1994

Integrity of rewelded thin wall 316L stainless steel tube

Odell McWane
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

McWane, Odell, "Integrity of rewelded thin wall 316L stainless steel tube" (1994). *Master's Theses*. 782.
DOI: <https://doi.org/10.31979/etd.s4me-6uxe>
https://scholarworks.sjsu.edu/etd_theses/782

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 1358206

Integrity of rewelded thin wall 316L stainless steel tube

McWane, Odell, M.S.

San Jose State University, 1994

U·M·I

**300 N. Zeeb Rd.
Ann Arbor, MI 48106**

**INTEGRITY OF REWELDED THIN WALL 316L
STAINLESS STEEL TUBE**

A Thesis

Presented to

**The Faculty of the Department of Materials Engineering
San Jose State University**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

by

Odell McWane

May, 1994

Thesis Advisor

Dr. Guna Selvaduray

Copyright May 1994
All rights reserved

Odell McWane

APPROVED FOR THE DEPARTMENT OF MATERIALS
ENGINEERING

Dr. Guna Selvaduray

Dr. Seth Bates

Dr. Nabil A. Ibrahim

APPROVED FOR THE UNIVERSITY

Serena J. Stanford

ABSTRACT

INTEGRITY OF REWELDED THIN WALL 316L STAINLESS STEEL TUBE

by Odell McWane

This study investigates the relationship between the number of reweld repair cycles, and their affect on the corrosion resistance of thin wall (0.065 inch) 316L stainless steel tube. The automatic and manual autogenous gas tungsten arc process is used to simulate the repair of welds by using up to five welding cycles to reweld existing welds.

The Electrochemical Potentiokinetic Reactivation test (EPR) and metallographic examination are used to evaluate the rewelded specimens.

No specimens for the heats of material in the study developed a sensitized microstructure.

Each heat of stainless steel tube in this study is capable of being rewelded using five welding cycles without loosing its corrosion resistance.

ACKNOWLEDGMENTS

Gratitude is expressed to my thesis advisor Dr. Guna Selvaduray, Professor Materials Engineering Department, and to my reading committee members, Dr. Seth Bates Associate Professor Division of Technology, and Dr. Nabil A. Ibrahim Chairperson General Engineering Department for their helpful comments and critique of the thesis project and manuscript.

Special recognition and thanks is given to Mr. William A. Bianco, President of Kinetic Systems inc., for providing the facilities, personnel, material and equipment in support of this project. I would also like to thank Mr. Douglas J. Galvin, Mr. Ken Burns, and Mr. Dan Likeness for their assistance in scheduling the shop welding activities. Thanks also goes to Mr. Rodney Belnap, Mr. Dave Rodriguez, Mr. Ken Snarr, and Mr. Johnny Martinez whose welding skills made this project a success.

From the General Electric Company, I would like to thank Mr. Barry Gordon for his generous supply of reference material on the EPR test, and Mr. Gail Dunning for his insight, experience and suggestions regarding the EPR test.

TABLE OF CONTENTS

CHAPTER	PAGE
ABSTRACT	
ACKNOWLEDGMENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
1. INTRODUCTION	1
1.1 Background	1
2. LITERATURE REVIEW	6
2.1 Sensitization	6
2.1.1 Effect of heat input	8
2.1.2 Effect of preheat	9
2.1.3 Effect of interpass temperature	9
2.1.4 Detection of sensitization	10
2.1.5 Correction of sensitization	12
2.2 Historical Review	13
2.2.1 Alloy development	14
2.2.2 Thermodynamics	17
2.2.3 Role of alloying elements	23
2.2.4 Role of ferrite	25
2.2.5 Effect of welding strain	27
2.2.6 Effect of cold work strain	29
2.2.7 Effect of grain size	29
3. OBJECTIVES	30

4.	HYPOTHESIS	31
5.	EXPERIMENTAL PROCEDURE	32
	5.1 General	32
	5.2 Materials	34
	5.3 Welding processes	35
	5.4 Corrosion test	36
6.	RESULTS	39
7.	DISCUSSION	58
8.	CONCLUSIONS	64
	REFERENCES	67
	BIBLIOGRAPHY	70
	APPENDIX A. Automatic Gas Tungsten Arc Parameters used for each heat of material	71
	APPENDIX B. Manual Gas Tungsten Arc Parameters used for each heat of material	72

LIST OF TABLES

Table	Page
I. Development of stainless steel for weldability and corrosion resistance	13
II. General affects of alloying, residual and minor elements on the sensitization of austenitic stainless steel	24
III. Chemical composition of 316L tube materials in wt%	34
IV. Automatic GTAW parameters for each heat of 316L material	35
V. Manual welding parameters for each heat of 316L material	36
VI. EPR test parameters and conditions	38
VII. Results of EPR tests	39
VIII. General interpretation for degree of sensitization based on Pa number	41
IX. EPR test results for unwelded heat treated specimens	51

LIST OF FIGURES

Figure	Page
1. Weld showing incomplete fusion	2
2. Weld showing inadequate joint penetration	3
3. Completed weld showing heat affected zone	4
4. Schematic showing log current density vs potential for a sensitized and unsensitized stainless steel	12
5. Degree of sensitization vs number of welding cycles for the automatic gas tungsten arc process	42
6. Degree of sensitization vs number of welding cycles for the manual gas tungsten arc process	43
7. Specimen No. 10 showing typical clean microstructure found in heat No. 913842 material .	44
8. Specimen No. 20 showing typical inclusions found in some specimens of heat No.'s 710954 and 855911 materials	45
9. As received, solution annealed 316L specimen number 12	46
10. One cycle automatic weld showing heat affected zone	47
11. Five cycle automatic weld showing heat affected zone	48
12. One cycle manual weld showing heat affected zone	49
13. Five cycle manual weld showing heat affected zone	50
14. Type 304 alloy, specimen no. 3A showing heavily sensitized microstructure.	52
15. Specimen no. 12HT, heat 710954, showing slightly sensitized microstructure	53

16.	One cycle automatic weld showing distribution of ferrite	54
17.	Five cycle automatic weld showing distribution of ferrite	55
18.	One cycle manual weld showing distribution of ferrite	56
19.	Five cycle manual weld showing distribution of ferrite	57

CHAPTER 1

INTRODUCTION

1.1 Background

The Food and Drug Administration's Good Manufacturing Practice (GMP) regulations for drug products state, in part, that constructed equipment used for the manufacture and transport of drug products shall be maintained in a sanitary condition. The sanitary requirements are to prevent contamination and harmful bacteria growth in the equipment used to manufacture the drug product.

To comply with the sanitary requirements of the Good Manufacturing Practice regulations, pharmaceutical manufacturers use equipment made of materials that can be easily cleaned and maintained in a sanitary condition, such as 316L austenitic stainless steel vessels, tube, pipe, fittings and valves.

Welded joints are used to make permanent connections in the stainless steel tube materials which not only carry the raw materials for processing, but also the finished products. Since permanent joints cannot be taken apart for cleaning, these joints must be capable of being cleaned in place. Therefore, welded joints must not contain defects which will reduce the effectiveness of the cleaning operation and thereby contribute to the contamination of the drug products. Those

joints which do contain defects must be repairable without reducing the corrosion resistance of the stainless steel materials.

In the pharmaceutical industry, thin wall (0.035" - 0.083") 316L austenitic stainless steel tube is the material of choice for transporting process fluids because of its cleanability, corrosion resistance and weldability. However, the welding process may produce incomplete fusion or inadequate penetration, as illustrated in Figures 1 and 2, respectively. Either of these weld defects must be repaired because they provide sites for bacterial growth and/or corrosion products to accumulate, thus reducing the ability of the pharmaceutical manufacturer to maintain a sanitary system.

Figure 1. Weld showing incomplete fusion

Figure 2. Weld showing inadequate joint penetration

When a repair is required, it may be accomplished in one of two ways:

- (1) Cut the weld out, prepare the tube for rewelding, then reweld. This method is time consuming and expensive, especially when access to the joint is limited. Typically two welds are required to replace one cut-out weld.
- (2) Reweld the joint by welding over the previous weld. This method is the least time consuming and least expensive.

Repair method 2 is desirable for practical and economic reasons. However, there is a concern regarding how many times

a joint can be rewelded by remelting the previous weld without adversely affecting the corrosion resistance of the base metal's heat-affected zone, which is shown in Figure 3.

Figure 3. Completed weld showing heat-affected zone

When austenitic stainless steel is heated such as by welding in the range between 427°C - 871°C (800°F - 1600°F) for a sufficient period of time, chromium carbide (Cr_{23}C_6) will precipitate at the grain boundaries in the base metal's heat-affected zone (HAZ). The precipitated carbides will leave a portion of the stainless steel grains at the grain boundaries depleted in the necessary 12% chromium content, which is required for corrosion resistance. Under these circumstances the HAZ is sensitized. That is, the HAZ is

susceptible to intergranular corrosion.

When austenitic stainless steels become sensitized, the steel is incapable of providing and maintaining the strong chromium oxide surface layer needed for corrosion resistance. In other words, those areas in the HAZ which have been depleted in chromium will not respond adequately to passivation, whether naturally occurring (by oxygen in air), or induced (by oxidizing solution). Pharmaceutical manufacturers use a variety of chemical solutions for cleaning, sterilizing, disinfecting, sanitizing and product formulation, in addition to pure water and water for injection. These solutions are potentially corrosive to a sensitized HAZ. Therefore, the repair method must not degrade the corrosion resistance of the HAZ.

Currently, for incomplete fusion and inadequate penetration defects, typical industry practice is to allow one reweld before a weld is cut out and replaced. If it can be shown that several rewelds are possible without sensitizing the base metal's HAZ, a substantial cost saving is possible. Therefore, this study proposes to determine the feasibility of rewelding 316L stainless steel using the automatic and manual autogenous gas tungsten arc welding processes, while maintaining the corrosion resistance and integrity of the joint for use in a pharmaceutical manufacturing environment.

CHAPTER 2

LITERATURE REVIEW

As a review of fundamentals and a aid in formulating and conducting the present study, a comprehensive literature review was undertaken to determine the state of the art of the carbide precipitation phenomena as it relates to welding, and the base metal heat affected zone. Therefore in addition to the theory of carbide precipitation, this chapter also contains a historical review of alloy development to control precipitation, factors which promote precipitation, and methods to detect and prevent precipitation.

2.1 Sensitization

Most sensitization studies⁽¹⁾ have been conducted by isothermal methods which simulate service conditions or heat treating. These studies are not very relevant to welding because of the continuous cooling in the weld heat-affected zone.

The most popular theory for the sensitization of austenitic stainless steels, including those sensitized by welding, is the chromium depletion theory, because it agrees with experimental observations and data. This theory states, in part, that when austenitic stainless steels such as 304 and 316 are heated to between 427°C - 871°C (800°F - 1600°F) for

a sufficient period of time, carbon combines with the chromium to form Cr_{23}C_6 which precipitates at the grain boundaries, leaving the iron depleted of the necessary 12% minimum chromium required for corrosion resistance.

Sensitization is time, temperature, and alloy composition dependent. The three main factors which promote sensitization in welding operations are preheat, interpass temperature and welding heat input. The first two variables are not applicable to this study because preheat is not used, and interpass temperature applies only to multiple weld passes being made in a single joint.

Between the two welding process methods being used, the manual method will tend to keep the base metal heat-affected zone in the sensitization temperature range the longest, because it produces the greater heat input. Heat input using the manual method is calculated using the following formula:⁽²⁾

$$\text{Heat Input (Joules/inch)} = \frac{V \times A \times 60}{T} \quad [1]$$

where V is the welding voltage, A the welding amperes, T the travel speed in inches/minute and 60 is a conversion factor to change minutes to seconds.

The automatic method produces the least heat input,

because it pulses the amperes between a high and low value rather than maintaining a relatively constant value as does the manual process. The high pulse amperes provides the weld penetration, whereas the low pulse value provides a cooling effect. Also the heat input is lowered because the travel speed is generally faster. Formula [1] is also used to calculate the heat input for the automatic process, except the value for the amperes is the weighted average value, determined as follows:⁽³⁾

$$I = \frac{I_B \times T_B + I_P \times T_P}{T_B + T_P} \quad [2]$$

I = average amperes

I_P = pulse peak amperes

I_B = background amperes

T_P = pulse peak time

T_B = background time

2.1.1.1 Effects of heat input

Welding heat input controls the time the base metal heat-affected zone remains in the critical sensitizing temperature range. High welding heat input promotes sensitization by promoting slow cooling rates and longer residence times in the critical temperature ranges. Low welding heat input promotes

high cooling rates and reduced times in the critical sensitizing temperature range.

2.1.2 Effects of preheat

Preheating is heating the weld joint to a predetermined temperature before welding. Preheating has the same effect as high welding heat input.

A recent study⁽¹⁾ of simulated welding of two 304 heats using the Gleeble test, showed that at a carbon level of 0.057%, the material showed insignificant sensitization when welded using 70KJ/in. heat input with up to 204⁰C (400⁰F) preheat, and 40KJ/in. heat input with up to 316⁰C (600⁰F) preheat. On the other hand, a 304 material with a carbon content of 0.078%C showed significant sensitization when welded using only 40KJ/in. at 22⁰C (77⁰F). This study confirms what has long been known, i.e., the higher the carbon content, the lower the tolerance for heat input and preheat. In other words, as the carbon content increases, the susceptibility of the steel to sensitization also increases, therefore the heat input and preheat must be held to lower levels.

2.1.3 Effects of interpass temperature

The interpass temperature is the temperature of the previous weld bead just before making another weld bead on top

of it. The interpass temperature has the same affect as high welding heat input. Interpass temperatures are associated with welding thick materials which require multiple weld beads and therefore multiple cycling. Studies^(1,4) have shown that multiple cycles which reached temperatures greater than 1204⁰C (2200⁰F) showed insignificant sensitization as compared to those which reached 870⁰C (1600⁰F). That is, the multiple cycling was additive for the lower peak temperature and not additive for the higher temperature. The explanation of this was that at the higher peak temperature any carbide precipitation in a previous weld HAZ was resolutioned at the higher temperature.

2.1.4 Detection of sensitization

Two methods were cited in the literature⁽¹⁾ for the detection of sensitization and carbide precipitation. The first method, ASTM A262 practice A, is an oxalic acid etch test which emphasizes the visual appearance of the grain boundary area for interpretation. The oxalic acid etch test is a qualitative test, and can be used only for screening or detecting the existence of chromium carbides along the grain boundary. It cannot measure the degree of sensitization.

The second test method, the Electrochemical Potentiokinetic Reactivation test (EPR) is based on measuring the amount of current required to reduce the thin passive

oxide film formed on the chromium depleted area at the grain boundaries.

The EPR method is performed by placing a sample of the material in a suitable oxidizing solution, then passivating the material at a positive electrochemical potential for a pre-determined length of time. The sample is then scanned in the negative direction at a controlled pre-determined rate. The resulting current is integrated, yielding the number of coulombs required to reduce the passive film.

A sensitized steel (unstable oxide), produces a curve with a high current density, whereas a nonsensitized steel (stable oxide) will produce a curve with a low current density as illustrated in Figure 4. Between the two test methods, the EPR test is considered to be a better quantitative method, and it also has a greater sensitivity to low degrees of sensitization.⁽¹⁾ It was also pointed out that for any test method the degree of sensitization is not directly correlated with the quantity of carbide precipitation in the grain boundary, but the distribution.

Figure 4. Schematic showing log current density vs potential for a sensitized and unsensitized stainless steel.⁽²⁰⁾

2.1.5 Correction of sensitization

To correct sensitization in 316L alloys, the carbide precipitation can be reversed by heating the affected material to between 1066°C - 1093°C (1950°F - 2000°F), holding at this temperature for approximately 1/2 hour per inch of material thickness, and rapidly cooling in water or inert gas. This corrective option is only practical for items small enough to be placed in a furnace, but not for tube welded in place. Sensitization can also be corrected by holding the material for an extended period of time at the temperature which caused

the precipitation.⁽⁵⁾ This self healing is caused by the diffusion of chromium from other grain areas into the chromium depleted area after the depletion of the available carbon due to carbide precipitation.

2.2 Historical Review

Because type 304 austenitic stainless steel has been the most widely used for welded fabrications requiring corrosion resistance, it has been the most widely studied with regard to carbide precipitation via welding. Table I lists the historical development of the most common austenitic stainless steels listed according to general weldability and corrosion resistance, beginning with the basic 304 alloy.

Table I. Development of stainless steel for weldability and corrosion resistance.

STAINLESS STEELS	APPLICABLE ELEMENTS IN WT% ⁽²¹⁾
304	0.08C Max.
304L	0.035C Max.
316	2.00 - 3.00 Mo. & 0.08C Max.
316L	2.00 - 3.00 Mo. & 0.035C Max.
317	3.00 - 4.00 Mo. & 0.08C Max.
317L	3.00 - 4.00 Mo. & 0.035C Max.
321	Ti 5 x C Min. (0.70% Max.)
347	Nb + Ta 10 x C Min. (1.0% Max.)

2.2.1 Alloy development

Since type 304 stainless steel has been the most popular material for welded fabrications requiring corrosion resistance, efforts were made to improve its corrosion resistance in the HAZ after welding. The first action taken was to lower the carbon content from approximately 0.08 wt.% maximum to 0.035 wt.% maximum, producing a 304L material, the reason being that a lower carbon content will provide less carbon to form chromium carbide, thereby slowing or eliminating the carbide precipitation process. From a kinetics point of view this makes sense when Fick's First Law is applied to real alloys, and where the diffusion coefficient D is considered to vary with composition.⁽⁶⁾ Under these circumstances interstitial carbon diffusion decreases as the concentration (percentage) of carbon decreases. The reasoning is that with a low percentage of carbon, statistically the movement of the carbon atoms is slowed, whereas with a high percentage of carbon atoms, the lattice structure is strained, providing more statistical freedom of movement for the atoms. Experience⁽¹⁾ has shown that lowering the carbon content does reduce the onset of carbide precipitation. How much the carbon is lowered depends on the time at temperature in the carbide precipitation range.

Additional improvements were made to the base metal HAZ for corrosion resistance by modifying the 304L alloy. This

improvement resulted in two new alloys: 316 and 316L. The 316L alloy contains the same low carbon content as the 304L, to reduce the availability of carbon for carbide precipitation. The basic difference between the 304 and 316 alloys is the addition of molybdenum to the 316 alloy. The addition of molybdenum does not prevent sensitization, but it does slow the reaction.

Researchers are not clear as to the exact role of molybdenum in the slower sensitization of 316 alloys. Briggs⁽⁷⁾ states that molybdenum increases the stability in the passive condition and the capability for passivation by forming an invisible protective oxide film. Colombier⁽⁸⁾ states that "...the alpha-forming molybdenum can cause the appearance of ferrite in the structure and we have seen that the austenitic-ferrite steels are not very susceptible to intergranular corrosion." He also states that "...molybdenum raises the tolerance for carbon in purely austenitic steels...this fact can be attributed to the fixation of part of the carbon in the form of molybdenum carbide, with molybdenum acting in this case like the other carbide-forming elements titanium and columbium."

Continued improvements to the base metal HAZ corrosion resistance resulted in the development of 317 and 317L. The low carbon in 317L serves the same purpose as in 316L. The difference between 316 and 317 alloys is the increase in

molybdenum from a maximum of 3% to a maximum of 4%.

The corrosion resistance of stainless steel alloys 321 and 347 are obtained by stabilizing the carbon with elements which have a greater affinity for carbon than chromium. Titanium is used as a stabilizer for alloy 321 and niobium plus tantalum for alloy 347. The sequence of events for carbide precipitation is different for these alloys than for types 304, 316, and 317. When received from the mill, the carbon in alloys 321 and 347 are in the form of titanium carbide, and niobium + tantalum carbides, respectively. These carbides form between 871°C - 1149°C (1600°F - 2100°F) and chromium carbides are dissolved in this temperature range. When the alloys are welded and rapidly cooled, the area adjacent to the weld which reaches 1427°C - 1482°C (2600°F - 2700°F) will dissolve all carbides and keep them in solution on cooling to room temperature. When the alloy is subsequently reheated to between 427°C - 871°C (800°F - 1600°F), the temperature range at which chromium carbides form, chromium carbide precipitation will occur because titanium, and niobium + tantalum carbides are in solution and not available for stabilization. However, chromium carbide precipitation can be prevented in these alloys by reheating above the chromium carbide precipitation temperature range, e.g. 871°C - 1149°C (1600°F - 2100°F) to form titanium and niobium + tantalum carbides, then cooled at any desired rate.

In summary, the development of the weldability and corrosion resistance in the stainless steel alloys consisted of lowering the carbon content, and/or adding molybdenum, titanium, niobium and tantalum to stabilize the alloy at high temperatures.

2.2.2 Thermodynamics

A search and review of the literature revealed very few articles treating welding and physical metallurgy from a thermodynamics point of view. A possible reason for the lack of literature may be that welding, and those physical metallurgical heat treating processes of commercial interest, are performed under nonequilibrium conditions, whereas most thermodynamic characterization of processes are done under equilibrium conditions. However, thermodynamics can be used as a general guide for some welding and heat treating applications since it does reveal the direction taken by a chemical reaction.

Thermodynamics is concerned with whether or not a given reaction will occur. It can be used to predict whether a chemical reaction is theoretically possible under a given set of conditions. The thermodynamic function used to determine the feasibility of a reaction is the change in Gibbs free energy, ΔG , for the reaction. The Gibbs free energy may be positive, zero, or negative.

When ΔG is positive a reaction is spontaneous in the opposite direction. For example, if the reaction

is assumed to occur between temperatures T_1 - T_2 , and written as shown, a positive ΔG would change the reaction to

which is not possible without a driving force such as a solution heat treatment between temperatures T_3 - T_4 , where $(T_3 - T_4) > (T_1 - T_2)$.

When $\Delta G = 0$ the reaction is in equilibrium. For the reaction

the chromium would be in equilibrium with the carbon and Cr_{23}C_6 . The temperature at which this occurs can be evaluated using the following formula:

$$\Delta G = \Delta G^0 + RT \ln K \quad [6]$$

where R is the universal gas constant, T the equilibrium temperature, K the equilibrium constant, and ΔG^0 the Standard

Gibbs free energy change for the reaction. Setting ΔG equal to zero results in

$$-\Delta G^0 = RT \ln K \quad [7]$$

Evaluating K leads to⁽¹⁾

$$K = \frac{a_{Cr_{23}C_6}}{a_{Cr}^{23} a_C^6} = \frac{1}{(\gamma_{Cr} X_{Cr})^{23} (\gamma_C X_C)^6} \quad [8]$$

where a is the activity of the species, γ the respective activity coefficients, and X the mole fraction. To evaluate K, the activity for chromium carbide is assumed to be 1.

The mole fractions X_{Cr} and X_C can be taken from the chemical composition of the material. However values for γ are not available in the literature.⁽⁹⁾ These values may be obtained by using the Wagner analysis,⁽⁹⁾ a complicated mathematical analysis using available experimental data and taking into consideration the effects of the other alloying elements in the material. Once these values are obtained and a value for ΔG^0 and R are taken from the literature, the equation can be solved for the equilibrium temperature. A less tedious and more direct method to determine the

equilibrium temperature is to use an Ellingham Diagram for the stability of carbides.⁽¹⁰⁾

When ΔG is negative the reaction is spontaneous in the direction written. The more negative the ΔG , the greater the tendency for the formation of the carbides. For ease of comparing the tendency for carbide formation, ΔG may be defined in terms of ΔH^0 , and ΔS^0 as

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad [9]$$

since values for these quantities are readily available in the literature.⁽¹¹⁾ ΔH^0 is the standard change in enthalpy, and ΔS^0 is the standard change in entropy, and T is the temperature of concern.

Consider the carbide reactions which occur in the stainless steels listed in Table I. For all alloys the chromium carbide formation reaction can be written as

The corresponding Standard Gibbs free energy change in the $427^0\text{C} - 871^0\text{C}$ ($800\text{F} - 1600^0\text{F}$) temperature range is:

$$\begin{aligned} \Delta G^0 &= -16,380 - 1.54T \text{ cal}^{(12)} \\ \Delta G^0 &= -17,458 \text{ cal to } -18,142 \text{ cal} \end{aligned} \quad [11]$$

For 316, 316L, 317, 317L the following additional reactions also occur between the above temperatures:

The corresponding Standard Gibbs free energy change in the temperature range of interest is:

$$\Delta G^0 = 4,200 - 4.8T \text{ cal}^{(13)} \quad [13]$$

$$\Delta G^0 = 840 \text{ cal to } -1291 \text{ cal}$$

For 321 stainless steel the following additional reaction occurs:

The corresponding Standard Gibbs free energy change in the temperature range of interest is:

$$\Delta G^0 = -186,000 + 10.0T^{(14)} \quad [15]$$

$$\Delta G^0 = -179,000 \text{ cal to } -174,560 \text{ cal}$$

For 347 stainless steel, the following additional reactions occur.

The corresponding Standard Gibbs free energy change in the temperature range of interest for NbC and TaC respectively are:

$$\begin{aligned} \Delta G^0 &= -141,000 + 4.98T^{(14)} & [18] \\ \Delta G^0 &= -137,514 \text{ cal to } -135,302 \text{ cal} \end{aligned}$$

$$\begin{aligned} \Delta G^0 &= -161,000 + 4.85T \text{ cal}^{(14)} & [19] \\ \Delta G^0 &= -157,605 \text{ cal to } -155,452 \text{ cal} \end{aligned}$$

For the 304 and 304L alloys, chromium carbide forms spontaneously in the temperature range of interest, as shown by Eqs. [10] and [11].

Chromium reduces the carbon activity more than molybdenum does at 1560°C.⁽¹⁵⁾ Assuming this is true for the 316 and 317 alloys in the temperature range of interest, carbon therefore will tend to combine with chromium rather than molybdenum. This is also indicated by the large negative ΔG^0 for chromium carbide, as shown by Eq. [11], as compared to molybdenum carbide, as shown by Eq. [13]. It also appears that the mechanism by which molybdenum provides corrosion resistance to the 316 and 317 alloys is other than by forming Mo₂C.

The stabilizing carbides, TiC, NbC, and TaC will form in alloys 321 and 347, respectively, in preference to the formation of Cr_{23}C_6 , as evidenced by the large negative ΔG^0 for these carbides, as shown by Eqs [15], [18], & [19], as compared to that for Cr_{23}C_6 , as shown by Eq. [11], provided these carbides are available through proper heating and cooling sequences.

2.2.3 Role of alloying elements

A review of the literature indicates that the exact mechanism by which the alloying elements influence chromium carbide precipitation is not known. However, in general researches have found that alloying elements can be classified in one of three categories with respect to their effect on the sensitization of austenitic stainless steel:

Beneficial - Cr, N, Mo, Mn, B, Nb, Ti, Ta

Detrimental - C, P, S, Ni, Si, Co

No Influence - O, H

Shown in Table II are the alloying elements typically found in austenitic stainless steel, and the proposed mechanism for influencing carbide precipitation and the sensitization of austenitic stainless steel.

Table II. General affects of alloying, residual and minor elements on the sensitization of austenitic stainless steel

ELEMENT	GENERAL AFFECTS OF THE ELEMENTS
Chromium	Increases the time for sensitization with contents ⁽²²⁾
Nitrogen	Increases the time for sensitization by retarding the nucleation and/or growth of carbides at the grain boundaries ⁽¹⁾
Molybdenum	Increases the ease of passivation in low chromium areas. Reinforces the beneficial affect of nitrogen by forming compounds with nitrogen ⁽¹⁾
Phosphorus	Retards the beneficial affect of nitrogen when both are segregated to the grain boundaries ⁽¹⁾
Carbon	Promotes sensitization by combining with chromium to form chromium carbide which precipitates at the grain boundary ^(1,22)
Nickel	Increases the potential to form carbide precipitation by increasing the carbon activity and reducing it's solubility in the austenite matrix ^(1,22)
Niobium	Retards the precipitation of chromium carbides at the grain boundaries by forming niobium carbides with the available carbon ^(1,22)
Titanium	Retards the precipitation of chromium carbides at the grain boundaries by forming titanium carbides with the available carbon ^(1,22)
Tantalum	Retards the precipitation of chromium carbides at the grain boundaries by forming tantalum carbides with the available carbon ^(1,22)
Manganese	Slows the chromium carbide precipitation rate by reducing the carbon activity and increasing its solubility in the austenite matrix ⁽²²⁾

Table II
(cont.)

Silicon	Increases the potential to form carbide precipitation by increasing the carbon activity ⁽²²⁾
Sulphur	No noticeable influence on the nucleation and growth of carbides ⁽²⁹⁾
Copper	The role of copper is not clear ⁽³²⁾
Boron	Tends to suppress grain boundary precipitates, exact mechanism employed is uncertain ⁽²⁸⁾
Oxygen	No noticeable influence on the precipitation processes occurring in stainless steel ⁽²²⁾
Hydrogen	No noticeable influence on the precipitation processes occurring in stainless steel ⁽²²⁾
Cobalt	Increases the activity and diffusivity of carbon and tenancy for precipitation ⁽²⁸⁾

2.2.4 Role of Ferrite

In 316L stainless steel delta ferrite is a single phase solid solution whose main elements are iron and chromium. Delta ferrite is formed in weld metals when welding austenitic stainless steel, including welds made without the use of weld filler metals (autogenous welds). The purpose of delta ferrite is to prevent hot cracking in a weld as it solidifies from the liquid state.⁽²³⁾ When welds made in austenitic stainless steels solidify on cooling from the liquid state, the weld will solidify as either primary austenite or primary

ferrite.

When the weld solidifies as primary austenite, low melting point impurities such as phosphorus and sulphur will concentrate at the dendrite interstices of the weld and fusion zone, and the grain boundaries of the HAZ, due to their low solubility in austenite. Upon continued cooling to room temperature, the austenite will contract, putting a shrinkage strain across the dendritic and grain boundaries. As a result of the shrinkage strain, a stress is developed in the semi-solidified low melting point impurities, thus causing interdendritic and intergranular cracking.^(24,25)

When the weld solidifies as primary delta ferrite, the low melting point impurities are absorbed by the delta ferrite phase due to their higher solubility in the ferrite phase, as compared to the austenite phase. Upon continued cooling to room temperature, the impurities remain in solution and no interdendritic or intergranular cracking occur.

The factors that determine whether the weld will solidify as primary austenite, or primary ferrite, are the cooling rate of the weld and the chemical composition of the weld filler metal and base metal, or the base metal, in the case when no filler metal is being used. High cooling rate welds (low heat input) tend to solidify as primary austenite. Low cooling rate welds (high heat input) tend to solidify as primary ferrite.⁽²⁴⁾

Manufacturers of weld filler metals, and base metals which are to be welded with and without the use of filler metals, design their metals to produce the ferrite phase in the weld bead. The metal manufacturers use the Welding Research Council (WRC) constitution diagram⁽²⁷⁾ as a guide to control the chemistry of deposited weld metals in order to produce the ferrite phase. Typically a minimum of 3 vol% (FN 3) ferrite is required to prevent hot cracking.^(23,26)

With respect to the influence of ferrite on carbide precipitation, it is generally agreed that the presence of ferrite in the weld metal has a beneficial effect on carbide precipitation and the resulting sensitization. Explanations given are:

- (1) The ferrite offers a large interphase boundary area for carbide precipitation; therefore, the chromium depletion at any one point is minimized.^(30,31)
- (2) The ferrite islands are distributed such that there are no continuous networks of precipitates in the austenite-ferrite grain boundaries.⁽³⁰⁾
- (3) The ferrite contains a greater amount of chromium than austenite and thus is not preferentially attacked.⁽³⁰⁾

2.2.5 Effect of Welding Strain

When a weld is being made in an unrestrained plate, the hot weld metal expands, pulling on the relatively cold

adjacent base metal, thus putting the base metal in tension. The base metal resists the expansion of the weld and therefore puts the expanding weld in compression.

On cooling the weld contracts, pulling the adjacent base metal in the opposite direction, and thus putting the base metal in compression. The base metal resists the contraction of the weld and therefore puts the weld in tension. These stresses become more complicated when considering volumetric expansions and contractions of real world welded joints, and the situation becomes more compounded by multiple welding cycles.

Researchers⁽¹⁾ have found that the affects of single and multiple cycle welding on sensitization are dependent upon the peak temperatures reached. At high peak temperatures, 1204⁰C (2200⁰F) or above, there is little affect. At a peak temperature of 871⁰C (1600⁰F) the strain is additive to the thermal affect. In other words, the degree of sensitization is increased due to the thermomechanical cycle. An explanation for this phenomenon is that the strain may increase the diffusivity through dislocation enhanced diffusion and pile-up, thereby providing favorable sites for nucleation of carbides and chromium depletion.

2.2.6 Effect of Cold Work Strain

Cold work, such as that which may occur in tube bending or straightening, tends to lower the temperature range at which carbide precipitation occurs. Cold work tends to increase the dislocation density in the grain boundary area, resulting in high energy areas which favor the precipitation and growth of carbides.⁽¹⁾

2.2.7 Effect of Grain Size

Sensitivity to intergranular corrosion is promoted by increased grain size. However since grain size is related to time at temperature, the effect of grain size cannot be separated from the fact that greater times at temperature also produce more carbide precipitation. Therefore, the grain size effect may be a combination of grain growth and carbide precipitation. From a practical point of view, grain coarsening as a result of welding has not been a problem,⁽³¹⁾ since the time at temperature in the HAZ zone is very short.

CHAPTER 3

OBJECTIVES

The objectives of this study were to:

- (1) Investigate the relationship between the degree of sensitization and the number of welding cycles for 316L stainless steel.
- (2) Use the information obtained to evaluate a welding repair alternative for joints containing incomplete fusion and inadequate penetration.

CHAPTER 4

HYPOTHESIS

Carbide precipitation is time, temperature, and composition dependent. In order for carbide precipitation to occur in the HAZ of welded 316L stainless steel, the HAZ must remain in the sensitization temperature range for a sufficient period of time to allow the carbon to combine with the chromium to form chromium carbide, and precipitate at the grain boundary.

The time the HAZ remains in the sensitizing temperature range increases with increasing welding heat input. The time in the sensitizing temperature range is also approximately additive for each welding cycle.

Therefore, since 316L stainless steel is stabilized with a low carbon content and molybdenum, it should not become sensitized using the five welding cycles proposed in this study because of the low welding heat input, and the brief time in the sensitizing temperature range for each welding cycle.

CHAPTER 5

EXPERIMENTAL PROCEDURE

5.1 General

To simulate actual field conditions, welding procedures for the automatic method were developed using the same methods (trial and error for appearance) as in the field for pharmaceutical construction.

Since field welding conditions are not ideal, field welding parameters (amperes and travel speed) were developed to obtain defect free weld joints under less than ideal conditions. For example, trial and error was used to obtain wide weld beads (more heat input) as opposed to narrow weld beads (less heat input). Past experience has shown the former to be more forgiving when there is a variation in the material thickness, or when the weld joint contains more than one heat of material, one or both of which may be less than ideal for welding. (16,17,18,)

When developing welding parameters by the trial and error method, typically the amperes and travel speed are set at a predetermined value based on passed experience with the thickness and type of base metal being welded, or based on the recommendations in the instruction manual supplied by the welding equipment manufacturer. If a satisfactory weld is made using the initial trial parameters, the parameters are

then used to make the final welds with no further adjustment. If the initial parameters produce unsatisfactory welds, the parameters are adjusted by increasing and/or decreasing the amperes and/or travel speed until a visually acceptable weld is produced. Several iterations of parameter adjustments may be necessary to obtain a satisfactory weld, depending on the skill and experience of the welding operator.

This study used journeymen welding operators who have had several years experience welding in the pharmaceutical industry. Therefore the number of parameter iterations were minimal. The trial and error method was not used to develop parameters for the manual method because the welder has control of the parameters, and he can adjust them as the weld is being made.

For both the automatic and manual welding methods, the general procedure for welding was to cut the tubes to twelve inch lengths, square the tube ends with a facing tool, deburr tubes, clean cut ends of tubes, tack weld tubes end to end, seal tube openings for inside diameter gas purging, purge inside diameter of tubes with argon gas, weld, clean outside diameter of weld with a stainless steel wire brush, and allow each weld bead to cool to room temperature before rewelding for multiple welding cycles. The required weld specimens were then removed and prepared for corrosion testing using the EPR method.

5.2 Materials

The materials used for this study were 316L stainless steel tubes, two inches in outside diameter, with a wall thickness of 0.065 inches. Each joint to be welded used two twelve inch lengths of tube, tack welded end to end to make a square groove butt joint, with no root opening.

The materials used and their respective specifications and chemical compositions are listed in Table III.

Table III. Chemical composition of 316L tube materials in wt%

Heat Number	918342	710954	855911
Specification	A269/A270	A249/A269	A269/A270
Carbon	0.015	0.018	0.018
Silicon	0.590	0.620	0.410
Manganese	1.72	1.66	1.91
Phosphorus	0.030	0.029	0.031
Sulfur	0.011	0.009	0.014
Chromium	16.38	16.43	16.72
Nickel	10.13	10.18	10.30
Molybdenum	2.08	2.09	2.18
Copper	0.32	0.03	0.25
Cobalt	0.20	0.11	0.14
Nitrogen	0.040	0.039	0.040

5.3 Welding processes

Welding was performed using automatic and manual autogenous gas tungsten arc processes. Automatic welding was performed using a programmable pulse arc welding machine. Welding parameters for welding each heat of material are listed in Table IV, and Appendix A for the automatic process, and Table V and Appendix B for the manual process.

Table IV. Automatic GTAW parameters for each heat of 316L material

Heat No.	Sample No.	No. Weld Cycles	Average Voltage	Average Amperes	Travel Speed in./min.	Heat Input Joules/in.
913842	2	1	9	45.3	3.8	6,437
	3	2	9	45.3	3.8	6,437
	4	3	9	45.3	3.8	6,437
	5	4	9	45.3	3.8	6,437
	6	5	9	45.3	3.8	6,437
710954	18	1	9	45.3	3.8	6,437
	19	2	9	45.3	3.8	6,437
	20	3	9	45.3	3.8	6,437
	21	4	9	45.3	3.8	6,437
	22	5	9	45.3	3.8	6,437
855911	29	1	9	45.3	3.8	6,437
	30	2	9	45.3	3.8	6,437
	31	3	9	45.3	3.8	6,437
	32	4	9	45.3	3.8	6,437
	33	5	9	45.3	3.8	6,437

Note: The heat input values represent the average heat input per cycle. For example, 5 welding cycles represents an average of 32,185 Joules/inch for the joint.

Table V. Manual welding parameters for each heat of 316L material

Heat No.	Sample No.	No. Weld Cycles	Average Voltage	Average Amperes	Travel Speed in./min.	Heat Input Joules/in.
913842	7	1	8.3	32.0	1.2	13,280
	8	2	9.4	41.5	2.2	10,639
	9	3	9.2	35.7	1.8	10,948
	10	4	8.9	38.0	2.0	10,146
	11	5	8.8	35.8	2.1	9,001
710954	13	1	8.5	40.0	2.7	7,555
	14	2	9.2	45.0	3.3	7,527
	15	3	9.7	51.0	3.7	8,022
	16	4	9.4	48.5	3.7	7,393
	17	5	9.7	49.4	3.9	7,372
855911	24	1	8.1	38.0	3.0	6,156
	25	2	8.5	43.0	2.7	8,122
	26	3	9.1	47.3	2.7	9,565
	27	4	9.0	44.3	2.7	8,860
	28	5	9.3	45.8	2.4	10,649

Note: The heat input values represent the average heat input per cycle. For example, sample no. 28 with 5 welding cycles represents an average of 53,245 Joules/inch for the joint.

5.4 Corrosion test

The HAZ and adjacent base metal which represented the specimen to be tested were carefully removed from each tube specimen so as to not include weld metal. The dimensions for the removed specimens were chosen based on the minimum area recommendations of ASTM G108-92, and for ease of handling.

The average dimensions for the EPR test specimens were 1.2 cm X 0.2 cm, which produced a total cross sectional area of 0.24 cm². The ASTM grain size of each specimen was measured using an austenite grain size reticle. Using the grain size and methods described in ASTM G108-92, the grain boundary area for each specimen was calculated. The average grain boundary area for the specimens was approximately 0.014 cm². The grain boundary area included HAZ and base metal. Therefore, the degree of sensitization values (P_a) represent an average of both base metal and HAZ.⁽³³⁾

Corrosion tests of the welded and unwelded samples were performed using the EPR test.⁽¹⁹⁾ The tests were performed using the standard electrochemical cell as illustrated in ASTM G108-92. Instrumentation consisted of the EG & G Princeton Applied Research Potentiostat/Galvanostat and Softcorr corrosion software version 2.38. Test parameters and conditions for the EPR test are listed in Table VI.

Table VI. EPR test parameters and conditions

PARAMETERS	CONDITIONS
Electrolyte	0.5M H ₂ SO ₄ + 0.01M KSCN
Temperature	30 ± 1°C
Sample Surface Finish	6 & 1 Micron diamond polish
Reactivation Rate	6 v/hr. (1.67 mv/hr.)
Passivation Potential	+0.200 mv vs SCE for 2 min.
Deaeration	Nitrogen
Auxiliary Electrode	Graphite
Reference Electrode	Standard Calomel
Degree of Sensitization	$P_a \text{ (C/cm}^2\text{)} = Q/\text{GBA}$
Note: C = Q = integrated charge in coulombs. GBA = Grain boundary area	

CHAPTER 6

RESULTS

Results of the EPR tests for each heat of material are shown in Table VII. P_a values marked with an asterisk are average values for specimens tested more than once. The measured ASTM grain size for all specimens was 7, as shown in Table VII. No specimens for the three heats of material developed a sensitized microstructure. As shown in Table VIII, a P_a number of at least 2 is required for a material to be considered sensitized.

Table VII. Results of EPR tests.

Heat No.	Specimen No.	GTAW Process	ASTM Grain Size	P_a (C/cm ²)
913842	1	SA	7	-0.09
	2	A	7	-0.04
	3	A	7	-0.03
	4	A	7	-0.02
	5	A	7	0.04
	6	A	7	0.06
	7	M	7	0.07
	8	M	7	0.07
	9	M	7	0.09
	10	M	7	0.28
	11	M	7	0.21
710954	12	SA	7	-0.17

Table VII
(cont.)

	13	M	7	0.92
	14	M	7	0.81*
	15	M	7	0.94
	16	M	7	1.57*
	17	M	7	1.64*
	18	A	7	0.67
	19	A	7	0.62
	20	A	7	0.96*
	21	A	7	0.94
	22	A	7	0.94
855911	23	SA	7	-0.04
	24	M	7	1.30
	25	M	7	1.38
	26	M	7	1.37
	27	M	7	1.48*
	28	M	7	0.29
	29	A	7	0.02
	30	A	7	0.26
	31	A	7	1.15
	32	A	7	1.30
	33	A	7	1.83

Notes: A = Automatic process, M = Manual process, SA =
Solution annealed

Table VIII. General interpretation for degree of sensitization based on P_a number⁽²⁰⁾

P_a Value	General Interpretation
< 2	unsensitized microstructure
2 - 5	slightly sensitized microstructure
6 - 15	sensitized microstructure
> 15	heavily sensitized microstructure

The plot of the results for the number of weld cycles vs the degree of sensitization (P_a) are shown in Figure 5 for the automatic welding method, and in Figure 6 for the manual method. For both welding methods and all three heats, the value of P_a increased from the value in the solution annealed condition.

Figure 5. Degree of sensitization vs number of welding cycles for the automatic gas tungsten arc process

Figure 6. Degree of sensitization vs number of welding cycles for the manual gas tungsten arc process

Figures 7 and 8 show the difference in a clean microstructure and a microstructure that contained inclusions as revealed in a pretest microstructural examination. Specimens which required repolishing due to inclusions are marked with an asterisk in Table VII.

Figure 7. Specimen No. 10 showing typical clean microstructure found in heat No. 913842 material. Unetched. 400X.

Figure 8. Specimen No. 20 showing typical inclusions found in some specimens of heat numbers 710954 and 855911 materials. Unetched. 400X.

Figures 9 to 13 show typical microstructural results for the as received solution annealed condition, one and five cycle automatic weld, and one and five cycle manual weld, respectively.

Figure 9. As received, solution annealed 316L specimen No. 12, heat 710954. Electrolytic etch with 10% oxalic acid. 400X.

Figure 10. One cycle automatic weld showing heat affected zone. Note ferrite stringers from weld on the left hand side. From specimen No. 18, heat 710954. Electrolytic etch with 10% ammonium persulfate. 400X.

Figure 11. Five cycle automatic weld showing heat affected zone. Note ferrite stringers from weld in lower left hand corner. From specimen No. 22, heat 710954. Electrolytic etch with 10% ammonium persulfate. 400X.

Figure 12. One cycle manual weld showing heat affected zone. Weld is shown on the left side. From specimen No. 13, heat 710954. Electrolytic etch with 10% ammonium persulfate. 400X.

Figure 13. Five cycle manual weld showing heat affected zone. Weld is shown on the left side. From specimen No. 28, heat 855911. Electrolytic etch with 10% ammonium persulfate. 400X.

Table IX shows the results of EPR tests performed on unwelded heat treated specimens in order to verify the accuracy of the test equipment and test setup, and to determine what approximate heat treat conditions are necessary to sensitize the 316L heats of material in this study. Specimens 1A and 3A were used to verify the accuracy of the test equipment and setup. The P_a values for specimens 1A (unsensitized) and 3A (heavily sensitized) are in agreement with reported literature values.^(19,33) The P_a number of specimens 1HT and 23HT increased from the value in the as received solution annealed condition, but not sufficiently for the materials to be considered sensitized. Specimen 12HT became slightly sensitized.

Table IX. EPR test results for unwelded heat treated specimens

Heat No.	Alloy	Specimen No.	ASTM Grain Size	P_a (C/cm ²)
N/A	304	1A	8	0.01
N/A	304	3A	8	24.00
913842	316L	1HT	7	1.40
710954	316L	12HT	7	3.37
855911	316L	23HT	7	0.55

Notes:

Specimen no. 1A was as received, solution annealed. Specimen 3A was heated to 750°C (1382°F), held for 3.5 hrs, furnace cooled to 450°C (842°F), and water quenched. Specimen 1HT, 12HT & 23HT were heated to 670°C (1238°F), held for 3 hrs, furnace cooled to 400°C (752°F), and water quenched.

Figures 14 and 15 show the microstructural results of specimens 3A and 12HT, respectively.

Figure 14. Type 304 alloy, specimen No. 3A, showing heavily sensitized microstructure (dark areas). Electrolytic etch with 10% oxalic acid. 400X.

Figure 15. Specimen No. 12HT, heat 710954 showing slightly sensitized microstructure (wider dark areas at grain boundaries). Electrolytic etch with 10% oxalic acid. 400X.

Figures 16 to 19 show the microstructural results of the ferrite distribution in the weld metal after one and five cycle automatic and manual welding.

Figure 16. One cycle automatic weld showing distribution of ferrite (dark areas). From specimen No. 2, heat 913842. Electrolytic etch with 10% oxalic acid. 400X.

Figure 17. Five cycle automatic weld showing distribution of ferrite (dark areas). From specimen No. 6, heat 913842. Electrolytic etch with 10% oxalic acid. 400X.

Figure 18. One cycle manual weld showing distribution of ferrite (dark areas). From specimen No. 7, heat 913842. Electrolytic etch with 10% oxalic acid. 400X.

Figure 19. Five cycle manual weld showing distribution of ferrite (dark areas). From specimen No. 11, heat 913842. Electrolytic etch with 10% oxalic acid. 400X.

CHAPTER 7

DISCUSSION

Although some recorded values for the P_a numbers are negative, as shown in Table VII (a result of the test specimens acting as an anode and cathode during the test scan) following standard conventions,⁽³⁴⁾ all values were plotted as positive, with the negative values assigned a value of zero. The zero values are in agreement with EPR values reported in the literature.^(19,35)

The reactivation current of the EPR test attacks chromium depleted grain boundary areas which have weak chromium oxide films. The wider the chromium depleted area the greater the attack, and therefore the higher the EPR P_a value. As shown in Figures 5 and 6, for heat number 913842, there was an increase in the P_a number for each welding cycle and method. This increase in P_a number indicates that there was activity between the chromium and carbon at the grain boundary area which affected the protective oxide film, but not enough activity to reach a condition of sensitization. Heat 913842 is a well behaved material, i.e. it agrees with what is expected for a stabilized stainless steel being welded with a low heat input process.

On the other hand, heat numbers 710954 and 855911, although not sensitized, were not as well behaved. The P_a

values for the weld cycles were slightly higher for these two heats. The obvious visual difference between the heats, as revealed by a pretest microstructural examination, was that heat 913842 was relatively clean as shown in Figure 7, as compared to heat numbers 710954 and 855911. Some specimens of the later heats contained numerous spherical and stringer inclusions as shown in Figure 8, which are known to affect EPR test results.⁽¹⁹⁾ Those specimens requiring repolishing and retesting due to inclusions are marked with an asterisk in Table VII. Another possible explanation or contributing factor for the slightly higher P_a values are that both heats also contain a slightly higher carbon and nickel content, both of which promote carbide precipitation.

Typically the P_a value for a welded specimen should be lower than the P_a value for a furnace heat treated specimen, because of the shorter time in the sensitization temperature range for the welded specimen. Both heats 710954 and 913842 are well behaved in this respect. The P_a values for welded specimens of heat 855911 are above the furnace heat treated values, except for four values as shown in Table VII and plotted in Figures 5 and 6. These four values may represent the true welded P_a values when unaffected by inclusions, since the specimens were relatively clean as compared to the other seven specimens of the heat.

In order for sensitization to occur, the HAZ must remain

in the sensitization temperature range for a sufficiently long period of time, to precipitate chromium carbides. A high welding heat input is a major contributing factor to the length of time the HAZ remains in the sensitizing temperature range. Since the range of heat input values for both the automatic and manual welding methods in this study are low compared to values which are reported⁽¹⁾ to have caused sensitization, the time the HAZ remained in the sensitization range is short, thereby producing a low P_a value. Further evidence for the low heat input and time at temperature is shown by the lack of grain growth, (ASTM grain size number in Table VII did not decrease) and no evidence of carbide precipitation in the heat affected zones of the specimen welds, as shown in Figures 10 through 13. This is in agreement with the low P_a values plotted in Figures 5 and 6.

Figures 9 through 13 show the typical microstructural conditions for all three heats of material with respect to grain growth and precipitation in the heat affected zone. Figure 9 shows the microstructure of an as received solution annealed 316L stainless steel material, which represents the typical microstructure of all three heats of material in the unsensitized condition. Figures 10 through 13 show the heat affected zone of a one and five cycle automatic weld, and a one and five cycle manual weld respectively. Due to the low heat input for each welding cycle, there is no change in the

HAZ grain size between the one cycle and five cycle welds, nor between the manual and automatic method. The heat affected zones in these four figures are also free of carbide precipitation. The micrographs in these figures confirm the low P_a values of Table VII.

Figures 14 and 15 show examples of carbide precipitation which may be compared with Figures 10 through 13, which do not show carbide precipitation. Specimens represented in Figures 14 and 15 were used to verify the accuracy of the test equipment and test setup. The corresponding P_a value in Table IX is in agreement with the microstructures of Figures 14 and 15, confirming the validity of the test results.

Due to the low heat input value for the welding methods employed, and the rate at which the P_a number increased with each welding cycle, as shown in Figures 5 and 6, it appears that these heats of material can be rewelded for repair several times without experiencing carbide precipitation. This is not to say that all heats of 316L materials will behave in a similar manner. Some heats may not be properly solution annealed and therefore develop carbide precipitation in fewer welding cycles. From a practical point of view, industrial practice would dictate that if a weld cannot be repaired after two or three attempts at rewelding, repair by rewelding would be abandoned, the weld cut out, and a new joint prepared and welded after adjusting the welding

procedure parameters.

Each time a welding cycle is performed and the previous weld bead is remelted, the ferrite phase in the previous weld goes into solution (is dissolved) and must reform when the weld solidifies again from the molten state. Therefore, another concern, although not addressed directly in this study, is the effect of multiple welding repair cycles on the ferrite content of the weld metal which controls solidification cracking and corrosion resistance in the weld. The ferrite content of a solidifying weld is a function of the weld's chemical composition and cooling rate. Since the welds in this study are autogenous and the chemical composition of the base metals do not change, the chemical composition of the welds do not change. Therefore there is no ferrite change due to the chemical composition variable. The cooling rate of the weld is a function of the base metal thickness and the welding heat input. Since the thickness of the base metal does not change, and the heat input for each welding cycle for each welding method is fairly constant (more so for the automatic method), the cooling rate also remains fairly constant. Therefore the ferrite content of the first weld cycle is essentially the same as the ferrite content of the last weld cycle, as shown in Figures 16 through 19. Also carbide precipitation does not occur in the type of welds made in this study because each weld bead is completely remelted and

rapidly cooled from the liquid state, thereby eliminating carbide precipitation due to a weld metal HAZ or slow cooling through the sensitization temperature range.

CHAPTER 8

CONCLUSIONS

The results of this study have lead to the following conclusions regarding the sensitization behavior of thin wall 316L stainless steel tube subjected to simulated reweld repair cycles.

EPR TEST METHOD

The EPR test method has a high sensitivity at low degrees of sensitization. That is, the test can detect chromium and carbon grain boundary activity at levels which are not detectable with the light microscope. The test is also quantitative, providing a definite value as a basis for comparison.

WELDING METHODS

Both the automatic and manual welding methods produced low welding heat inputs. The automatic method produced a constant low heat input, whereas the manual method's heat input fluctuated slightly due to the different welding techniques of each welder. Since both methods produced a low heat input, the time in the sensitization temperature range for the first weld cycle, as well as for the fifth weld cycle, was short. Therefore no grain growth or carbide precipitation

occurred in the HAZ for either method or cycle.

For both welding methods and each welding cycle, the ferrite content in the autogenous weld metal remained constant due to the constant base metal chemical composition, welding heat input, and weld cooling rate. Therefore, the welds in this study are not susceptible to hot cracking or carbide precipitation due to a reduction in the ferrite content.

MATERIALS

Material with heat number 913842 had a slow increase in the degree of sensitization values as the number of welding cycles increased. This material was well behaved. That is, the material behaved as expected for a low carbon stainless steel being welded with a low heat input process. On the other hand, for materials with heat numbers 710954 and 855911 the degree of sensitization values increased at a more rapid rate as the number of welding cycles increased. These latter two heats of material were not as well behaved as the former. However, inclusions and stringers in the materials may have contributed to the rapid rise in the degree of sensitization values.

SUMMARY

Using the EPR test method and metallographic examination, this study found that there was a general increase in the

degree of sensitization values below the critical value of 2, as the number of welding cycles increased. This study also found that due to the low heat input and short time in the sensitization temperature range, the three heats of material are capable of being repaired by rewelding using up to five welding cycles with both the automatic and manual welding methods without becoming sensitized. Therefore, a welding repair alternative for incomplete fusion and inadequate penetration defects by rewelding existing welds is feasible, provided the welds are made in materials which are similar to those in this study with respect to heat treat condition and chemical composition.

REFERENCES

1. Lundin, C. D., et al., Sensitization of Austenitic Stainless Steels; Effect of Welding Variables on HAZ Sensitization of AISI 304 and HAZ Behavior of BWR Alternative Alloys 316NG and 347. Welding Research Council Bulletin No. 319. The Welding Research Council, New York: 1986.
2. Patton, W. J. The Science and Practice of Welding. P. 239. Prentice - Hall: New Jersey: 1967.
3. Heiro, H., et al., The Influence of Welding Parameters on Droplet Temperature During Pulsed Arc Welding. Welding and Metal Fabrication. P. 482., September 1976.
4. Solomon, H. D., Continuous Cooling Sensitization of Type 304 Stainless Steel. Corrosion, 34 (6) June 1978.
5. Strawstrom, C. and Hillert, M., An Improved Depleted-Zone Theory of Intergranular Corrosion of 18-8 Stainless Steel. Journal of the Iron and Steel Institute. P. 77, January 1969.
6. Porter, D. A. and Easterling, K. E., Phase Transformations in Metals and alloys. Chapman and Hall: New York: 1992.
7. Briggs, J. Z., The Role of Molybdenum in Corrosion Resistance Materials. Corrosion Prevention and Control. Vol. 9, Oct. Dec. 1992.
8. Colombier, L., Molybdenum in Stainless Steels and Alloys. Climax Molybdenum Company LTD., London
9. Tedmon, C. S., et al., Intergranular Corrosion of Austenitic Stainless Steel. Journal Electrochemical Society. P. 192, Vol. 118, No. 2, February 1971.
10. Richardson, F. D. The Thermodynamics of Metallurgical Carbides and of carbon in iron. Journal of the Iron and Steel Institute. P. 33, Vol. 175, September 1953.
11. Kubaschewski, O. & Alcock, C. B., Metallurgical Thermochemistry. Pergamon Press: New York: 1979.

12. Cihal, V. and Jarman, R. A., Knife-Line Corrosion in Stainless Steel Structures. Metal Construction, P. 134, March 1979.
13. Wicks, C. E. and F. E. Block., Thermodynamic Properties of 65 Elements-Their Oxides, Halides, Carbides, and Nitrides. Bureau of Mines Bulletin 605. U.S. Department of the Interior. Washington. 1963.
14. Cihal, V., Intergranular Corrosion of Steels and Alloys. Elsevier: New York: 1984.
15. Lankford, W. T., et al., The Making, Shaping and Treating of Steel. 10th ed. United States Steel Corp: Pittsburgh: 1985.
16. Shirali, A. A., and Mills, K. C., The Effect of Welding Parameters on Penetration in GTA Welds. Welding Journal. P. 347-S., July 1993.
17. Sundell, R. E., et al., Minor Element Effects on Gas Tungsten Arc (GTA) Weld Penetration-Weld Pool Physics. Advances in Welding Science and Technology Conference Proceedings. ASM International, Metals Park, OH: 1986.
18. Walsh, D. W., and Savage, F. W., The Mechanism of Minor Element Interaction in Autogenous Weld Pools. Advances in Welding Science and Technology Conference Proceedings. ASM International, Metals Park, OH: 1986.
19. Standard Test Method for Electrochemical Reactivation (EPR) for Detecting Sensitization of AISI Type 304 and 304L Stainless Steels. ASTM G108. ASTM. Phila: 1992.
20. Jones, D. A., Principles and Prevention of Corrosion. P. 302. Macmillan: New York: 1992.
21. ASTM. A269-90 Standard Specification for Seamless and Welded Austenitic Stainless Steel Tubing for General Service. ASTM Standard Section 1, Vol. 01.01 Steel Piping, Tubing & Fittings. ASTM. Phila: 1992.
22. Folkhead, E., Welding Metallurgy of Stainless Steel. Springe - Verlage: New York: 1984.
23. Kotecki, D. J., Understanding Delta Ferrite. Welding Design and Fabrication. P. 33., December 1990.

24. David, S. A., et, el. Characterization of Heat - Affected Zone cracking in Austenitic Stainless Steel Welds. Welding Journal. Vol. 66, No. 8, August 1987.
25. Lundin, C. D, and Chou, C. P. D., Fissuring in the "Hazard Haz" Region of Austenitic Stainless Steel Welds. Welding Journal. Vol. 64, No. 4, April 1985.
26. Siewart, T. A., et, el. Ferrite Number Prediction to 100 FN in Stainless Steel Weld Metal. Welding Journal. Vol. 67, No. 12, December 1988.
27. Kotecki, D. J., and Siewart, T. A. WRC - 1992 Constitution Diagram for Stainless Steel Weld Metals: A Modification of the WRC - 1988 Diagram. Welding Journal. Vol. 71, No. 5, May 1992.
28. Peckner, D., & Bernstein, I. M. Handbook of Stainless Steels. McGraw - Hill. New York: 1977.
29. Briant, C. L., The Effects of Sulfur and phosphorus on the Intergranular corrosion of 304 Stainless Steel. Corrosion. Vol. 36, No. 9. September 1980.
30. Pawel, S. J., The Sensitization Behavior of Cast Stainless Steels Subjected to Weld Repair. M. S. Thesis., University of Tennessee: 1983.
31. Gooch, T. G., Stress Corrosion Cracking of Welded Austenitic Stainless Steel. Welding in the World. Vol. 22, No. 3/4, 1984.
32. Hann-Tuw, L., et, el. The Electrochemical and Corrosion behavior of Austenitic Stainless Containing Copper. Corrosion Science. Vol. 33, No. 5, pp 691-697, 1992.
33. Clarke, W. L., et, el. Detection of Sensitization in Stainless Steel Using Electrochemical Techniques. Paper No. 180, Corrosion '77. NACE, San Francisco, CA.
34. Trethewey, K. R., & Chamberlain, J., Corrosion for Students of Science and Engineering. John Wiley & Sons: New York: 1988.
35. Bruemmer, S. M., Sensitization Development in Austenitic Stainless Steel - Measurement and Prediction of Thermomechanical History Effects. Corrosion Science. Vol. 44, No. 7, PP 427 - 434, July 1988.

BIBLIOGRAPHY

ASM International, Corrosion. Metals Handbook, Ninth Edition. Vol. 13. ASM International. OH: 1981.

Cihal, V. and Kasora, I. Relation Between Carbide Precipitation and Intercrystalline Corrosion of Stainless Steels. Corrosion Science. Vol. 10, P. 875. 1970.

DeBold, T. A., Which Corrosion Test for Stainless Steels? Materials Engineering. Vol. 2 (No.1), July 1980.

Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels. ASTM A262. ASTM, Phila, Pa. 1985
Hetzl, D. E., Intergranular Stress Corrosion Cracking in Welded, Unstabilized Austenitic Stainless Steel. Metal Progress. P. 73., March 1984.

Robinson, J. L., Preferential Corrosion of Welds. The Welding Institute Research Bulletin. P. 46., February 1979.

Sedriks, A. J., Corrosion of Stainless Steels, John Wiley and Sons, New York: 1979.

Steigerwald, R. F., Intergranular Corrosion of Stainless Alloys. ASTM STP 656. ASTM. Phila, Pa. 1977.

APPENDIX A

AUTOMATIC GAS TUNGSTEN ARC PARAMETERS USED FOR EACH HEAT OF MATERIAL

Arc Length	0.050"
Tungsten Type	2% thorium
Tungsten Diameter	1/16"
Shielding Gas	Argon at 25 CFH
Purge Gas	Argon at 10 CFH
Pulse High and Low Time	0.02 seconds
Pulse Low Amperes	13
Average Pulse High Amperes	78
Average Voltage	9

Notes;

- (1) Welding voltage, amperes and travel speed were preset using trial and error.
- (2) Weld heat input as shown in Table IV was calculated using equations (1) and (2).
- (3) Welding equipment used was Arc Machines Model 107 and 207.

APPENDIX B

MANUAL GAS TUNGSTEN ARC PARAMETERS USED FOR EACH HEAT OF MATERIAL

Arc Length	Variable
Tungsten Type	2% thorium
Tungsten Diameter	1/16"
Shielding Gas	Argon at 25 CFH
Purge Gas	Argon at 10 CFH
Average Voltage	9
Average Amperes	42.4

Notes:

- (1) The voltages and amperes were read directly from a digital meter on the welding machine while the welder was welding.
- (2) The travel speed was obtained using the seconds hand on a watch.
- (3) The heat input shown in Table V was calculated using equation (1).
- (4) Welding Equipment used was Miller Maxstar 151 with a constant ampere DC invertor power supply.