Properties of a Fully Austenitic Stainless Steel Weld Metal for Severe Corrosion Environments

Development is successfully carried out on a new material for urea plants and on a corresponding filler metal which is available as a bare wire, covered electrode or strip

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Introduction

There are many instances involving the chemical industry where the common standardized stainless CrNiMo-steels do not have satisfactory corrosion resistance for economical operation of the equipment. This is so in the most critical parts of reactors for the production of the important fertilizer urea.

For many years AISI Type 316L stainless steel has been used as construction material for such parts. The rapidly increasing demand for urea has forced producers to increase the production considerably. Besides building further production plants, it was evident that a better construction material could contribute to increased production by giving the plants a longer service-life.

Against this background a new material was developed. The material is fully austenitic and has the composition C max 0.020%, Cr 25%, Ni 22%, Mo 2.1%, N 0.12%. Nowadays it is widely used as stripper tubes in urea plants.

Since welding is extensively used in plant fabrication it is necessary that the construction material has good weldability. This was proved by several tests which showed that the heat-affected zone (HAZ) did exhibit properties equal to those of base metal. This is due to:

1. Low carbon content minimizing the risk for carbide precipitation during welding.
2. High nickel content and nitrogen addition minimizing the ferrite formation.
3. Low contents of impurities ($P \leq 0.015\%$, $S \leq 0.015\%$) which counteracts cracking.

Since a chain is not stronger than its weakest link, it is evident that a material having excellent corrosion resistance has to be welded with a filler giving a weld metal with comparable properties. In a case like this, where for corrosion reasons ferrite practically is not allowed in the weld metal, the well-known difficulties to get crack-free welds are likely to arise. The development work of a filler metal for gas tungsten-arc welding (GTAW) and covered electrodes for manual shielded metal-arc welding (SMAW) giving weld metal with corresponding corrosion resistance and strength properties is described in this paper; also described is how its cracking resistance was optimized.

Austenitic ELC filler metals of the type 19Cr/16Ni/Mn are used for surfacing in urea plants. However, the corrosion resistance of the material is not as good as that of the above mentioned higher alloyed base metal. Therefore, the filler metal developed was also manufactured as strip for submerged-arc surfacing. The tests with this are described, and the results are presented and discussed.

Resistance to Cracking

A well-known characteristic of common fully austenitic weld metal is its sensitivity to cracking. Two types of cracking, solidification cracking and micro-cracking in reheated weld metal of multipass weldments are reported. The composition of the weld metal does indeed influence the crack sensitivity and the following statements have been published (Ref. 1):

1. Carbon should be below 0.1%.
2. Silicon should be below 0.3%.
3. Manganese should be between 3 and 6%.
4. Phosphorus and sulphur should each be maximized to 0.015%.
5. Molybdenum should be between 2 and 3%.
6. Nitrogen should be between 0.1 and 0.2%.
7. Trace impurity elements should be avoided.

The base metal fulfills these requirements except in the case of manganese. Also, since raw materials of very high purity are used, trace impurity elements are at very lowest level which is practically possible. The same authors have also shown (Ref. 2) that the crack sensitivity has a minimum in the manganese range 4 to 5%—Fig. 1. Also, another paper (Ref. 3) shows that nitrogen counteracts cracking.

Evidently, to obtain a filler metal with an analysis matching that of the base metal the manganese content should be increased in order to minimize the risk for cracking. Therefore, filler metals of the type 25Cr/22Ni/2.1Mn/N were manufactured with three different manganese levels (namely 1.6%, 4.1% and 6.4%) and

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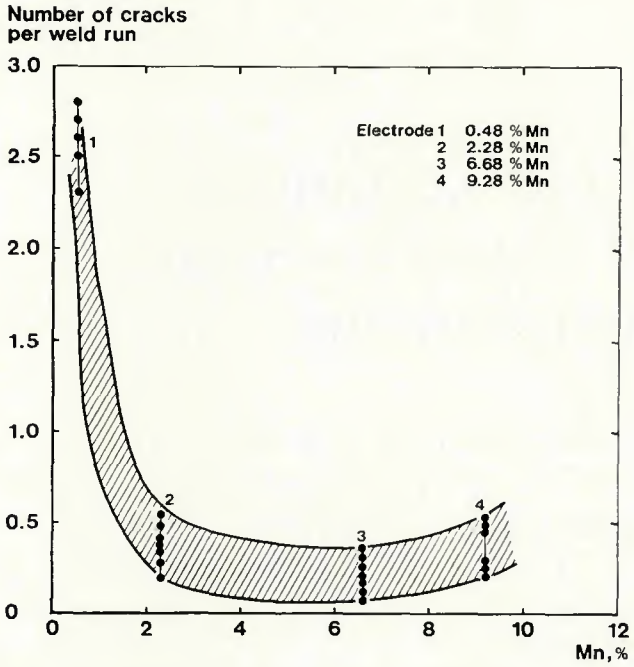

Fig. 1—Relationship between incidence of cracking in weld pads and manganese content

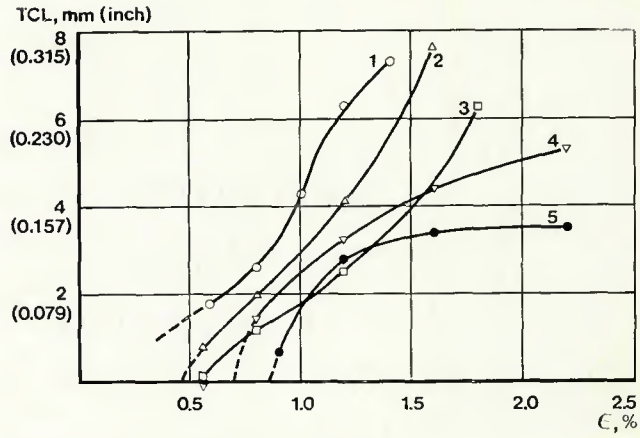

Fig. 2—Total crack length (TCL) vs. elongation (E) and cracking threshold in Varestraint test

Note The curves are drawn on the mean values of three tests

Filler metal	Cracking threshold, % Remelted material	Reheated material
1. AWS ER 310	not predictable	$0.60 < \varepsilon < 0.85$
2. 25/22/2.1/N/1.6Mn	0.45[1]	$0.85 < \varepsilon < 1.15$
3. 25/22/2.1/N/4.1Mn	0.55[1]	$1.15 < \varepsilon < 1.70$
4. 25/22/2.1/N/6.4Mn	0.70[1]	$1.70 < \varepsilon < 2.20$
5. 20/16/2.8/N/8.3Mn	0.85[1]	$\varepsilon > 2.20$

1) extrapolated value from curve

tested. Varestraint testing (Ref. 4) was chosen as test method, and the trials also involved a 20Cr/16Ni/2.8Mo/N filler metal with 8.3% manganese and a filler metal corresponding to AWS ER 310. The compositions of the all weld metals from the fillers used are given in Table 1.

The test material was prepared in the following way. An 8 mm (5/16 in.) deep 90 deg V-groove was machined in the 10 mm (0.4 in.) thick base metal which then was completely filled using GTAW in 5 runs with the filler metal to be tested. This welding was carried out at 180A, 14V and 120 mm/min (4.5 ipm). The composition was checked in the top layer (Table 1), and the test plates were machined to the size 50 × 9 × 250 mm (2 × 0.35 × 12 in.). The Varestraint test was carried out as melting of the top layer in the test weld by GTAW without filler metal and simultaneous bending. Welding data consisting of 250A, 17V and 150 mm/min (6 ipm) were used. The test plates were pickled, and the presence and sizes of cracks were investigated under microscope at 40 times magnification.

In Fig. 2 the total crack length in the remelted weld metal vs. elongation of the top layer of the test plate is given. The elongation (E) is defined as:

$$E = [t/(2R + t)][100(\%)]$$

where t = thickness of test plate (mm), and R = bending radius (mm).

The cracking threshold, i.e., the elongation limit where cracks appear,

Table 1—Materials Used for Crack Tests

Test	Type of material	Chemical composition, % C	Si	Mn	P	S	Cr	Ni	Mo	N
Varestraint	Base metal	.014	.22	1.6	.011	.003	25.0	22.0	2.07	.13
Varestraint	Weld metal AWS ER 310	.094	.52	1.7	.013	.006	25.5	20.4	≤.06	.047
Varestraint	Weld metal 25/22/2.1/N/1.6Mn	.019	.16	1.6	.012	.010	24.6	21.5	2.14	.119
	Check in Varestraint specimen			1.6			24.7	21.8		
Varestraint	Weld metal 25/22/2.1/N/4.1Mn	.014	.16	4.1	.009	.011	24.3	21.8	2.20	.104
	Check in Varestraint specimen			3.7			24.6	21.8		
Varestraint	Weld metal 25/22/2.1/N/6.4Mn	.018	.08	6.4	.013	.012	23.6	21.8	2.06	.068
	Check in Varestraint specimen			5.5			23.9	21.8		
Varestraint	Weld metal 20/16/2.8/N/8.3Mn	.016	.38	8.3	.010	.010	19.7	16.0	2.84	.106
	Check in Varestraint specimen			7.6			20.4	16.8		
Examination of surfacing	Weld metal 25/22/2.1/N/4.5Mn	.020	1.09	2.58	.010	.009	23.3	22.1	2.16	.16

Table 2—Welding Data for SAW Strip Surfacing

Type of strip	Bead no.	Current, A[a]
25/22/2.1/N/4.5Mn	1	650
60 × 0.5 mm	2[b]	700
20/16/2.8/N/8.3Mn	1	650
60 × 0.5 mm	2[b]	700

(a) Other conditions held constant as follows: voltage—28 V; speed—100 mm/min; stickout—30 mm; overlap—7-8 mm; neutral flux (Messer Griesheim LW 412).
(b) Interpass temperature 150 C (302 F).

Table 3—Welding Data for Corrosion and Tensile Test Specimens

Method[a]	Filler metal diameter, mm	Current, A	Voltage, V	Speed, mm/min
GTAW	1.6	90-100	11-12	240
SMA	2.5	80-85	25	250

(a) The same welding data were used for all filler metals tested.

is also given in Fig. 2 for remelted as well as reheated material. The threshold values for remelted material are extrapolated from the curves but for practical reasons, very short total crack length, the values for reheated material are given as intervals in which the threshold is located.

The tests show very clearly that the crack sensitivity is decreased when the manganese content is increased. The cracking threshold for remelted as well as reheated metal is increased with the manganese content, and all the welds made of the special filler metals are far better than those from AWS ER 310. It is interesting to note that the filler metal with 4.1% manganese gives the lowest total crack length at elongation values around 1% and that the filler metals with 6.4 and 8.3% manganese exhibit almost constant total crack length at elongations above 1.5%.

The differences in cracking threshold are small as absolute values. However, it has been shown (Ref. 5) that this is typical for Varestraint testing of material belonging to the same group. Thus the results shown in Fig. 2 should be considered as significant for different cracking behavior.

To further control the crack sensitivity circular groove tests were carried out with SMA welding as well as with GTAW. Covered electrodes, 2.5 mm diameter (3/32 in.) of the type 25Cr/22Ni/2.1Mo/N and with different manganese contents, 1.5%, 4.5%, 5% and 6%, were used in SMA welding, which was carried out in one layer at 80 A, 25 V and 150 mm/min (6 ipm). No cracks were found in weld metal from the electrodes with 4.5%, 5% and 6% manganese, but some small cracks appeared in weld metal with 1.5% manganese. One-layer GTAW was performed at 200 A, 14 V and 50 mm/min (2 ipm) with 25Cr/22Ni/2.1Mo/N filler metals having manganese contents 1.6%, 4.1%, 6.4% and 8.3%. No cracks were found in these welds.

This is further evidence that increased manganese content is beneficial. The absence of cracks despite higher heat input in GTAW with 1.6% manganese filler metal is probably due to the lower phosphorus and sulphur contents (Ref. 6).

Special crack tests are specified in connection with surfacing. One of these (Ref. 7) which is involved in a procedure test for the surfacing of urea plant equipment has been chosen for crack testing of submerged-arc strip weldments.

The welding was carried out in two layers with 60 × 0.5 mm (2.36 × 0.019 in.) strip filler metal of the type 25Cr/22Ni/2.1Mo/N/4.5Mn on a 50 mm (2 in.) thick mild steel plate. Welding data are given in Table 2.

A test piece 130 × 80 mm (5.12 × 3.15 in.) containing material from four different weld layers and thus three transitions between layers was cut out. After grinding parallel to the surface and etching the whole surface, the test piece was investigated with respect to cracks under microscope at X24 magnification. This was made at surfaces located 0,1,2 and 3 mm (0, 0.039, 0.078 and 0.118 in.) below the original weld surface.

No cracks could be found at the 1, 2 and 3 mm levels. At the zero level only two very small cracks were found, one on each side of a transition between two layers. The length of the cracks was only 0.35 mm (0.0137 in.) and 0.1 mm (0.0039 in.) respectively. According to the present requirements, cracks of a length of max 0.6 mm (0.0236 in.) are ignored.

These results indicate good crack resistance for the filler metal in connection with strip surfacing. The crack sensitivity of this fully austenitic weld metal may be considered comparable to ferrite-containing austenitic surfacing of AISI 304 type.

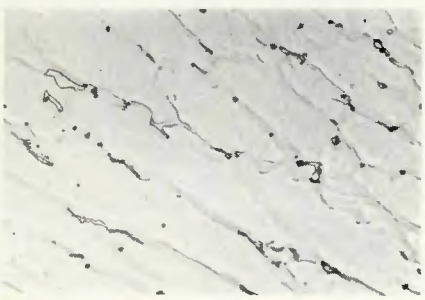

Fig. 3—Structure of weld metal from Varestraint test with filler metal type 25/22/2.1/N/4.5Mn. ×800 (reduced 46% on reproduction)

Metallographic Investigations

The metallographic investigations were made in order to determine the weld metal structure and the mechanism for the crack formation in the Varestraint test.

Material from Varestraint tests and strip surfacing was examined. The investigated material is of the types 25/22/2.1/N/1.6Mn, 25/22/2.1/N/4.1Mn, 25/22/2.1/N/6.4Mn and 20/16/2.8/N/8.3Mn. The analyses of weld metal are given in Table 1.

There are several investigations (Refs. 8, 9, 10) which have shown that Mn increases the tendency of σ-phase formation. Morlay *et al* (Ref. 9) investigated a fully austenitic 25Cr20Ni-steel with 0.1% C. The addition of 4% Mn doubled the σ-phase content.

In fully austenitic welds of 25Cr20Ni-type, so-called segregation cracks and hot ductility cracks have been reported (Ref. 12) of which the former type is the most common one. These cracks are normally formed at high temperatures, about 1300 C (2372 F), owing to segregations and the formation of phases having low melting temperature. As shown in Fig. 1, a Mn content between 2 and 6% seems to decrease the tendency to hot cracking (Ref. 1). A possible reason for this may be the formation of manganese sulfides (melting point 1530 C or 2786 F) instead of the low-temperature melting phases FeS and NiS (melting at 1190 C and 992 C or 1994 and 1818 F).

Structure Studies

The structure of the welds has been studied in a light microscope and electron microscope. All the welds made in the Varestraint test have a heavily segregated structure containing a primarily solidified austenite with a secondary phase in the interdendritic areas—Fig. 3. With linear analysis the

Fig. 4—Sigma phase determined in the structure of the Varestraint test with filler metal 25/22/2.1/N/4.5Mn. ×21000 (reduced 46% on reproduction)

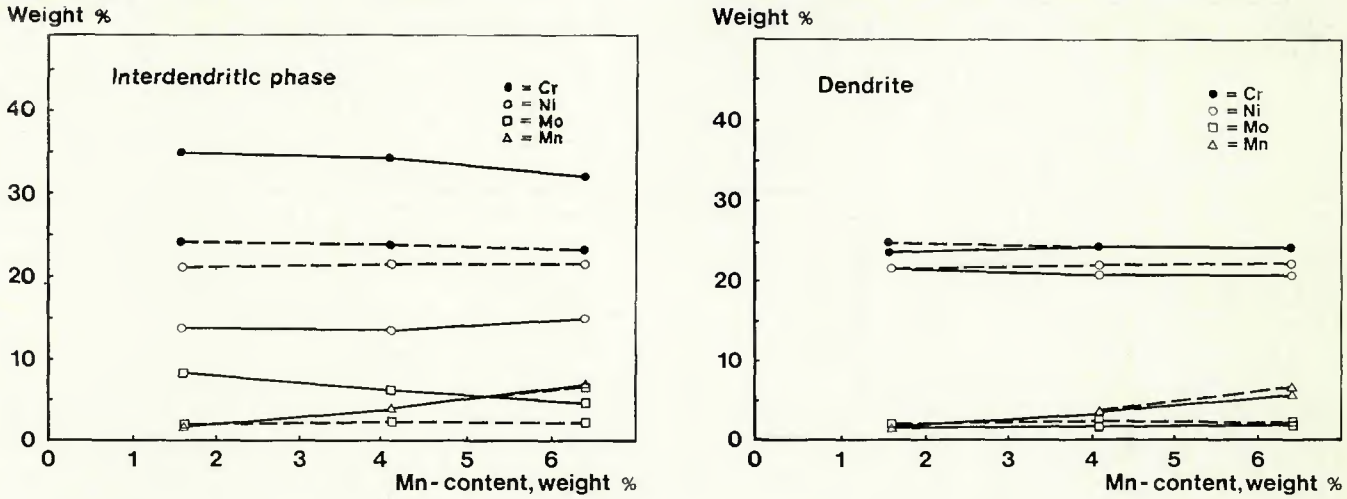

Fig. 5—Cr, Ni, Mn and Mo content as a function of the weld metal Mn-content determined in microprobe analysis. Samples from Varestraint tests. Continuous lines give results from microprobe analyses; broken lines give average values from wet chemical analyses

contents of this phase were determined to 0.4, 0.6, 0.5 and 0.2% respectively. The amount of magnetic phase, i.e. ferrite, was determined by a magnetic balance to 0.4, 0.4, 0.4 and 0.3%.

When comparing the values measured by linear analysis with those obtained with the magnetic balance it is obvious that the secondary phase mainly consists of ferrite. By electron microscope diffraction studies it was, however, determined that small amounts of σ-phase existed in all samples—Fig. 4. From the above it can be concluded that the amount of σ-phase is in the order of 0.1%.

The weld metal obtained in strip surfacing has a similar segregated structure but without secondary phases such as σ-phase or ferrite.

Microprobe Analysis

By microprobe analyses the composition in the middle of the dendrites and in the interdendritic phases was determined. The results are given in Table 4 and Fig. 5. As can be seen, Mn is the least segregated element of the four elements determined (Cr, Ni, Mo and Mn). With increased Mn content the segregation of Mo seems to decrease. As Mo is considered to increase the tendency to σ-phase formation more than Mn does (Refs. 9–11), one can expect that the tendency to σ-phase formation will decrease with an increase in Mn content.

The analysis variations in the dendritic and interdendritic areas were determined. The results in Table 5 show that the SAW welds in comparison with the GTAW samples have lower Cr, Mn, Mo contents and higher Ni-content, but the segregations seem to be of the same magnitude.

Fracture Studies

The cracks obtained in the Varestraint tests were studied in a scanning electron microscope. The cracks found in the remelted weld metal are of a so-called liquation or segregation type—(Fig. 6). The fracture surfaces and the surroundings of the cracks were investigated by microprobe analyses and Guinier determinations. Neither could increased contents of S and P be determined around the cracks and in the cracks, nor could manganese sulfides or iron sulfides be found. This does not necessarily mean that these phases are absent since they normally occur as very thin films and have to be traced with more advanced methods.

All investigated cracks that were created in the Varestraint test were found in the interdendritic areas—Fig. 7. In all cases the cracks were found in connection with the σ-phase and/or the ferrite phase.

In the reheated weld metal from the Varestraint test samples also cracks of the ductility-dip type were found. Those cracks follow the grain boundaries and are located to the interdendritic areas.

Solidification Behaviour

As the structure obtained in welding is determined among other things by the cooling rate, some studies were

Table 4—Microprobe Analysis of Varestraint Test Samples

Type		Composition, wt-% Cr	Mn	Ni	Mo
25/22/2.1/N/1.6Mn	Dendrite	23.3	1.4	21.3	1.4
	Phase	35.5	1.9	14.0	8.2
25/22/2.1/N/4.5Mn	Dendrite	24.0	3.1	20.4	1.5
	Phase	34.9	3.9	13.5	6.1
25/22/2.1/N/6.4Mn	Dendrite	23.7	5.0	20.5	1.5
	Phase	32.5	7.0	15.0	4.7

Table 5—Microprobe Analysis of Weld Metal

Method	Type of filler		Composition, wt-% Cr	Mn	Ni	Mo
GTAW[a]	25/22/2.1/N/4.5Mn	Dendrite	24.0	3.1	20.4	1.5
		Interdendrite	26.3	4.3	22.8	2.2
SAW[b]	25/22/2.1/N/4.5Mn	Dendrite	21.4	2.5	26.3	1.1
		Interdendrite	24.0	3.1	27.3	1.9

(a) Sample from Varestraint test.
(b) Sample from strip surfacing.

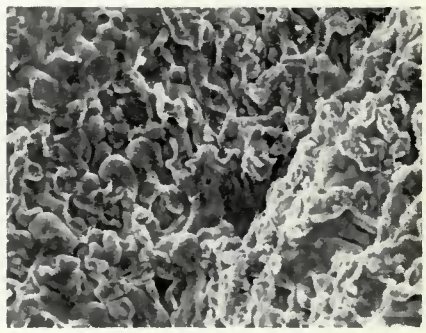

Fig. 6—Fracture surface obtained in the Varestraint test with filler metal type 25/22/2.1/N/4.5Mn. ×800 (reduced 46% on reproduction)

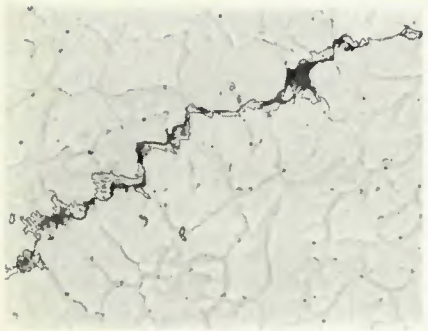

Fig. 7—Liquation cracks obtained in the Varestraint test with filler metal type 25/22/2.1/N/4.5Mn. ×800 (reduced 46% on reproduction)

made in order to determine the solidification behavior of the three investigated fillers. Samples of the three wires were quenched from a temperature approximately 5 C (9 F) below the liquidus temperature. By micro-studies it was found that all samples primarily solidified as austenite which was followed by a ferrite solidification in the interdendritic areas. A similar structure as the one shown in Fig. 3 was determined.

The ferrite content in the three samples was determined by a linear analysis. The results given in Table 6 show that Mn acts as a ferrite former at the temperatures investigated. The fact that Mn acts as ferrite former in chromium-nickel steels with high Mn or N contents has earlier been shown among others by F.C. Hull (Ref. 13).

Table 6—Ferrite Content in Quenched Samples With Varying Mn-Content

Type	Mn, %	Quench temperature, C	Ferrite, %
25/22/2.1/N/1.6Mn	1.6	1405	2
25/22/2.1/N/4.5Mn	4.5	1386	3.2
25/22/2.1/N/6.4Mn	6.4	1379	3.5

Summary of the Metallographic Investigation

The metallographic investigations revealed that the structure obtained with filler metal of type 25/22/2.1/N/Mn is austenitic with nil or a very small amount of ferrite. The quenching tests indicated that an increased Mn-content may increase the tendency to ferrite formation. In order to avoid such a tendency in this type of weld metal, the Mn-content should consequently be as low as possible.

The absence of ferrite in the SAW samples may be explained by the somewhat more stable austenitic composition. The difference in cooling rate between SAW and GTAW samples may also have contributed to decreased ferrite content. This will be further investigated. The weakest part of the structure has been determined to be the segregated interdendritic areas.

Corrosion Resistance and Mechanical Properties

Sample Preparation

For tensile tests as well as for corrosion tests of welded joints 4 mm (0.157 in.) thick strips in 25Cr/22Ni/2.1Mo/N material were prepared with a 60 deg V-groove and butt-welded in two layers. The welding data are given in Table 3. For the corrosion tests of all-weld metal, 4 mm (0.157 in.) thick test pieces were cut out in the upper part

Table 7—Chemical Composition of Material for Corrosion and Tensile Tests

Type	Form	C	Si	Mn	P	S	Cr	Ni	Mo	N
25/22/2.1/N/1.6Mn[a]	Wire	.012	.14	1.61	.013	.019	25 2	22.2	2.10	.11
25/22/2.1/N/4.5Mn[a]	Wire	.014	.10	4.50	.010	.010	24.8	22.8	2.16	.11
25/22/2.1/N/5Mn[a]	Wire	.016	.14	5.00	.018	.007	24.7	22.4	2.10	.12
25/22/2.1/N/6.3Mn[a]	Wire	.018	.06	6.32	.010	.007	24.1	21.7	2.10	.11
25/22/2.1/N/4.5Mn[b]	Electrode	.040	.33	3.42	.018	.005	24.9	21.0	2.28	.12
25/22/2.1/N/4.5Mn[b]	Strip	.020	1.09	2.58	.010	.009	23.3	22.1	2.16	.16
20/16/2.8/N/8.3Mn[b]	Strip	.022	1.35	6.1	.010	.008	19.3	16.1	2.80	.13

(a) Filler metal.
(b) Weld metal.

Table 8—Corrosion Test Results (Corrosion Rate in mm/year)

Material tested	Huey test[a]		40% H_2SO_4 25 C (1+3+3)×24h	60% H_3PO_4 boiling (1+3+3)×24h	99% HNO_3 60 C (1+3+3)×24h
	Not heat treated	Heat treated at 580 C/4h+650 C/10h			
Base metal 25/22/2.1/N	0.10[b]	–	0.65	0.05	0.48
GTAW weld metal 25/22/2.1/N/4.5Mn	0.07[b]	–	–	–	–
GTAW welded joint 25/22/2.1/N/4.5Mn	0.10[b]	–	0.70 (0)[d]	0.06 (0)[d]	0.39 (50)[d]
SMA weld metal 25/22/2.1/N/4.5Mn	0.09[b]	–	–	–	–
SMA welded joint	0.08[b]	–	0.73 (0)[d]	0.13 (8)[d]	0.30 (20)[d]
SAW weld metal, strip 25/22/2.1/N/4.5Mn	0.16[b]	0.26[b]	–	–	–
SAW weld metal, strip 20/16/2.8/N/8.3Mn	0.54[b]	1.87[c]	–	–	–

(a) ASTM A262 Practice C 5×48h, average value given.
(b) Decreasing corrosion rate.
(c) Increasing corrosion rate.
(d) Values in brackets indicate selective attack in μm.

Table 9—Mechanical Properties

Type of filler	Weld method	Tested part	σ_B, N/mm²	Reduction of area, %	Elongation,[a] %	Location of fracture
25/22/2.1/N/1.6Mn	GTAW	Welded joint	685	54		Base metal
	GTAW	Weld metal	685		65	
25/22/2.1/N/4.5Mn	GTAW	Welded joint	650	56		Base metal
	GTAW	Weld metal	760		73	
25/22/2.1/N/5Mn	GTAW	Welded joint	683	37		Weld metal
	GTAW	Weld metal	765		69	
25/22/2.1/N/6.3Mn	GTAW	Welded joint	701	21		Weld metal
	GTAW	Weld metal	713		69	
25/22/2.1/N/1.5Mn	SMA	Welded joint	626	46		Fusion line
	SMA	Weld metal	687		66	
25/22/2.1/N/4.5Mn	SMA	Welded joint	618	49		Fusion line
	SMA	Weld metal	669		50	
25/22/2.1/N/6Mn	SMA	Welded joint	599	38		Fusion line
	SMA	Weld metal	704		39	

(a) Elongation of hole 3.5 mm (0.138 in.) diameter.

of 15 mm (0.6 in.) thick weld pads. For corrosion tests of SAW weld metal from surfacing, 4 mm (0.157 in.) thick specimens were also used. According to the specification they were cut out so that one of the specimen surfaces was the untreated weld metal surface.

Tensile testing was performed on 20 mm (0.78 in.) wide specimens cut across the weld. For testing the weld metal two 3.5 mm (0.137 in.) diameter holes were drilled in the weld in order to predetermine the location of the failure.

Corrosion Test Results

The welded specimens have been corrosion tested in 40% H_2SO_4 at 25 C (77F), 60% boiling H_3PO_4, 99% HNO_3 at 60 C (140 F) and in Huey-test. The weld metal compositions are given in Table 7 and the results obtained in Table 8.

Weld metals from GTAW and SMA show corrosion rates almost of the same magnitude as those obtained for the base metal. The corrosion rate data are relatively low compared with what is obtained with ordinary stainless steels. The corrosion rates for the SAW weld metals are somewhat higher than for the base metals but are still very low.

The difference is explained by the difference in chemistry. The difference in corrosion rate between the 25/22/2.1/N/4.5Mn and type 20/16/2.8/N/8.3Mn should be noted. When corrosion properties of weld metal from the different filler metals with varying Mn content were determined, no influence whatsoever of the Mn content could be found.

Mechanical Testing

Tensile Testing

The results from the tensile tests are given in Table 9. As can be seen the tensile strength is at a fairly high level, about 700 N/mm². It can also be noted that the best ductility (reduction of area and elongation values) is shown by a filler metal of 25/22/2.1/N/4.5Mn type.

Bend Tests

Bend tests were performed on 20 mm (0.78 in.) wide GTAW specimens with the weld placed across the width of the specimens and over a mandrel with a radius of 2.5 times the 10 mm (0.39 in.) thickness. For each filler three face-bend and three root-bend tests were carried out. No cracks were detected.

Conclusion

On the basis of the test results reported here and information in the literature, it was possible to design an optimal filler metal composition with regard to corrosion and crack resistance, mechanical properties and structure stability, namely: C max 0.020%, Cr 25%, Ni 22%, Mo 2.1%, N 0.12%, Mn 4.5% and P and S max 0.015% each.

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