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Manganese and Nitrogen in Stainless Steel SMA Welds for Cryogenic Service

The roles of Mn and N in filler metals for cryogenic service are clarified, and a formula for more accurate FN calculation is proposed

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ABSTRACT. Evaluation of a shielded metal arc (SMA) weld test matrix in which manganese (1.5 to 10 wt-%) and nitrogen (0.04 to 0.26 wt-%) were varied independently has clarified the effect of these elements on cryogenic mechanical properties and predicted ferrite number (FN). Several molybdenum and boron additions were also made, but they had no observable effect on strength or Charpy V-notch (CVN) absorbed energy. The matrix was based on a type 308L stainless steel weld metal composition. Desired compositions and constant FN were attained through alloy additions to the electrode coating. For each weld, one all-weld metal 4-K tensile specimen and five 76-K CVN impact specimens were tested.

Increasing the nitrogen content from 0.05 to 0.25 wt-% linearly increased the 4-K yield strength from 600 to 1300 MPa (87 to 188.5 ksi) and decreased the 76-K lateral expansion from 0.6 to 0.1 mm (0.24 to 0.04 in.). Nitrogen reduced the 76-K CVN absorbed energy but not linearly. The addition of manganese slightly increased the yield strength and slightly decreased the lateral expansion. The 4-K tensile strength was relatively unaffected by alloy additions; values varied between 1300 and 1500 MPa (188.5 and 217.5 ksi).

The DeLong FN predictive equation was improved by substituting the Szumachowski-Kotecki constant manganese term of 0.35 into the DeLong nickel equivalent. Analysis of the remaining FN deviation revealed an interaction between nitrogen and manganese. Addition of manganese-nitrogen interactive terms to the nickel equivalent increased the accuracy of the FN prediction.

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Introduction

Toughness values for 300 series stainless steel welds at cryogenic temperatures have consistently been lower than those for base materials of equal strength (Refs. 1, 2). Several studies have attempted to understand this phenomenon by statistically determining predictive equations for Charpy V-notch (CVN) toughness on the basis of the weld composition (Refs. 3-5). Although these studies have resulted in tougher welds through optimized electrode compositions, the welds still do not match the toughness of the base material. Recently, controlled additions of nitrogen (along with additions of manganese to reduce the tendency to form porosity) have increased the plate strength at cryogenic temperatures with little loss in toughness (Ref. 6). However, this increased base material strength cannot be totally utilized until welds of comparable toughness at these elevated strengths are developed.

KEY WORDS

Cryogenic SMA Welds
Stainless SMA Welds
Manganese + Nitrogen
Mn+N in 308L Welds
SMAW Test Matrix
Cryogenic Toughness
Predictive Equations
308L+316L Cryogenics
Cryogenic CVN Energy
Cryogenic FN Effects

This study was intended to contribute to the development of welds with properties comparable to those of the nitrogen-strengthened base materials. We investigated the strength-toughness relationship in a series of SMA welds. The nitrogen and manganese contents were varied to evaluate their effect on the weld properties. Several welds with varying boron and molybdenum contents were also included.

Factors Influencing Strength, Toughness and Ferrite Number

Strength

The strengthening potential of nitrogen in stainless steel increases with decreasing temperature (Refs. 5, 7-11). Nitrogen occupies interstitial sites and expands the lattice in a manner similar to carbon (Ref. 12). Unlike high carbon contents, high nitrogen contents do not result in sensitization problems. The nitrogen content can be increased until porosity occurs at the solubility limit (Ref. 9). It can be introduced to the deposit through shielding gas mixtures with the GMA or GTA processes or through nitrogen-containing alloy additions to the coating with the SMA process. With 0.05 wt-% nitrogen additions in type 308 stainless steel welds, increases in yield strengths of approximately 120, 150 and 175 MPa (17.4, 21.8 and 25.4 ksi) were reported by Mukai, *et al.* (111 K), Enjo, *et al.* (76 K), and Onishi, *et al.* (76 K), respectively (Refs. 10, 11, 13). Onishi reports a similar increase in yield strength at 4 K. In comparison, only slight increases in weld yield strength (< 50 MPa/7.3 ksi) have been found at room temperature (Refs. 10, 11, 13, 14).

The influence of nitrogen on the tensile strength is disputed. In 304 and 316 austenitic base material (Ref. 11), and in both fully austenitic and ferrite-containing stainless steel welds (Ref. 15), increases in 76-K tensile strengths of 100 and 300 MPa (14.5 and 43.5 ksi) were found when nitrogen content was increased from 0.05 to 0.15, and 0.20 to 0.40, wt-%, respectively. Enjo, *et al.,* reported a 76-K tensile strength increase of only 20 MPa (2.9 ksi) when the nitrogen content was raised from 0.05 to 0.15 wt-% (Ref. 10) in type 308 stainless steel welds. In all cases, the magnitudes of tensile strength increases reported were less than those observed for the yield strength. The influences of other elements (such as manganese, molybdenum and boron) on cryogenic weld strength have not been published, but Sakamoto, *et al.,* reported that manganese increased yield strength in stainless steel base material at 76 K (Ref. 16).

Toughness

The cryogenic toughness of type 308L and 316L stainless steel welds is determined by the interrelated and sometimes opposing effects of the individual alloying elements and the ferrite number (FN). The FN has been found to be the dominant factor in determining CVN toughness in these materials (Refs. 4, 17-20). Lower FN tends to raise the toughness. On the other hand, increased nitrogen contents, which lower the FN, have been reported to lower the CVN absorbed energy and lateral expansion (LE) values in SMA welds (Ref. 4). These differences and the variations in toughness values near 0 FN indicate that the role of nitrogen (and other alloying elements) with respect to toughness requires further study. Several researchers (Refs. 4, 20) have studied the effect of alloying elements that influence the ferrite content on the absorbed energy at 76 K. Nickel reportedly increased toughness, whereas carbon and chromium reduced toughness. Nitrogen is generally believed to reduce toughness, but it has been suggested that the effect of nitrogen on CVN toughness may be dependent on the specific alloy composition (Ref. 19). Manganese has been reported to decrease 76-K CVN energy in stainless steel base material (Ref. 16). The effects of molybdenum are not clear.

Ferrite Number

The strong influence of FN on cryogenic toughness dictates the use of an accurate method for predicting FN in the new high-nitrogen and -manganese stainless steel electrodes. The diagrams developed by Schaeffler (Ref. 21) and DeLong (Ref. 22) are currently the best methods available for the prediction of FN. These diagrams were not designed for use with high-manganese alloys; they tend to underestimate FN for higher alloy contents because the austenitizing power of manganese decreases at high manganese concentrations (Refs. 23, 24).

Whether the various FN diagrams or the corresponding mathematical expressions for these diagrams are used, nickel and chromium equivalents represent the relative austenitizing and ferritizing tendency for a given alloy composition. The DeLong nickel and chromium equivalents are:

$$Ni_{eq} = Ni + 30\,(C + N) + 0.5\,Mn$$
$$Cr_{eq} = Cr + Mo + 1.5\,Si + 0.5\,Nb$$

where the elements are in wt-%.

Numerous studies have determined the dependence of FN on alloying elements. The coefficients and constants that have been proposed to model the effects of nitrogen and manganese are given in Table 1. At high nitrogen contents, Espy, in particular, found that the nitrogen coefficient decreases (Ref. 24). Most studies involving high manganese contents have proposed constants to represent the effect of manganese and replace DeLong's 0.5 Mn term (Refs. 23, 25). The Hull study (Ref. 26) was the only high manganese matrix to yield a manganese coefficient. However, its second-order term does reduce the influence of manganese on the nickel equivalent at high concentrations. A review of the alloy ranges used in the various studies did not disclose the reason different terms (either constants or coefficients) were proposed to model the influence of the manganese and nitrogen in the nickel equivalent expression.

Materials and Procedure

To clarify the role of manganese and nitrogen on the cryogenic strength, toughness and FN, and to understand the reason for the varying and sometimes conflicting effects reported in the litera-

Table 1—Various Manganese and Nitrogen Coefficients Determined in Previous Studies

Researcher	Coefficient or Constant: N	Coefficient or Constant: Mn	Principle Matrix Variations (wt-%)	Comments
Schaeffler (Ref. 21)	–	0.5 Mn	Ni (0 to 30)	308, 309, 310, 316, 410 and 502
DeLong (Ref. 22)	30 N	–	N (0.03 to 0.22)	309, 308L, 316, 316L, 347 (low Mn)
Hull (Ref. 26)	18.4 N	$0.11\,Mn - 0.0086\,Mn^2$	Ni (0 to 22) Mn (0 to 20) N (0 to 0.15)	70 chill – cast stainless steel alloys. Mo, Si, V, W, Ti, Cb, Ta, Aℓ Co, Cu, C also varied. Cr = 14 to 20 wt-%
Espy (Ref. 24)	30 (N-0.045) 22 (N-0.045) 20 (N-0.45)	0.87	Mn (5 to 12.5) N (0.13 to 0.33)	4 nitronic series alloys N and Mn not varied systematically. The 3 N coeff. are for < 0.20, < 0.25 and < 0.35 wt-% N, respectively.
Hammar and Svenson (Ref. 25)	14.2 N	0.31	Ni (9.0 to 14) N (0.01 to 0.20) C (0.04 to 0.10)	130 austenitic alloys (Ingots) Mn content = 1 to 2 wt-% Cr = 17 to 25 wt-%
Mel'Kumor and Topilin (Ref. 27)	20 N	–	Ni (10 to 16) N (0.05 to 0.46)	Austenitic stainless steel 0.5 Mn, 25 Cr, 0.09 C
Szumachowski and Kotecki (Ref. 23)	–	0.35	Mn (1 to 12)	308, 309L, 316L, 307 Low nitrogen (0.05 wt-%)
Okagawa, *et al.* (Ref. 28)	13.4 N	–	N (0.04 to 0.29)	GTA weld (no filler metal) on 304L base metal. N added through shielding gas.

Table 2—Chemical Composition(a) and Ferrite Numbers of the Welds

Alloy No.	C	Mn	Si	P	S	Cr	Ni	Mo	N	B	FN Pad	FN Plate(c)	FN Calculated DeLong
1	0.033	1.57	0.29	0.013	0.006	17.58	9.19	0.02	0.047	(d)	2.8	4.9	1.35
2	0.034	1.49	0.34	0.020	0.006	15.37	9.06	2.03	0.034	(d)	3.4	4.4	2.2
3	0.034	3.23	0.39	0.014	0.006	17.87	9.02	0.02	0.035	(d)	4.0	4.7	2.07
4	0.036	6.54	0.37	0.015	0.007	17.61	9.13	0.02	0.046	(d)	2.8	4.2	−4.3
5R(b)	0.039	6.31	0.34	0.021	0.007	15.39	9.14	1.99	0.047	(d)	2.8	3.6	−5.4
5	0.039	6.31	0.34	0.021	0.007	15.39	9.14	1.99	0.047	(d)	2.8	3.6	−5.4
6A	0.036	6.27	0.34	0.027	0.007	15.17	9.14	3.84	0.162	(d)	2.6	2.9	−8.06
7	0.032	1.66	0.32	0.014	0.006	18.36	8.94	0.02	0.103	(d)	1.8	3.1	0.6
8	0.033	2.96	0.36	0.013	0.006	18.13	9.12	0.02	0.037	(d)	3.6	5.1	0.02
9	0.038	6.46	0.35	0.015	0.007	18.51	9.17	0.02	0.098	(d)	2.6	3.6	−5.35
10	0.037	9.52	0.38	0.017	0.009	17.71	9.10	0.02	0.106	(d)	1.5	2.7	−12.16
11	0.031	3.18	0.34	0.015	0.006	18.99	9.05	0.02	0.153	(d)	1.4	1.9	−2.93
12	0.037	6.62	0.38	0.016	0.008	19.51	9.06	0.02	0.151	(d)	2.2	3.6	−5.53
13	0.035	6.61	0.32	0.021	0.007	17.77	9.10	1.66	0.166	(d)	2.5	3.5	−7.25
14	0.038	9.38	0.35	0.017	0.009	18.98	9.14	0.02	0.163	(d)	1.7	2.8	−12.16
15	0.032	6.11	0.36	0.016	0.007	20.90	9.29	0.02	0.252	(d)	1.6	2.0	−7.92
16	0.038	9.56	0.37	0.019	0.009	20.22	9.07	0.02	0.265	(d)	1.2	1.8	−14.75
17	0.031	2.90	0.30	0.013	0.006	18.79	9.12	0.02	0.104	(d)	2.0	3.8	2.83
18	0.033	3.25	0.39	0.014	0.006	17.58	9.00	0.02	0.032	0.015	3.2	3.7	1.38
18R(b)	0.032	3.16	0.42	0.013	0.006	17.90	9.05	0.02	0.041	0.006	3.0	4.6	2.04
19	0.039	9.55	0.34	0.017	0.009	17.70	9.26	0.02	0.037	(d)	3.6	4.8	−7.81
20	0.033	3.10	0.36	0.015	0.006	17.75	9.07	0.02	0.152	(d)	0.8	1.0	−7.17
21	0.033	3.46	0.37	0.014	0.006	17.82	9.10	0.02	0.150	0.008	0.6	0.5	−7.25
22	0.032	9.72	0.34	0.018	0.009	17.60	9.06	0.02	0.259	(d)	0.2	0.7	−24.00

(a)Weight percent.
(b)Repeated welds.
(c)FN plate is the average of FN bead surface and FN impact specimen surface.
(d)Not determined.

Table 3—Mechanical Properties of the Welds

	4-K Tensile Properties				76-K CVN Properties	
Alloy	σ_y (MPa)	σ_T (MPa)	Elongation (%)	Reduction (%)	LE(a) (mm)	AE(a) (J)
1	469	1586	26(b)	16.6	0.686	46
2	527	1570	20	13.5	0.711	39
3	504	1432	25(b)	23.8	0.584	41
4	455	1341	26	22.7	0.584	42
5R	619	1346	27(b)	18.0	—	—
5	665	1489	37	29.1	0.533	37
6	1169	1447	12	14.1	0.127	16
7	787	1412	21(b)	14.3	0.483	39
8	502	1387	24(b)	14.9	0.686	43
9	864	1410	24(b)	22.4	0.432	42
10	871	1395	32	23.8	0.406	37
11	932	1376	20	16.8	0.406	40
12	1020	1376	18.8	15.3	0.305	37
13	1129	1410	12.0	13.5	0.229	33
14	1075	1527	28.5	26.6	0.305	34
15	1344	1627	16.5	18.9	0.127	20
16	1306	1622	20.0	13.3	0.127	24
17	748	1438	25(b)	10.2	0.508	42
18	502	856	6.5	10.8	0.610	43
18R	491	1267	19(b)	14.5	0.610	38
19	635	1299	27	23.1	0.483	37
20	888	1261	16(b)	15.1	0.457	42
21	874	1125	11.3	9.6	0.432	41
22	1250	1498	15.5	15.4	0.152	21

(a)LE = lateral expansion; AE = absorbed energy.
(b)Fractured outside the gauge marks.

ture, a test matrix based on a type 308 stainless steel weld composition was evaluated. Alloy additions were made to the SMA electrode coating. Manganese (1.5 to 10 wt-%) and nitrogen (0.04 to 0.26 wt-%) were varied independently within the matrix. Several molybdenum (2 and 4 wt-%) and boron (0.006 and 0.015 wt-%) additions were also made to the matrix.

The weld matrix was designed with a variable chromium content. The chromium content was adjusted to compensate for the manganese, molybdenum, boron or nitrogen additions so that welds with a nearly constant FN value were produced. The FN of weld pads and the welds were measured magnetically. The measurement device was calibrated with ANSI/AWS Standard A4.2-74.

The weld metal carbon and nitrogen were determined with individual element analyzers; the phosphorus and sulfur, by an optical emission spectrophotometer; and the remaining elements, by conventional analytical techniques. The chemical composition and measured FN for the 24 welds included in this study are listed in Table 2. Molybdenum interference in the optical emission spectrograph probably caused the variations in measured phosphorus contents.

Test welds were produced using a series of 3.2-mm (1/8-in.) diameter electrodes that had core wires from a single heat of type 308 stainless steel. The base material was 13-mm-thick by 305-mm-long (0.5-in.-thick by 12-in.-long) mild steel plate. To overcome the effect of dilution by the base material, the exposed faces and backing strip were buttered with two layers of weld metal prior to beginning the test weld, as specified in AWS A5.4-78. The same welding machine, power supply, and welding variables (110 A, 22 V, an identical bead sequence, and a heat input of approximately 0.6 kJ/mm, or 15 kJ/in.) were used to minimize weld variations. The interpass temperature was maintained at

93°C (199°F).

Two all-weld metal, 6-mm (0.23-in.)-diameter tensile specimens, oriented along the axis of the weld, were machined from each weld. The second specimen, reserved as a spare, was tested in a number of cases to check the repeatability of the results; in these cases, the average value is reported. Tensile specimens were tested at 4 K (liquid helium) with a strain rate of $9 \times 10^{-5}\ s^{-1}$. A 25-mm (1-in.) gauge length was used. Specific details on the 4-K tensile testing equipment and procedures have been reported previously (Ref. 29). Five A-type ASTM CVN specimens, with their notches oriented perpendicular to the plate surface and located along the weld centerline, were removed from each weld and tested at 76 K.

Results and Discussion

Strength

The yield and tensile strengths determined for the various welds at 4 K are given in Table 3 and plotted for the various nitrogen contents of the welds in Fig. 1. The yield strength increased linearly with the nitrogen content. The equation relating the yield strength to the nitrogen content was:

Weld Yield Strength (MPa at 4 K) = 400 + 3700 (wt-% N) (1)

The F value (a test of the significance of the model) was 256 and the coefficient of determination R^2 (a measure of the quality of the regression) was 0.92. This equation corresponds closely with a previously determined equation relating the yield strength to nitrogen content for stainless steel plate (Ref. 6):

Plate Yield Strength (MPa at 4 K) = 350 + 3400 (wt-%) (2)

The tensile strength remained near the average of 1400 MPa (203 ksi) for nitrogen contents up to 0.16 wt-% and averaged 1500 MPa (217.5 ksi) for the three alloys that had about 0.26 wt-% nitrogen. This slight increase in the tensile strength was not statistically related to the nitrogen contents.

Yield strength as a function of the weld manganese content is shown in Fig. 2. The nitrogen contents were coded, since they are the dominant strengthener. At the 0.05, 0.10 and the 0.15 wt-% nitrogen concentrations the yield strength was found to increase as the manganese content of the welds increased. The equation including both the nitrogen and manganese effects on yield strength is:

Weld Yield Strength (MPa at 4 K) = 360 + 3400 (wt-% N) + 14 (wt-% Mn) (3)

The F value was 154 and the R^2 value was 0.94. There was some evidence that the strengthening tendency of manganese changes as a function of nitrogen content (Fig. 2), but linear terms express the relative effects of manganese and nitrogen contents quite well for the scope of this study.

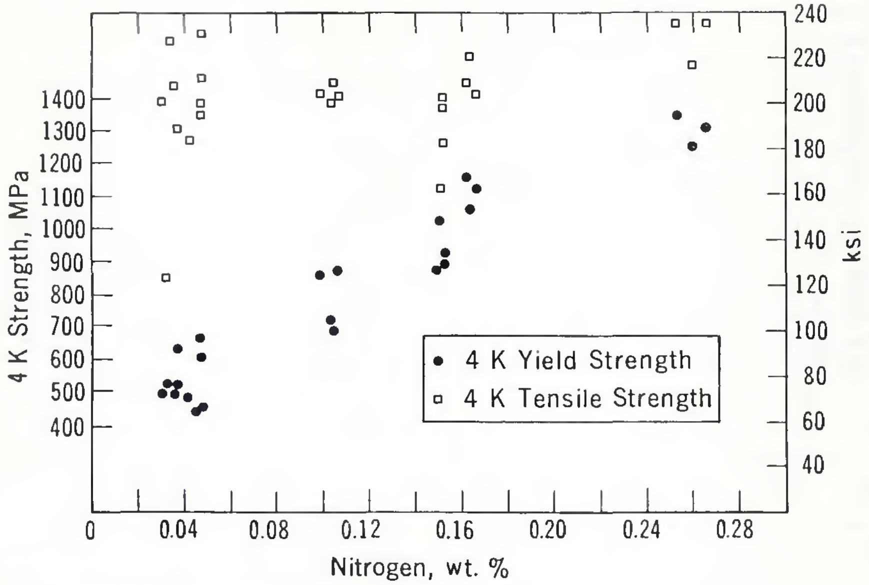

Fig. 1—Strength versus weld nitrogen content at 4 K

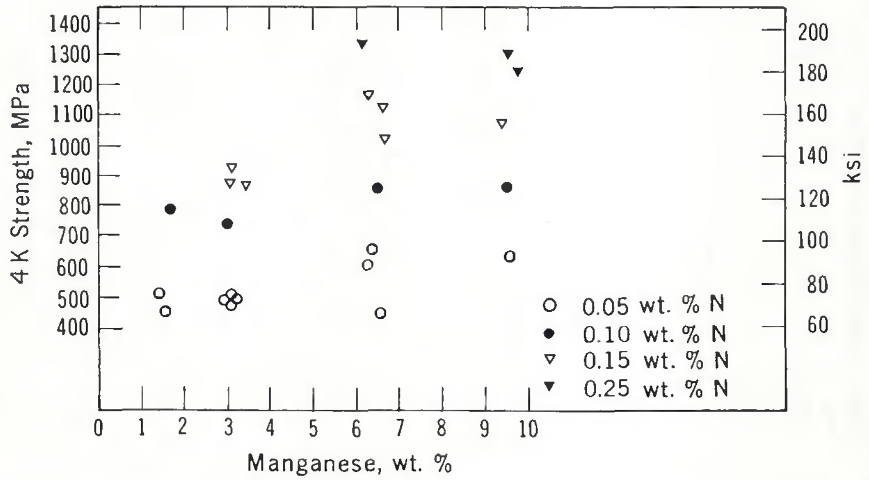

Fig. 2—Yield strength versus weld manganese content at 4 K

Toughness

Figure 3 shows that the CVN absorbed energy at 76 K decreases only slightly as nitrogen content is increased up to 0.16 wt-%. The average absorbed energy value in this region was approximately 40 J (29 ft-lb). Nitrogen contents above 0.16 wt-%, however, caused a substantial decrease in absorbed energy. At 0.25 wt-% nitrogen, the absorbed energy is reduced approximately 50%. All compositions followed this trend closely, with the exception of the 3.84 wt-% molybdenum alloy, which fell far below the trend. No effect of manganese on the CVN energy was determined.

Unlike the CVN absorbed energy, lateral expansion values decreased linearly as a function of nitrogen content—Fig. 4. A decrease in lateral expansion of approximately 86% occurred when the nitrogen content was raised from 0.03 to 0.26 wt-%. The manganese content also affected lateral expansion. The lateral expansion of Alloy 12 is 0.1 mm (0.004 in.) less than that of Alloy 11 in Table 3 (both ≈ 19 wt-% Cr, 0.15 wt-% N, 1.5 FN); we attribute this to its significantly greater manganese content. The alloys with molybdenum additions generally fit the observed trends; however, the lateral expansion values of alloys with combined high nitrogen, manganese and molybdenum contents (particularly Alloys 13 and 6) were low.

The CVN absorbed energy and lateral expansion have been reported to be

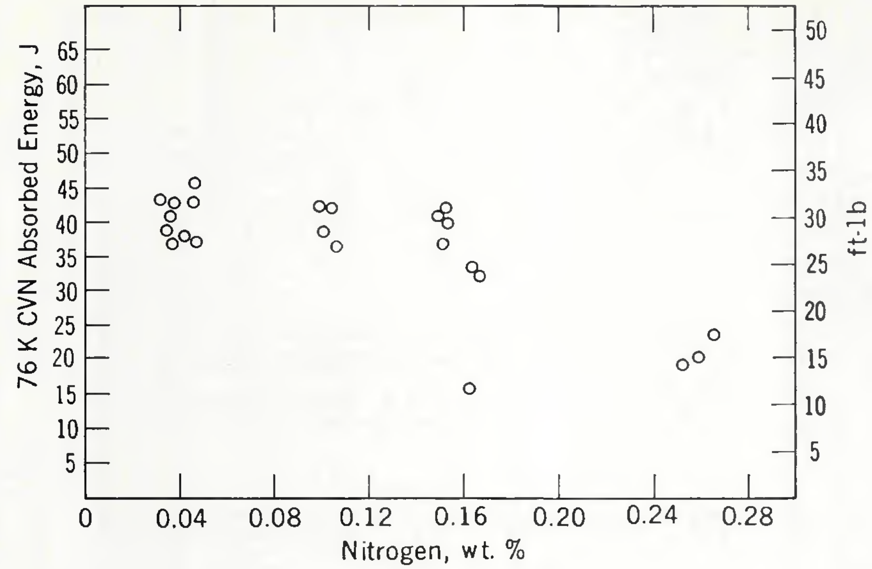

Fig. 3 — CVN absorbed energy versus weld nitrogen content at 76 K

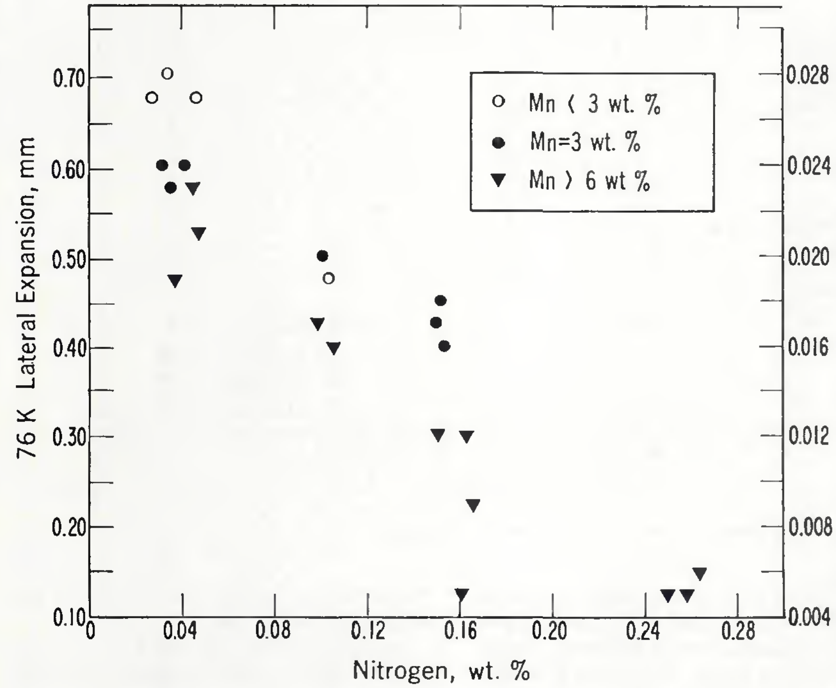

Fig. 4 — Lateral expansion versus weld nitrogen content at 76 K

linearly related for the common type 308L and 316L stainless steel compositions (Refs. 3, 4). The nonlinear relationship observed in this study between CVN absorbed energy and lateral expansion when the nitrogen content was below 0.16 wt-% was therefore unexpected, and its cause was not determined. We suspect that oxygen content, inclusion density, ferrite content, or other factors characteristic of these compositions are responsible for limiting the impact energy to 40 J (30 ft-lb). If this is indeed the case, the effect of nitrogen would become apparent only at nitrogen contents high enough to lower the CVN absorbed energy below the 40-J shelf. The nonlinear relationship found in this study indicates a need to re-evaluate the use of the 76-K CVN test to screen material for 4-K toughness testing.

The yield strength-lateral expansion relationship for these alloys is illustrated in Fig. 5. This relationship is better than that for alloy content-lateral expansion and indicates that the strengthening mechanisms (interstitial for the nitrogen and substitutional for the manganese) are controlling the lateral expansion. Relating the lateral expansion to the yield strength by linear regression techniques produced the equation:

Table 4—Deviation Between the Measured FN and the FN Calculated Using DeLong's Equation

Alloy	N (wt-%)	Mn (wt-%)	ΔFN[a]
1	0.047	1.57	1.45
2	0.034	1.47	1.20
3	0.035	2.23	1.93
4	0.046	6.54	7.10
5R	0.047	6.31	8.20
5	0.047	6.31	8.20
6	0.162	6.27	10.66
7	0.103	1.66	1.20
8	0.037	2.96	3.58
9	0.098	6.46	7.95
10	0.106	9.52	13.66
11	0.153	3.18	4.33
12	0.151	6.62	7.73
13	0.166	6.61	9.75
14	0.163	9.38	13.86
15	0.252	6.11	9.52
16	0.265	9.56	15.95
17	0.104	2.90	−0.83
18	0.032	3.25	1.82
18R	0.041	3.16	0.96
19	0.037	9.55	11.45
20	0.152	3.10	7.97
21	0.150	3.46	7.85
22	0.259	9.72	24.20

(a) ΔFN is defined as the difference between the measured FN (FNP) and the FN calculated with the DeLong predictive equation.

$$\text{LE (mm at 76 K)} = 0.95 - 6 \times 10^{-4} \text{ [Weld Yield Strength (MPa at 4 K)]} \quad (4)$$

This equation had an F value of 344 and an R^2 value of 0.94.

To put the mechanical property data into perspective, the data determined for these weld metal alloys need to be compared to type 316LN base metal. In general, type 316LN base metal has a yield strength greater than 1000 MPa (145 ksi) and fracture toughness (K_{Ic}) above 200 MPa · $m^{1/2}$ at 4 K (Ref. 1). Correspondingly, 76-K CVN absorbed energy and lateral expansion values are typically near 90 J (66 ft-lb) and 1 mm (0.04 in.), respectively, for this material.

The weld compositions evaluated in this study had CVN absorbed energy values (30 to 40 J/22 to 30 ft-lb) similar to previous weld studies at these strength levels, but far below the base metal value (90 J). Therefore, we find a continuing need for a better understanding of the factors that determine toughness in the weld metals. Studies to evaluate the effect of inclusions on toughness are suggested.

Ferrite Number

Table 4 gives the difference between the value of FN measured magnetically on the weld pads (FNP) and that calculated using the DeLong predictive equation for the various welds. The ΔFN, or deviation between the measured and predicted FN, increases as nitrogen and manganese concentrations increase. Three approaches were used to examine and minimize these deviations.

A graphical method was used to express the influence of manganese and nitrogen on the nickel equivalent. In Fig. 6, the difference in nickel equivalents (ΔNi_{eq}) is plotted versus the manganese and nitrogen contents (Ref. 23). The ΔNi_{eq} is a measure of the difference between the DeLong diagram nickel equivalent, found using the measured FN and calculated chromium equivalent, and a calculated partial nickel equivalent in which either the manganese or nitrogen term is deleted. The difference between the two equivalents measures the effect of the manganese or nitrogen. The slopes of the best fit lines through the manganese-ΔNi_{eq} or nitrogen-ΔNi_{eq} graphs define the respective manganese and nitrogen coefficients. A nitrogen coefficient ($R^2 = 0.91$) of 21 is obtained when Alloy 22 is excluded from data. Alloy 22 is excluded due to its deviation from the trend established by nearly identical compositions. Also, by replotting all the data as the DeLong diagram nickel equivalent versus nitrogen, a nitrogen coefficient of 21 is obtained ($R^2 = 0.93$). A nitrogen coefficient of 21 agrees well with those reported by Hull, Espy and Mel'Kumor—Table 1.

The data (in Fig. 6B) indicate a slightly negative manganese coefficient. A negative slope has not previously been proposed; but this concept is also supported by the Szumachowski-Kotecki type 309 Ni_{eq} data (Ref. 23). It is clear that the Espy, Szumachowski-Kotecki and Hull terms and the line representing this study all predict manganese effects better than the 0.5 DeLong manganese coefficient. If a constant manganese term is fitted, the manganese constant (−0.25) is less than that proposed by either Espy (0.87) or Szumachowski and Kotecki (0.35) (Refs. 24, 25).

Stepwise linear regression, the second method of analysis, was used to determine the accuracy of existing predictive FN equations and to examine possible improvements to these equations by changing the coefficients and adding new variables. In this approach, 20 variations of the DeLong (Refs. 22, 30), Schaeffler (Refs. 21, 30) and Seferian (Ref. 31) equations were evaluated and ranked in order of their significance by the stepwise regression program. Within each equation type, different combinations of nitrogen and manganese terms were used. For nitrogen, coefficients of 30, 24, 18, 13 and 0 were included. For manganese, DeLong's 0.5 manganese coefficient and constant manganese terms of 0.35 and 0.74 were included. One equation that contained Hull's manganese terms was included. From this wide variety of predictive equations and modifications, the best equation was selected for the manganese and nitrogen ranges in this study.

In addition to these FN predictive equations, compositional terms such as Mn, N, Si, Mn^2, MnN and CN were also available for selection by the regression program. Selection of one of these terms following the selection of a predictive equation indicated that its influence was not properly modeled in the predictive equation. As an example of the notation for the predictive equations, FNCSK indicates the ferrite number calculated using a Schaeffler diagram equation modified to include nitrogen and using the Szumachowski-Kotecki manganese constant (0.35). The D in FNCD represents the DeLong diagram FN equation.

Figure 7 shows the predicted values for three of these equations (FNCD, FNCDK, FNCSK) plotted against the FN measured on the weld pad (FNP) and illustrates the substantial differences between the predicted and measured FN values. These equations are defined by:

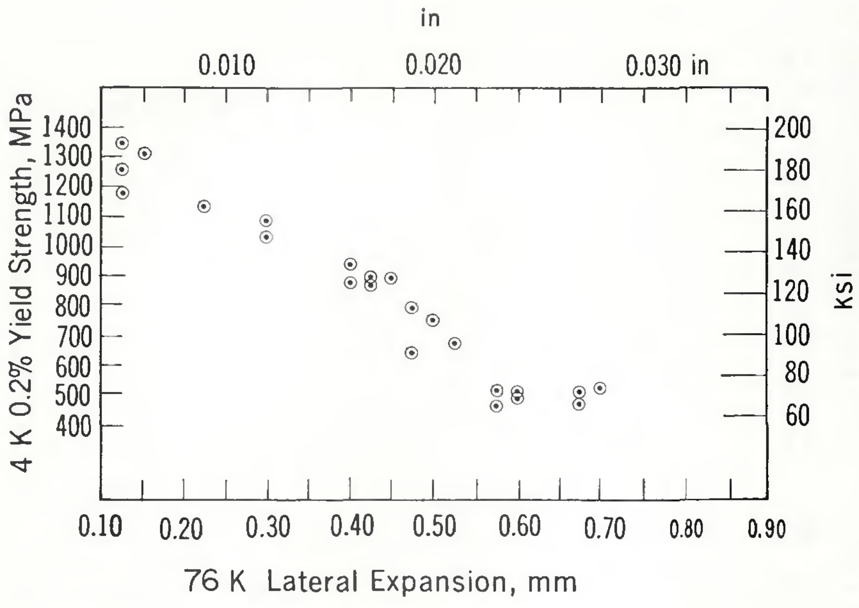

Fig. 5 — Yield strength at 4 K versus lateral expansion at 76 K

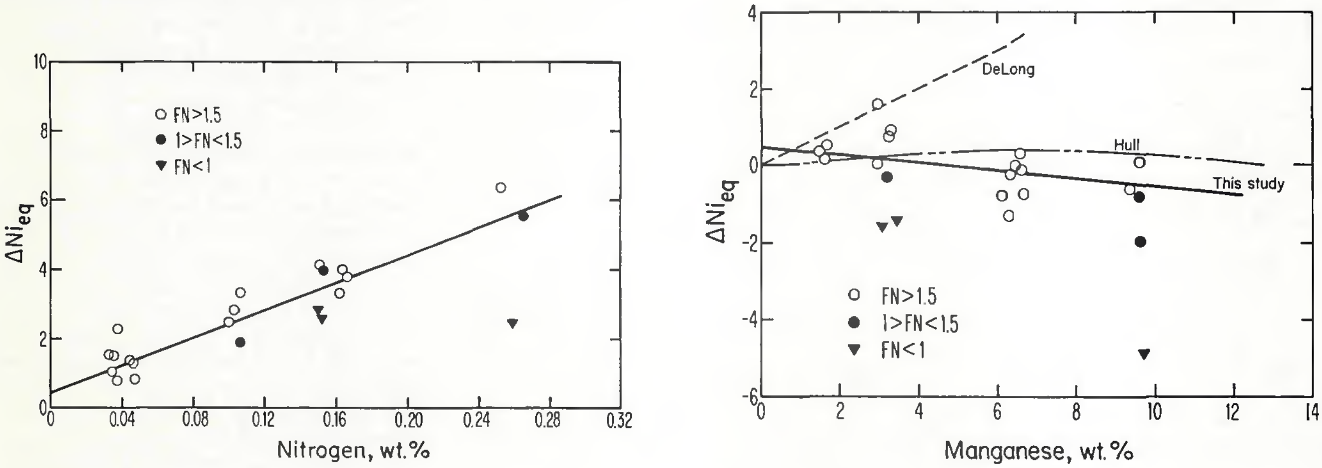

Fig. 6 — Difference in nickel equivalent. A — Versus weld nitrogen content; B — Versus weld manganese content

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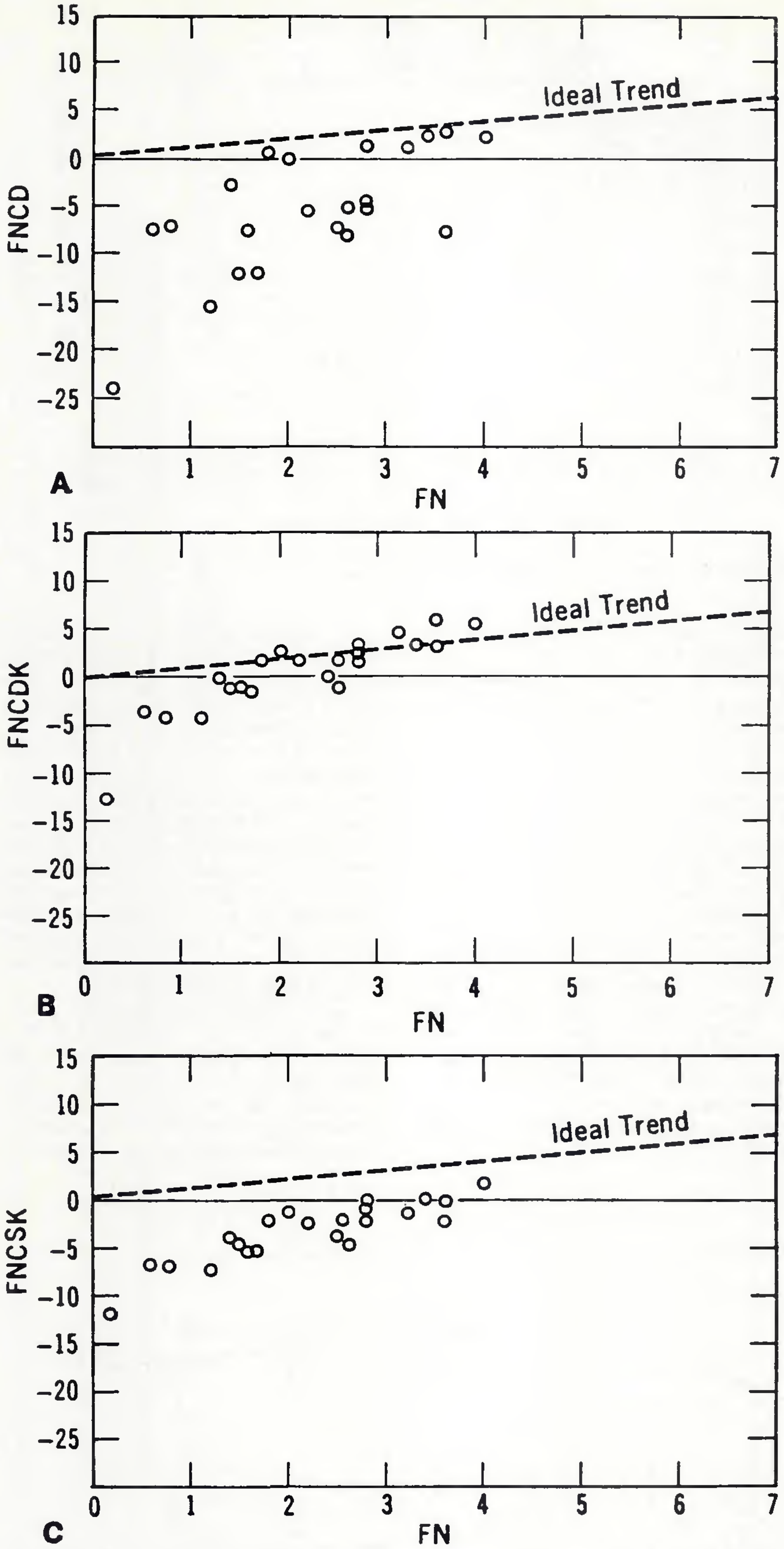

Fig. 7—A—Ferrite number calculated using the DeLong equation; B—Ferrite number calculated using the Szumachowski-Kotecki 0.35 constant to replace the manganese term in the DeLong equation; C—Ferrite number calculated using the Schaeffler equation modified to include a nitrogen term

$$\mathrm{FNCD} = -30.65 + 3.49\,(\mathrm{Cr} + \mathrm{Mo} + 1.5\mathrm{Si}) - 2.5\,[\mathrm{Ni} + 30(\mathrm{N} + \mathrm{C}) + 0.5\,\mathrm{Mn}] \qquad (5a)$$

$$\mathrm{FNCDK} = -30.65 + 3.49\,(\mathrm{Cr} + \mathrm{Mo} + 1.5\,\mathrm{Si}) - 2.5\,[\mathrm{Ni} + 30(\mathrm{N} + \mathrm{C}) + 0.35] \qquad (5b)$$

$$\mathrm{FNCSK} = -37.1 + 43.5\,(\mathrm{Cr} + \mathrm{Mo} + 1.5\mathrm{Si}) \,/\, 2.5\,[\mathrm{Ni} + 30(\mathrm{N} + \mathrm{C}) + 0.35] \qquad (5c)$$

where all elements are given in wt-%.

The unmodified DeLong equation (FNCD) underestimated the measured FN by as much as 24 FN when the nitrogen and manganese contents exceeded the ranges for which the equation was proposed—Fig. 7A. Figure 7B shows the improved FN predictions resulting from the replacement of DeLong's 0.5 manganese coefficient with the 0.35 constant manganese term (FNCDK). Although the FN values generated from the FNCDK expression agree well with the measured FN values at lower manganese and nitrogen content, overall the FNCSK equation produces a more linear data set. When modified with a coefficient to adjust its slope and given the appropriate intercept, FNCSK could therefore predict the effect of manganese and nitrogen most accurately. For this reason, FNCSK was always chosen as the best predictor of FNP by stepwise linear regression analysis. A similar result was found using the ferrite number measured on the actual welds (FNW). Because the results using FNP or FNW are so similar, they will be used interchangeably and are simply identified as FN. The equation found through this method of analysis was:

$$\mathrm{FN} = 3.0 + 0.26\,(\mathrm{FNCSK}) \qquad (6)$$

This equation had an F value of 98 and an R^2 value of 0.82. In each calculation, the program indicated the need for an additional nitrogen- or nitrogen-manganese-containing term in the predictive equation. Overall, this method of analysis showed that although FN prediction is greatly improved by using the modified Schaeffler equation, the manganese and nitrogen terms within the FNCSK expression require further study.

Modification of DeLong's nickel equivalent was the third and final approach to reduce the FN deviations. The nickel equivalent was calculated from the chromium equivalent and measured FN. Only compositional variables associated with the present DeLong nickel equivalent and boron were allowed as choices during linear regression analysis with this method. Here, it was possible to determine which compositional terms were statistically significant and their respective coefficients. A revised nickel equivalent was found that better predicted FN in these high manganese-nitrogen alloys:

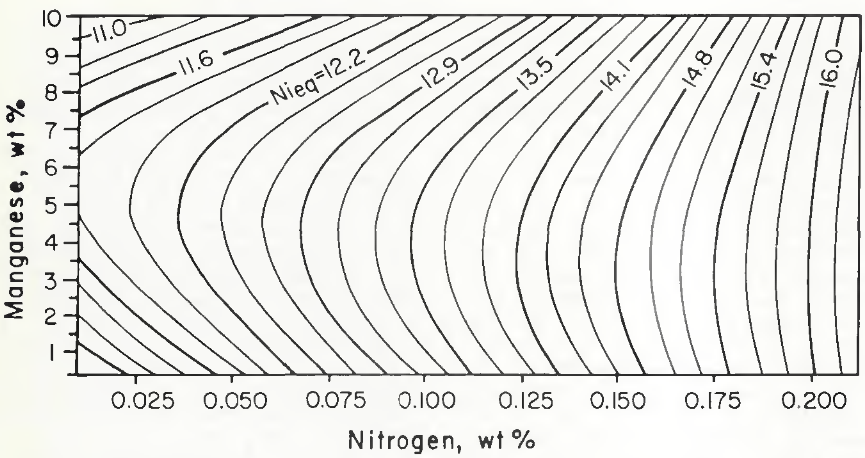

Fig. 8 — The nitrogen-manganese interaction expressed in terms of the nickel equivalent

$$Ni_{eq} = Ni + 29(C + N) + 0.53(Mn) - 0.05(Mn) - 2.37(MnN) + 0.94(MnN)^2 - 0.71 \quad (7)$$

where all elements are represented in wt-%. An F value of 220 and an R^2 value of 0.98 indicate a high statistical significance for the equation. This modified nickel equivalent can be substituted for the DeLong nickel equivalent to determine FN using the DeLong diagram, or it can be substituted in a mathematical representation of the DeLong diagram (Equation 5a), yielding:

$$FN = -30.65 + 3.49(Cr + Mo + 1.5\ Si) - 2.5[Ni + 29(C + N) + 0.53(Mn) - 0.05(Mn)^2 - 2.37(MnN) + 0.94(MnN)^2 - 0.71] \quad (8)$$

In developing this nickel equivalent, alloys with nitrogen contents greater than 0.22 wt-%, or FN of less than 1.0, were not included. Since the DeLong equation was shown to have a large scatter at very high nitrogen or manganese contents in Fig. 6 and accurate measurements of FN near zero are difficult, these limitations seem reasonable.

The manganese effect is decidedly dependent on the nitrogen level, as shown on the contour map of the equation in Fig. 8. At a low nitrogen content, the nickel equivalent first increases as the manganese content is increased. As manganese contents exceed the 4 to 5.5 wt-% range, however, the nickel equivalent begins to decrease. The observation of a change in the austenitizing power for manganese within this concentration range has been reported by Suutala (Ref. 32), Hull (Ref. 26), and Guiraldenq (Ref. 33). The fact that increased nitrogen contents modify the behavior of manganese has not previously been reported. At 0.20 wt-% nitrogen, for example, no characteristic change in the nickel equivalent takes place as the manganese content is increased. The nickel equivalent slowly and continuously decreases to lower values. On the other hand, at 0.06 wt-% nitrogen, the nickel equivalent increases from 12 to 12.7 and then decreases to 11.4 as the manganese content is raised. A change in the nickel equivalent from 12 to 13 at the average chromium content of 19.5 results in an FN change of 3 on the DeLong diagram.

If either of the MnN terms is removed from Equation 7, the other becomes insignificant, the magnitudes of their coefficients are reduced, and the coefficient for nitrogen approaches 22. Such an equation is in agreement with those found by Hull (Ref. 26) and Mel'Kumor and Topilin (Ref. 27). It could be argued that Equation 7 is in fact an extension of those developed by Hull, Mel'Kumor and Topilin and is also related to that found by DeLong (Ref. 22) at lower manganese levels.

In summary, the DeLong manganese coefficient of 0.5 is inaccurate for these high manganese-nitrogen alloys. The replacement of DeLong's coefficient with the Szumachowski-Kotecki constant manganese term (0.35) improves FN prediction, but it still does not completely describe the behavior of manganese. The revised nickel equivalent proposed in Equation 6, however, improves FN predictions by quantifying the nitrogen-manganese interactions. From the various manganese and nitrogen terms reported by researchers and the seemingly contradictory nitrogen coefficients indicated through graphical versus computer methods in this study, it is clear that interactions between alloy elements must be more fully understood before better (and, one hopes, simpler) FN predictive equations can be written.

Conclusions

1. The 4-K yield strength of these welds is primarily a function of the nitrogen content. Manganese increases the strength slightly. Both effects can be expressed by:

$$\text{Weld Yield Strength (MPa)} = 360 + 3400\ (\text{wt-\% N}) + 14\ (\text{wt-\% Mn}) \quad (3)$$

2. The 76-K lateral expansion had a more linear correlation to the strength and the alloy content than the CVN absorbed energy. The lateral expansion was expressed best by:

$$\text{LE (mm at 76 K)} = 0.95 - 6 \times 10^{-4}\ [\text{Weld Yield Strength (MPa at 4 K)}] \quad (4)$$

3. Present FN predictive equations are inaccurate for 18Cr-9Ni stainless steels with high manganese and nitrogen levels. Two equations were found to improve FN prediction for these alloys. The first is simpler; the second is more accurate:

$$FN = 3.0 + 0.26[-37.1 + 43.5(Cr + Mo + 1.5\ Si)/2.5(Ni + 30(N + C) + 0.35)] \quad (6)$$

$$Ni_{eq} = Ni + 29(C + N) + 0.53(Mn) - 0.05(Mn)^2 - 2.37(MnN) + 0.94(MnN)^2 - 0.71 \quad (7)$$

The second equation is a modified Ni_{eq}, which is to be used with the DeLong diagram.

Acknowledgment

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