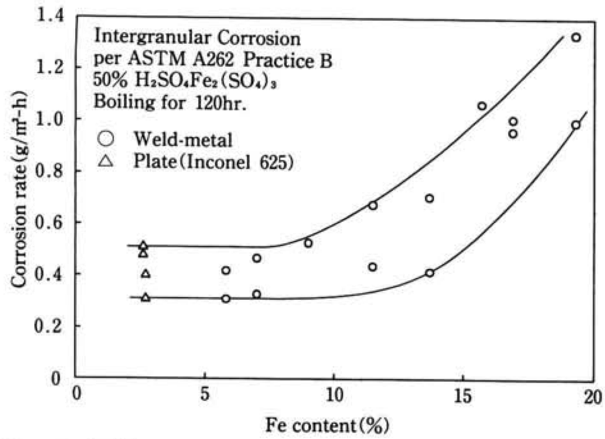


Fig. 4 Effect of Fe content on the intergranular corrosion resistance of alloy 625 weld metal

Table 5 Comparison of corrosion test results for C-276 and C-22 alloy clad steel plates and solid materials

Testing Condition \ Material	C-276		C-22	
	Cladding	Solid	Cladding	Solid
General Corrosion (Boiling in 5% or 10 % H_2SO_4 for 4h)[1]	0.33 0.36	0.16 0.20	0.20 0.18	0.22 0.22
General Corrosion (Boiling in 10%HCL for 4h)	5.15 5.30	5.60 7.30	9.24 9.31	9.44 9.74
Intergranular Corrosion (Boiling in 50%H_2SO_4 +42g/l $Fe_2(SO_4)_3$ for 24h)	5.30 5.84	5.83 6.27	0.73 0.73	0.62 0.62
Pitting Corrosion (Boiling in 11.5%H_2SO_4 +1.2%HCL+1%$FeCl_3$ 1%$CuCl_2$ for 24h)	0.31 (Nopits) 0.34 (Nopits)	0.35 (Nopits) 0.35 (Nopits)	0.08 (Nopits) 0.07 (Nopits)	0.07 (Nopits) 0.08 (Nopits)

1) 5%H_2SO_4 for C-276 and 10%H_2SO_4 for C-22 (Unit, mm/year)

owing to the fact that the solution heat treatment is performed at high temperatures. **Figures 2** and **3** show the cross-sectional microstructure and the carbon distributions near the interface before and after solution heat treatment for C-276 clad steel plate. In Fig. 2, the area which appears black on the cladding side of the interface is an area of carbon diffusion from the base material (carburized layer). The width of this carburized layer after solution heat treatment is 0.3mm or less (Fig. 3).

Table 5 compares the results of various corrosion tests for cladding layer of C-276 and C-22 clad steel plate with those for the solid materials. The corrosion resistance of the cladding layer of the clad steel plate is essentially the same as that of the solid materials, and no deterioration in corrosion resistance is evident in the process of manufacturing the clad steel plates. The results of pitting corrosion tests in the environment simulating an FGD system, a boiling solution of 11.5% H_2SO_4+1.2% HCl+1% $FeCl_4$+1% $CuCl_2$ ("green death solution"), revealed that C-22 has superior corrosion resistance to C-276 in this environment.

5. Welding of Ni-Base Alloy Clad Steel Plates for FGD Systems and Corrosion Resistance of Welds

Regarding the welded joints of clad steel plates, the corrosion resistance of the surface on the cladding-material side exposed to corrosive environments must be comparable or superior to that of the cladding layer of the clad plate. In general, the corrosion resistance of high-alloy stainless steel welds is inferior to that of the plate or forging of the same composition, due to microscopic compositional segregation[10, 11]. In the welding of clad steel plates, there is dilution of Fe from the carbon or low-alloy steel base material, and it is commom to use welding material with a higher alloy content than the cladding material. Ni-base alloys undergo a significant degradation of corrosion resistance as a result of Fe dilution, so that in addition to the use of a welding material with excellent corrosion resistance, dilution must be minimized. **Figure 4** shows the effect of Fe content on the intergranular corrosion resistance of alloy 625 (UNS-N06625) weld metal. When the Fe content of alloy 625 increases above 10%, the resistance to intergranular corrosion drops sharply (the specified uppper Fe limit for alloy 625 is 5%). In this case, however, the C content increases together with the amount of Fe dilution, and C dilution is also thought to affect the decline in corrosion resistance.

The effect of welding conditions on the corrosion resistance of welds was studied for C-276 clad steel plate (thickness;1.6+4.8 mm). The resistance to intergranular corrosion, which poses the greatest problem

Table 6 Welding conditions in welding tests of C-276 alloy clad steel plates

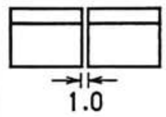
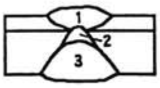
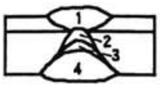
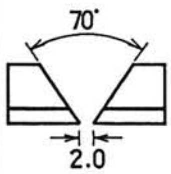
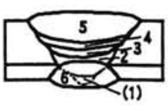
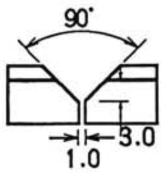
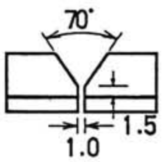
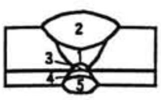
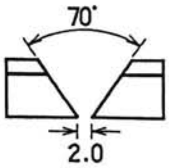
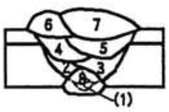
Type	Welding groove	Stacking	Pass	Welding material	Welding method	Current and polarity	Welding current (A)	Welding voltage (V)	Travelling speed (mm/min)
I			1	HC-22, ϕ1.2	P-GMAW	DC,RP	195/205	28/30	550/650
			2				175/185	26/28	
			3		GMAW	DC,RP	195/205	29/31	550/650
I'			1	HC-22, ϕ1.2	P-GMAW	DC,RP	195/205	28/30	550/650
			2~4	Alloy625, ϕ1.2	GMAW	DC,RP	250/260	30/32	550/650
II			1~2	Alloy686, ϕ2.4	GTAW	DC,SP	115/125	11/13	100/140
			3~5	Alloy625, ϕ1.2	GMAW	DC,RP	250/260	30/32	550/650
			6	Alloy686, ϕ2.4	GTAW	DC,SP	120/130	12/13	100/140
III			1	Alloy686, ϕ2.4	GTAW	DC,SP	115/125	11/13	100/140
			2~6				135/145	13/15	
			7~9	Alloy625, ϕ1.2	GMAW	DC,RP	250/260	30/32	550/650
IV			1~2	LB52N, ϕ3.2	SMAW	AC	110/130	–	140/160
			3~5	Alloy686, ϕ2.4	GTAW	DC,SP	115/125	11/13	100/140
V			1	LB52N, ϕ3.2	SMAW	AC	110/130	–	140/160
			2~7	Alloy686, ϕ2.4	GTAW	DC,SP	115/125	11/13	100/140
			8	LB52N, ϕ3.2	SMAW	AC	110/130	–	140/160

Table 7 Chemical composition of welding materials used in the tests

Welding materials	Chemical composition (wt.%)											
	C	Si	Mn	P	S	Ni	Cr	Mo	V	Fe	W	Co
HC-22 ϕ2.4mm (for GTAW)	0.004	0.01	0.13	0.010	<0.010	Bal.	21.20	13.2	0.03	3.50	3.00	0.80
HC-22 ϕ1.2mm (for Pulse GMAW)	0.003	0.03	0.26	0.010	<0.010	Bal.	21.50	13.2	0.14	4.90	3.00	1.00
Alloy 625 ϕ1.2mm (for GMAW)	0.027	0.14	0.01	0.003	0.002	BaL.	21.40	8.5	Ti 0.23	0.35	Al 0.30	Nb 3.42
Alloy 686 ϕ2.4mm (for GTAW)	0.004	0.01	0.24	0.004	<0.001	Bal.	20.53	16.3	–	1.04	3.88	–

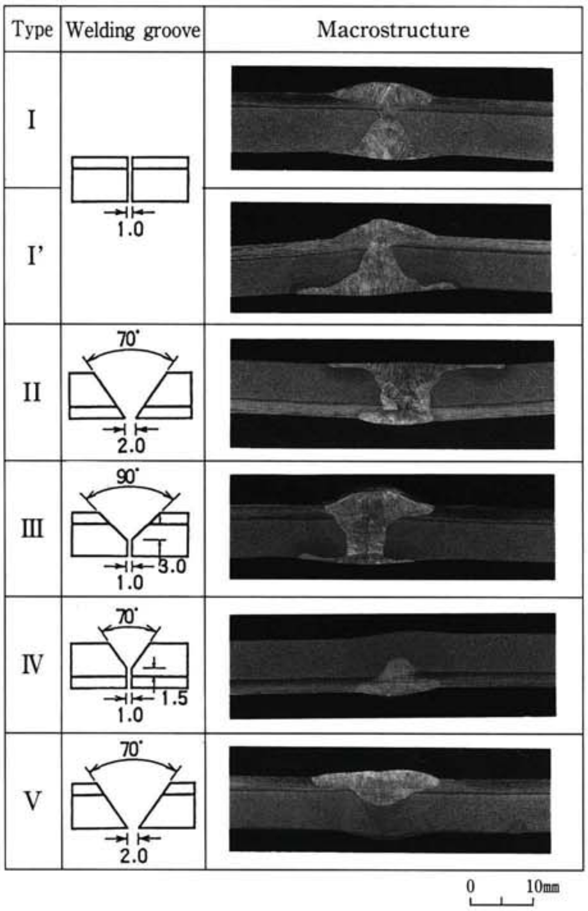


Fig. 5 Macro-etched structure of the welded joints

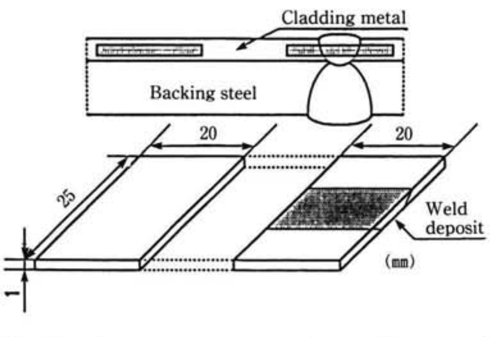


Fig. 6 Corrosion test specimens from welds and sampled region

at welds and heat-affected zone, was evaluated. As indicated in **Table 6**, the welding bevel shape, stacking method, welding materials and welding method were varied. The chemical compositions of the welding materials used appear in **Table 7**. The welding on the surface of cladding side was performed using C-22 or alloy 686 welding material, with better corrosion resistance than C-276. Alloy 686 (UNS-N06686) has lower Fe content than C-22, and improved corrosion resistance[9]. **Figure 5** shows the macro-etched structures of each weld, and **Table 8** gives the distri-

Table 8 Chemical composition distribution in depth direction from the cladding material surface at the centers of the welds

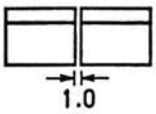
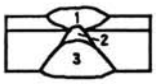
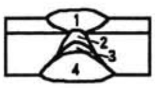
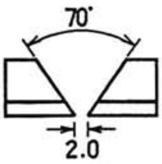
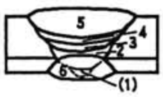
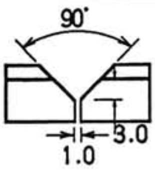
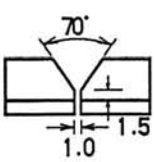
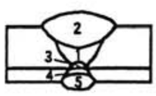
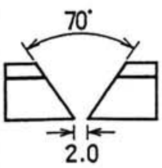
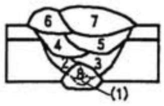
Type	Welding groove	Depth[1] (mm)	Cr (wt.%)	Mo (wt.%)	Fe (wt.%)	PI (Cr+3.3Mo)
I	1.0	0 ~0.5	17.4	15.1	9.1	67.2
		0.5~1.0	17.4	14.3	9.1	64.6
		1.0~1.5	17.3	14.6	9.1	65.5
		1.5~2.0	17.3	14.3	9.1	64.5
		2.0~3.0	17.0	14.3	9.1	64.2
I'		0 ~0.5	19.1	14.3	5.1	66.3
		0.5~1.0	18.9	14.3	5.1	66.1
		1.0~1.5	18.7	14.6	5.1	66.9
		1.5~2.0	18.4	14.6	5.4	66.9
		2.0~3.0	19.0	12.6	5.1	60.6
II	70°, 2.0	0 ~0.5	17.7	15.7	6.0	69.5
		0.5~1.0	17.6	15.2	6.3	67.8
		1.0~1.5	17.4	15.1	6.3	67.2
		1.5~2.0	17.3	15.1	6.0	67.1
		2.0~3.0	18.6	12.0	6.3	58.2
III	90°, 3.0, 1.0	0 ~0.5	17.0	14.9	8.3	66.2
		0.5~1.0	17.1	15.7	8.3	68.9
		1.0~1.5	17.1	15.7	8.0	68.9
		1.5~2.0	17.0	15.1	8.6	66.8
		2.0~3.0	17.0	16.3	9.7	70.8
IV	70°, 1.5, 1.0	0 ~0.5	16.7	15.7	9.4	68.5
		0.5~1.0	16.7	16.0	9.1	69.5
		1.0~1.5	16.9	16.3	9.4	70.7
		1.5~2.0	17.0	16.6	9.7	71.8
		2.0~3.0	15.7	14.9	14.9	64.9
V	70°, 2.0	0 ~0.5	16.7	14.9	11.4	65.9
		0.5~1.0	16.7	15.1	11.1	66.5
		1.0~1.5	16.9	15.4	10.6	67.7
		1.5~2.0	16.9	15.4	10.6	67.7
		2.0~3.0	15.7	14.9	16.0	64.9

*: Checked by X-ray line analysis
1) Distance from top surface of weld metal

butions of Cr, Mo and Fe in the depth direction from the cladding material surface at the center of the weld. From Table 8 we can see that there is dilution by the cladding material C-276 and the base carbon steel, although the extent differs with the welding conditions. In other words, the Cr contents reduced in the weld metal of C-22, while Mo and Fe increased. In the 686 alloy weld metal, the Cr contents reduced, while the Mo content did not significantly change, and the Fe content increased. Comparing type I and type I', the extent of dilution is different despite the fact that the welding conditions for cladding layer are same. This is probably due to the melting of the base material in type I welds, resulting from slight differences in the amount of heat input during welding. Comparing types II through V, Fe dilution from the base carbon steel is smallest in type II, and greatest in type V welds.

Corrosion test specimens (1×25×20mm) were taken from the center of the cladding layer of each weld, as shown in **Figure 6**, and intergranular corro-

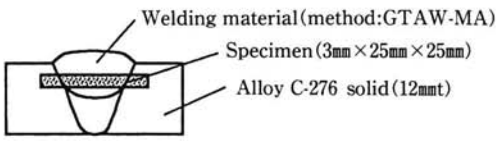
Table 9 Results of intergranular corrosion tests for C-276 alloy clad steel plate welds

Type	Welding groove	Stacking	Pass	Welding material	Welding method	Intergranular corrosion (mm/year) *1
I			1	HC-22, ϕ1.2	P-GMAW	5.958, 6.235
			2			
			3		GMAW	
I'			1	HC-22, ϕ1.2	P-GMAW	7.979, 6.138
			2~4	Alloy625, ϕ1.2	GMA	
II			1~2	Alloy686, ϕ2.4	GTAW	5.255, 5.153
			3~5	Alloy625, ϕ1.2	GMAW	
			6	Alloy686, ϕ2.4	GTAW	
III			1	Alloy686, ϕ2.4	GTAW	8.574, 8.573
			2~6			
			7~9	Alloy625, ϕ1.2	GMAW	
IV			1~2	LB52N, ϕ3.2	SMAW	6.316, 6.643
			3~5	Alloy686, ϕ2.4	GTAW	
V			1	LB52N, ϕ3.2	SMAW	8.403, 7.469
			2~7	Alloy686, ϕ2.4	GTAW	
			8	LB52N, ϕ3.2	SMAW	
Base cladding layer						5.303, 5.842

*1: ASTM G28A (50% H_2SO_4 + 42g/l $Fe_2(SO_4)_3$, Boil, 24hr)

Table 10 Results of intergranular corrosion tests for C-276 alloy solid material and welds

Welding material	Corrosion rate (mm/year)	
Alloy C-22	6.354,	7.027
Alloy 686	8.052,	7,293
Alloy C-276	12.156,	13.313
Alloy C-276 base material	7,886,	7.926



2) ASTM G28A
50% H_2SO_4 + 42g/l $Fe_2(SO_4)_3$, Boil, 24hr)

sion tests were performed. The results appear in **Table 9**. These results include the effect of dilution from the base carbon steel. In order to determine the corrosion resistance of the welds for each welding material in the case of no dilution from the base carbon steel, C-276 solid material was welded using alloys C-22, 686, and C-276 welding material. The welds and C-276 base material were subjected to the same intergranular corrosion tests as mentioned above. The results are given in **Table 10**. We can see that the welds using C-22 and alloy 686 exhibit the same corrosion resistance as the C-276 base material. However, the corrosion resistance of the welds using the same C-276 material was clearly poorer than that of the C-276 base material. As already explained, this is attributed to the microscopic segregation in the weld metal. Even when the nominal chemical composition is same, the weld metal causes the differences in alloying elements concentrations in dendrite and interdendritic region, so that dendrite with less concentration of the corrosion-resistant elements (Cr, Mo and W) are selectively corroded[10, 11]. Comparing the results of Table 10 with the results for the weld of clad steel plate (Table 9), all of the clad steel welds show the corrosion resistance comparable to that of the solid material welds, within the range of data scattering. However, types I and II are difficult to control the welding conditions in actual fabrication, and it is, at present, considered that types III through V are suitable for practical use.

Based on the above welding test results, it is clear that welds with excellent corrosion resistance can be obtained by performing multilayer welds with low heat input through the use of appropriate bevel shapes and welding materials. However, these methods involve numerous passes and suffer from insufficient productivity. Further improvement of welding productivity is needed.

6. Conclusion

To protect the global environment from pollution, power plants which burn coal with high sulfur contenttend to be obliged to install flue gas desulfurization (FGD) system, and consequently numerous FGD systems are being constructed around the world. As FGD equipment is used in a severe acidic chloride environment, it employs Ni-base alloys with excellent corrosion resistance; but recently clad steel plates have been increasingly applied because of the greater economy of the material itself, the reduced fabrication costs and the superior safety. In this paper the characteristics and weldability of Ni-base alloys C-276 and C-22 clad steel plates used in FGD equipment were introduced, and it was shown that these materials are suitable for use in FGD equipment.

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