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SUITABILITY OF INCONEL FOR CORROSION PROTECTION ON WATER SIDE OF SODIUM COMPONENT STEAM GENERATOR

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ABSTRACT

The heat exchanger and steam generator for the U.S. Atomic Energy Commission Sodium Components Project will be constructed entirely of type 316 stainless steel. Because of the susceptibility of this alloy to stress corrosion cracking, it is proposed to clad all areas of the steam generator with Inconel where the stainless steel will be exposed to water and steam. This report includes a discussion of the work by numerous investigators that justify the selection of Inconel for this service. A discussion of Inconel type welding alloys is also included.

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INTRODUCTION

AISI type 316 stainless steel was selected as the material best suited for fabrication of a steam generator operating with 1140°F secondary sodium. However, the material is considered undesirable for water-steam exposure because of susceptibility to stress corrosion cracking in dilute caustic and chloride environments. Chlorides can be introduced by condenser leakage or inadequate feedwater purification and dilute caustic can be produced on the steam side of the unit as a result of a water to sodium leak. In order to increase reliability of the unit, a thin clad of Inconel will shield the stainless steel from water-steam exposure. This will be done by the use of bimetallic tubes and through deposition of an Inconel weld overlay on the tube sheet and channel ends.

This report summarizes information in the literature which indicates the reliability of Inconel for this application. Information summarized concerns stress corrosion cracking resistance of Inconel in chloride or caustic environments, high temperature steam corrosion resistance, and properties of Inconel type weld overlay materials which are available.

STRESS CORROSION CRACKING RESISTANCE

There is an abundance of experimental data which demonstrate the resistance of Inconel to stress corrosion cracking in chloride environments. Some of the test work by different sources was very repetitious in respect to exposure conditions and testing techniques. The following discussion makes reference to reports on some of the Inconel corrosion data and briefly describes the test or service results reported.

The only implication of chloride stress corrosion failure of an Inconel type material known to the authors is reported in the Corrosion and Wear Handbook (1). The material which failed had chemical composition limits overlapping the chemical composition limits of conventional Inconel. Intergranular cracking of a spring which had been in steam service for four years at a temperature of 750°F and stress of 77,000 psi was reported. Another intergranular failure occurred on heat exchanger tubes immersed in hot water. The cracks originated within a sludge on the bottom tube sheet and failure was attributed to the presence of a continuous intergranular precipitate. A test specimen of the alloy was immersed in aerated natural sea water, containing approximately 20,000 ppm chlorides, and autoclave tested at 550°F. Failure of the specimen during 24 days of testing was attributed to stress corrosion cracking. Another test specimen did not fail during 45 days exposure to the same environment at 350°F.

Tilting autoclave tests were performed on stressed and welded Inconel specimens by the Martin Company(2). Standard U-bend specimens were suspended in the water and steam phases of autoclaves half filled with water. Welded specimens tested were placed at the vapor-liquid interface. Environmental conditions were varied in concentrations of chlorides, oxygen, and method of pH adjustment. The most severe environment was water containing 1000 ppm chlorides with air trapped over the liquid in the autoclave. Tests were run for 500 hours at 500°F and 680 psi. A dull brown adherent coating was formed on all specimens, but none of the specimens cracked or pitted. The average penetration for all specimens was 0.35 mils per year and the highest penetration for a single specimen was 0.90 mils per year. Type 304 stainless steel subjected to similar autoclave tests failed within 120 hours with test water containing less chlorides at 380°F and 200 psi (3).

Heat exchangers which simulated the design of the steam generator employed at Fort Belvoir in the SM-1 reactor plant were tested under various environmental conditions by Martin (4). Inconel was one of the structural materials investigated. Heat exchangers designated as model heat exchangers consisted of a single tube sheet with three U-shaped tubes in a shell and tube vertical unit. Heat exchangers designated as minature heat exchangers consisted of horizontal shell and tube units with two U-tubes extending from a single tube sheet. Secondary water was on the shell side of all units. Model heat exchangers, heated by a pressurized water loop, were tested in sets, each set consisting of a steam generator and superheater. Miniature units were tested in a static secondary system with vapor being condensed and reboiled. The secondary systems were maintained at 200 psi pressure with about 40^{o}F of superheat being attained in the model superheater. Secondary water flowing to the model heat exchangers containing Inconel tubes (MOD SG-6 and MOD SH-6) had an average chloride content of approximately 1000 ppm. Oxygen was controlled by sulfite scavenging. The units were service tested for 3819 hours. The pH was controlled at 8.3 to 9.5 with phosphates. Inconel tubes were in excellent condition at completion of test despite formation of a thick boiler scale. These test results are in contrast to similar tests with type 304 stainless steel model heat exchangers which showed stress corrosion failure in water containing only 50 ppm chlorides (5).

Additional tilting autoclave stress corrosion tests were reported by White and Johnson (7). A number of nuclear power plant steam generator tubing materials were tested by the National Aluminate Corporation for Bettis Atomic Power Laboratory. Stressed U-bend specimens were exposed for 24 hours to both the liquid and vapor phases of a high pH synthetic boiler water solution containing oxygen, phosphate, and 500 ppm chlorides, at a temperature of 500^{o}F. Seventy-two Inconel specimens were tested with no stress corrosion cracks developing. Sixty-four specimens of type 347 stainless steel were tested under the same conditions, and all of them cracked.

Model boiler tests were performed at Babcock and Wilcox Research Center as a followup to the autoclave screening tests at National Aluminate Corporation. This work is reported by Howells, McNary, and White (8). Heat exchanger models and test operation were nearly identical with model heat exchanger tests performed at Martin. The secondary water temperature was 480-490^{o}F and chloride concentration was 500 $\pm$ 50 ppm. Stress corrosion cracks occurred in all twelve tube-to-tube sheet junctions of a stainless steel boiler model. Secondary surfaces of Inconel tubing in an Inconel boiler model were in excellent condition at conclusion of testing. Mild general corrosion and scattered small pits were observed in crevice areas.

A report by Denhard (9) describes a study of relative stress corrosion cracking resistance of several alloys in boiling 42% magnesium chloride solution. Variations in composition, heat treatment, and surface condition were studied as to effect on cracking resistance. Inconel was found to be completely resistant to chloride stress corrosion cracking in boiling magnesium chloride. One test on this alloy at 100,000 psi failed in slightly over 1000 hours, but examination showed the cause to be pitting corrosion, which increased the stress by reducing the cross-sectional area. Stresses of 50,000 to 90,000 psi did not cause cracking in time periods up to 3500 hours.

McGoff and Glaser (10) heated a stressed Inconel specimen to 600-650^{o}F and dripped a 9 percent magnesium chloride solution onto the surface for

560 hours. No cracking occurred, although austenitic stainless steel cracked in four hours in a similar test. They were also unable to crack stressed Inconel specimens by thermal cycling 133 times in 733 hours by heating to 650°F in air and cooling to 200°F with synthetic sea water containing approximately 19,300 ppm chlorides.

McGoff (11) also reports on tests performed on ten stressed one inch schedule 40 Inconel pipe specimens. Specimens were exposed in a high humidity sea water - warm air compartment for 100 hours. Constant temperature specimens were held at 400, 200, 165, and 125°F and cyclic specimens were varied between 550 and 125°F in a compartment where ambient temperature was 125°F. The Inconel pipe specimens showed no evidence of stress corrosion cracking by the high chloride atmosphere and pitting was not observed in an atmosphere which had caused corrosion of type 304 stainless steel.

Copson (12) has reported on the effect of nickel content on stress corrosion cracking resistance of alloys containing iron, nickel, and chromium as major alloying elements. Stressed wire specimens were exposed to boiling 42% magnesium chloride solution and the time to cracking as a function of nickel content was observed. The time to cracking increased rapidly with nickel content over eight percent, and alloys with more than 45 to 50 percent nickel seemed immune to cracking. Copson states that Inconel is completely resistant to this type of stress corrosion cracking. Additional tests were reported on iron-nickel alloy U-bend specimens of various nickel contents in boiling 33% sodium hydroxide containing 0.13% lead oxide and 0.13% sodium chloride for 14 days. Results in caustic were similar to those obtained in chlorides. Cracking did not occur in specimens containing 38% nickel and 99% nickel, while a specimen containing 8.5% nickel cracked in two. Specimens of lesser nickel content had micro cracks after exposure.

Copson and Berry (13) investigated the corrosion resistance of Inconel for service in the steam generation system of pressurized water nuclear power plants. Tests conducted in simulated secondary boiler water were performed in autoclaves with a thermal leg to insure circulation of the water during tests. Stress and crevice specimens were exposed in the liquid, in the vapor, and at the liquid-vapor interface of water containing approximately 50 ppm chlorides with air trapped over it. Specimens were exposed for 2000 hours at 500°F. An adherent tarnish film was formed on tested Inconel specimens. There was no pitting or local attack and corrosion rates were exceedingly low. Corrosion results were essentially the same as for other autoclave and simulated boiler tests described herein. Although stress corrosion cracking did not occur, these tests cannot be considered as good stress corrosion tests since stainless steel specimens also did not crack. MND-E-1322 (3) indicates that greater than 100 ppm chlorides would be required to crack stainless steel in such a test. The authors (13) state that Inconel is resistant to stress corrosion cracking in chloride and alkaline environments. Unpublished data of the International Nickel Company, Incorporated is cited as evidence of resistance to alkaline environments. The paper concludes that Inconel is an excellent construction material for primary and secondary water of pressurized water reactor plants.

Qualitative statements are made concerning stress corrosion cracking resistance of Inconel in several International Nickel Company technical publications. Extracts from two of these publications (14, 15) follow in order of cited references:

> "Experience with nickel, Monel, and Inconel used under stress in a great variety of services has shown that these materials are not subject to season cracking, while stress-corrosion cracking has been observed only when they are in contact with a few specific chemicals, such as salts of mercury and fused caustic soda. No caustic embrittlement of nickel, Monel, or Inconel has been encountered in concentrations of caustic soda under 75 percent; and embrittlement by fused caustic can be avoided entirely by annealing the metal prior to exposure."

> "Inconel is one of the few materials suitable for use in contact with hot, strong solutions of magnesium chloride. In addition to the low rate of corrosion, Inconel shows no tendency toward stress corrosion cracking during exposure to the solution. Because of its high nickel content, Inconel is practically free from corrosion by alkaline solutions; for example, tests in 70 percent caustic soda at 260°F showed a rate of corrosion of only 0.00004 ipy."

Strauss and Thum's results for corrosion resistance of nickel base alloys in several media are presented in The National Bureau of Standards Circular #485 (16). Inconel is rated as fair to excellent in sea water and brackish water with chlorides, and excellent in one to twenty percent alkaline solutions.

CORROSION RESISTANCE IN HIGH TEMPERATURE STEAM

Qualitative statements concerning corrosion resistance of Inconel in high temperature steam appear in several technical publications of the International Nickel Company, Incorporated. Typical remarks are the following which appear in reference publications.

> "It (Inconel) is completely resistant to all mixtures of steam, air, and carbon dioxide and is especially useful in contact with steam at high temperatures in excess of 800°F. Inconel coils are used successfully for heating steam up to 1500°F..." (p. 12 of Reference 15).

> "...The upper useful limit for Inconel in steam has not been established, but it is above 1500°F..."(17).

Inconel was among the materials tested in a high temperature steam power station at Detroit (18). Corrosion data were as follows, with results on a type 304 stainless steel specimen included for comparison.

Material	Test (hrs.) Duration	Test Temperature	Calculated Inches Penetration/10000 Hrs	% Wt. Loss
Inconel	8000	1100°F	.00094	0.57
304 ss	15000	1100°F	.00020	0.20

Station steam contained no carbon dioxide and less than .01 ppm oxygen. The corrosion values given are for single specimens, and therefore, are not significant except to indicate that the corrosion rate was very low. Some pitting was found in Inconel after exposure.

Additional quantitative data concerning corrosion resistance of Inconel in high temperature steam (1050°F) could not be found. A high pressure - high temperature loop will be operated for six months at Alco Products, Incorporated as part of the Research and Development program for design of a once-through steam generator. Additional high temperature steam corrosion data will be obtained from this test.

DISCUSSION OF CORROSION DATA

The Inconel failures reported in the Corrosion and Wear Handbook (1), which has received wide circulation, have probably led to unwarranted concern over the stress corrosion resistance of Inconel. The information presented is very sketchy and it is probable that failures resulted from increased stress due to reduction in cross-section by pitting in the severe environments. Such a failure was reported by Denhard (9). Most of the other tests reported herein were severe enough to crack any materials susceptible to cracking in a chloride environment. Since no other instances of cracking are reported, it seems reasonable to conclude that the failures reported by the one source were not due to chloride stress corrosion cracking.

None of the corrosion tests reported were conducted at the high service temperature (1050^{o}F) which will be required of Inconel for this application. It is known that temperature will accelerate cracking of alloys which are susceptible to stress corrosion cracking. However, no instances are known where stress corrosion cracking was promoted by temperature if the material in question was immune to such cracking at lower temperature. Tests on Inconel have furnished sufficient evidence of such immunity to conclude that it will not be cracked by a chloride environment at high temperature.

Inconel has not been subjected to as much testing in dilute caustic environment because of its known corrosion resistance to alkaline solutions. Consequently, most of the evidence presented on resistance to caustic stress corrosion cracking is qualitative. The data reported by Copson (12) indicate that Inconel is immune to such cracking because of high nickel content.

INCONEL TYPE WELDING ALLOYS

There are several welding electrodes and filler wires commercially available which are capable of depositing a metal composition basically equivalent to Inconel (ASTM B-168). These welding alloys as listed below differ slightly in their composition with respect to iron, manganese, columbium and other minor elements, however the nickel content which influences the resistance to stress corrosion cracking is essentially the same.

Chemical Composition

Elements	Inco 62 (MIL-EN62)	MIL-EN87	Inco Weld A (MIL-EN60)	MIL-4N85
Carbon	.10	.10	.10	.10
Manganese	1.0	2.5/3.5	2.0/2.75	5.0/9.5
Silicon	.75	.50	.35	1.0
Sulphur	.015	.015	.015	.015
Chromium	14/17	18/22	14/17	13/17
Nickel	70 min	67 min	67 min	Bal
Iron	6/10	3	10	6/10
Columbium	Min 4 x Si	2/3	-	1/2.5
Aluminum	-	-	.10	-
Others	-	.75 Ti	2.5/3.5 Ti	1.0 Ti

The Alco welding laboratory and other organizations have investigated the welding characteristics of these alloys for nuclear and high temperature steam generator service. The results of these investigations were reviewed and the electrode composition for the electric arc process and filler wire for inert-gas-shielded metal and tungsten-arc processes were selected as applicable for the service intended. Several electrodes and filler wires were given a cursory consideration and were subsequently rejected because of weld metal chemistry, hardening tendencies at service temperature, susceptibility to fissuring and other welding difficulties.

The Alco Welding Laboratory (19) have evaluated both Inco Weld A (MIL E-21562, Type EN6A) and Inco 62 (MIL E-21562 Type EN62) for overlaying A212-grade B carbon steel and type 304 stainless steel plate. These overlays were made by the automatic inert-gas-shielded-metal-arc-process. It was concluded by these investigations that both Inco Weld A and Inco 62 overlays have satisfactory soundness and required mechanical, metallurgical, and chemical properties to meet applicable ASME and Navy Qualification Standards. Because of the titanium content of Inco Weld A wire, precipitation hardening will occur from exposure to temperatures in the range of 1000°F to 1400°F. The resulting stress rupture ductility is almost nil at 1200°F and is therefore unsatisfactory for the anticipated service conditions.

KAPL (20) reports that Inco 62 wire MIG - deposited in moderately thick (1 1/8") to heavy (2 5/8") Inconel structural weldments, is disposed to fissuring to about the same degree as the 300 series stainless steels. Fissures are undisclosed by the usual nondestructive inspections (liquid penetrant and radiographic), but are readily observed in side bends of weld sections, or upon metallographic examination. The extent of fissures does not exceed the requirements of applicable welding procedure qualification codes or specifications. This report leaves doubt as to the complete reliability of Inco 62 for this application, even though Alco work with Inco 62 has proved satisfactory.

Alco production experience and laboratory investigations have also concluded that the MIL-4H85 coated electrode is superior to all other Inconel type materials for manual metal-arc welding. Investigations conducted by KAPL (20) have concluded that Inconel electrodes usually produce slags that are tenacious and difficult to remove and there is no tendency for slag to float out during subsequent passes. This will require a complete removal of slag between each weld pass. The MIL-4H85 electrode is an exception as the slag produced is friable and almost self removing.

Recently the Alco Welding Laboratory completed an evaluation of the MIL-EN87 wire for automatic inert-gas metal-arc-overlays. This alloy was specifically designed for dissimilar metal welds. In regard to the quality of the weld deposit, this alloy showed satisfactory soundness and the required mechanical, metallurgical and chemical properties to meet applicable ASME and Navy Qualification Standards.

KAPL (21) has also evaluated the MIL-EN87 wire for naval nuclear applications and have concluded that it is acceptable for power plant application and cladding and that structural welds can meet current naval nuclear qualification requirements. The MIL-EN87 wire is superior to Inco Weld A wire for weld cladding from the aspect of arc characteristics and overlay quality and the cladding quality is not impaired by high base metal dilution.

At stress relieving and service temperature of 1050° to 1400°F, MIL-EN87 does not show any significant response to age hardening. The corrosion properties of MIL-EN87 in a water environment are comparable to wrought Inconel, even with a high iron dilution.

International Nickel Company (22) reports that MIL-EN87 filler wire for inert-gas-shielded-metal-arc welding has produced crack free or porosity free welds under conditions of high restraint in 15% chromium, 7% iron, nickel alloy and between nickel-chromium iron alloy and carbon steel and is well suited for overlaying carbon steel in heavy sections. Inco also reports that tube-to-tube sheet welds free of cracking and porosity have been made successfully between MIL-EN87 overlays and nickel-chromium - iron tubes with the inert-gas-tungsten-arc process without filler metal addition.

The high temperature strength properties of Inconel type welds and overlays are also of interest to establish allowable design stresses. The following short-time-high-temperature tensile data compare the properties of cold rolled, annealed Inconel with overlay deposits of MIL-EN87 and MIL-4N85 at 1200°F.

	MIL-EN87	MIL-4N85 (1100°F)	Inconel
Tensile Strength, psi	67,700	68,400	62,000
Yield Strength, psi	42,500	41,400	20,000
Elong %	29.5	40	30-40

Even though creep and stress-rupture data are not available, the above short-time - high temperature tensile properties indicate that both alloys have slightly higher strength than cold rolled annealed inconel. Since the chemical compositions are quite similar, allowable design stresses for annealed inconel will be used for both EN87 and 4N85 weld deposits. Although consideration of the cladding strength is not permitted in determination of material thicknesses for tubes or tube sheets, the high temperature properties of Inconel type welds must be defined for design of the tube-to-tube sheet joints.

On the basis of the above information, the MIL-4N85 coated electrode and the MIL-EN87 wire for electric arc and metal-inert-gas-shielded-arc (MIG) processes, respectively, are considered to be the most applicable for developing welding and overlaying procedures for the steam generator.

HIGH TEMPERATURE STRENGTH OF WROUGHT INCONEL

The effects on the strength properties of Inconel after exposure to air and steam at 1200, 1350 and 1500°F are reported in the ASME paper 59-PWR-1, "Metallurgical Evaluation of Superheater Tube Alloys After Six Months Exposure at Temperatures of 1100 to 1500°F". (23) Corrosion by the air and steam environments was not indicated, but was assumed to be very slight. The short-time tensile, hardness and impact properties reported in this paper are listed below:

Test Temperature		Tensile Strength psi	0.2% Yield psi	Elongation in 1.5", %	Reduction of Area, %	Brinell Hardness	Charpy V-notch ft-lb
Room	(1)	84,500	24,500	56.0	66.0	128	207, 202, 218
	(2)	89,400	28,600	48.0	65.0	132	144, 146, 141
	(3)	88,700	27,100	49.0	64.0	126	184, 217, 200
	(4)	86,000	26,200	50.0	68.0	121	184, 192, 187
1200°F	(1)	64,900	15,800	56.0	63.0		174, 171, 170
	(2)	59,500	17,350	44.0	56.0		181, 165, 162
1350°F	(1)[a]	61,000	15,500	54.0	58.0		168, 184, 172
	(3)	61,350	15,400	42.0	47.0		202, 175, 219
1500°F	(1)	42,750	14,500	67.0	74.0		167, 174, 170
	(4)	51,500	14,500	45.0	42.0		167, 170, 162

(1) Unexposed.
(2) After 6 months at 1200°F.
(3) At 1350°F.
(4) At 1500°F.
a 1300°F rather than 1350°F. The Inconel was solution quenched from 2050°F before exposure.

From these data, it is evident that previous exposure to elevated temperatures has little effect on the room or high temperature mechanical properties of Inconel. The slight increase in room temperature tensile and yield strength and reduction in impact properties, may be a result of a precipitation hardening reaction, or the presence of a grain boundary constituent, but the effect is insignificant. The 1200°F short-time tensile properties are slightly reduced after six months exposure to 1200°F, but this effect is also of little consequence. It may, therefore, be concluded that the long-time exposure to the design temperatures of the steam generator will have little or no effect on the mechanical properties of Inconel.

CONCLUSIONS

Consideration of the information presented in this report has led to the following conclusions.

(1) Inconel is resistant to stress corrosion cracking in chloride and dilute caustic environments.

(2) Inconel affords good corrosion and erosion resistance under all conditions of steam exposure anticipated in the steam generator.

(3) Inconel is not subject to deleterious precipitation hardening and has satisfactory mechanical properties for the intended application.

(4) An Inconel type welding wire, EN-87, or 4N85 electrode can be used to deposit an overlay on tube sheet and channel ends with adequate corrosion resistance and mechanical properties for the intended service.

It is expected that these conclusions will be verified by metallurgical analysis of a once-through boiler model which will be tested under simulated service conditions at Alco Products, Incorporated.

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