The Welding Characteristics of a New Ni-Cr-Mo Alloy Designed to Resist Wet Process Phosphoric Acid

Hastelloy® G-35® alloy was studied using the Varestraint weldability test, evaluating mechanical properties, and determining corrosion behavior

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ABSTRACT. This paper concerns the welding characteristics of a new, high-chromium nickel alloy designed specifically for use in concentrated wet process phosphoric acid, a key chemical in the agrichemical industry. The alloy was also designed to resist chlorides and other oxidizing acids. The study involved use of the Varestraint weldability test, to assess the susceptibility of the alloy to solidification cracking, and evaluation of the mechanical properties of gas tungsten arc and gas metal arc weldments. In addition, the corrosion properties of weldments were determined by immersing all-weld-metal samples of the alloy in a number of acid media. For perspective, this paper also includes Varestraint test data for several well-established, corrosion-resistant nickel-based alloys, and defines the corrosive conditions under which the new alloy excels.

Introduction

About ten million tons of phosphoric acid is produced annually in the United States, 80% of which is used in the production of agricultural fertilizers. Most of this acid is made by the "wet process" involving a reaction between sulfuric acid and phosphate rock, which generates impure phosphoric acid and calcium sulfate. Impurities include fluoride ions, chloride ions, silica, aluminum, iron, calcium, and sodium. The concentration of the phosphoric acid so produced is determined by the amount of rinse water needed to separate it from the calcium sulfate, and is normally in the range of 30 to 32 wt-% P_2O_5.

To increase the concentration of this product, for ease of transportation and use, it is taken through a series of evaporation steps. The evaporators are of the heat-exchanger type and operate at temperatures in excess of 90°C. Some evaporation steps are beyond the capability of metallic materials; others involve use of high-chromium stainless steels and high-chromium nickel-based alloys. The alloy described in this paper, Hastelloy® G-35® alloy (UNS N06035), was designed to extend the use of metallic materials in phosphoric acid evaporators. It has the following nominal composition (in wt-%):

Chemical Composition

Ni	Cr	Mo	Fe *	Si *	Mn *	Al *	C *
Bal.	33	8	2	0.6	0.5	0.4	0.05

* Maximum

Fortuitously, this composition has many other potential uses, mainly in the chemical process industries, but also in metal pickling. Tests so far indicate high resistance to oxidizing acids, chloride salts, and alkalis. With pressure vessel applications in mind, the material has been approved for use by ASME and is covered by several ASTM standards.

To assess the solidification cracking (fusion zone hot cracking) propensity of this new alloy, the Varestraint test developed by Savage and Lundin (Ref. 1) was used. Solidification cracking occurs when partitioning of elements during solidification causes low-melting-point films to form along solidification grain boundaries (Ref. 2). As the weld metal cools and shrinks, a level of strain may develop that exceeds the ductility of the partially solidified material, resulting in separation of the grain boundaries along the liquid films. This type of cracking normally appears along the centerline of highly restrained welds. The Varestraint test provides a means of applying augmented strains to small laboratory samples to simulate highly restrained production weldments. There are two types of Varestraint test — the "full scale" and the "subscale." The former is for samples thicker than 6.4 mm (0.25 in.); the latter is for samples 1.5 to 3.2 mm (0.06 to 0.125 in.) thick. Since most previous work on nickel-based alloys has involved the "subscale" test, this was also selected for the present work, so that comparisons could be made easily.

Evaluation of the mechanical properties of G-35 welds involved two types of samples, namely transverse samples from welded plates and cylindrical, all-weld-metal samples taken from AWS B4 Cruciform assemblies. Similar all-weld-metal samples were used to provide discs for corrosion testing in a range of environments.

KEYWORDS

Varestraint Test
Solidification Cracking
All-Weld Metal
G-35 Alloy
GMAW
GTAW
Alloy 625

Experimental Procedure

The actual composition of the G-35 material used in these tests is given in Table 1, along with the actual compositions of the comparative alloys used in previous tests. In the subscale Varestraint test, an autogeneous gas tungsten arc weld bead is deposited down the length of a sheet sample. At a predetermined location during welding, the sheet sample is bent over a die block of known radius, by means of a cable attached to the free end of the sample. This introduces a controlled amount of strain in the vicinity of

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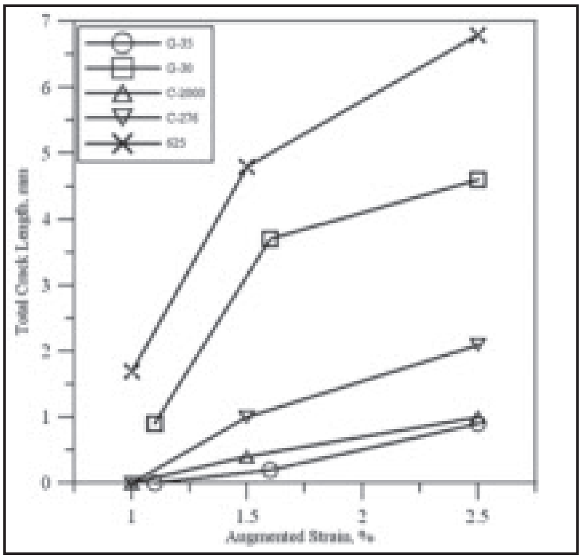

Fig. 1 — Total crack length vs. augmented strain.

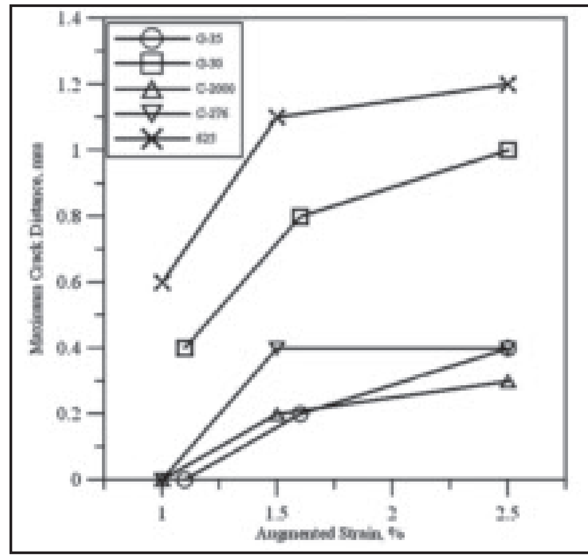

Fig. 2 — Maximum crack distance vs. augmented strain.

Table 1 — Actual Compositions of G-35 and Comparative Alloys

Alloy	G-35	G-30	C-276	C-2000*	625
Heat No(s).	2334-2-2450	8103-8-8517	2760-8-3657	2316-4-8000 2316-9-8024 2316-6-8005	2650-6-6993
UNS No.	N06035	N06030	N10276	N06200	N06625
Al	0.31	0.26	0.23	0.27	0.19
B	<0.002	<0.002	0.002	< 0.002	0.004
C	0.004	0.01	0.0031	0.003	0.02
Nb	<0.05	0.74	0.05	0.03	3.65
Co	0.06	2.75	1.53	0.05	0.17
Cr	33.09	28.62	15.55	22.83	21.55
Cu	0.03	1.82	0.07	1.61	0.04
Fe	1.07	14.27	5.99	0.70	4.40
Mg	0.008	0.028	0.019	0.042	0.03
Mn	0.24	1.09	0.5	0.21	0.27
Mo	7.71	5.25	15.41	15.95	9.07
N	0.06	0.06	0.024	0.03	0.03
Ni	57.38	42.6	55.34	57.78	59.27
P	<0.005	0.01	0.007	0.003	0.006
S	0.001	0.002	0.0014	0.004	0.002
Si	0.18	0.19	0.04	0.02	0.17
V	<0.01	0.05	0.15	0.05	—
W	0.01	2.81	3.98	0.07	0.11

*Average composition of three heats of material

the trailing edge of the weld pool. There are two ways to quantify the resistance of a given alloy to solidification cracking. The first is to measure the lengths of all visible cracks induced by the test, and to calculate the total crack length (the sum of the lengths) and/or maximum crack distance (the length of the longest crack), as a function of augmented strain. The second is to determine the minimum amount of augmented strain needed to induce cracking. In this work, it was decided to determine both the total crack length (TCL) and the maximum crack distance (MCD), at three levels of augmented strain. Details of the sample geometry and welding conditions used in the "subscale" Varestraint test are given in Table 2.

To evaluate the mechanical properties of G-35 weldments, plates of 12.7 mm (0.5 in.) thickness were joined with a matching (ERNiCrMo-22) welding wire using gas metal arc welding (GMAW) and gas tungsten arc welding (GTAW), and transverse tensile and Charpy impact samples were removed for testing. SingleV-grooves, with 70-deg included angles and 3.2-mm (0.125-in.) root opening, were used for the plate welds. Joint angles were created by use of the plasma arc cutting process, then finished with a manual grinder equipped with an aluminum oxide grinding wheel. Prior to welding, the samples were cleaned using acetone. The welding parameters used to make the welds are given in Table 3. All welding was performed manually in the flat position, with a maximum interpass temperature of 93°C (200°F). For the all-weld-metal tests, cylindrical samples of 12.7 mm (0.5 in.) diameter were electrical discharge machined from AWS B4 Cruciform assemblies filled manually using the GMAW process and the welding parameters defined in Table 3, again with a maximum interpass temperature of 93°C (200°F). Similar cylinders of 15.9 mm (0.625 in.) diameter were used for the corrosion tests.

To assess the corrosion behavior of G-35 welds, discs of 3.2-mm (0.125-in.) thickness were taken from these cylinders and tested in four inorganic acids (hydrochloric, hydrofluoric, nitric, and sulfuric), wet process phosphoric acid (from a plant in Florida), and two ASTM standard acid mixtures. Except in hydrofluoric acid, the discs were tested in glass flask/condenser systems for 96 hours, with interruptions every 24 hours, during which the samples were weighed. The hydrofluoric acid tests were performed in Teflon®–coated flask/condenser systems for 240 hours (uninterrupted), shorter times having proved inappropriate for nickel alloys.

Results and Discussion

The Varestraint test results, generated for G-35 alloy in this work and for com-

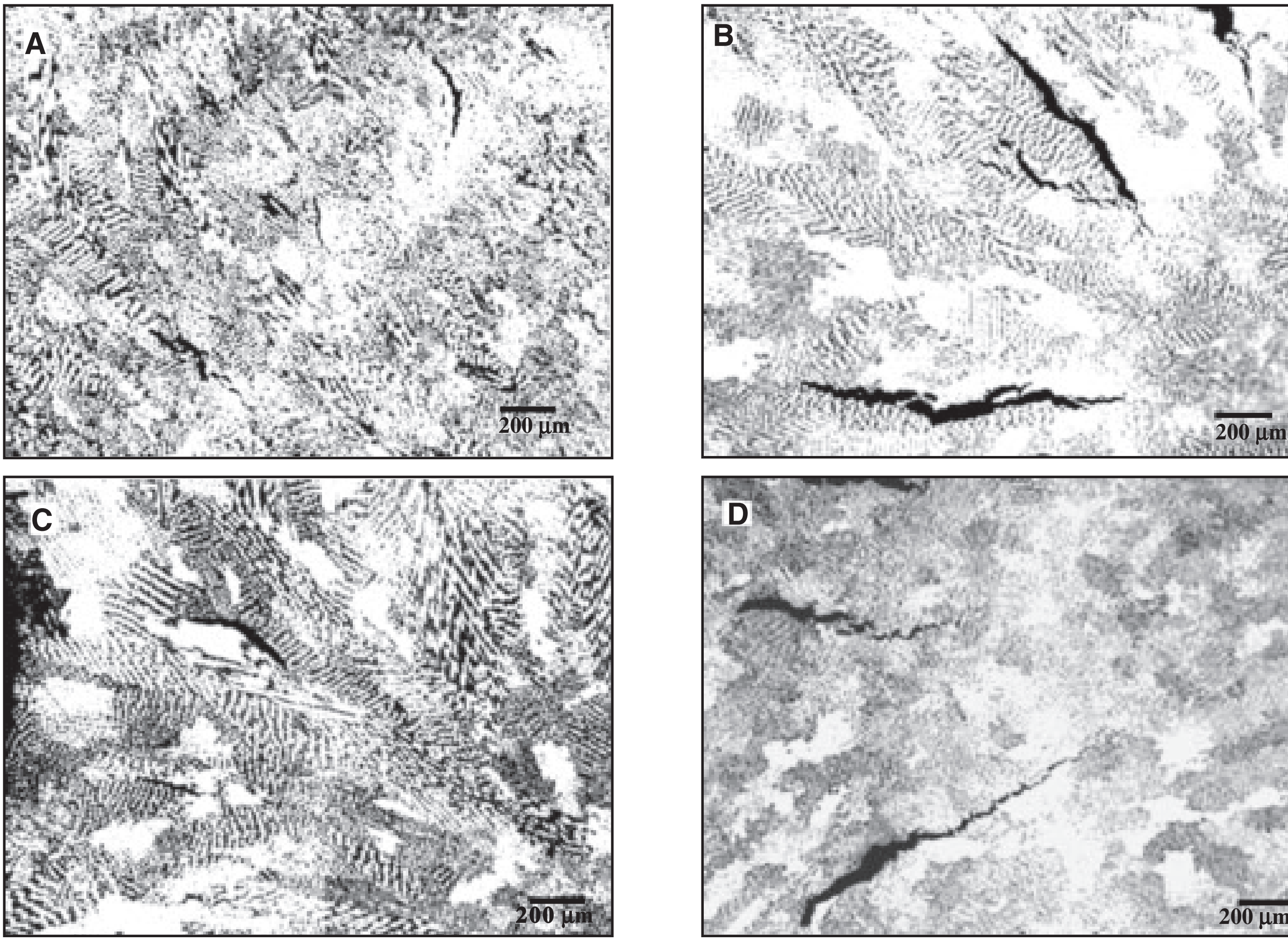

Fig. 3 — Low magnification photomicrographs of the weld fusion zones as follows: A — G-35 alloy; B — G-30 alloy; C — C-2000 alloy; and D — 625 alloy.

parative alloys in previous work (Ref. 2) are given in Table 4. These data are presented graphically in Figs. 1 and 2. The results indicate that, of the nickel alloys tested, G-35 alloy is among the most resistant to solidification cracking. The solidification characteristics of Alloy 625, which exhibited the highest average TCL and MCD values, are described in Refs. 3–5. These references suggest that the low-melting-point films in 625 alloy are closely associated with niobium, an essential ingredient of the alloy. Depending on the carbon and silicon levels, gamma/MC, gamma/Laves, and/or gamma/M6C eutectic-like constituents are formed in 625 alloy during solidification. That niobium may be responsible for the higher susceptibility of 625 alloy to solidification cracking is supported by the results for G-30® alloy (the second most susceptible material), which also has deliberate, albeit smaller, addition of niobium. For perspective, 625 alloy is generally regarded as having good weldability (Ref. 6), so performance of C-276, C-2000®, and G-35 alloys can be considered excellent.

Table 2 — Welding Parameters Used for Subscale Varestraint Tests

Sample Dimensions	25.4 × 152.4 × 3.2 mm (1.0 × 6.0 × 0.125 in.)
Current	70 A
Travel Speed	1.9 mm/s (4.5 in./min)
Arc Length	0.94 mm (0.037 in.)
Shielding Gas Flow (100% Argon)	0.28 L/s (35 ft^3/h)
Electrode Type	Tungsten, 2% Thoriated
Electrode Diameter	2.4 mm (0.094 in.)
Electrode Angle	60 deg

Table 3 — Welding Parameters Used for Mechanical Test Specimens

Sample Type	Welding Process	ERNiCrMo-22 Welding Wire Diameter mm	in.	Shielding Gas	Current A	Voltage V
Transverse Tensile	GTAW	3.2	0.125	100% Argon	155–220	14–16
Transverse Tensile	GMAW (Synergic)	1.1	0.045	75% Ar + 25% He	175	28
All-Weld-Metal Tensile	GMAW (Synergic)	1.1	0.045	75% Ar + 25% He	175	28

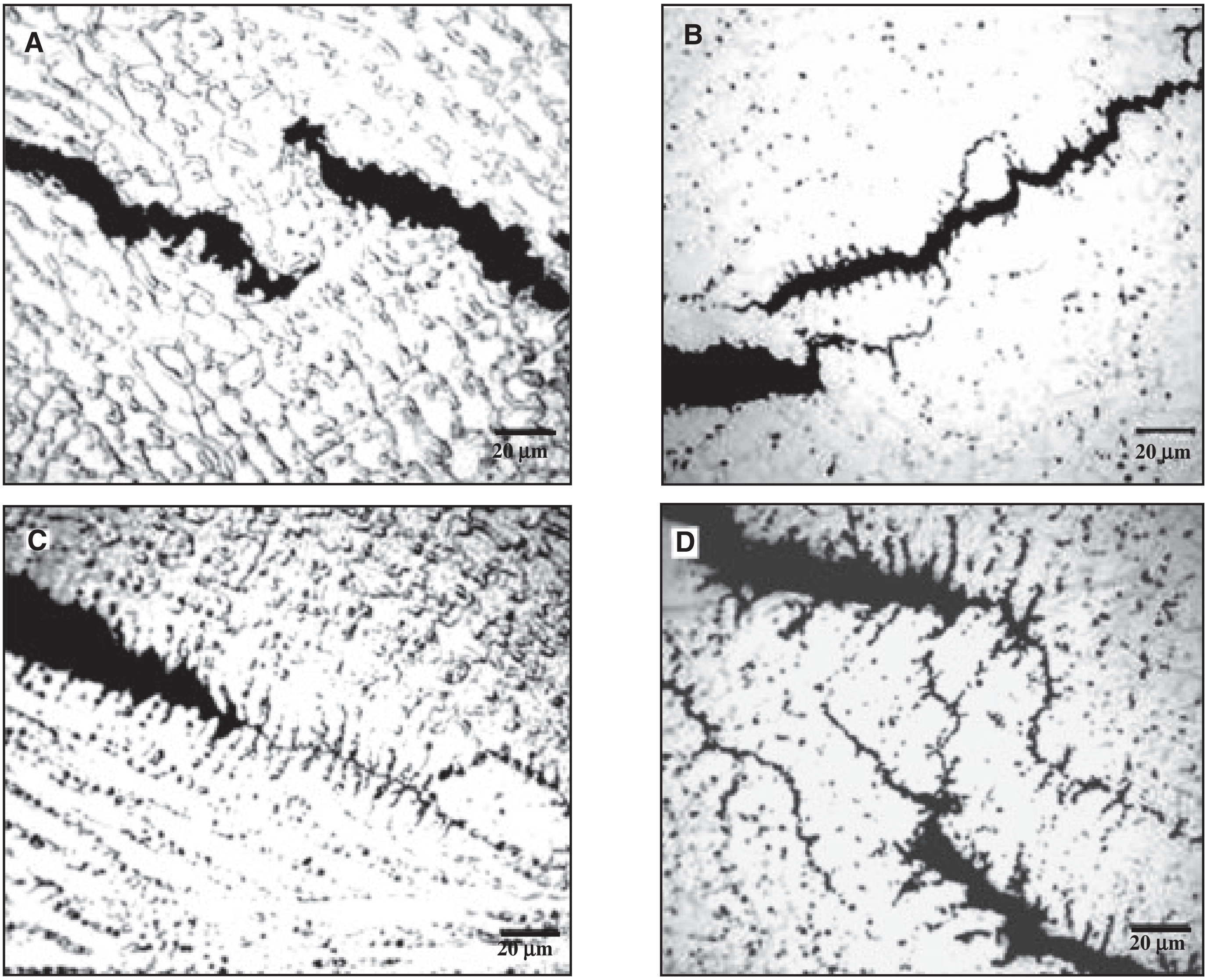

Fig. 4 — High-magnification photomicrographs of the weld fusion zones as follows: A — G-35 alloy; B — G-30 alloy; C — C-2000 alloy; and D — 625 alloy.

Table 4 — Average Total Crack Lengths and Maximum Crack Distances

Alloy	Strain	Number of Tests	TCL mm	TCL in.	MCD mm	MCD in.
G-35	1.1	4	0.0	0.000	0.0	0.000
G-35	1.6	4	0.2	0.007	0.2	0.007
G-35	2.5	3	0.9	0.035	0.4	0.014
G-30	1.1	4	0.9	0.037	0.4	0.016
G-30	1.6	4	3.7	0.145	0.8	0.030
G-30	2.5	4	4.6	0.182	1.0	0.038
C-2000	1.0	6	0.0	0.000	0.0	0.000
C-2000	1.5	9	0.4	0.017	0.2	0.010
C-2000	2.5	16	1.0	0.040	0.3	0.012
C-276	1.0	3	0.0	0.000	0.0	0.000
C-276	1.5	3	1.0	0.040	0.4	0.015
C-276	2.5	6	2.1	0.084	0.4	0.018
625	1.0	3	1.7	0.067	0.6	0.024
625	1.5	3	4.8	0.188	1.1	0.043
625	2.5	6	6.8	0.269	1.2	0.049

Low- and high-magnification photomicrographs of fusion zone cracks in several of the test alloys are shown in Figs. 3 and 4. The high-magnification photomicrographs in particular indicate the low-melting-point eutectic-like constituents along which the cracks propagate. The mechanical properties of G-35 weldments are given in Tables 5 and 6. These indicate moderate strengths and high ductilities, typical of corrosion-resistant nickel alloys. The Charpy V-notch results at –196°C indicate that the alloy can be used, in welded form, in cryogenic applications, without fear of embrittlement.

With regard to the corrosion resistance of G-35 weldments, the results of corrosion tests are given in Table 7. These indicate excellent resistance to 2.5% hydrochloric acid, 10% sulfuric acid, 65% nitric acid, and 5% hydrofluoric acid, at the test temperatures, and excellent resistance to a boiling mixture of 50% sulfuric acid and 42 g/L ferric sulfate (ASTM G 28A test). They also indicate that welds of G-35 alloy are equivalent to G-35 base metal in terms of their resistance to wet process phosphoric acid (at least when the concentration of the P_2O_5 constituent is 52 wt-%). The high test temperature in phosphoric acid was at the request of a potential customer. Normally, the temperature limit for metallic materials in 52% P_2O_5 is just above 120°C, at which corrosion rates of about 0.1 mm/year would be expected for G-35 weld and base metal.

Table 7 does indicate significant performance differences between the weld and base metals of G-35 alloy in 10% hydrochloric acid and in a mixture of 6% ferric chloride and 1% hydrochloric acid. The latter solution is recommended by ASTM Standard G 48 in assessing the resistance of stainless steels and nickel alloys to pitting and crevice corrosion. The term critical pitting temperature (CPT) in Table 7 refers to the lowest temperature at which pitting is observed in this solution, in tests of 72 hours duration. In this work, it was determined by testing samples of G-35 weld and base metal at different temperatures in mixtures of 6% ferric chloride and 1% hydrochloric acid. To identify the CPT (40°C) for G-35 weld metal, testing in duplicate at 40°, 45°, 50°, and 60°C was required. To establish the G-35 base metal CPT (95°C), duplicate testing at 80°, 90°, 95°, and 100°C was needed. As to a reason why G-35 weld metal should be significantly less resistant than the base metal to pitting in this mixture, and to uniform attack in 10% hydrochloric acid, this is likely due to segregation in the weld microstructure and the criticality of these two tests.

Table 5 — Tensile Data for Weldments

Welding Process	Test Temperature °C	°F	0.2% Offset Yield Strength MPa	ksi	Ultimate Tensile Strength MPa	ksi	Elongation %
GTA (Transverse Sample from Welded Plate of 12.7-mm Thickness)	RT		438	63.5	696	101.0	44.0
	260	500	310	44.9	545	79.0	40.0
	538	1000	249	36.1	448	65.0	37.0
Synergic GMA (Transverse Sample from Welded Plate of 12.7-mm Thickness)	RT		459	66.5	724	105.0	31.5
	260	500	335	48.6	555	80.5	43.0
	538	1000	246	35.7	501	72.7	51.0
Synergic GMA (All Weld Metal Sample of 12.7-mm Diameter)	RT		486	70.5	696	101.0	43.0
	260	500	336	48.8	538	78.0	46.0
	538	1000	302	43.8	441	64.0	42.0

Table 6 — Charpy V-Notch Impact Data for Weldments

Welding Process	Notch Position	Test Temperature °C	°F	Impact Strength J	ft lbf
Synergic GMA (Transverse Sample from Welded Plate of 12.7-mm Thickness)	Midweld	RT		273	201
		–196	–320	207	153
	Heat-Affected Zone	RT		>358	>264
		–196	–320	>358	>264

Table 7 — Corrosion Rates and Critical Pitting Temperatures of G-35 Weld and Base Metal

Solution	Temp.	Corrosion Rate, mm/y G-35 Weld Metal	G-35 Base Metal
G 28A	Boiling	0.10	0.09
2.5% HCl	79°C	0.01	<0.01
10% HCl	38°C	0.77	0.17
10% H_2SO_4	Boiling	0.15	0.11
65% HNO_3	Boiling	0.08	0.07
5% HF	52°C	0.11	0.10
52% P_2O_5	162°C	1.59	1.65
		Critical Pitting Temperature, °C	
6% $FeCl_3$ + 1% HCl		40	95

Conclusions

1. G-35 alloy possesses excellent resistance to solidification cracking, being equivalent to C-276 and C-2000 alloys in this regard.

2. The marked susceptibilities of 625 and G-30 alloys to solidification cracking are probably related to their deliberate niobium additions.

3. G-35 weldments are characterized by moderate strengths and high ductilities, even at cryogenic temperatures.

4. In most environments, and in particular wet process phosphoric acid, the corrosion resistance of G-35 weldments is equivalent to that of the base metal.

Acknowledgments

The authors would like to acknowledge the contributions of Mark Britton and Mark Rowe to this study. Britton performed the Varestraint tests and Rowe analyzed the results.

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