NICKEL ALLOYS AND WELDING PRODUCTS FOR POLYTHIONIC ACID AND CHLORIDE CONTAINING REFINERY ENVIRONMENTS

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ABSTRACT

The selection of materials of construction is a major factor in the success of many processes in an oil refinery. Three areas which have substantial impact in selection of materials are corrosion resistance, mechanical properties and economics. Several materials are considered for reactor vessels, heaters, feed-effluent exchangers and hot transfer lines of the hydrotreating processes. Although hydrotreating and hydrodesulfurization processes vary, they all involve using hydrogen to remove sulfur and other impurities from petroleum products at elevated temperatures. There are several corrosion mechanisms which are possible in these processes. Three of these mechanisms are high temperature sulfide corrosion, polythionic acid (PTA) stress corrosion cracking (SCC) and chloride SCC.

INTRODUCTION

Austenitic stainless steels and high nickel alloys are used in refinery and petrochemical applications where superior corrosion resistance and high temperature strength are required. Resistance to corrosion plays an important role in selecting construction materials. Temperature, in turn, plays an important role in the severity of many corrosive environments. Materials intended to resist high temperature hydrogen sulfide in refineries include a range from carbon steel to high nickel alloys. The chemical compositions of the materials discussed in this paper are listed in Table 1. Severe problem areas for this type of corrosion include applications such as heater tubes and transfer lines, piping exchangers and air coolers. Carbon steel is commonly used for temperatures up to about 500°F (260°C), and then materials such as 5 percent Cr-1/2 percent Mo and 9 percent Cr-1 percent Mo are substituted to provide better resistance to the hydrogen sulfide attack.[1,2] Even these materials suffer from heavy corrosion and metal wastage as temperatures, pressures and sulfide concentrations are increased. The environmental mechanism involves the reaction of the sulfide with the iron in the steels to form iron sulfide. This gives rise to heavy metal wastage and scaling.[3] The scaling causes two detrimental results. First is the reduction of material thickness, and second is the fouling and plugging of lines from the material which spalled off and entered the process stream. McCoy[4] reported the effects of this type of corrosion on 9Cr-1Mo and showed the increased corrosion resistance of the austenitic stainless steels and nickel alloys. The results listed in Table 2 show that the austenitic stainless steels have a substantial reduction in corrosion rate as compared to 9Cr-1Mo, and Fe-32Ni-21Cr alloy has a slight increase in corrosion resistance over the austenitic stainless steels in this service. When the severity of the process is deemed too aggressive for steels, the austenitic stainless steels, and high nickel alloys are specified. The remainder of this paper deals with these severe applications and the materials that are specified for use in them.

The PTA and chloride SCC resistance of several stainless steels and high nickel alloys were examined. Welding products used to join these materials were also evaluated for their resistance to these conditions.

EXPERIMENTAL

U-Bend SCC and intergranular attack (IGA) tests were conducted using 0.062-0.150 inch (2.44-5.90mm) thick mill annealed material. All specimens were prepared for testing by sanding to a 120 grit dry surface finish prior to testing.

Polythionic acid solution was prepared by bubbling sulfur dioxide gas through distilled water for three hours followed by hydrogen sulfide gas for one hour. The resulting solution was checked for potency by exposing a Type 304 SS U-Bend sensitized by heat treatment at 1250°F (677°C) for two hours. Cracking within one hour indicated a solution suitable for use. Test duration is indicated in the applicable tables.

In evaluation of U-Bend SCC tests, time to crack was defined as the time required for formation of cracks large enough to be visible at 20X magnification. Time to fail was defined as the time required for cracking to advance to the point where tension was lost in the legs of the U-Bend specimens.

IGA (sensitization) tests were conducted according to ASTM test procedure A262-85, Practice C. This consisted of exposure to boiling 65% nitric acid for five consecutive 48 hour periods.

RESULTS

Polythionic Acid Stress Corrosion Cracking

Under certain conditions, sulfur compounds, moisture and oxygen can combine in service to form polythionic acid - $H_2S_xO_6$ where x = 3,4 or 5.[2] These conditions exist in hydrotreaters during shutdown as a result of the interaction of moisture and oxygen with the sulfide scale formed on the equipment surface during operation.[5,6] If this acid is present in areas where intergranular sensitization has been produced in an alloy component, there is a chance for PTA SCC. Intergranular sensitization is produced by the formation of chromium carbides and resulting chromium depletion along the grain boundary region during exposure to service temperatures in the range of 900-1500°F (482-816°C). Welding and processing can affect carbide precipitation and resulting susceptibility to PTA SCC. Nickel base alloys and austenitic stainless steels stabilized with columbium or titanium have improved resistance to intergranular sensitization and PTA SCC. The performance of these materials can be influenced by mill heat treatment.

Figure 1 is a photomicrograph of Type 347 Stainless Steel with typical intergranular SCC cracking which resulted from exposure to polythionic acid (apparently after an improper heat treatment).

Nickel alloys and austenitic stainless steels will generally have good resistance to hydrogen sulfide attack in the normal operating temperature of hydrotreating processes. All of these materials do not , however, have good resistance to PTA SCC. The results of SCC testing of several materials is listed in Table 3. AISI Types 321 and 347 SS are stabilized with Ti and Cb, respectively, which provides for good resistance to PTA SCC when given the proper final anneal.

AISI Type 304 SS and nickel alloy UNS N08800 are not stabilized materials and are susceptible to PTA SCC. A relation exists between the degree of sensitization in nickel alloys and their susceptibility to PTA SCC.[9] Even low carbon heats (0.03 max.) of alloy UNS N08800 have adequate carbon available to result in sensitization and subsequent PTA SCC.[6]

Nickel alloys UNS N08801, N08825 and N06625 are stabilized with Ti or Cb and resist PTA SCC when given a proper final anneal. Results for these alloys are also contained in Table 3.

Final anneal is important because it reduces the amount of carbon available to precipitate as $M_{23}C_6$ carbides at the grain boundaries during exposures to sensitizing temperatures. When these stabilized alloys are given a high temperature final anneal, or solution anneal, much of the carbon is in solution and they become susceptible to sensitization and subsequent PTA SCC.

Susceptibility to intergranular attack is commonly measured by a Huey Test (ASTM A262-C). An average corrosion rate of less than 3 mils per month (36 mpy) for the five periods is considered to be satisfactory performance. Substantially higher rates indicate sensitization of the material.

Alloys UNS N08801 and N08825 are two stabilized nickel alloys that are used in this type of service. Figures 2 and 3 compare corrosion rates for alloy UNS N08801 and Figures 4 and 5 compare the corrosion rates for alloy UNS N08825 in ASTM A262-C (Huey Test), where stabilized andunstabilized material was exposured to sensitizing temperatures for various times prior to testing. The stabilized materials, Figures 2 and 4, show the resistance to sensitization. The unstabilized materials, Figures 3 and 5, show sensitization after brief exposure to sensitizing temperatures.

Materials used for welding are also an important consideration in this type of application. Types 321 and 347 SS can be welded with ER347 but generally require post-weld heat treatment to prevent cracking.

Nickel alloys UNS N08801, N08825 and N06625 can all be welded with *INCONEL Welding Electrode 112 (AWS A5.11 Class ENiCrMo-3) and INCONEL Filler Metal 625 (AWS A5.14 Class ERNiCrMo-3) and generally do not require any post-weld heat treatment. *INCOLOY Welding Electrode 135 can also be used for welding alloys UNS N08801 and N08825. Again, post-weld heat treatment is generally not required. Table 4 contains the results of PTA SCC testing for nickel alloy welding products.

Chloride Stress Corrosion Cracking

Some austenitic stainless steels resist PTA SCC but are still subject to service failure by chloride SCC. The level of stress, residual and applied, chloride concentration, and temperature are the main factors that contribute to chloride SCC. All of the austenitic stainless steels, including the stabilized grades , are susceptible to this failure mechanism.[7] The classic curve by Copson[8], Figure 6, shows the beneficial effect of nickel on chloride SCC resistance. Thus, only the higher nickel stabilized alloys would resist both PTA and chloride SCC in refinery and petrochemical environments. Figure 7 is a photomicrograph of Type 304 Stainless Steel which shows the typical transgranular chloride SCC.

CONCLUSIONS

1. Austenitic stainless steels and high nickel alloys have good resistance to hydrogen sulfide attack. Alloyed steels, such as 5Cr-1/2Mo and 9Cr-1Mo, are subject to heavy metal wastage at severe hydrotreating conditions.

2. Stabilized nickel alloys UNS N08801, N08825 and N06625 and stabilized austenitic stainless steels AISI Type 321 and 347 have good resistance to PTA SCC when given the proper final anneal.

3. Nickel alloys UNS N08800, N08801, N08825 and N06625 have good resistance to chloride SCC. The austenitic stainless steels do not have adequate nickel content to have good resistance to chloride SCC.

4. Nickel alloys UNS N08801, NO8825 and N06625 have good resistance to hydrogen sulfide, PTA SCC and chloride SCC conditions found in hydrotreating processes.

5. Nickel alloys UNS N08801, N08825 and N06625 can be joined with ERNiCrMo-3 and ENiCrMo-3 welding products. Generally, post-weld heat treatment is not required, and both the parent and weld metal have good resistance to the corrosion mechanisms of hydrotreating processes.

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Table 1
Nominal Chemical Composition

	UNS Number	C	Fe	Cr	Ni	Mo	Al	Ti	Cb	Cu	Si	P	S	Mn
Carbon Steel		0.3	Bal								0.2	0.01	0.02	0.7
5Cr - 1/2 Mo		0.1	Bal	5		0.6					0.3	0.012	0.01	0.5
9Cr - 1 Mo		0.1	Bal	9	0.4	1.0	0.03			0.1	0.5	0.015	0.01	0.5
304	S30400	0.08[1]	Bal	18.5	9.5			5xC[2]						
321	S32100	0.08[1]	Bal	18	11				10xC[2]					
347	S34700	0.08[1]	Bal	18	11									
800	N08800	0.05	Bal	21	32.5		0.4	0.4						
801	N08801	0.05	Bal	20.5	32			1.1						
825	N08825	0.03	30	21.5	Bal	3	0.1	0.9		2.2				
625	N06625	0.06	3	21.5	Bal	9			4					
AWS A5.14 Class ERNiCrMo-3		0.06	3	21.5	Bal	9			4					
AWS A.511 Class ENiCrMo-3		0.05	4	21.5	Bal	9			3.65					
INCOLOY Welding Electrode 135		0.04	Bal	28.5	36.5	4		0.2		1.7	0.5			2

[1]Max.
[2]Min.

Table 2
Comparison of Short Term Rates Vs. Long Term Calculated Rates

Alloy	Corrosion Rate, mils per year					
	600°F (315°C)		750°F (400°C)		900°F (480°C)	
	Long Term*	330 Hour Test	Long Term*	330 Hour Test	Long Term*	330 Hour Test
9 Cr - 1 Mo	17.1	37.9	64.7	172.2	128.0	383.2
304L	0.9	2.1	2.6	15.1	5.7	36.8
321	0.9	1.9	3.3	14.6	5.3	38.1
800	0.6	1.1	2.3	8.7	5.8	28.2

H_2S Content: 5-7% by volume
* Calculated from slope of mass loss-time curves for each alloy.
(Reference 1)

Table 3
PTA SCC and Average IGA Results

Alloy	PTA Results		IGA Test Results	
	TTC	TTF	mpy	mm/y
800	5 Hr	30 Hr	1668	(42.4)
801	NC	NF	468	(11.9)
825	NC	NF	13	(0.3)
800H	5 Hr	30 Hr	1692	(43.0)
625	NC	NF	55	(1.4)
321	NC	NF	137	(3.5)
347	NC	NF	43	(1.1)
304	<24	-	-	-

IGA Tests per ASTM A262-C.
All specimens tested in mill annealed plus 1250°F (672°C) for 1 hour and AC.

Table 4
PTA SCC Results of Welded Specimens (1000 Hours Total Exposure)

Base Material	Thermal Treatment	Cracking Time, hr.		
		ENiCrMo-3	ERNiCrMo-3	Electrode 135
UNS N08800	1000°F/ 50 hr	-	-	74
	1000°F/100 hr	-	-	166
	1100°F/ 50 hr	16	16	-
	1100°F/100 hr	16	16	-
	1200°F/ 50 hr	240	DNC	-
	1200°F/100 hr	DNC	DNC	-
UNS N08001	1000°F/ 50 hr	-	-	DNC
	1000°F/100 hr	-	-	DNC
	1100°F/ 50 hr	DNC	DNC	DNC
	1100°F/100 hr	DNC	DNC	DNC
	1200°F/ 50 hr	DNC	DNC	DNC
	1200°F/100 hr	DNC	DNC	DNC
UNS N08825	1000°F/ 50 hr	-	-	DNC
	1000°F/100 hr	-	-	DNC
	1100°F/ 50 hr	IP	IP	DNC
	1100°F/100 hr	IP	IP	DNC
	1200°F/ 50 hr	IP	IP	DNC
	1200°F/100 hr	IP	IP	DNC

IP = In Progress DNC = Did Not Crack

Table 5
Summary of Materials and Their Corrosion Behavior In Hydrotreating Media

Material	Resistance To High Temperature Sulfide Attack	Resistance to Stress Corrosion Cracking	
		Polythionic Acid	Chloride Ion
9 Cr-1 Mo	Poor	Immune	Immune
304L	Satisfactory	Poor	Unsatisfactory
321	Satisfactory	Satisfactory	Unsatisfactory
347	Satisfactory	Satisfactory	Unsatisfactory
800	Satisfactory	Poor	Satisfactory
801	Satisfactory	Satisfactory	Satisfactory
825	Satisfactory	Satisfactory	Satisfactory
625	Satisfactory	Satisfactory	Satisfactory
ENiCrMo-3	Satisfactory	Satisfactory	Satisfactory
ERNiCrMo-3	Satisfactory	Satisfactory	Satisfactory
Electrode 135	Satisfactory	Satisfactory	Satisfactory

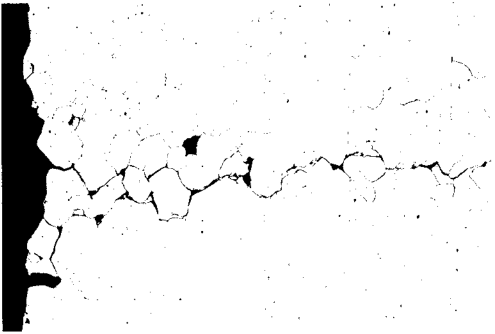

Figure 1. Intergranular PTA SCC produced in Type 347 Stainless Steel reformer tube. Heavy intergranular carbide precipitation was present, apparently as the result of improper heat treatment. Magnification 100X, Etchant: 10% oxalic, electrolytic

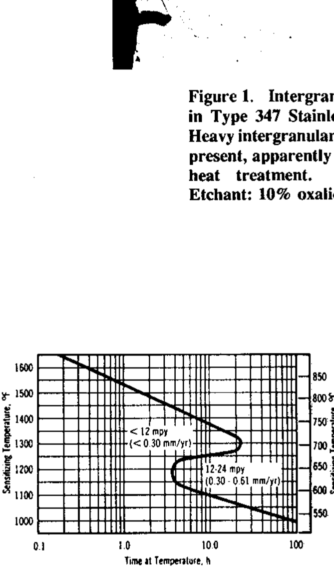

Figure 2. Effect on corrosion rate in Huey Test of reheating stabilized alloy UNS N08801. Stabilizing anneal was 1750°F (955°C)/1 hr/WQ.

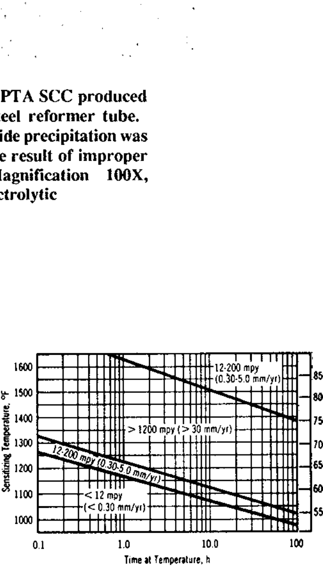

Figure 3. Effect on corrosion rate in Huey Test of reheating unstabilized alloy UNS N08801. Material was annealed at 2000°F (1090°C)/1 hr/WQ.

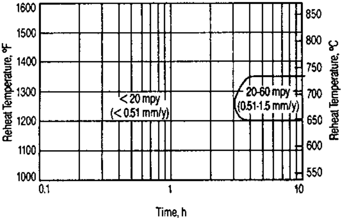

Figure 4. Effect on corrosion rate in Huey Test of reheating stabilized alloy UNS N08825. Stabilizing anneal was 1725°F (940°C)/5 min/AC.

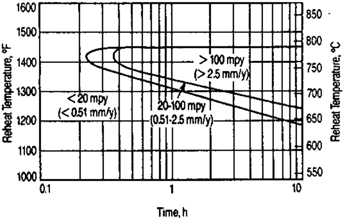

Figure 5. Effect on corrosion rate in Huey Test of reheating unstabilized alloy UNS N08825. Material was annealed at 2000°F (1090°C)/5 min/AC.

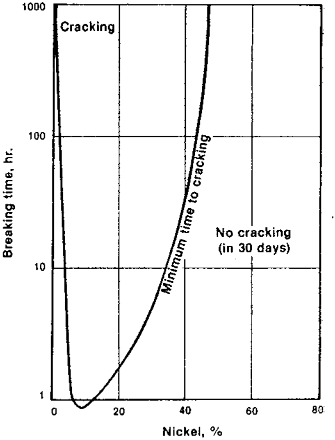

Figure 6. Effect of nickel content on SCC of Fe-Ni-Cr alloys in boiling 42% Magnesium Chloride. (Reference 8)

Figure 7. Welded Type 304 Stainless Steel U-bend specimen showing transgranular branching cracks adjacent to the weld. Magnification 100X Etchant: Glycergia