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EFFECT OF SMALL VARIATION IN THE COMPOSITION OF PLATES AND WELD FILLER WIRES ON THE GENERAL CORROSION RATE OF Ni-Cr-Mo ALLOYS

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ABSTRACT

The ASTM standard B 575 provides the requirements for the chemical composition of Nickel-Chromium-Molybdenum (Ni-Cr-Mo) alloys such as Alloy 22 (N06022) and Alloy 686 (N06686). The compositions of each element are given in a range. For example, the content of Mo is specified from 12.5 to 14.5 weight percent for Alloy 22 and from 15.0 to 17.0 weight percent for Alloy 686. It was important to determine how the corrosion rate of welded plates of Alloy 22 using Alloy 686 weld filler metal would change if heats of these alloys were prepared using several variations in the composition of the elements even though still in the range specified in B 575. All the material used in this report were especially prepared at Allegheny Ludlum Co. Seven heats of plate were welded with seven heats of wire. Immersion corrosion tests were conducted in a boiling solution of sulfuric acid plus ferric sulfate (ASTM G 28 A) using both as-welded (ASW) coupons and solution heat-treated (SHT) coupons. Results show that the corrosion rate was not affected by the chemistry of the materials within the range of the standards.

Keywords: N06022, Heat-to-Heat Variability, Corrosion Rate, solution heat treatment, ASTM G 28A

INTRODUCTION

The composition of engineering alloys such as Alloy 22 (N06022) and 686 (N06686) is given by ASTM standards (B 575). [1] When the alloys are commercially produced their chemical composition can vary slightly from heat to heat while still within the boundaries of the standard specification. It was of interest to determine if a small variation in the composition of the alloys was important enough, for example, to result in a different corrosion resistance.

The fabrication history of the original welded plates is given elsewhere. [2-3] Basically, wrought plates with seven different heats (A through G) of Alloy 22 (Table 1) were welded with weld wire from seven different heats (1 through 7) of Alloy 686 (Table 2). The Alloy 22 plates were nominally 1-inch thick. The Alloy 686 or ERNiCrMo-14 weld wire was 0.0625-inch diameter and met the specifications of ASME SFA-5.14. [4] The welding method was gas tungsten arc welding (GTAW). Welded specimens from these 49 resulting plates were studied both in the as-welded (ASW) condition and in the solution heat-treated (SHT) (annealed) condition. The solution annealing was carried in air at 2075°F for 1 h plus rapid cooling (water spraying). [2-3] Immersion corrosion tests were carried out in a boiling solution of sulfuric acid and ferric sulfate (ASTM G 28 A). [5]

EXPERIMENTAL

Preparation of the Corrosion Coupons

The test material was delivered to Lawrence Livermore National Laboratory in the form of 1-inch thick welded plates. There were two types of plate strips: (1) As-Welded (ASW) and (2) ASW plus solution heat-treated (SHT). The welding and heat treatment were carried out in the primary metal producer plant. [2-3] Table 3 shows the identification of the coupons prepared from the welded plates. These plates were water-jet cut perpendicularly to the weld in approximately 1-inch thick slices. Then, the test coupons were abrasion wheel cut to immersion corrosion testing sizes from the plate slices. Each coupon contained the weld seam on its center and base material at each side of the weld seam. The testing coupons were approximately 0.5 to 1-inch wide, 0.25 to 0.5-inch thick and 2-inch long. These sizes were constrained by the testing apparatus (ASTM G 28) and specimen holder. [5] That is, each coupon had six surfaces. Five of the surfaces were as-cut surfaces (abrasion wheel of water jet) and one surface (top surface) had the mill finish condition. In the case of the ASW + SHT coupons the top surface had also the characteristic black annealing oxide scale.

The surface area of the coupons varied generally from 20 to 35 cm^2 and the weight in the varied from 30 to 60 g. The coupons were degreased in acetone, rinsed in de-ionized water and let dry. Each coupon was labeled, photographed, dimensioned and weighed three times before the corrosion testing started. In the initial plan it was intended to corrosion test 98 specimens, one for each condition of chemistry and heat treatment. However, at the time of this report, the tests were only approximately 2/3 finished due to a laboratory eviction.

Immersion Corrosion Tests (G 28 A)

ASTM G 28 A method measures the susceptibility of nickel alloys to intergranular attack. It is often used to determine preferential intergranular attack near welds or in heat affected zones (HAZ). The guidelines are specified in the Annual Book of ASTM standards. [5] Figure 1 shows the setting for the tests. The ASTM G 28 A method for Alloy 22 consists in immersing coupons of the alloy for 24 h in a boiling solution of 42 g/L $Fe_2(SO_4)_3$ (ferric sulfate) plus 50% H_2SO_4 (sulfuric acid). This is a highly acidic and oxidizing solution. The difference in the mass of the coupon between before and after the test can be used to calculate the uniform corrosion rate (Equation 1) [5]

$$CR(mm/y) = \frac{8.76 \times 10^4 \cdot (W_i - W_f)(g)}{A\left(cm^2\right) \cdot t(h) \cdot d\left(g \cdot cm^{-3}\right)} \qquad (1)$$

Where W_i is the initial mass of the coupon, W_f is the mass of the coupon after the 24-h immersion test, A is the surface area of the coupon, t is the testing time (24 h) and d is the density of Alloy 22 (8.69 g/cm^3). [5] Only one coupon was tested for each base-weld combination.

Figure 1. Set-up for Immersion Corrosion Testing

PRELIMINARY RESULTS AND DISCUSSION

The results discussed here are preliminary since the entire matrix of the tests has not been completed yet. The testing coupons were approximately parallelepipeds, that is, they had six faces. Five faces were as-cut faces and were of the same nature for both types of coupons (ASW and ASW + SHT). Whenever comparing surface characteristics after corrosion testing only the face of interest (top face) is discussed. Figure 2 shows the general appearance of the top face of ASW 28R5 coupon, before and after the immersion test. Coupon 28R5 corresponded to Base Heat G welded with Wire Heat 7 (Table 3). Before the test, the coupon had a slight heat tint in the heat affected zone (HAZ) area. After the test, the HAZ appeared darker than the rest of the coupon, suggesting enhanced attack in this area. This can be seen as two darker bands at each side and parallel to the weld seam (Figure 2). The attack in the HAZ is generally intergranular attack (IGA).

Figure 3 shows the general appearance of the top face of the ASW + SHT 73R5 coupon. Before the immersion test, the coupon was covered by a dark (black + dark green) oxide scale. After the immersion test, most of the oxide scale was washed away and only the weld seam contained remnants of this scale. Many times there were islands of uneven attack in the weld seam within the area covered by the scale. In some weld seams, cavities were found. It is not clear if these cavities were formed during the immersion tests of were weld porosity formed during welding. The black HAZ bands of IGA present in the

ASW coupons (Figure 2) were absent in the ASW + SHT coupons (Figure 3).

Figure 2. ASW Coupon 28R5 before (top) and after (above) the immersion test

Figure 3. ASW + SHT Coupon 73R5 before (top) and after (above) the immersion tests

Table 4 shows the corrosion rate results from the immersion testing. The tests are approximately 2/3 complete (there are still 35 coupons –out of 98- to be tested). Figure 4 shows the corrosion rate for all the ASW coupons. Corrosion rate data are single values for each base-weld wire chemistry combination. Nonetheless, it is apparent from Figure 4 that the corrosion rate for most plate-weld wire pairs was between 1.0 and 1.1 mm/year. The corrosion rate of wrought and welded Alloy 22 is approximately 1 mm/year (40 mpy). [6-11] Figure 4 shows that there were a few coupons in the middle of the graph that had slightly higher corrosion rates. These coupons were prepared using Weld Wire 4 and base metal with "rich" chemistry (Heats E, F and G) (Table 1). It is likely that the rich chemistries accelerated the precipitation of deleterious ordered phases during welding, which later increased the corrosion rate of the coupons in the HAZ.

Figure 5 shows the corrosion rates for the ASW + SHT coupons. Figure 6 shows comparatively the corrosion rates for the ASW coupons (Figure 4) and the ASW + SHT coupons (Figure 5). In general the corrosion rates of the ASW + SHT coupons were higher than the ASW coupons, probably because of the dissolution (or detachment) of the oxide scale from the top surface of the ASW + SHT coupons (Figure 3). Also, the testing electrolyte was darker after the tests for the ASW + SHT coupons than for the ASW coupons, suggesting more contamination of the electrolyte in the case of the ASW + SHT coupons. Mori et al. have shown that the corrosion rate of Ni-Cr-Mo alloys in ASTM G 28 solutions is highly dependent on the surface finish of the coupons. [12] Figure 5 shows that the corrosion rate seemed to increase for higher number weld wire heats. The higher number weld wire heats correspond to "richer" chemistries (Table 2), that is, the material that contained the highest amounts of Cr, Mo and W. Again, similarly to the data for ASW coupons (Figure 4), the ASW + SHT coupons welded with Wire 4 had higher than expected corrosion rates.

It has been reported previously that the Base Heat G did not meet the elongation to failure during mechanical testing required for wrought N06022 material. [2-3] Weldments produced using Wire 4 produced poor mechanical properties of the material (e.g. reduced tensile strength and low elongation to failure). [2-3] Poor mechanical properties of welded plates were also reported using wires 4 and 7 with plate D. [2-3] For most of the welded plates, a SHT process increased the Charpy toughness of the materials. The toughness of the welded coupons, both ASW and SHT were the lowest for the E, F and G plates welded with wire 4. [2-3] The poor performance of weld Wire 4 was attributed to the high content of residual elements. [2-3]

Figure 7 shows the relationship between the corrosion rate of the ASW coupons and the weight percent factor (WPF) %Cr/(%Mo + %W). The WPF was calculated by averaging the weight percent content of the elements in the base (N06022) and weld seam (N06686). Figure 7 shows that, as expected, as the WPF increases the corrosion rate of a Ni-Cr-Mo alloy in an acidic oxidizing solution decreases. [12, 13]

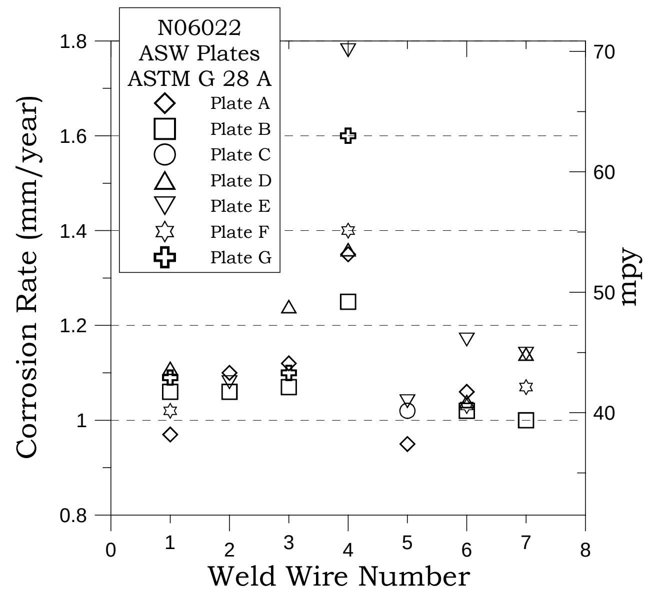

Figure 4. Corrosion Rate for ASW Coupons

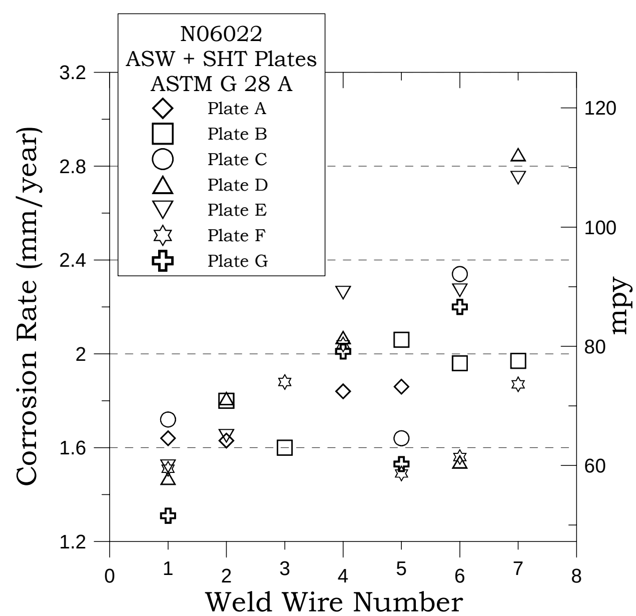

Figure 5. Corrosion Rate for ASW + SHT Coupons

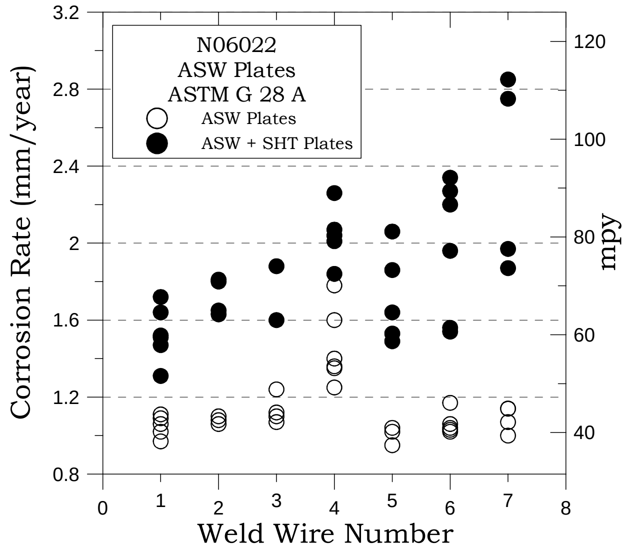

Figure 6. Corrosion Rate for ASW and ASW + SHT Coupons

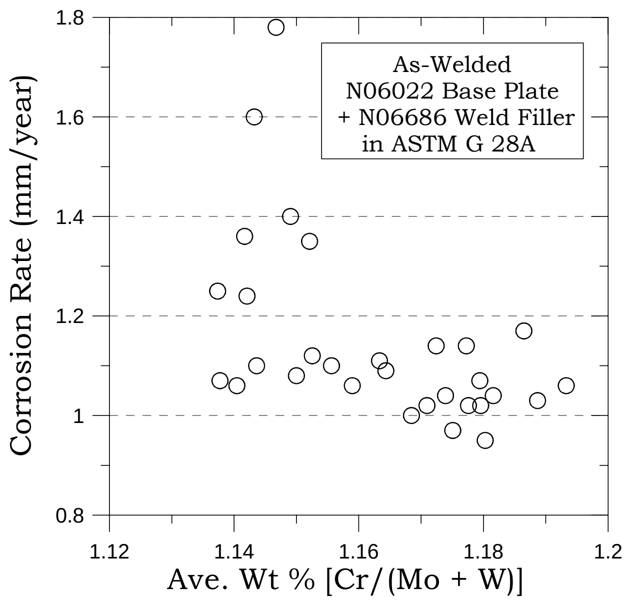

Figure 7. Corrosion Rate for ASW Coupons as a function of the WPF

CONCLUDING REMARKS

Results from the current testing shows that variations in the chemistry of both Alloy 22 and Alloy 686 within the range provided by the guiding standards do not affect the corrosion performance of these alloys. This is not surprising since when a primary metal producer develops and patents a new alloy, many different chemical compositions of the developed alloy are tested both for mechanical properties and for corrosion resistance in several types of electrolytes, generally from acidic reducing to acidic oxidizing. Later, the ranges of the chemical composition that give the desirable mechanical and corrosion properties are written into the standards which are presented to and accepted by societies such as ASTM of ASME. That is, the fact that the current test program failed to detect a change in the corrosion resistance of the alloys when their composition is varied within the margins of the approved standard could have been predicted based on the industrial experience. Even though some rich chemical compositions (when all important alloying elements such as Cr, Mo and W and maxed out) gave slightly different behavior, it is unlikely that a commercial heat will have the maximum content of all the important elements, purely for economical reasons.

CONCLUSIONS

- Corrosion rate of as-welded coupons of Alloy 22 plates with Alloy 686 wires in ASTM G 28 A solution were comparable to published data and in the order of 1 mm/year (40 mpy)
- The corrosion rate of welded plus solution heat treated (ASW + SHT) coupons were higher than for ASW coupons, because the former contained an oxide scale in the surface that disintegrated during corrosion testing
- Corrosion rate results depended only slightly with the chemistry of both the base alloy and the weld wire
- In the range of the accepted chemistry of commercial materials the corrosion rate of one heat usually is indistinguishable from the corrosion rate of another heat

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Table 1. Approximate Average Chemical Composition of the N06022 Plates (Heats A-G)

Element ↓ Heat →	A	B	C	D	E	F	G
Ni	61.6	59.6	58.5	56.00	56.3	58.1	53.9
Cr	20.3	20.8	21.1	21.3	21.6	21.8	22.5
Mo	12.7	13.3	13.1	13.6	13.7	13.8	14.2
W	2.7	3.0	3.0	3.0	3.0	3.0	3.4
Fe	2.5	3.0	4.0	3.0	5.0	3.0	5.8
Co	0.15	ND	ND	2.23	ND	0.03	ND
Mn	0.02	0.02	0.01	0.4	0.04	0.02	0.03
Al	0.18	0.15	0.17	0.15	0.15	0.19	0.20
V	ND	ND	ND	0.25	0.01	0.01	0.01
Cu	0.01	0.01	ND	0.02	ND	0.01	ND
Si	0.03	0.03	0.03	0.07	0.04	0.05	0.05
C	0.004	0.004	0.006	0.005	0.01	0.014	0.007
S	0.0003	ND	ND	ND	ND	ND	ND
P	0.003	0.004	0.004	ND	0.006	0.005	0.006
ND = Not Detected (Below the Detection Limit)							

Table 2. Approximate Average Chemical Composition of the N06686 Weld Wires (1-7)

Element ↓ Heat →	1	2	3	4	5	6	7
Ni	61.9	60.4	58.8	53.6	57.8	56.8	55.6
Cr	19.3	19.8	20.5	20.6	21.6	22.3	22.9
Mo	15.1	15.8	16.3	16.3	16.3	16.3	16.8
W	3.2	3.5	3.7	3.8	3.8	4.0	4.3
Fe	ND	0.42	0.39	4.03	0.28	0.35	0.14
Co	ND	ND	ND	0.02	ND	ND	ND
Mn	ND	ND	ND	0.89	ND	ND	ND
Al	0.15	0.16	0.17	0.06	0.18	0.16	0.16
V	ND	ND	ND	0.11	ND	ND	ND
Cu	ND	0.01	0.01	0.43	0.01	0.01	0.01
Si	0.02	0.02	0.03	0.08	0.02	0.03	0.03
C	0.004	0.005	0.002	0.005	0.001	0.001	0.002
S	ND	ND	ND	ND	ND	ND	ND
P	ND	0.006	0.007	ND	0.008	0.008	0.01
ND = Not Detected (Below the Detection Limit)							

Table 3. Welded Plate Designation Based on the Chemistry of Base Plate and Weld Wire

Chemistry of Base and Weld	ASW Plate ID	ASW + SHT Plate ID		Chemistry of Base and Weld	ASW Plate ID	ASW + SHT Plate ID
A1	4R5	5R5		E1	8R5	9R5
A2	14R5	15R5		E2	18R5	19R5
A3	64R5	65R5		E3	70R5	71R5
A4	84R5	85R5		E4	190R5	91R5
A5	42R5	43R5		E5	46R5	47R5
A6	50R5	51R5		E6	58R5	59R5
A7	30R5	31R5		E7	34R5	135R5
B1	6R5	7R5		F1	2R5	3R5
B2	17R5	16R5		F2	12R5	13R5
B3	66R5	67R5		F3	72R5	73R5
B4	82R5	83R5		F4	88R5	89R5
B5	44R5	45R5		F5	38R5	39R5
B6	56R5	57R5		F6	54R5	55R5
B7	32R5	33R5		F7	26R5	127R5
C1	10R5	11R5		G1	24R5	25R5
C2	120R5	21R5		G2	122R5	23R5
C3	168R5	69R5		G3	162R5	63R5
C4	92R5	93R5		G4	98R5	99R5
C5	148R5	49R5		G5	40R5	41R5
C6	60R5	61R5		G6	52R5	53R5
C7	36R5	37R5		G7	28R5	29R5
D1	94R5	95R5				
D2	96R5	97R5				
D3	80R5	81R5				
D4	86R5	87R5				
D5	78R5	79R5				
D6	74R5	75R5				
D7	176R5	177R5				

Table 4. Corrosion Rate of Coupons Prepared from Welded Plates

ASW Plate ID	Corrosion Rate (mm/year)	ASW + SHT Plate ID	Corrosion Rate (mm/year)		ASW Plate ID	Corrosion Rate (mm/year)	ASW + SHT Plate ID	Corrosion Rate (mm/year)
4R5	0.97	5R5	1.64		8R5	ND	9R5	1.52
14R5	1.10	15R5	1.63		18R5	1.08	19R5	1.65
64R5	1.12	65R5	ND		70R5	ND	71R5	ND
84R5	1.35	85R5	1.84		190R5	1.78	91R5	2.26
42R5	0.95	43R5	1.86		46R5	1.04	47R5	ND
50R5	1.06	51R5	ND		58R5	1.17	59R5	2.27
30R5	ND	31R5	ND		34R5	1.14	135R5	2.75
6R5	1.06	7R5	ND		2R5	1.02	3R5	1.51
17R5	1.06	16R5	1.80		12R5	ND	13R5	ND
66R5	1.07	67R5	1.60		72R5	ND	73R5	1.88
82R5	1.25	83R5	ND		88R5	1.40	89R5	2.04
44R5	ND	45R5	2.06		38R5	ND	39R5	1.49
56R5	1.02	57R5	1.96		54R5	1.03	55R5	1.56
32R5	1.00	33R5	1.97		26R5	1.07	127R5	1.87
10R5	ND	11R5	1.72		24R5	1.09	25R5	1.31
120R5	ND	21R5	ND		122R5	ND	23R5	ND
168R5	ND	69R5	ND		162R5	1.10	63R5	ND
92R5	ND	93R5	ND		98R5	1.60	99R5	2.01
148R5	1.02	49R5	1.64		40R5	ND	41R5	1.53
60R5	ND	61R5	2.34		52R5	ND	53R5	2.20
36R5	ND	37R5	ND		28R5	NA	29R5	ND
94R5	1.11	95R5	1.47					
96R5	ND	97R5	1.81					
80R5	1.24	81R5	ND					
86R5	1.36	87R5	2.07					
78R5	ND	79R5	ND					
74R5	1.04	75R5	1.54					
176R5	1.14	177R5	2.85					
ND = Not Determined Yet, NA = Not Available (Data lost)								