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Effects of welding on the metallurgy of electropolished 316L stainless steel

Steve Trigwell
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**EFFECTS OF WELDING ON THE METALLURGY OF
ELECTROPOLISHED 316L STAINLESS STEEL**

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 of

Master of Science

by

Steve Trigwell

May 1998

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ABSTRACT

EFFECTS OF WELDING ON THE METALLURGY OF ELECTROPOLISHED 316L STAINLESS STEEL

by Steve Trigwell

In this study, electropolished 316L stainless steel specimens from various heat lots were welded under identical parameters, but with varying concentrations of oxygen leaked into the purge gas during the welding (0 ppm, 1.2 ppm, 6.3 ppm, and 31.6 ppm). Discoloration in the Heat Affected Zone (HAZ) was determined to be proportional to the oxygen concentration and to be composed of an iron enriched oxide layer. The composition of the original steel was found to be only a minor factor in the extent of discoloration. Consequent corrosion studies in a 3.5% NaCl solution showed the HAZ to be slightly more susceptible to corrosion regardless of the extent of discoloration. No evidence of carbide precipitation in the grain boundaries was observed in the HAZ. It is postulated that the cause of the discoloration was due to iron diffusing through the chromium oxide layer in the HAZ in the sensitizing temperature range and forming an iron oxide layer, the thickness of which depended upon the concentration of oxygen available in the purge gas.

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I would also like to thank Marion Tooke, for her optimism and encouragement through the difficult times.

I wish to dedicate this work to my parents, Joy and the late Arthur Henry, who encouraged myself and my brothers, Dave and Andy, to pursue our dreams, and to be the best we can be, in whatever our chosen fields may be.

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CHAPTER 1: INTRODUCTION

Trends in semiconductor manufacturing are focused upon producing smaller and more complicated devices, while continuing to improve reliability and increase yield. Consequently, contaminants and small defects on dies that only a few years ago were considered insignificant are now becoming unacceptable for current IC production. The purity of chemicals and gases used in semiconductor manufacture have therefore been subject to heavy scrutiny. Similarly, the methods of distributing these fluids are also now being subjected to the same scrutiny, particularly where corrosive fluids are often used, so that any possible contribution to contamination, corrosion, or particle generation can be minimized.

The gas delivery system for semiconductor fabrication has long been a source of contamination on wafers.⁽¹⁾ Outgassing from the piping and the generation of particles can cause seriously reduced yields. Methods for characterizing particles on silicon wafers, to determine their origins, are in themselves a big industry where scanning Auger Electron Spectroscopy (AES) has been extensively used to characterize steel particles, on the order of a few microns in size, on silicon wafers.⁽²⁾ Advanced welding technology has been carefully employed for welding passivated tubing,^(3, 4) as well as methods for the detection of particles and impurities in ultra pure gas delivery systems.^(5, 6) The use of polymer-type filters, and recently the adoption of stainless steel filters,⁽⁷⁾

have led to a high level of cleanliness in corrosive gas lines. The Semiconductor Equipment and Materials Institute (SEMI) has established specifications for contaminant levels in various semiconductor grade gases.⁽⁸⁾ However, with the trends in semiconductor manufacturing moving towards producing smaller and more complicated devices while trying to improve yield and reliability, contamination levels that were once considered insignificant are now becoming a cause for concern.

Due to its superior corrosion resistance and low carbon content,⁽⁹⁾ electropolished 316L austenitic stainless steel has become the industry standard for use in delivery systems for ultra-high-purity gas transportation, especially where extensive welding is to occur. Although strict specifications have been developed by SEMATECH^(10, 11, 12, 13) to ensure quality for semiconductor grade stainless steel tubing, concerns have been expressed by manufacturers and vendors of tubing regarding the often observed discoloration in the Heat Affected Zone (HAZ) near the weld joint. Examples of weld zone discoloration are shown in Figures 1 and 2. This discoloration can vary from a faint blue to a deep brown.

Scanning Electron Microscopy (SEM) and Field Emission AES (FEAES) analyses have shown the extreme brown discoloration observed in disassembled corrosive gas lines to be composed of sub-micron particles composed of iron, oxygen, and chlorine.⁽¹⁴⁾

Figure 1: Example of weld zone discoloration on electropolished 316L stainless steel

Figure 2: Higher magnification micrograph showing the blue discoloration in the Heat Affected Zone (HAZ)

Preliminary experiments have also shown that large variations in the discolorations were observed for different heat lots of stainless steel welded under the same conditions.⁽¹⁵⁾ This discoloration is now being treated seriously as possible sources of particulate contamination.

CHAPTER 2: MATERIALS USED IN ULTRA PURE GAS DELIVERY SYSTEMS

The common characteristics of the 300 series alloys are a composition of about 18% chromium and 8% nickel and an austenitic microstructure. The most important characteristic is their ability to resist corrosion. They also possess good mechanical properties, and can be readily fabricated by commercial processing, namely, drawing, forging, forming, and machining.

Type 316 has 2 - 3% molybdenum added which improves the corrosion resistance, particularly resistance to pitting corrosion. The benefit of Type 316 over Type 304 steel is lost as the molybdenum is depleted from the surface when electropolishing. Type 316L is used where extensive welding is to occur; it has lower levels of carbon (0.03% max. versus 0.08% for Type 316) to reduce the tendency toward carbide precipitation at the grain boundaries during welding. However, it is important to note that adding or subtracting alloying elements to the base metal can affect the material's performance. By restricting the carbon content in Type 316L steel, the metal becomes slightly less strong, less ductile, and harder to machine. Stabilizing elements such as titanium (Type 321) or niobium and tantalum (Type 347) are added to other alloys; these tend to stabilize the carbon by forming carbides in solution and preventing precipitation of chromium carbide at the grain boundaries.⁽¹⁶⁾ The higher carbon concentration in Type 321 allows for smoother drawing and for the best fusion

techniques. However, the overall corrosion resistance of Type 321 is slightly lower compared to Type 316.

Nickel alloy C-276 (Hastelloy) has also been used in some chemical process industries where the corrosion resistance of the 300 series stainless steel is inadequate.⁽¹⁷⁾ But for the semiconductor industry, Type 316L stainless steel has become the standard. A comparison of composition and physical properties of the 300 series steels Type 304L, Type 316L, and Type 321, is shown in Table 1. Before the steel can be used in delivery lines, it has to be prepared to produce an end product that possesses a smooth, passive surface that is corrosion resistant.

2.1 Manufacturing methods

The overall quality of the tubing used in semiconductor process lines is governed firstly by the melting and drawing of the metal, and secondly, but to a lesser degree, by the processing (electropolishing and passivation). There are four main methods of melting used today: electric arc furnace, vacuum arc remelting, vacuum oxygen decarburization, and argon oxygen decarburization.⁽¹⁶⁾ The electric arc furnace is a primary melt and the most popular method used for stainless steels. However, it does not produce a steel of the quality required for the semiconductor industry and further refining of the metal is required by supplemental melting operations. Vacuum arc remelting provides for a finer

Table 1a: Elemental compositions of the 300 series stainless steels

Elemental compositions											
Alloy type	C	Cr	Ni	Mn	Si	P	S	Fe	Ti	Mo	
	max. (%)	(%)	(%)	max. (%)	max. (%)	max. (%)	max. (%)	(%)	max. (%)	(%)	
304	0.08	18.0/20.0	8.0/12.0	2	1	0.045	0.03	Balance	---	---	
304L	0.03	18.0/20.0	8.0/12.0	2	1	0.045	0.03	Balance	---	---	
316	0.08	16.0/18.0	10.0/14.0	2	1	0.045	0.03	Balance	---	2.3	
316L	0.03	16.0/18.0	10.0/14.0	2	1	0.045	0.03	Balance	---	2.3	
321	0.08	17.0/19.0	9.0/12.0	2	1	0.045	0.03	Balance	5 x C	---	

Table 1b: Mechanical properties of the 300 series stainless steels

Mechanical properties				
Alloy type	Ultimate strength (psi)	Yield strength (psi)	Elongation in 2" (%)	Hardness (RB)
304	85000	35000	60	80
304L	75000	30000	60	75
316	80000	40000	55	80
316L	75000	30000	60	75
321	85000	40000	55	80

Table 1c: Elevated temperature properties of the 300 series stainless steels

Elevated temperature data: Creep strength @ 10000 hrs. with with % elongation					
Alloy type	Temp. (F)	Ultimate strength (psi)	Alloy type	Temp. (F)	Ultimate strength (psi)
304	1000	17000	304L	1000	17000
	1100	12000		1100	12000
	1200	7000		1200	7000
	1300	4000		1300	4000
316	1000	22400	316L	1000	22400
	1100	16800		1100	16800
	1200	11200		1200	11200
	1300	6900		1300	6900
321	1000	18000			
	1100	13000			
	1200	8000			
	1300	4500			

grain size and vacuum oxygen decarburization remelting is a chemical adjusting procedure.

Argon oxygen decarburization is a preferred method for producing semiconductor grade stainless steel, providing for a homogenous grain structure and chemistry control. It also provides an absence of inclusions which occur in electric arc furnace produced steel; the inclusions are a major problem when electropolishing.

After melting, the metal is poured into molds and prepared for the tube drawing process. First, the metal is hot extruded into a hollow tube. When it has cooled, the tube is cold drawn. The metal now is worked only at ambient conditions and is only heated in the final annealing. The three main drawing practices for semiconductor grade tubing are rod drawing, floating plug drawing, and fixed plug drawing. However, a further method known as radial ultrasonic tube drawing is gaining favor, providing for a smoother finished surface and closer tolerances which are a benefit during orbital welding procedures. As well as selecting the proper drawing method, in-process steps to maintain the cleanliness of the steel are also critical to make sure no residual lubricant or solvents are baked into the metal in the final anneal.

2.2 Electropolishing and passivation

Although stainless steel in air possesses a native oxide layer that is naturally chromium rich, the surface roughness of the steel plays a significant

part in the effectiveness of this layer in corrosion. The thickness of the native oxide layer may vary and be non-uniform. In order to produce a smooth surface, with a uniform chromium-enriched oxide layer which is chemically inert and corrosion resistant, a further process is required. The most common is electropolishing and passivation, which are preceded by a surface preparation step. A typical process flow for the electropolishing and passivating process is shown in Figure 3.

Electropolishing removes small amounts of material from the steel surface, leaving a smooth surface relatively free of inclusions, rough surfaces, and contamination. In the case of stainless steel, iron is selectively removed from the surface. This enriches the chromium level, which brightens the metal. It is accomplished by immersing the steel into an acid bath tank with an electrode attached to the metal, thus providing an electric current. The surface to be treated is configured as the anode. A d.c. power source drives electrons from the anode to the cathode, resulting in surface atoms leaving the anode as metal cations and diffusing into the electrolytic bath. New atoms are continuously exposed, and the process continues. A high potential is applied to the electrodes so that oxygen is liberated by the oxidation of hydroxyl radicals; this prevents an insulating oxide layer from forming at the surface.

The electropolishing process requires a proper balance between voltage and current. If the current is too high, both the peaks and valleys of the

Figure 3: A typical electropolishing process

rough surface will be etched, leading to pitting and a high generation of gases, particularly oxygen. If the current is too low, electroetching occurs, leading to the non-selective removal of material. The ideal balance between current and voltage is depicted in Figure 4. Bath temperatures are also important; too low a temperature results in a slow process with poor brightening and surface smoothness. Too high a temperature can lead to an active process, resulting in etching and surface defects. A schematic microscopic view of a stainless steel surface before and after electropolishing is shown in Figure 5.

Passivation is the next step, with the objective of oxidizing the metal surface using a strong oxidizer. The use of a wet oxidizer, e.g. nitric acid, produces a chromium oxide enriched surface layer which enhances the corrosion resistance. The finished surface should now be smooth and as free as possible from machining marks, grooves and pits.

These treatment steps have the dual objective of improving the physical and chemical inertness of the surface. The improvement of the physical inertness (reducing the surface roughness) occurs mostly in the electropolishing stage, while the passivation step has the greatest effect on the chemical inertness.

Although the resulting surface may be smoothed, brightened, dehydrogenized, stress-relieved, cleaned and de-burred, there are some factors

Figure 4: Idealized relationship between current density and voltage in an electropolishing bath

Figure 5: Microscopic view of metal surface before and after electropolishing

that still have to be considered. Surface defects in the base material may still be visible even though they are clean and smooth, and scratches due to fabrication prior to electropolishing may show up under the buffing. Also, contaminants such as phosphates, sulfates, and chlorides from the electropolishing process may be left as residues. However, in spite of these minor realities, the electropolishing process provides for a functionally superior surface.

2.3 Welding of 316L stainless steel

The austenitic microstructure of Type 316L stainless steel is obtained by the use of the high quantity of nickel (over 8%) which stabilizes the usually transient austenite and prevents the formation of ferrite, martensite, or carbides. The 300 series of steels have a reputation of being easy to weld⁽⁴⁾ due to the formation of delta ferrite (δ) after welding. Type 316L steel is hyper-peritectic, with initial solidification as austenite after welding, and with reduced ferrite forming with faster cooling. A minimum amount of ferrite is required to promote good weldability; however, corrosion resistance is reduced as ferrite increases. This has been attributed to galvanic attack occurring due to the potential difference between the austenite and ferrite, but may also be due to solidification segregation.⁽⁴⁾

Improper heat treatment during welding of austenitic stainless steels can cause the grain boundaries to become susceptible to corrosion. This is due to segregation of impurities such as phosphorus and sulfur to the grain boundaries,

or the formation of chromium carbide that depletes the chromium in the regions adjacent to the grain boundaries below that necessary for passivity. The metal then is known to have become sensitized. For austenitic alloys, the sensitizing temperature range is 400 - 850°C. During welding, the sensitizing temperature range is usually a few millimeters away from the weld bead, the latter usually being above the melting point. The extent of sensitization depends upon the carbon content of the steel; where considerable welding is a concern, the reduction of the carbon content (less than 0.03%) allows for the alloy to be heated in the sensitizing temperature range with less susceptibility to carbide precipitation. These alloys are designated with an "L" such as Type 304L and Type 316L.

Welding of Type 316L stainless steel is usually performed by pulsed-arc gas tungsten-arc (GTA) welding, also known as tungsten inert-gas (TIG) welding. In the welding process, an arc discharge takes place between the tungsten electrode and the base metal. The latter is melted at a temperature of up to 1600°C and is fused together without the use of an added filler. The weld head forms an enclosed chamber which is filled with an inert gas, commonly argon, or more recently an argon/hydrogen mixture, to protect the molten weld metal from air during the welding sequence. A rotor inside the weld head holds the tungsten electrode and rotates around the tubing to complete the weld. The start of the weld sequence begins with a timed prepurge, followed by a timed delay once the

arc is struck to form the weld puddle and allow it to nearly penetrate the tube. The welding current is reduced as the weld proceeds through a series of steps to prevent overpenetration. The welding current is pulsed between a primary current and a background current to better control the weld puddle. At the end of the rotation, there is an overlap to complete the weld, and the current is gradually reduced to prevent a hole being burned through the tubing. The purge gas continues through the tubing until the tubing has cooled sufficiently to prevent excessive oxidation when exposed to air.⁽³⁾

Since the welding involves the melting of the base metal itself, the chemical composition of the base metal itself is also of critical importance. Variations in difficulty in the weldability of different heat lots of Type 316L stainless steel have been observed,⁽¹⁵⁾ resulting in cases of bead meander which manifests as a deviation of the weld bead from a perfect circle around the tube, and/or a tendency to oxidize (also known as “heat tint” or discoloration) at the heat affected zone.

The technology that centers around the automatic welding technique is also important in determining the overall performance of an ultra-high purity gas delivery system, and therefore it is not just the material that has to be considered. However, improvements in welding technology and materials together are allowing for quality tubing for the semiconductor industry.

2.4 Characterization methods for quality control

Electropolished stainless steel has to meet the strict specifications developed for semiconductor grade stainless tubing and fittings to ensure quality. Methods for testing the interior surface of stainless steel tubing to measure the effectiveness of electropolishing have been developed by SEMATECH.^(10, 11, 12, 13) The objective was to provide test methods by which comparable data among components considered for use in ultra-high purity gas distribution systems could be obtained. The test methods are currently undergoing review for industry standardization by ASTM.

The analytical methodology for characterizing passivated stainless steel surfaces is a relatively straightforward multi-technique approach which measures the surface contamination, composition and structure of the oxide passivating film, and evaluates the morphology of the passivated surface. The three analytical techniques used are Electron Spectroscopy for Chemical Analysis (ESCA), Auger Electron Spectroscopy (AES), and Scanning Electron Microscopy (SEM).

ESCA, also known as X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with the capability of detecting all elements with an atomic number greater than helium ($Z = 2$). X-rays are used to interact with a sample surface, causing photoelectrons to be ejected from the surface atoms. The kinetic energies of these electrons are characteristic of the elements from

which they originate, and by measuring the kinetic energies, the binding energies of the surface atoms can be calculated and hence identified. Each element has a unique set of binding energies, and elemental compositions can be obtained by integrating the area under the peaks. The escape depth of the ejected photoelectrons is about 50 - 100 Å, depending on the element, and hence is a very surface sensitive technique. The sensitivity is in the order of 0.5 atomic percent. One of the main strengths of ESCA is the ability to determine chemical state information from the small shifts in binding energy associated with the chemical environment of the atom. For example, the oxides of the transition metals can be clearly distinguished from the metal, and quantified by deconvoluting the peaks. An example of an ESCA spectrum from the surface of electropolished Type 316L stainless steel showing the elemental composition is shown in Figure 6, and summarized numerically in Table 2. The main constituents of the steel, namely, chromium, nickel, iron, and molybdenum are evident, as well as surface oxidation and carbonaceous contamination. The phosphorus, silicon, and nitrogen are probably residues from the processing. High-resolution scans of the carbon, chromium, and iron peaks are shown in Figure 7. From these spectra the chemistry (Cr/Fe ratio, Cr(oxide)/Fe(oxide) ratio) of the outer 20 - 50 Å was determined, and is summarized in Table 3. The carbon spectrum shows a high hydrocarbon content (C-C, C-H), suggesting the

Figure 7: High resolution ESCA scans of the carbon, chromium, and iron peaks from the surface of electropolished stainless steel

Table 2: Typical ESCA surface composition of electropolished stainless steel

	P	Si	Mo	C	N	O	Cr	Mn	Fe	Ni
Atomic conc. (%)	3.1	0.5	0.6	34	2.1	46	7.8	1.0	3.7	1.1

Table 3: Typical ESCA high resolution data showing iron and chromium oxidation states

	Cr ^o	Cr-O	Fe ^o	Fe-O	$\frac{\text{Total Cr}}{\text{Total Fe}}$	$\frac{\text{Cr-O}}{\text{Fe-O}}$
Atomic conc. (%)	0.48	7.32	1.9	1.79	2.11	4.09

All values are atomic percent abundance of Cr as Cr^o and Cr-O and Fe as Fe^o and Fe-O

Table 4: Typical AES data

Oxide layer thickness (1) (Å)	Cr:Fe ratio (2)	Depth of enrichment (3) (Å)	Iron oxide layer thickness (4) (Å)
25	1.73	22	4

presence of machining oil. The values shown for this example are within the typical range for well electropolished Type 316L stainless steel.

AES is also a surface sensitive technique and utilizes a focused electron beam to induce electron emission. In this case, after the emission of a core electron, a higher energy electron falls into the vacancy and releases energy. This energy is either given off as a photon (X-Ray Fluorescence (XRF)), or released as a third (Auger) electron. Measurement of the kinetic energies of these ejected Auger electrons provides compositional information about the surface. As in ESCA, AES can detect all elements except hydrogen and helium. One of the advantages of AES is that the escape depth of the Auger electrons is shallower than for ESCA, on the order of 5 - 40 Å, and allows for slightly greater surface sensitivity. Also because of the ability to focus an electron beam down to very small spot sizes (150 Å in the case of a field-emission source), sub-micron analysis is possible. In addition, when combined with inert gas ion etching, composition with depth can be readily obtained. This is known as depth profiling. It is this feature that is especially utilized in the qualification of stainless steel.

AES is employed to provide a measure of the oxide layer thickness, and determine the elemental composition as a function of depth through the electrochemically altered region. A disadvantage of AES is that chemical information is not readily obtained. However, with the advances in software data

processing, techniques allowing for identification of chemical states and phases are now available. A typical depth profile of electropolished stainless steel is shown in Figure 8, and indicates several features of interest, which are summarized in Table 4. The most important features for this study are:

- 1) Oxide thickness. This is defined as the depth at which the oxygen signal has fallen to half-maximum. For well electropolished stainless steel, this value is in the range of 20 - 50 Å.
- 2) Maximum Cr:Fe ratio. The maximum ratio of the chromium to the iron signal in the oxide layer and the depth at which it occurs is used as an indication of the effectiveness of the electropolishing and chromium enrichment. Typically this value is greater than 1.5:1 and occurs at about the midpoint of the oxide thickness.
- 3) Maximum depth of enrichment. The chromium enrichment layer thickness encompasses the region where the chromium concentration is greater than iron, and is typically 20 - 25 Å.
- 4) Surface iron oxide layer. A thin iron oxide layer is sometimes present (< 5 Å thick); too thick a layer may indicate the presence of corrosion.

Due to the different escape depths for ejected electrons for ESCA and AES, the Cr:Fe ratios obtained from either technique are usually quite different. Also, as the sensitivity factors used for AES are obtained from elemental NIST

Figure 8: Typical AES depth profile of electropolished stainless steel. The data is presented as a) peak-to-peak counts, and b) as relative atomic concentration

traceable standards, there exists a systematic error due to the chromium and iron being in the oxide state. The ESCA values are therefore considered the more accurate values. However, the Cr:Fe ratios obtained in the AES depth profiles do provide a useful numerical comparison relative to known good electropolished stainless steel.

SEM is a finely focused electron beam technique which utilizes the secondary electrons and backscattered electrons from the sample surface to obtain images of the surface at extremely high magnifications, up to 300000 times, when scanned at TV raster rates. SEM is used in the qualification of electropolished stainless steel to characterize the morphology of the surface and evaluate the effectiveness of the electropolishing. The magnifications used are 1000x and 3600x, at which anomalies such as pits, crack, inclusions, and machining marks can be photographed and counted. Too many pits or striations on the surface that can indicate the surface has been overpolished.

Each of these tests outlined above can be performed relatively quickly and cheaply, and provided the SEMATECH protocols are followed, can be used to compile a database and compare lots. However, at present all the qualification tests are routinely performed on samples that have been cut out of unwelded tubing components such as fabricated pipes and valve fittings. Once the tubing has passed the qualification procedure, it is ready to be used and welded into the process lines. In the typical case of gas delivery lines in

semiconductor fabrication, several miles of tubing are used in which the tubing is welded at an average of every foot in length.⁽¹⁵⁾ The substantial number of welded joints raises the concern for the likelihood of corrosion of the HAZ and the generation of particulates. At present there exists no test for qualifying the quality of the weld zones once the tubing is installed in the process line. It is only when there is excessive contamination in the end product, or a suspicion that the gas delivery system is the cause of a problem, that it is dismantled, cut open, and the weld zones examined and analyzed. This is, of course, at considerable cost in time and production.

It is therefore of great interest to understand the corrosion behavior of the steel in the welded zone, so that steps can be taken before the construction of a high-purity gas delivery system to ensure the possibility that corrosion is minimized to the utmost.

CHAPTER 3: PREVIOUS RESEARCH ON CORROSION OF STAINLESS STEELS

Several studies have been done on the pitting corrosion of stainless steels, specifically of the 300 series, under various conditions,^(18, 19, 20, 21) The need for superior corrosion resistance for use in the semiconductor industry has led to considerable development of post fabrication treatments to enhance the passivation of the surface, namely, in the electropolishing followed by wet chemical or dry oxygen passivation.^(22, 23, 24, 25) The development and use of surface analytical techniques such as ESCA, Atomic Force Microscopy (AFM), and AES in the application of characterizing passive films and corrosion on stainless steels,^(26, 27, 28, 29, 30) has made a big impact on the understanding of corrosion mechanisms.

Susceptibility to intergranular corrosion in the HAZ of welded stainless steels has been known for a long time,^(31, 32, 33) and is principally caused by the diffusion of carbon in the steel to the grain boundaries in the sensitized region, a short distance from the actual weld. This forms chromium carbide precipitates which deplete the regions adjacent to grain boundaries of the necessary chromium for passivity. Specific analyses on the HAZ using AES have also suggested that intergranular corrosion is caused by segregation of impurities such as sulfur and phosphorus to the grain boundaries.^(34, 35) However, in the study by Joshi and Stein,⁽³⁴⁾ the bars were quenched after welding and fractured

through the HAZ after cooling to liquid nitrogen temperature. This would render them non-sensitized and eliminate carbide precipitation as a cause. The results of Pilous et al.⁽³⁵⁾ were obtained after annealing the welded samples at high temperatures (575 - 680°C) for 43 to 100 hours, and then analyzing the surface of the fracture plane. Although they also observed carbides at the exposed grain boundaries, the sulfur and phosphorus concentrations were particularly high and were attributed to the failure. A study by Von Moltke et. al.⁽³⁶⁾ using AES, showed that the discoloration rings in the HAZ in Type 304 stainless steel were high in iron oxide and susceptible to pitting corrosion in 3.5% NaCl due to lower levels of chromium. The analysis was performed using AES depth profiles to analyze the oxide layers, and SEM imaging to analyze the pits; but apart from a mention that chromium depleted metal is more susceptible to pitting, no explanation of the cause was discussed.

The use of low carbon content (<0.03% C) steels has been developed to try to eliminate this problem, and are generally labeled with an L suffix to distinguish them. Consequently, the L grade stainless steels, particularly Types 304L and 316L have been extensively used in corrosive environments. However, recent work on the microbiologically influenced corrosion of Types 304L and 316L has shown that pitting corrosion in the HAZ was dependent upon the extent to which the HAZ was oxidized.⁽³⁷⁾ More specific work by Henon and Jekel⁽³⁸⁾ showed that various discolorations could be obtained in the HAZ of Type

316L electropolished stainless steel by varying the oxygen leak into the argon purge during the welding, which in turn resulted in an increasing amount of corrosion at the weld site when exposed to aggressive gases (HCl, HBr, WF₆). No attempt was made in this study to determine the composition of the discolorations; the authors instead argued that as Type 316L tubing was used and that the heat input used in the welding was so low, carbide precipitation was just simply not possible. They also reported previous work by T. Mehalko, using AES, that showed similar discolorations were simply thicker oxide layers, the color of which was an optical effect dependent upon the thickness and the formation of an interference color. Again, no explanation was given regarding the cause - only that it occurred and an oxide thickness less than 1000 Å forming a smooth integral part of the protective passive oxide layer should be considered acceptable.

More recent work by Grant et al.^(39, 40) showed that the amount of surface etching, and pitting, was directly proportional to the amount of heat tint present in the HAZ. They also observed that the amount of discoloration, and therefore amount of etching was greatly reduced by treating the post-welded tubing with a mixed chelant solution.⁽³⁹⁾ Auger line scans performed across the weld zones still showed lower Cr:Fe ratios in the HAZ, but the effects of chelant passivation did clearly demonstrate a significant decrease in the effects of heat tint. However, as they pointed out, treatments for removing the heat tint are not

practical in real life as most tubing in gas delivery systems are installed in the “as-welded” condition. Their discussion of the blue ring observed in the HAZ suggested that it may result from manganese that has been vaporized during welding and redeposited in the HAZ and it is this that is corroded preferentially. This is supported by the observation of the blue ring predominantly on the downstream side of the weld zone. However, they reported that Auger analysis of the HAZ showed a lower manganese concentration in the blue ring that was adjacent to clean areas. For deep brown colored heat tint in the HAZ, associated with high oxygen levels in the purge gas, the composition was reported as oxides of chromium and iron, formed when these elements are vaporized from the metal and redeposited on the surface, leaving a chromium depleted layer in the HAZ, which is more subject to localized corrosion.

Several other researchers have also shown that slight variations in the composition of the alloying elements in Type 316L can have a significant effect on the welding characteristics.^(39, 40, 41) This has been collaborated in preliminary experiments by Ralph Cohen at Intel Corporation⁽¹⁵⁾ where variations in discoloration and even no discernible discoloration were observed for different heat lots of steel welded under the same conditions. Using AES, Cohen also showed that there existed variations in the oxide layer thickness and chromium content across the weld zone region, even for no observable discoloration.⁽¹⁵⁾ This data suggests that steel considered acceptable for corrosive gas lines due

to no discoloration upon welding, may be susceptible to future corrosion. However, Cohen's work was performed on a single set of samples and has not yet been reproduced.

The need for consistency and uniformity of welded Type 316L stainless steel for ultra-high-purity gas lines is demanded by the industry, and even though no direct evidence that particulates on wafers have come from corrosion of the weld zones has been found, the first observation of corrosion in the gas lines has led to them being ripped out and replaced.^(15, 42)

At present, discoloration free weld zones are considered satisfactory in the installation of gas delivery lines, especially for use with corrosive gases (HCl, HBr). However, the lack of any discoloration does not guarantee they are not susceptible to future corrosion. At present, observance of any corrosion results in immediate replacement of the entire piping system. Several analyses have been undertaken at Surface Science Laboratories to characterize the corrosion, but as of yet, no evidence has been found in the literature to correlate the post installation corrosion with heat lots and welding parameters. There also does not appear to be much work reported on the corrosion mechanisms in the HAZ of electropolished Type 316L stainless steel when welded. The choice of Type 316L is assumed to eliminate carbide precipitation, but observations suggest otherwise. At present, care is taken by the installers of ultra-high-purity gas lines that tubing from the same heat lots is welded together to avoid discoloration on

one side of the weld zone for the same welding parameters⁽⁴²⁾. However, that is not always possible when the tubing is welded to valves or junctions, that although electropolished, may have come from a different manufacturer.

CHAPTER 4: RESEARCH OBJECTIVE

It is well established in the welding of steel that the HAZ becomes susceptible to intergranular corrosion. The temperature range that can induce this susceptibility, known as the sensitizing range, is less than the melting point required during arc welding, and extends several millimeters from the weld zone. For austenitic stainless steels this temperature range is 400 - 850°C. The extent of HAZ formation is also a factor of welding time. Therefore slow cooling through the sensitizing temperature after welding can increase the susceptibility for corrosion. On exposure to an oxidizing/corrosive environment, corrosion occurs in this region rather than the weld itself. This susceptibility to corrosion is principally caused by diffusion of carbon, in the steel, to the grain boundaries in this sensitizing region, forming chromium carbide (Cr_{23}C_6) precipitates along the grain boundaries, thus depleting the adjacent regions of the necessary 12% chromium content for passivity.

In the welding of electropolished Type 316L stainless steel, a band of discoloration approximately 1 millimeter from the weld joint is often observed, ranging from a faint gold band, to an opaque blue-gray haze. Optical micrographs showing typical discoloration in the HAZ are shown in Figures 1 and 2. AES analyses of these discolorations have determined them to be simply thicker oxide layers than that present on the rest of the tubing surface, and that the extent of the discolorations was an optical effect dependent on the thickness

of the oxide film.⁽³⁸⁾ Large variations in the discolorations have been observed under identical welding conditions, indicating that a different sensitivity occurs between tubing samples made from different heats of stainless steel.⁽¹⁵⁾ Variations in the oxide layer thickness and chromium content across the weld/HAZ region were also determined for weldments with no discoloration.⁽¹⁵⁾

The research and reports in the literature to date leave several important questions that are unanswered at the present. The most important topics that need to be addressed are as follows:

- 1) How much does the amount of discoloration depend upon the elemental composition of the steel?
- 2) What exactly is the nature of the discoloration in the HAZ?
- 3) How susceptible to corrosion are weldments with various levels of discoloration?

Great interest has been expressed by the electropolishers and the semiconductor industry in answers to the above. Preliminary work undertaken at Surface Science Laboratories has indicated a strong need to unravel the parameters governing weld oxidation. The overall intent of this study was to address the above topics.

The objective, therefore, was to weld several different heat lots of electropolished 316L stainless steel while leaking minute, controlled amounts of air into the argon purge, thus producing different amounts of heat tint (discoloration in the HAZ). The HAZ region and a reference area upstream from the weld on each specimen were then analyzed by AES to characterize the surface and oxide layer compositions to determine the nature of the discoloration. Each specimen was then cross-sectioned, and the corrosion current (corrosion rate) at 1 mm steps from the weld bead through the HAZ was measured in a 3.5% NaCl solution. The objective of this experiment was to determine the localized susceptibility to corrosion of the bulk and weld zones of the material.

Cross-sectioned specimens of the tubing showing the heaviest discoloration were then etched in oxalic acid. The objective was to observe the grain boundary structure of the inner tubing surface and of the bulk surface in the cross-sections to determine if carbide precipitation at the grain boundaries was in fact occurring.

CHAPTER 5: EXPERIMENTAL PROCEDURE

In order to obtain the best results from this study, it was required to prepare welded specimens of electropolished Type 316L stainless steel tubing under controlled conditions as would be performed in a “real life” situation. The development of a mixing panel to supply the purge gas for the welding was designed and built in Portland, Oregon, by Ralph Cohen of Intel Corporation. The welding operations were performed in a high-purity gas fabrication shop, again under the supervision of Ralph Cohen. The electropolished Type 316L stainless steel tubing used was supplied by commercial vendors.

The analysis of the tubing was performed at Surface Science Laboratories by X-Ray Fluorescence (XRF) and Auger Electron Spectroscopy (AES) in accordance with the SEMATECH Test Method 91060573B-STD for such testing.

The corrosion testing was carried out in the Corrosion Laboratory of the Materials Engineering Department at San Jose State University.

5.1 Materials used

Five heat lots of 1/4 inch diameter Type 316L stainless steel tubing, including two heat lots that did not weld satisfactorily at a FAB project in 1995,⁽¹⁵⁾ were used in this study. The heat lots selected included a typical “normal” heat (labeled V20892 and V40639), an Electron Beam Remelt (labeled EBR R3040),

a heat having a higher than normal tendency to oxidize ("heat tint") in the HAZ (labeled Trouble 1 V30110), a heat characterized as having severe weld bead meander¹, and a heat with a higher than normal chromium concentration (labeled High Cr 432958). The specimens of the first normal heat (V20892) were used to test and set up the parameters for the analysis, and were not included in the final data. The elemental bulk compositions of each heat lot as given by the suppliers are shown in Table 5.

5.2 Welding parameters

5.2.1 Equipment

The welding was done in a high purity gas fabrication shop using an ARC machine Model 207 power supply. The Mass Flow Controller (MFC) panel used to mix purified argon with compressed air in controlled amounts was designed by Ralph Cohen and also fabricated by the contractor. A schematic of the mixing panel is shown in Figure 9. Compressed air was used to better simulate a typical leak in the purge system during field welding. The mixing panel consisted of four Sierra model 840 MFC's with a four channel Sierra model 904 MFC controller. The purified argon was obtained from a cryogenic source

¹ Bead meander is defined as deviation of the weld bead from a perfect circle around the tube by a deflection of up to 25% of the bead width from the ideal circle.

Table 5: Elemental compositions measured by XRF

Element Wt. %	Normal V40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High Cr 432958	
	Supplier	SSL	Supplier	SSL	Supplier	SSL	Supplier	SSL	Supplier	SSL
Carbon	0.020	---	0.029	---	0.018	---	0.017	---	0.015	---
Nitrogen	0.010	---	0.001	---	---	---	0.036	---	0.033	---
Aluminium	0.002	---	0.009	---	0.004	---	0.004	---	0.003	---
Silicon	0.590	---	0.005	---	0.400	---	0.690	---	0.530	---
Phosphorus	0.027	---	0.001	---	0.024	---	0.026	---	0.022	---
Sulfur	0.009	---	0.005	---	0.010	---	0.011	---	0.007	---
Titanium	0.010	---	---	---	---	---	---	0.390	---	---
Vanadium	---	382 ppm	---	---	---	460 ppm	---	549 ppm	---	442 ppm
Chromium	16.490	16.690	16.290	16.630	16.950	16.940	16.640	16.780	17.300	17.230
Manganese	1.310	1.440	0.030	0.420	1.510	1.590	1.640	1.580	1.600	1.510
Iron	67.030	66.370	66.838	65.770	66.174	66.070	65.166	64.660	63.634	63.630
Cobalt	0.030	914 ppm	0.030	0.130	0.100	984 ppm	0.150	0.110	0.071	886 ppm
Nickel	12.270	13.070	14.580	14.690	12.480	13.150	12.990	13.710	14.000	14.830
Copper	0.030	---	0.002	---	0.280	---	0.470	0.480	0.200	---
Niobium	---	---	---	---	---	---	---	147 ppm	---	---
Molybdenum	2.170	2.310	2.180	2.360	2.050	2.100	2.160	2.220	2.580	2.670

SSL - Surface Science Laboratories

Figure 9: Schematic of the mixing panel used to supply the purge gas for the welding

purified with a Millipore Megaline model WPLV20251 purifier. The argon was certified from the supplier to be 0.4 ppm O₂, and < 1 ppm H₂O. The compressed air was supplied from a Campbell Housefield oil free compressor. The panel permitted blending to form a mixture where the air volume ranged from 0 - 0.008 liters per minute (lpm), and the argon volume ranged from 0 - 5.0 lpm. This mixture was mostly vented, but a small amount of the mixture (flow rate up to 0.05 lpm) was blended again with purified argon to form the very low concentrations of air:argon mixtures (down to 1 ppm O₂ in argon). All the gases were filtered using Mott Metallurgical sintered metal filters. The derived ratios of O₂:Ar were checked with a Delta-F Platinum Nanotrace O₂ analyzer and the mixture values determined, as shown in Appendix 1.

5.2.2 Procedure

Sections of tubing were welded in a high purity gas fabrication shop using an ARC machine Model 207 power supply. A total of 73 welding runs were performed including runs to establish the welding parameters. The total welding experimental data is shown in Appendix 2. After the welding, each tube was then classified according to the extent of oxidation in keeping with the recommendations in ASTM Standard D5531-94.⁽¹⁵⁾ The problem termed "oxidation" manifests itself as a faint blue-gray ring around the inside diameter of the tube either side of the weld bead approximately 1 mm from the weld bead. It tends to be more prominent on the downstream side of the weld, relative to the

direction of the purge gas. Acceptability is defined and the weld is considered “color free” when no ring is observed when viewed with a fluorescent lamp of a known wattage or a 3 volt halogen lamp at a fixed distance.

From the total number of welded tubes, the number of samples included in the sampling plan was limited in order to first determine if any major trends could be found. Also, due to the complexity of, and problems with, the welding process not all specimens were available. The sampling plan was established after review of the experiment’s objectives with an Intel process statistician.⁽¹⁵⁾ A total of 31 welded tubes were chosen for the analysis, covering all the different heats and purge gas levels. The sampling plan is shown in Table 6, where the samples from each heat are referred to by their run number.

The tubes were cut into lengths of approximately 8 to 12 inches long, cleaned with deionized water (including blowing two urethane foam plugs through each tube), and dried by blowing one urethane foam plug through each tube and then blowing dry with cryogenic, unpurified argon for three minutes. The tubes were packaged into individual nitrogen purged polyethylene bags after capping the end of each tube with an aclar swatch and cap and shipped to Surface Science Laboratories for analysis.

Table 6: Sampling plan

Oxygen content in purge gas (ppm)	Pass/Fail criteria		Oxidation level	Material welded					
	Fluorescent	Maglite		Normal 1 V20892	Normal 2 V40639	EBR R3040	Trouble 1 V30110	Trouble 2 V30112	High Cr 432958
0	Pass	Pass	None	#14, #15	#73	#12, #13	#21, #22	#25, #26	#29, #32
1.2	Pass	Pass	Light	NA	#69, #70	#53	NA	NA	#55, #56
6.3	Pass	Fail	Medium	NA	#67, #68	#52	#40, #41	#49, #50	#59, #60
31.6	Fail	Fail	Heavy	NA	NA	NA	#43, #44	#46, #47	#62, #63

5.3 Analysis techniques

5.3.1 Equipment

For this study, the analysis techniques used were X-Ray Fluorescence (XRF) and Auger Electron Spectroscopy (AES). XRF was used to determine the bulk composition of the stainless steel as supplied and compared with compositional data reported by the vendor. A full description of XRF as an analysis technique is given in Appendix 3. The AES was used to determine the surface and oxide composition of the tubing in the HAZ and on a reference area upstream from the weld joint. The AES was performed in accordance with the SEMASPEC Test Method 91060573B-STD as this is the most commonly used method for qualifying electropolished stainless steel accepted by the semiconductor industry, and allows for comparisons to be made to other data held in data bases.

The XRF equipment used was a Kevex Omicron small spot analyzer utilizing a rhodium X-ray tube operating at 30 kV.

For this analysis, an NIST certifiable standard of Type 316L stainless steel was used (see Appendix 3). Only the major constituents of the supplied specimens were determined for this analysis, as limited by the reported composition of the NIST standard.

The AES experiments were performed on a VG Scientific Microlab 310-F equipped with a field emission source and a background pressure of 10^{-10} torr. The depth profiles were acquired utilizing an EX05 scanning ion gun using argon

ions at an a energy of 3 kV, 1 μ A, rastered over a 4 mm² area. The argon etch rate was calibrated against a thermally grown layer of Ta₂O₅ of 1000 Å thickness on Ta. Due to the varying stoichiometry of the oxide layer on stainless steel, it was not possible to determine the exact oxide layer thickness as the relative etch rates to Ta₂O₅ are not known. Therefore the oxide layer thicknesses, defined as the depth at which the oxygen signal falls to half-maximum, are reported as Ta₂O₅ equivalent thicknesses, as accepted by the SEMATECH protocol. The basic principles of AES have been described in Section 2.4 under characterization methods for quality control.

5.3.2 Procedure

The stainless steel tubes were removed from their protective environment, and placed whole in the XRF analyzer. As this is a bulk technique, the outer diameter of the tubes were analyzed at locations away from the weld zone.

After the XRF analysis and prior to the AES analysis, the tubing samples were cut to approximately 3/4" in length. This was due to the maximum limitation of the sample size that can be inserted in the AES spectrometer. The samples were then cut along their axis to expose the inner diameter surface. The cutting was performed using a clean hacksaw blade, and care was taken to prevent any contamination getting on to the surfaces. The blades were of a fine cut with 32 teeth per inch to allow for smooth cutting, and minimizing any heat build up in the tubing.

The samples were analyzed with an electron beam energy of 10 kV and sample current of 50 nA at a magnification of 10000x. The analysis area was approximately 5 μm square in size. The sensitivity factors used in the quantification were obtained from an NIST certified standard of Type 316L stainless steel (Appendix 3).

5.4 Corrosion studies

5.4.1 Materials and equipment

Six representative specimens were chosen for the corrosion analysis. A section of the normal tubing (heat #V40639) with no weldments was used as the reference (control) sample. The other specimens were chosen to represent the various levels of oxidation, rather than the particular heat lot, as determined by the optical examinations of the HAZ, the AES data, and the availability of specimens from each heat lot.

The other specimens tested were: normal tubing with no visible discoloration (heat #V40639 - run #73), high chromium content tubing with no visible discoloration (heat #432958 - run #32), high chromium content tubing with medium discoloration (heat #432958 - run #60), trouble tubing with no discoloration (heat #V30112 - run #26), and trouble tubing with heavy discoloration (heat #V30112 - run #46).

The electrochemical data were collected using an EG&G Par 273 system using 342 Softcorr corrosion software. The measurements were carried out in a

3.5% NaCl solution at pH = 7 +/- 0.1 at room temperature (23°C). A standard KCl calomel electrode with a 1 mm porous plug was used as the reference electrode, and a graphite rod was used as the counter electrode.

5.4.2 Procedure

A thin stainless steel wire which would act as the working electrode, was spot-welded onto the back of each specimen. The specimens were then mounted in epoxy molding compound and mechanically polished with successive grits down to a final 0.3 μm alumina polish, producing a mirror finish on the cross-sectional surfaces. After polishing, the specimens were mounted in additional epoxy, and held in a spring loaded arm device on a flat granite table until the epoxy cured. The spring loaded arm was parallel to the surface of the granite so that the exposed polished surfaces were parallel to the bottom of the entire epoxy block.

The specimens were prepared so that measurements of the corrosion current could be taken along the exposed polished cross-sectional surface from the weld zone at 1 mm intervals, as shown schematically in Figure 10.

Each specimen in turn was placed in a fresh NaCl solution and set up as shown in Figure 11. The calomel reference electrode was held approximately 1 mm from the surface of the weld joint for each specimen in the solution, and a special rig with a micrometer screw was used to move the specimen 1 mm at a time under the reference electrode. The specially made epoxy block allowed for

Figure 10: Example of sample preparation for the corrosion analysis

Figure 11: Schematic of the experimental apparatus for the electrochemical analysis

the distance from the specimen surface to the reference electrode to be held constant along the tubing.

The measurements were run by biasing the specimens to -250 mV below the corrosion potential, E_{corr} , and then stepping the voltage to +250 mV above E_{corr} at a scan rate of 1 mV/sec. for each point along the specimen. Tafel plots were used to determine the corrosion current density (nA/cm^2) at each of the five points. The corrosion current was obtained by extrapolating the linear portion of each cathodic region of the curve to E_{corr} . The corrosion current density is directly proportional to the corrosion rate as given by Equation [1];⁽⁴³⁾

$$\text{Corrosion rate (mils per year)} = 0.13I_{\text{corr}}(\text{EW})/d \quad [1]$$

where

I_{corr} = corrosion current density, nA/cm^2

EW = equivalent weight of the corroding species, g

d = density of the corroding species, g/cm^3

For the purpose of this analysis, higher measured values for I_{corr} would indicate a greater susceptibility to corrosion, since only the relative corrosion current along the tube and between samples was of interest; the data are therefore reported as corrosion current density only. To determine the accuracy of the testing, several runs were taken along a reference sample with no weld. The reproducibility and variation of the measurements was determined to be within 10% of the value measured.

Finally, the cross-sectioned specimens were removed from their epoxy molds and subjected to an oxalic acid etch test, according to ASTM Practice A, a standard practice for detecting susceptibility to intergranular attack in austenitic stainless steel AISI grade Type 316L.⁽⁴⁴⁾

CHAPTER 6: RESULTS

In this section, the results of the bulk composition of specimens from all the heat lots as determined by XRF are presented. The thickness and composition of the oxide layer in the HAZ and adjacent reference areas of specimens from each heat, determined by AES, are presented and discussed. The corrosion susceptibility of the HAZ and reference areas on the inner surface and bulk of these specimens determined by Tafel plots are presented. Finally, the results of an oxalic acid etch on selected specimens to determine the presence of chromium carbide precipitation at the grain boundaries are discussed.

6.1 XRF data

The data for the XRF analysis, compared to the material composition for each sample type as reported by the vendors, is shown in Table 5. Fewer elements were scanned for in the XRF analysis and hence, after normalizing to 100%, the values obtained are slightly higher than those reported by the vendors. However, the data obtained at SSL show good agreement with that reported by the vendors. It was found that the chromium concentration in the high chromium (432958) specimen was not significantly higher than that of the specimen with the meander problem, Trouble 2 (V30110) (17.23% versus 16.94%) and was still well within the specification for chromium concentration in Type 316L stainless steel as indicated in Table 1a. It was also found that the

nickel concentration in both heat lots EBR R3040 and High chromium 432958 was above the upper limit for nickel in Type 316L stainless steel. The values measured were 14.69% and 14.83%, respectively, compared to an upper specified limit of 14%. The levels of other constituents of the specimens were reported by the vendors to be below the maximum allowed in the specification.

6.2 AES data

The results of the AES analysis of the surface in the HAZ and reference area of the as-received specimens, and of the resulting surface at the end of the depth profiles, are shown in Tables 7, 8, 9, 10, and 11, for specimens Normal V40639, EBR R3040, Trouble 1 V30110, Trouble 2 V30112, and High Chrome 432958, respectively. The data were obtained by measuring the elemental peak-to-peak heights in each spectrum and normalizing with sensitivity factors for each element that had been previously derived from standards. The AES data are presented as relative atomic percents and therefore cannot be correlated directly with the XRF data which are reported as weight percent.

From the peak shape and energy of the silicon peak, it was determined that the silicon was present in the oxide form on the as-received surface wherever it was detected. Silicon is one of the few elements that has a significant difference in peak shape and position between the elemental and chemical state, thus allowing for easy determination. All the other elements were reported in their elemental form. The etch depths reported in Tables 7 through 11 for the end of the profiles are Ta_2O_5 equivalent depths. At the end of the

Table 7: Normal V40639 - Relative atomic concentrations derived from the survey scans

Spectrum number	Sample description	Etch depth	Si(O)	Si	P	S	Mo	Cl	C	Ca	N	Sn	O	Cr	Mn	Fe	Ni	Mg
1	0 ppm ref	0A	0.3	---	1.9	0.6	---	0.1	49.	---	2.5	---	26	6.9	0.3	9.1	3.3	---
3	0 ppm ref	110A	---	---	---	---	1.2	---	8.8	---	---	---	0.7	15.	---	62.	12.	---
4	0 ppm HAZ	0A	0.6	---	---	0.2	---	0.5	39.	---	1.6	0.5	29	0.7	---	16.	2.9	1.3
6	0 ppm HAZ	120A	---	0.6	---	---	1.6	---	2.3	---	---	---	2.3	18.	---	63.	11.	0.7
7	1.2 ppm ref	0A	0.4	---	3.8	0.4	---	---	20.	---	2.3	---	39.	11.	---	16.	6.1	---
9	1.2 ppm ref	85A	---	---	---	---	1.5	---	2.5	---	---	---	2.6	17.	---	66.	11.	---
10	1.2 ppm HAZ	0A	1.2	---	0.5	0.1	---	0.4	25.	---	---	1.0	37	0.8	8.7	20.	3.8	0.9
12	1.2 ppm HAZ	120A	---	0.4	---	---	1.5	---	2.3	---	---	---	3.1	17.	0.9	63.	11.	1.2
13	6.3 ppm ref	0A	0.5	---	3.6	0.4	---	---	21.	---	2.3	---	39.	11.	---	16.	5.7	---
15	6.3 ppm ref	115A	---	0.4	---	---	1.9	---	1.3	---	---	---	0.5	18.	---	67.	11.	---
16	6.3 ppm HAZ	0A	1.9	---	---	0.1	---	0.1	25.	---	---	0.8	40.	0.5	4.7	21.	3.8	1.4
18	6.3 ppm HAZ	120A	---	0.3	---	---	1.5	---	2.1	---	---	---	4.1	15.	---	64.	12.	---

Table 8: EBR R3040 - Relative atomic concentrations derived from the survey scans

Spectrum number	Sample description	Etch depth	Si(O)	Si	P	S	Mo	Cl	C	Ca	N	Sn	O	Cr.	Mn	Fe	Ni	Mg
19	0 ppm ref	0A	---	---	5.7	0.4	---	---	24.	---	4.1	---	34.	11.	---	14.	5.9	---
21	0 ppm ref	115A	---	---	---	---	1.6	---	2.6	---	---	---	---	17.	---	66.	13.	---
22	0 ppm HAZ	0A	---	---	---	0.4	---	---	19.	0.8	1.4	---	37.	7.5	---	28.	5.5	---
24	0 ppm HAZ	90A	---	---	---	---	1.2	---	3.2	---	---	---	1.1	16.	---	65.	13.	---
25	1.2 ppm ref	0A	---	---	4.7	0.5	---	---	18.	---	4.2	---	39.	12.	---	15.	7.0	---
27	1.2 ppm ref	115A	---	---	---	---	1.9	---	2.4	---	---	---	1.5	17.	---	64.	13.	---
28	1.2 ppm HAZ	0A	---	---	---	0.2	---	---	16.	---	1.0	---	40.	7.2	---	30.	5.4	---
30	1.2 ppm HAZ	120A	---	---	---	---	1.6	---	1.2	---	---	---	1.7	17.	---	65.	13	---
31	6.3 ppm ref	0A	---	---	4.3	0.6	---	---	22.	---	3.6	---	38	11.	---	14.	6.7	---
33	6.3 ppm ref	115A	---	---	---	---	2.0	---	1.7	---	---	---	1.8	18.	---	64.	13.	---
34	6.3 ppm HAZ	0A	---	---	---	0.2	---	---	18.	---	1.4	---	45	6.3	---	26.	3.4	---
36	6.3 ppm HAZ	120A	---	---	---	---	1.4	---	1.0	---	---	---	4.9	18.	---	62.	13.	---

Table 9: Trouble 1 V30110 - Relative atomic concentrations derived from survey scans

Spectrum number	Sample description	Etch depth	Si(O)	Si	P	S	Mo	Cl	C	N	Sn	O	Cr	Mn	Fe	Ni	Cu	Mg
37	0 ppm ref	0A	---	---	3.7	0.6	---	0.2	33.	2.6	---	33.	9.5	3.2	9.9	4.7	---	---
39	0 ppm ref	115A	---	---	---	---	1.0	---	2.9	---	---	---	17	---	67.	13	---	---
40	0 ppm HAZ	0A	---	---	---	0.2	---	0.4	28.	---	1.3	37.	0.5	7.4	20.	4.2	---	1.6
42	0 ppm HAZ	90A	---	---	---	---	0.8	---	3.6	---	---	1.5	18.	---	64.	12.	---	---
43	6.3 ppm ref	0A	---	---	2.7	0.4	---	---	20.	2.9	---	41.	12	---	15.	6.8	---	---
45	6.3 ppm ref	85A	---	---	---	---	1.1	---	2.7	---	---	0.8	18.	---	65.	12.	---	---
46	6.3 ppm HAZ	0A	2.2	---	---	0.2	---	0.7	27.	---	1.2	37.	0.2	8.9	19.	3.3	---	---
48	6.3 ppm HAZ	120A	---	---	---	---	1.4	---	1.6	---	---	2.3	18	---	65.	12.	---	---
49	31.6 ppm ref	0A	---	---	3.0	0.5	---	---	20.	2.2	---	44.	11	1.0	12.	6.1	---	---
51	31.6 ppm ref	85A	---	---	---	---	0.9	---	1.9	---	---	1.1	19	---	66.	11.	---	---
52	31.6 ppm HAZ	0A	1.9	---	---	0.2	---	---	29.	---	1.0	39.	---	4.3	23.	1.9	---	---
54	31.6 ppm HAZ	340A	---	---	---	---	1.2	---	---	---	---	5.8	18.	---	64.	11.	---	---

Table 10: Trouble 2 V30112 - Relative atomic concentrations derived from survey scans

Spectrum number	Sample description	Etch depth	Si(O)	Si	P	S	Mo	Cl	C	N	Sn	O	Cr	Mn	Fe	Ni	Cu	Mg
55	0 ppm ref	0A	0.6	---	3.2	0.3	---	0.1	30.	2.8	---	34.	11.	---	13.	5.8	---	---
57	0 ppm ref	115A	---	---	---	---	2.3	---	3.3	---	---	---	18	---	65.	12.	---	---
58	0 ppm HAZ	0A	0.7	---	---	0.2	---	0.5	29.	---	0.7	36.	0.4	7.7	20.	4.2	0.7	1.0
60	0 ppm HAZ	90A	---	0.3	---	---	1.3	---	2.4	---	---	3.4	17.	2.1	61.	11.	0.5	0.6
61	6.3 ppm ref	0A	0.5	---	3.4	0.3	---	0.1	19.	2.3	---	42.	11.	---	14.	6.8	---	---
63	6.3 ppm ref	85A	---	0.3	---	---	1.3	---	1.0	---	---	0.6	18.	---	67.	12.	---	---
64	6.3 ppm HAZ	0A	2.1	---	---	0.2	---	0.2	20.	---	1.6	42	0.4	7.8	21.	3.5	---	0.4
66	6.3 ppm HAZ	120A	---	0.9	---	---	1.2	---	1.8	---	---	5.3	17.	2.2	59.	11.	0.6	1.0
67	31.6 ppm ref	0A	---	---	3.1	0.5	---	0.2	22.	2.5	---	42.	10.	---	12.	6.5	---	---
69	31.6 ppm ref	85A	---	---	---	---	2.5	---	3.4	---	---	1.4	18.	---	63.	12.	---	---
70	31.6 ppm HAZ	0A	2.8	---	---	---	---	0.3	18.	---	---	50.	0.9	12	17.	---	---	---
72	31.6 ppm HAZ	340A	---	0.5	---	---	1.7	---	---	---	---	2.9	18.	---	66.	11.	---	---

Table 11: High chrome 432958 - Relative atomic concentrations derived from the survey scans

Spectrum number	Sample description	Etch depth	Si(O)	Si	P	S	Mo	Cl	C	N	Sn	O	Cr	Mn	Fe	Ni	Mg
73	0 ppm ref	0Å	0.9	---	2.9	0.2	---	0.1	19.	2.9	---	41.	13.	---	12.	6.9	---
75	0 ppm ref	115Å	---	---	---	---	1.8	---	4.1	---	---	1.0	18.	---	63.	12.	---
76	0 ppm HAZ	0Å	1.7	---	---	0.3	---	0.4	29.	2.2	0.7	34.	1.4	3.5	22.	5.8	---
78	0 ppm HAZ	115Å	---	---	---	---	1.4	---	2.4	---	---	1.5	15.	---	65.	14.	---
79	1.2 ppm ref	0Å	0.9	---	2.7	0.3	---	0.1	15.	3.1	---	43.	14.	---	14.	7.5	---
81	1.2 ppm ref	85Å	---	---	---	---	2.1	---	1.8	---	---	0.5	19.	---	63.	13.	---
82	1.2 ppm HAZ	0Å	2.0	---	---	0.2	---	0.1	20.	2.5	---	38.	3.5	2.0	25.	6.3	---
84	1.2 ppm HAZ	85Å	---	---	---	---	2.3	---	---	---	---	---	20.	---	64.	14.	---
85	6.3 ppm ref	0Å	0.4	---	3.1	0.2	---	---	16.	2.9	---	43.	14.	---	13.	7.1	---
87	6.3 ppm ref	85Å	---	---	---	---	1.5	---	1.5	---	---	---	19.	---	64.	13.	---
88	6.3 ppm HAZ	0Å	4.8	---	---	0.3	---	0.2	23.	1.4	---	37.	2.7	3.2	21.	6.4	---
90	6.3 ppm HAZ	120Å	---	---	---	---	1.8	---	1.8	---	---	1.7	20.	---	62.	13.	---
91	31.6 ppm ref	0Å	0.4	---	2.3	0.2	---	---	22.	3.2	---	40.	12.	---	13.	6.7	---
93	31.6 ppm ref	85Å	---	---	---	---	1.9	---	2.2	---	---	1.9	19.	---	62	13.	---
94	31.6 ppm HAZ	0Å	2.5	---	---	0.3	---	0.1	56.	1.1	1.0	23	0.6	---	14	1.8	---
96	31.6 ppm HAZ	335Å	---	0.5	---	---	2.9	---	---	---	---	---	20.	---	63	13	---

depth profiles, minor carbon and oxygen were still detected in some cases. This has been observed to be typical for metal surfaces that have been inert gas ion etched with a unidirectional beam. This is due partly to the surface roughness induced by the ion beam with depth, resulting in shadowing of some parts of the surface. Examination of the compositions for all the specimens at the end of the depth profiles showed them to agree with the reported atomic concentrations for the major constituents: iron, chromium, nickel, and molybdenum, within the experimental error of the technique. The reproducibility of AES data at Surface Science Laboratories has been determined to be within 5% of the reported value when using certifiable standards. For comparison of the compositions of selected elements in the HAZ and in the reference area on the as-received surface, the concentrations of silicon (oxide), phosphorus, sulfur, carbon, tin, oxygen, chromium, manganese, iron, and nickel are summarized in Tables 12 through 21, and plotted in Figures 12 through 21, respectively. The actual AES data is included in Appendix 4.

Silicon oxide was detected in greater concentrations in the HAZ than the reference areas on all the specimens except EBR (R3040). The concentration of silicon in the EBR heat lot, as reported by the supplier, was significantly lower than the other heats. The silicon oxide content was also found to increase in the HAZ with increasing O₂ concentration in the purge gas.

Phosphorus was not in general found within the detection limits (approximately 0.2 - 0.5 atomic %) in the HAZ, and it did not seem to be a factor

Table 12: Atomic concentrations of surface silicon oxide

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	0.3	0.6	—	—	—	—	0.6	0.7	0.9	1.7
1.2 ppm	0.4	1.2	—	—	—	—	—	—	0.9	2.0
6.3 ppm	0.5	1.9	—	—	—	2.2	0.5	2.1	0.4	4.8
31.6 ppm	—	—	—	—	—	1.9	—	2.8	0.4	2.5

Figure 12: Silicon oxide variation for different levels of O₂ in weld purge

Table 13: Atomic concentrations of surface phosphorus

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	1.9	—	5.7	—	3.7	—	3.2	—	2.9	—
1.2 ppm	3.8	0.5	4.7	—	—	—	—	—	2.7	—
6.3 ppm	3.6	—	4.3	—	2.7	—	3.4	—	3.1	—
31.6 ppm	—	—	—	—	3.0	—	3.1	—	2.3	—

Figure 13: Phosphorus variation for different levels of O₂ in weld purge

Table 14: Atomic concentrations of surface sulfur

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	0.6	0.2	0.4	0.4	0.6	0.2	0.3	0.2	0.2	0.3
1.2 ppm	0.4	0.1	0.5	0.2	—	—	—	—	0.3	0.2
6.3 ppm	0.4	0.1	0.6	0.2	0.4	0.2	0.3	0.2	0.2	0.3
31.6 ppm	—	—	—	—	0.5	0.2	0.5	—	0.2	0.3

Figure 14: Sulfur variation for different levels of O₂ in weld purge

Table 15: Atomic concentrations of surface carbon

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	49	39	24	19	33	28	30	29	19	29
1.2 ppm	20	25	18	16	—	—	—	—	15	20
6.3 ppm	21	25	22	18	20	27	19	20	16	23
31.6 ppm	—	—	—	—	20	29	22	18	22	56

Figure 15: Carbon variation for different levels of O₂ in weld purge

Table 16: Atomic concentrations of surface tin

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	—	0.5	—	—	—	1.3	—	0.7	—	0.7
1.2 ppm	—	1.0	—	—	—	—	—	—	—	—
6.3 ppm	—	0.8	—	—	—	1.2	—	1.6	—	—
31.6 ppm	—	—	—	—	—	1.0	—	—	—	1.0

Figure 16: Tin variation for different levels of O₂ in weld purge

Table 17: Atomic concentrations of surface oxygen

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	26	29	34	37	33	37	34	36	41	34
1.2 ppm	39	37	39	40	—	—	—	—	43	38
6.3 ppm	39	40	38	45	41	37	42	42	43	37
31.6 ppm	—	—	—	—	44	39	42	50	40	23

Figure 17: Oxygen variation for different levels of O₂ in weld purge

Table 18: Atomic concentrations of surface chromium

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	6.9	0.7	11	7.5	9.5	0.5	11	0.4	13	1.4
1.2 ppm	11	0.8	12	7.2	—	—	—	—	14	3.5
6.3 ppm	11	0.5	11	6.3	12	0.2	11	0.4	14	2.7
31.6 ppm	—	—	—	—	11	—	10	0.9	12	0.6

Figure 18: Chromium variation for different levels of O₂ in weld purge

Table 19: Atomic concentrations of surface manganese

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	0.3	8.1	—	—	3.2	7.4	—	7.7	—	3.5
1.2 ppm	—	8.7	—	—	—	—	—	—	—	2.0
6.3 ppm	—	4.7	—	—	—	8.9	—	7.8	—	3.2
31.6 ppm	—	—	—	—	1.0	4.3	—	12	—	—

Figure 19: Manganese variation for different levels of O₂ in weld purge

Table 20: Atomic concentrations of surface iron

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	9.1	16	14	28	9.9	20	13	20	13	22
1.2 ppm	16	20	15	30	—	—	—	—	14	25
6.3 ppm	16	21	14	26	15	19	14	21	14	21
31.6 ppm	—	—	—	—	12	23	12	17	12	14

Figure 20: Iron variation for different levels of O₂ in weld purge

Table 21: Atomic concentrations of surface nickel

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	3.3	2.9	5.9	5.5	4.7	4.2	5.8	4.2	6.9	5.8
1.2 ppm	6.1	3.8	7.0	5.4	—	—	—	—	7.5	6.3
6.3 ppm	5.7	3.8	6.7	3.4	6.8	3.3	6.8	3.5	7.1	6.4
31.6 ppm	—	—	—	—	6.0	1.9	6.5	—	6.7	1.8

Figure 21: Nickel variation for different levels of O₂ in weld purge

of the O₂ concentration in the purge gas. Phosphorus is often detected on the surface of electropolished stainless steel as a residue from the electropolishing process. The lack of phosphorus in the HAZ suggests it volatilizes during welding and is carried downstream with the purge gas.

Sulfur was detected in all regions and was higher in the reference areas than the HAZ except for the High Chrome (432958) heat lot where it was found to be of approximately equal amounts in both regions. Sulfur is also typically found as a residue from the electropolishing process. It was detected in higher concentrations than reported to be found in the bulk of the material. Sulfur has been attributed to bead meander,⁽⁴⁵⁾ but heat lot Trouble 2 (V30112) which was reported to exhibit bead meander did not have a higher concentration of sulfur in the bulk or on the surface.

The carbon concentration showed a trend of decreasing with increasing O₂ concentration in the purge gas for all the heat lots except for High Chrome (432985). The amount of carbon typically observed on a metal surface exposed to the environment can vary from 30 - 50 relative atomic %. The exception here was the High Chrome (432958) specimen (56 atomic %) with the highest amount of O₂ in the purge gas and heaviest discoloration.

Tin was not reported in the mill certification as reported by the suppliers, or determined by XRF at SSL, but it appeared in the HAZ of all heats except EBR (R3040). Further analysis by XRF by Cohen⁽⁴⁵⁾ has shown the presence of tin in all heats except EBR, with the concentration somewhat higher in the two

Trouble heats (V30110 and V30112). Finding tin on the surface of the HAZ was unexpected and warrants further study to determine if it is significant.

The oxygen surface concentration showed a trend of increasing with increasing O₂ in the purge gas for all heat lots except for High Chrome (432958). There did not appear to be any difference in the oxygen concentration between the reference areas and the HAZ except for the High Chrome (432958) heat, in which the oxygen was lower in concentration in general in the HAZ.

The chromium concentration was significantly lower in the HAZ for all specimens, although somewhat less so in the High Chrome (432958) heat, and much less so in the EBR (R3040) heat. There did not appear to be any correlation between the concentration of chromium detected in the HAZ and the level of O₂ in the purge gas.

Manganese was present in the HAZ of all the heats except for EBR (R3040). The composition as determined by XRF and reported by the supplier showed the EBR heat to have a significantly lower manganese concentration in the bulk than the other heats. The level of manganese on the surface of the HAZ is significant in all cases and appeared to decrease at higher O₂ concentrations in the purge gas except for the Trouble 2 (V30112) heat where the level increased. Recent literature^(46, 47) has suggested that the discoloration in the HAZ of welded electropolished stainless steel was caused by redeposition of manganese, which had volatilized from the weld zone, downstream of the weld. However, from this data it was observed that the level of manganese in

the HAZ for the normal heat (V40639) with no O₂ in the purge gas was the same as that for the Trouble 1 heat (V30110) with medium to heavy discoloration.

The iron concentration was higher in the HAZ than in the reference area for all heats, but no correlation was observed between the iron concentration and the level of O₂ in the purge gas.

The nickel concentration was lower in the HAZ than in the reference area for all heats and tended to decrease with increasing O₂ in the purge gas.

Copper was detected in the HAZ of the heat Trouble 2 (V30112) which exhibited a bead meander problem when welded. The XRF data and supplier certification both show that the copper concentration was significantly higher in this heat as compared to the others. It is thought that copper is an impediment to successful welding of 1/4 inch tubing.⁽⁴⁵⁾ As previously mentioned, sulfur is often attributed to bead meander, but heats showing the same sulfur content did not exhibit a bead meander problem.

The chromium to iron ratios and the oxide layer thicknesses for each specimen were measured as defined in Section 2.4. The depth profile in the reference area for specimen V40639 (normal) is shown as an example in Figure 22. The oxide layer thickness was measured to be 29 Å which is in the correct range for typical well electropolished stainless steel (20 - 50 Å). The oxide layer was found to be chromium enriched with the chromium concentration higher in the oxide layer than in the bulk of the material, compared to the iron

Figure 22: AES depth profile data for Normal V40639

concentration. The maximum chromium-to-iron ratio in the oxide layer was measured as 1.66:1, which is well above the minimum of 1.5:1, and is typical of well electropolished stainless steel. This specimen can be considered as a good example of well electropolished stainless steel. By contrast, the depth profile for the heavily discolored HAZ for the specimen 432958 (High chrome) is shown in Figure 23. For this specimen, a thick oxide layer of 92 Å, which was predominantly iron with no chromium enrichment, was observed. The maximum chromium-to-iron ratio in the oxide layer was estimated to be 0.38:1. This specimen can be considered an extreme bad sample of electropolished stainless steel, and an iron enriched oxide layer like this may well be susceptible to corrosion in the presence of a corrosive fluid and moisture.

The chromium-to-iron ratios for all the specimens are summarized in Table 22, and shown in Figure 24. In general, the chromium-to-iron ratios were typical for the reference areas (> 1.5:1) with no oxygen in the purge gas, but were borderline or below typical for all levels of oxygen in the purge gas, and tended to be lower as the O₂ purge gas level increased. It was found that the High Chrome specimens showed on average slightly higher chromium-to-iron ratios for all specimens. The chromium-to-iron ratios for the HAZ regions for all specimens were considerably less, with no significant difference observed between the specimens.

Figure 23: AES depth profile data for High Chrome 432985

Table 22: Cr:Fe ratios derived from the depth profiles

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	1.66	0.40	1.51	0.52	1.69	0.43	1.51	0.36	1.71	0.47
1.2 ppm	1.16	0.38	1.34	0.41	—	—	—	—	1.45	0.39
6.3 ppm	1.25	0.24	1.42	0.50	1.41	0.11	1.32	0.2	1.65	0.45
31.6 ppm	—	—	—	—	1.54	0.05	1.52	0.32	1.50	0.38

Figure 24: Cr:Fe ratios for different levels of O₂ in weld purge

The oxide layer thicknesses for all the specimens are summarized in Table 23 and shown in Figure 25. From this data, a difference in the oxide layer thicknesses was found between the reference area and the HAZ region as the level of oxygen in the purge gas increased, with the highest level (31.6 ppm) producing significantly thicker oxide layers. The thickest oxide layers were determined for the Trouble (V30110 and V30112) and the High Chrome (432958) heat lots which also showed the heaviest discoloration. This data indicates that the level of discoloration is dependent on the oxide layer thickness. The oxide layer thickness measured for the reference areas of the bulk material was determined to be similar between specimens for all oxygen leak levels.

6.3 Corrosion data

For the corrosion data, an example of the Tafel plot for the High Chrome specimen (432958) at the weld zone is shown in Figure 26. This plot was typical for the data collected. A summary of the data collected for all the specimens tested is shown in Table 24, and plotted for each specimen in Figures 27 through 32. The complete corrosion data is included in Appendix 5.

For the normal (V40639) specimen, in the reference area and in the HAZ zone showing no discoloration, very little variation in the corrosion data along the surface was found within the limits of accuracy ($\pm 10\%$) of the technique. The variation in the absolute values obtained between the two specimens was probably due to the different thickness of the tubing walls exposed by the cross-

Table 23: Oxide layer thicknesses derived from the depth profiles in A

	Normal 40639		EBR R3040		Trouble 1 V30110		Trouble 2 V30112		High chrome 432958	
O ₂ in purge	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ	REF	HAZ
0 ppm	29	26	19	16	21	22	20	21	21	16
1.2 ppm	17	21	18	14	—	—	—	—	19	15
6.3 ppm	19	31	19	29	18	30	18	29	19	18
31.6 ppm	—	—	—	—	19	84	19	110	18	92

Figure 25: Oxide layer thickness for different levels of O₂ in weld purge

Figure 26: Typical Tafel plot data (High Chrome 432985)

Table 24: Measured corrosion current (I_{corr})

Distance from weld (mm)	Normal 40639 Ref. area	Normal 40639 None	High chrome 432958 None	High chrome 432958 Medium	Trouble V30112 None	Trouble V30112 Heavy
	(nA/cm ²)	(nA/cm ²)	(nA/cm ²)	(nA/cm ²)	(nA/cm ²)	(nA/cm ²)
0	13	31	42	41	28	12
1	12	31	45	49	39	22
2	10	32	22	39	30	18
3	9	33	24	42	34	19
4	9	34	21	32	30	21

Figure 27: Corrosion current versus distance from weld

Figure 28: Corrosion current versus distance from weld

Figure 29: Corrosion current versus distance from weld

Figure 30: Corrosion current versus distance from weld

Figure 31: Corrosion current versus distance from weld

Figure 32: Corrosion current versus distance from weld

sections, resulting in different current density readings. However, it is the relative values along the length of the tubing walls, from the weld zone, that are of interest, and therefore this difference in current density between the specimens was not considered.

For the High Chrome (432958) and Trouble 2 (V30112) specimens, showing no and medium or heavy discoloration, higher corrosion currents were measured at approximately one millimeter from the weld zone, in the vicinity of the HAZ, in all cases. The specimen showing the largest variation along the tube length was the High Chrome (432958) with no discoloration (0 ppm O₂ leak). These data indicate that an increased susceptibility to corrosion was observed in the bulk of the material corresponding to the HAZ, regardless of the level of discoloration on the inner surface of the tubing in the HAZ. These data also correlates with the AES data, in that low Cr:Fe ratios, i.e. Fe enriched oxide layers in the HAZ, were found even on specimens with no visible discoloration. This suggests the lack of presence of discoloration in the HAZ does not indicate less susceptibility to corrosion.

6.4 Oxalic acid etch analysis

Micrographs, taken in the SEM mode in the field emission Auger spectrometer, showing the grain structure in the HAZ and reference area on the inner tubing wall surface, are shown in Figures 33 and 34, respectively. Similarly, micrographs taken of the bulk surface in the HAZ and reference area

on the cross-sectioned surfaces, are shown in Figures 35 and 36, respectively. The subsequent SEM analysis and micrographs showed evidence of step structures, with steps observed at the grain boundaries, but no evidence of any ditch structures which would be characteristic if there was carbide precipitation at the grain boundaries.

The oxalic acid etch is such that the lack of ditch structuring around the grain boundaries, and presence of steps, would confirm that there is no carbide precipitation in the HAZ for these Type 316L stainless steel specimens that would be responsible for the HAZ corrosion.

Figure 33: Micrograph of the inside tubing surface in the HAZ after oxalic acid etch. Specimen V30112 (#46). Magnification = 1000x

Figure 34: Micrograph of the inside tubing wall in a reference area after oxalic acid etch. Specimen V30112 (#46). Magnification = 1000x

Figure 35: Micrograph of the bulk tubing surface in the HAZ after oxalic acid etch. Specimen V30112 (#46). Magnification = 1000x

Figure 36: Micrograph of the bulk tubing surface in a reference area after oxalic acid etch. Specimen V30112 (#46). Magnification = 1000x

CHAPTER 7: DISCUSSION

Five different heat lots of electropolished stainless steel were used in this study, and were welded under similar conditions. Heat lots V40639 and R3040 were examples of typical weldments, the difference between these two was that heat lot R3040 was Electron Beam Remelted (EBR). Heat lot V30110 was characterized as having a higher than normal tendency to oxidize (HAZ discoloration), and heat lot V30112 was characterized as having severe weld bead meander. Heat lot 432958 was included as a heat having an elevated chromium composition. In this section, the effects of the elemental composition, the amount of oxygen in the purge gas, and the effects of corrosion on the welded specimens are discussed.

7.1 Effects of elemental composition

The levels of discoloration optically observed in the HAZ for the various levels of oxygen in the purge gas were similar for all the heat lots. Similarly, the results of the corrosion testing showed an increase in the corrosion susceptibility in the HAZ for all the welded specimens, regardless of the oxygen exposure and composition. However, there were significant differences detected in the results of the AES data for certain elements among the different heat lots that correlated with the bulk elemental compositions. These differences may have an effect on the long-term corrosion resistance or on the corrosion susceptibility to severely corrosive environments.

The Cr:Fe ratios in the HAZ were on average slightly higher for the high chromium concentration heat lot (432958) and the EBR heat lot (R3040) than the other heats. The relative chromium and iron concentrations in the HAZ were significantly higher in the EBR heat (R3040) for all oxygen exposures. The nickel concentration was also higher in the HAZ for the high chromium heat (432958) and the EBR heat (R3040). However, significant amounts of silicon oxide and manganese were detected in the HAZ of all the specimens except for the EBR heat (R3040). These data correlate with the bulk composition determination for each heat by XRF. Tin was also detected in the HAZ for each heat except for the EBR heat (R3040), although it was not detected initially in the bulk by XRF. The effects of tin and silicon on the corrosion performance of electropolished stainless steel are not known at present, but are not immediately considered a problem. However, the amounts of manganese detected were significant (up to 12 relative atomic %). There is considerable debate regarding the role of manganese in the corrosion of the HAZ in electropolished stainless steel. Kobayashi,⁽¹⁾ Miyoshi et. al.,⁽⁴⁶⁾ and Grant et. al.⁽⁴⁷⁾ all report that manganese is released during welding and re-deposited in the vicinity of the weld forming the blue-brown discoloration observed. This then acts as a catalyst for corrosion in the HAZ, especially in the presence of moisture. Manganese has a relatively high vapor pressure compared to the other major constituents of stainless steel, as shown in Table 25. However, Miyoshi⁽⁴⁶⁾ reported that the maximum manganese concentration occurred on 316L stainless steel at a distance of

**Table 25: Table of vapor pressures of respective elements in 316L stainless steel
(After Kubaschewski and Evans; ref. 51)**

$P_{\text{STD}}^{\text{Mn}} = 6.170 \text{ mm Hg.}$	$P_{\text{alloy}}^{\text{Mn}} = 0.02P_{\text{STD}}^{\text{Mn}} = 123 \times 10^{-3} \text{ mm Hg}$
$P_{\text{STD}}^{\text{Cr}} = 0.013 \text{ mm Hg.}$	$P_{\text{alloy}}^{\text{Cr}} = 0.17P_{\text{STD}}^{\text{Cr}} = 2.11 \times 10^{-3} \text{ mm Hg}$
$P_{\text{STD}}^{\text{Fe}} = 0.020 \text{ mm Hg.}$	$P_{\text{alloy}}^{\text{Fe}} = 0.66P_{\text{STD}}^{\text{Fe}} = 1.32 \times 10^{-3} \text{ mm Hg}$
$P_{\text{STD}}^{\text{Ni}} = 0.002 \text{ mm Hg.}$	$P_{\text{alloy}}^{\text{Ni}} = 0.13P_{\text{STD}}^{\text{Ni}} = 0.26 \times 10^{-3} \text{ mm Hg}$

For stainless steel of approximate composition:

66 % Fe, 17% Cr, 13% Ni, and 2% Mn and at a melting point of 1387°C (1662°K)⁵⁹

5 - 10 mm downstream from the weld bead. AES analyses were performed on a specimen of heat lot V30110 (highest tendency to oxidize) which showed the highest level of discoloration. Survey scans were taken 1 mm apart starting from the edge of the weld zone, and the data is shown in Table 26 and Figure 37. The manganese concentration reached a maximum at a point 6 mm from the weld zone, well past the observed discoloration in the HAZ. Optical measurements of the observed discoloration for all the specimens showed it generally to be between 1.5 to 3.5 mm from the weld bead. Manganese was detected at a very low concentration in the base metal (0.03 wt. %) of the EBR heat (R3040) compared to the other heats (1.31 - 1.64 wt. %), but no manganese was detected for the EBR heat (R3040) in the HAZ. The levels of discoloration and measured surface oxide layers for the heat were similar to the other heats, and combined with the data shown in Figure 37, suggests that the presence of manganese by itself cannot be the cause for the oxidation in the HAZ of weldments. As stated earlier, this conclusion derives from the measurement of manganese content from the weld bead, showing the deposits occur increasingly away; there is no high manganese concentration corresponding to the HAZ.

Copper was prominent in the bulk analysis (0.47 - 0.48 wt. %) for the Trouble 2 heat (V30112) which had a bead meander problem when welded. Copper was detected in the HAZ of this heat. Tracking of the welding and chemical composition of 14 other heats by Cohen⁽¹⁵⁾ exhibited neither bead

Table 26: Relative atomic concentrations across HAZ

Specimen V30110 (#44)	C	O	Cr	Mn	Fe	Ni
Pt. 1 Edge of weld zone	15.	47.	5.1	1.1	28.	1.5
Pt. 2 Between weld zone and HAZ	14.	48.	5.6	3.1	24.	1.3
Pt. 3 Blue zone HAZ	17.	42.	2.4	7.6	25.	1.9
Pt. 4 Brown zone HAZ	15.	46.	0.9	9.9	24.	1.9
Pt. 5 1 mm past HAZ	14.	45.	3.1	13.	20.	1.9
Pt. 6 2 mm past HAZ	14.	44.	4.6	17.	16.	1.2

Figure 37: Plot of surface composition versus distance from the weld bead

meander or as high a copper content. Bead meander or arc deflection (arc blow) is one of the most troublesome problems encountered in welding and also is the least understood.⁽⁴⁸⁾ It is generally attributed to an imbalance of magnetic forces within the weld pool in ferromagnetic materials, but can also be encountered with non-magnetic materials. The role of copper in the mechanism of bead meander is therefore a target for further study.

7.2 Effects of O₂ concentration in the argon purge gas

A direct correlation between the amount of discoloration in the HAZ and the amount of oxygen in the purge gas was observed. All of the tested samples welded with a concentration of 1.2 ppm O₂ in the purge gas, showed a degree of oxidation low enough to pass the in-house QC optical inspection, but levels above that produced optically observable discoloration that was proportional to the amount of oxygen in the purge gas and resulted in thicker oxide layers.

The Cr:Fe ratios, as determined from the AES depth profiles, which are considered a general measure of the state of the oxide layer, were significantly reduced in the HAZ of all the specimens. The Cr:Fe ratios tended to decrease with increasing oxygen concentration in the purge gas. The AES data showed the chromium concentration in the HAZ was considerably less than the reference area, while the iron concentration was higher for all the specimens. Previous analyses^(15, 36, 38, 47, 49, 50) have also reported lower Cr:Fe ratios in the HAZ.

At the high temperatures used in the welding process, it would be expected that the chromium would preferentially oxidize to form Cr_2O_3 over iron in the vicinity of the weld zone.⁽⁵⁰⁾ This mechanism is supported by the standard free energies of formation (ΔG°_f) of the relevant oxides⁽⁵¹⁾ at 289°K as shown in Table 27. Observation of the data shows that the ΔG°_f for Cr_2O_3 is far more negative and therefore more thermodynamically stable than for FeO , Fe_2O_3 , and Fe_3O_4 . The following oxidation-reduction reactions will occur for the constituents in their standard state:

However, the chromium and iron are not in their standard states, but their concentrations are relatively high so that it is assumed that their activities are equal to their mole fraction and the above directions of the reactions hold true.

It is therefore expected that Cr_2O_3 would be formed on the surface of the stainless steel in the vicinity of the weld zone, but this was not the case observed in the HAZ in this study. In the weld itself, the temperature is that of the melting point of the stainless steel, and there is a temperature gradient away from the weld along the tubing. It was therefore of interest to determine the temperature gradient going away from the weld zone, to estimate the actual temperature of

**Table 27: Table of free energy of formation of respective oxides in 316L stainless steel
(After Kubaschewski and Evans; ref. 51)**

Reaction	ΔG_f°(kcal/mole O₂) 298°K	ΔG_f(kcal/mol O₂) 298°K	ΔG_f°(kcal/mole O₂) 873°K	ΔG_f(kcal/mole O₂) 873°K
$4/3\text{Cr} + \text{O}_2 = 2/3\text{Cr}_2\text{O}_3$	-166.1	-163.7	-142.3	-135.4
$\text{Ni} + \text{O}_2 = \text{NiO}$	-51.4	-49.2	-37.9	-31.6
$2\text{Fe} + \text{O}_2 = 2\text{FeO}$	-115.2	-113.8	-97.8	-93.6
$4/3\text{Fe} + \text{O}_2 = 2/3\text{Fe}_2\text{O}_3$	-117.0	-115.7	-93.6	-89.8
$3/2\text{Fe} + \text{O}_2 = 1/2\text{Fe}_3\text{O}_4$	-119.3	-118	-97.8	-93.9

Where $\Delta G_f = \Delta G_f^\circ + RT \ln K$

the metal in the HAZ. This was simulated mathematically as described in Appendix 6, with the results shown in Figure 38. Optical observations of the discolored region in the HAZ on the specimens showed the blue and brown coloring to be approximately between 1.5 mm and 3.5 mm from the edge of the weld zone. From Figure 38, this correlates to a temperature range of approximately 480°C to 760°C with a mid-point at around 600°C. This also correlates with the sensitized zone in steel occurring between 400 - 850°C.⁽³²⁾ Calculations of the ΔG°_f at 600°C (873°K) are also presented in Table 27, where it was observed that Cr_2O_3 formation is still favored. Therefore the presence of an iron oxide top layer in the HAZ needs to be explained.

Work by G. Betz et al.⁽⁴⁹⁾ showed that when a Type 304 stainless steel sample without an oxide layer was heated in vacuum, the Cr:Fe ratio was a function of the temperature of treatment, with a significant drop in the Cr:Fe ratio occurring in the temperature range of 400°C to 700°C. Similar studies by T. Von Molte et al.⁽³⁶⁾ on Type 304 stainless steel, also showed a significant drop in the Cr:Fe ratio for specimens heated in air in a weld simulator. In this case the drop was noted between 300°C and 600°C.

It was suggested by Betz et al.⁽⁴⁹⁾ that the presence of an iron oxide layer in this temperature range is due to the rapid growth kinetics involved with the formation of FeO, compared to that of Cr_2O_3 and the other iron oxides. The growth rate of FeO has been reported to vastly exceed that of Fe_2O_3 and

Figure 38: Plot of temperature versus distance from weld

Fe_3O_4 ,⁽⁵²⁾ and since Cr_2O_3 and Fe_2O_3 have similar crystal structures and mutual solid solubility, this would indicate a slower growth rate for Cr_2O_3 than FeO . The iron enriched zone in the HAZ is postulated to be caused by this rapid growth of FeO at the surface. However, no evidence was shown in their work, or in this present study, to support this hypothesis.

Unfortunately, oxide chemical state differences cannot be readily determined by AES for the transition metals, and so it was not possible from these data to confirm the presence of FeO rather than the other iron oxides in the outer surface region of the specimens. Although ESCA can resolve chemical state differences for transition metal oxides, the depth of the information (50 - 100 Å) obtained by ESCA is far greater than the thickness of the surface oxide layer (typically 20 - 30 Å) and hence it would not be possible to differentiate the outer layer composition. Advances in the hardware (e.g. field emission sources) and software (e.g. Target Factor Analysis (TFA)) now make it possible to perform AES depth profiles and determine different chemical state compositions with depth, even for thin oxide layers due to the shallow escape depth of Auger electrons (typically 5 - 40 Å).

The use of Field Emission AES and TFA to determine the composition of the iron-enriched oxide layer in the HAZ in the temperature range around 600°C, would be a target for further study on Type 316L stainless steel and other 300 series alloys.

7.3 Effects on corrosion properties

The corrosion data showed a higher susceptibility to corrosion at a distance of approximately 1 mm from the edge of the weld zone for all the welded specimens tested, regardless of the level of discoloration in the HAZ. This data indicates that all weld zone HAZs are susceptible to corrosion, and unaffected by the level of discoloration, which has been shown to be an optical effect depending upon the thickness of the oxide layer. The oxide layer thicknesses for the low levels of O₂ in the argon purge gas during welding (1.2 and 6.3 ppm) were similar to that for the reference areas, but the Cr:Fe ratios were significantly lower, indicating iron-rich regions. So even though no discoloration was observed on these specimens, the HAZs were iron-rich compared to the reference areas.

The tests were performed in a standard 3.5% NaCl solution with a pH of 7 at room temperature (23°C). However, in actual usage in a semiconductor FAB, the tubing may actually meet a far more corrosive environment such as WF₆ or HCl. Work performed by T. Von Molte et al.⁽³⁶⁾ in 3.5% NaCl solution adjusted to pH 1 with HCl on Type 304 stainless steel, showed severe pitting corrosion in the vicinity of the HAZ of simulated weld specimens where they also reported a significant decrease in the Cr:Fe ratio and iron-rich oxide layer. The mechanism for the pitting corrosion observed with an iron-rich layer was attributed to the iron-rich layer acting as an ion-selective membrane and allowing the migration of chloride ions from the electrolyte to the metal surface, but inhibiting outward

diffusion of the chlorides. This leads to a build up of chloride ions, acting as the trigger for pitting. However, such a mechanism depends upon the maintenance of an iron oxide layer on the surface. They also observed that for slower potential scan rates, the pitting was not observed, which was attributed to the iron oxide layer being chemically dissolved from the surface during the scan, leaving a surface composition similar to that of the bulk.

CHAPTER 8: CONCLUSIONS

The discoloration in the HAZ commonly observed in welded electropolished stainless steel is caused by contamination by O_2 of the argon purge gas used during welding. The amount of discoloration is a function of the concentration of O_2 in the purge gas. It was determined that the nature of the discoloration was a thick iron enriched oxide layer, with the severity of the discoloration proportional to the thickness of the oxide layer.

The extent of discoloration was also affected by the chemical composition of the original steel. The Electron Beam Remelt (EBR) heat lot showed the lowest chromium depletion in the HAZ than even the High Chromium heat lots. The EBR heat also showed the lowest concentration of contaminants such as sulfur and phosphorus in the bulk, although no correlation between the level of discoloration and the presence of these contaminants was observed.

The corrosion data indicated an increase in the corrosion susceptibility for the HAZ, relative to the weld edge, and that this was true not only for the inner tubing surface, but also through the thickness of the tubing. The level of discoloration on the inner surface was shown not to be a factor. However, to increase the statistical reliability of the data, it is recommended for future work that more corrosion current measurements be taken.

Significant amounts of manganese were detected in the HAZ of all the specimens, although again the level of discoloration was not dependent on the manganese concentration. The HAZ regions on all the heat lots were

determined to be iron enriched and chromium depleted and it has been reported that the presence of manganese on these regions acts as the catalyst for corrosion in the presence of a corrosive agent and moisture. However, the exact mechanism of how this happens has not yet been determined. No evidence of carbide precipitation at the grain boundaries for the worst discolored cases was observed, which would rule this mechanism out as being the cause for the higher susceptibility for corrosion. It is postulated that the iron rich layer in the HAZ is due to the kinetics of the formation of iron oxide over that of chromium oxide in the sensitizing temperature range found in the HAZ. It is recommended that future work be performed to determine if similar results are obtained among other alloys of the Type 300 series, and of different alloys.

In summary, the sensitization of electropolished stainless steel in the HAZ cannot be avoided and is a fact of life. These areas will continue to be of concern as future corrosion sites, but steps to reduce this can be taken. The discoloration, which at present can lead to the rejection of welded joints just by its presence, can be avoided by tighter controls of the contamination of the inert purge gas during welding. Levels of 1.2 ppm O₂ and below do not appear to affect the degree of oxidation in the samples that passed the QC inspection. Electron Beam Remelting the steel, although producing a composition that did not show a higher chromium composition in the bulk, showed a HAZ with lower chromium depletion than the other heats after welding.

Materials of compatible composition should be specified when welding materials from different heats, and closer attention to details of manufacturing, handling and welding parameters is needed to produce the highest quality stainless steel tubing for ultra-high purity applications.

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APPENDIX 1: Dilution Calculator

Example Oxygen concentration for Run #57 (Heat High Chrome 432958)

Calculate flow rate required for 1st stage dilution:

Dilution required:	155	
Main argon flow:	1.24 slpm	= FLOW 3
Air flow required	0.008 slpm	= FLOW 4

Calculate flow rate required for 2nd stage dilution:

Dilution required:	215	
I.D. purge flow required:	4.41 slpm	= FLOW 1+2
Flow of air/argon required:	0.021 slpm	= FLOW 2
Flow of 2nd stage ar required:	4.389 slpm	= FLOW 1
Corrected dilution:	214	

FLOW 4	=	0.008 where flow 4 is main air MFC
FLOW 3	=	1.24 where flow 3 is main argon MFC
FLOW 2	=	0.021 where flow 2 is MFC amount of flow used for 2nd dilution after combining 4 + 3
FLOW 1	=	4.389 where flow 1 is MFC amount af argon used in 2nd dilution

PPM of air in purge = $30.148 [(1000000 * F4 * F2) / (F3 * F1)]$

PPM of oxygen in purge = 6.3

APPENDIX 2: WELD EXPERIMENT DATA

WELDING PARAMETERS: O2 LEAK VS. DISCOLORATION: VARIOUS HEATS									
PHYSICAL PARAMETERS:	RUN 8	RUN 11	RUN 16	RUN 17	RUN 18	RUN 19	RUN 20	RUN 21	RUN 22
HEAT #:	V20892	B3040	V20892		V30110				
HEAT DENOTER	"typical"	"EBR"	"typical"		"oxide"				
DATE	7/7/95				7/19/95				
TIME	15:15	15:40	16:45	17:00	08:30	08:45	08:55	10:30	10:45
WELD MACHINE (ARC 207)	13448								
HEAD #:	15723								
TUBE SIZE	0.25"								
TUBE WALL	0.035"								
AMBIENT TEMPERATURE (F)	70				72				
TUNGSTEN DIAMETER	1/18"								
ARC GAP	0.03"								
ORIFICE DIAMETER	1/16"								
WELD PROGRAM:									
ROTATION DELAY	1.5								
PULSE HIGH TIME	0.1								
PULSE LOW TIME	0.1								
LEVEL 1 AMPS	34								
L1 BACKGROUND AMPS	12								
LEVEL 2 AMPS	31					34			
L2 BACKGROUND AMPS	12								
LEVEL 3 AMPS	29	27	29						
L3 BACKGROUND AMPS	7								
LEVEL 4 AMPS	26	24	26		27				
L4 BACKGROUND AMPS	7								
TIME 1	3								
TIME 2	3								
TIME 3	3								
TIME 4	4								
DOWNSLOPE	6	6.5	6						
TOTAL REVLTN. less D5	0.55								
TOTAL REVLTN. incl. D5	1.34								
RPM	9.2								
PURGE PARAMETERS									
PREPURGE TIME (secs.)	120						600		
PURGE FLOW: HEAD (slpm)	35								
PURGE FLOW: ID (slpm)	6.89		6.59	6.89	6.88				
POST PURGE TIME (secs.)	20								
FLOWMETER: AIR (F4)	0		0.005	0.005	0				
FLOWMETER: AR MAIN (F3)	0.05		5	2.5	0.24				
AIR 1ST DILUTION RATE	0		1000	500					
FLOWMETER: 1ST MIX (F2)	0.05		0.014		0.05				
FLOWMETER: AR 2ND (F1)	6.84		6.88		6.89				
AIR 2ND MIX DILUTION RATE	0		499		0				
O2 ANAL. READING (ppb)	NA								
CALC. O2 CONC. (ppm)	NA		2	4	0				
MAIN AIR	40				40				
MAIN AR	30				32				
BLEEDOFF FLOW (slpm)	0				1				
I.D. PRESSURE READING	3.5								
OBSERVATIONS									
COLOR (downstrm of weld)	none	sit. haze	none			sit. blue			
IRREGULARITIES (bead ext.)	none								
BEAD WIDTH	2 mm	2.8 mm	2 mm		1.5-2 mm	1.5-2 mm			
BEAD CONTOUR	flat	slight concave	flat						

WELDING PARAMETERS: O2 LEAK VS. DISCOLORATION: VARIOUS HEATS									
PHYSICAL PARAMETERS:	RUN 23	RUN 24	RUN 27	RUN 28	RUN 29	RUN 30	RUN 31	RUN 32	RUN 37
HEAT #:	V30112		432958						V30110
HEAT DENOTER	meander		"high Cr"						"oxide"
DATE	7/7/95								7/27/95
TIME	11:30	11:50	14:10	14:30	14:55	15:10	15:30	15:45	10:45
WELD MACHINE (ARC 207)	13448								
HEAD #:	15723								
TUBE SIZE	0.25"		0.5"						
TUBE WALL	0.035"		0.049"						
AMBIENT TEMPERATURE (F)	72								
TUNGSTEN DIAMETER	1/18"								
ARC GAP	0.03"		0.032"						
ORIFICE DIAMETER	1/16"								
WELD PROGRAM:									
ROTATION DELAY	1.5								
PULSE HIGH TIME	0.1								
PULSE LOW TIME	0.1								
LEVEL 1 AMPS	34		54				52		35
L1 BACKGROUND AMPS	12		18						12
LEVEL 2 AMPS	34		50	45					36
L2 BACKGROUND AMPS	12		18						12
LEVEL 3 AMPS	29		45						30
L3 BACKGROUND AMPS	7		18						7
LEVEL 4 AMPS	27		43						28
L4 BACKGROUND AMPS	7		18						7
TIME 1	3		6						3
TIME 2	3		5						3
TIME 3	3		5						3
TIME 4	4		5						4
DOWNSLOPE	6								
TOTAL REVLTN. less D5	0.55		1.04						
TOTAL REVLTN. incl. D5	1.34		1.36						
RPM	9.2		3.2						9.2
PURGE PARAMETERS									
PREPURGE TIME (secs.)	600	300							600
PURGE FLOW: HEAD (slpm)	35								
PURGE FLOW: ID (slpm)	6.88	6.57	4.41						
POST PURGE TIME (secs.)	20		30						
FLOWMETER: AIR (F4)	0								0.008
FLOWMETER: AR MAIN (F3)	0.24								1.24
AIR 1ST DILUTION RATE	500								155
FLOWMETER: 1ST MIX (F2)	0.05								0.021
FLOWMETER: AR 2ND (F1)	6.89	6.52	4.36						6.88
AIR 2ND MIX DILUTION RATE	0								328
O2 ANAL. READING (ppb)	NA								300
CALC. O2 CONC. (ppm)	0								4.1
MAIN AIR	40								
MAIN AR	32								30
BLEEDOFF FLOW (slpm)	1								0.25
I.D. PRESSURE READING	3.5		1.5						3.5
OBSERVATIONS									
COLOR (downstrm of weld)	OK	OK	OK	OK		OK	OK		ok mag
IRREGULARITIES (bead ext.)	dress	dress	none	none		none	none		
BEAD WIDTH	1.8 mm	1.5 mm	2.5-3 mm	2.5 mm		flat	2.5 mm		
BEAD CONTOUR	concave	flat	flat	flat			flat		

WELDING PARAMETERS: O2 LEAK VS. DISCOLORATION: VARIOUS HEATS									
PHYSICAL PARAMETERS:	RUN 38	RUN 39	RUN 42	RUN 45	RUN 48	RUN 51	RUN 53	RUN 54	RUN 57
HEAT #:	V30110			V30112		B3080		432958	
HEAT DENOTER	"oxide"			meander		"EBR"		"high Cr"	
DATE	7/27/95								8/4/95
TIME	11:20	11:40		14:00		15:10	15:40	16:15	11:00
WELD MACHINE (ARC 207)	13448								
HEAD #:	15723								
TUBE SIZE	0.25"							0.5	
TUBE WALL	0.035"								
AMBIENT TEMPERATURE (F)	72								
TUNGSTEN DIAMETER	1/18"								
ARC GAP	0.032								
ORIFICE DIAMETER	1/16"								
WELD PROGRAM:									
ROTATION DELAY	1.5								
PULSE HIGH TIME	0.1								
PULSE LOW TIME	0.1								
LEVEL 1 AMPS	35							54	
L1 BACKGROUND AMPS	12							18	
LEVEL 2 AMPS	36					32		50	
L2 BACKGROUND AMPS	12							18	
LEVEL 3 AMPS	30							45	
L3 BACKGROUND AMPS	7							18	
LEVEL 4 AMPS	28					26		43	
L4 BACKGROUND AMPS	7							16	
TIME 1	3							6	
TIME 2	3							5	
TIME 3	3							5	
TIME 4	4							5	
DOWNSLOPE	6								
TOTAL REVLTN. less D5	1.04								
TOTAL REVLTN. incl. D5	1.36								
RPM	9.2							3.2	
PURGE PARAMETERS									
PREPURGE TIME (secs.)	600			300		120		300	
PURGE FLOW: HEAD (slpm)	35								
PURGE FLOW: ID (slpm)	4.41								
POST PURGE TIME (secs.)	20								
FLOWMETER: AIR (F4)	0.008						0.005		0.008
FLOWMETER: AR MAIN (F3)	1.24		0.4		1.24		2		1.24
AIR 1ST DILUTION RATE	155		50		155		400		155
FLOWMETER: 1ST MIX (F2)	0.042	0.032	0.051		0.032		0.015	0.01	0.021
FLOWMETER: AR 2ND (F1)	6.84		6.85		6.84		6.89	4.4	
AIR 2ND MIX DILUTION RATE	163	214	134		214		450		214
O2 ANAL. READING (ppb)	618	470	2350		475		96	109	475
CALC. O2 CONC. (ppm)	3.4	6.3	31.6		6.3	5.3	1.2		6.3
MAIN AIR	40								
MAIN AR	30								
BLEEDOFF FLOW (slpm)	0.25		2		6.25			9	6.2
I.D. PRESSURE READING	3.5							1.5	
OBSERVATIONS									
COLOR (downstrm of weld)	fail fluo.	ok fluor.	very ox.	very ox.	ok fluor.	ok fluor.		ok fluor.	ok fluor.
IRREGULARITIES (bead ext.)	fail mag	fail mag	meander	deposits	fail mag	ok mag		ok mag	fail mag
BEAD WIDTH	1.5-2 mm	1.8-2 mm		1.8-2 mm	1.8-2 mm	2-2.5 mm		2.5 mm	1.5-2mm
BEAD CONTOUR	flat							flat	flat

WELDING PARAMETERS: O2 LEAK VS. DISCOLORATION: VARIOUS HEATS									
PHYSICAL PARAMETERS:	RUN 58	RUN 61	RUN 64	RUN 65	RUN 66	RUN 69	RUN 71	RUN 72	RUN 73
HEAT #:	432958		40639						
HEAT DENOTER	"high Cr"		"typical"						
DATE	8/4/95								
TIME	12:45	13:40	14:40			15:50	16:20		
WELD MACHINE (ARC 207)	13448								
HEAD #:	15723								
TUBE SIZE	0.5"								
TUBE WALL	0.035"								
AMBIENT TEMPERATURE (F)	74								
TUNGSTEN DIAMETER	1/18"								
ARC GAP	0.03"								
ORIFICE DIAMETER	1/16"								
WELD PROGRAM:									
ROTATION DELAY	1.5								
PULSE HIGH TIME	0.1								
PULSE LOW TIME	0.1								
LEVEL 1 AMPS	53		35		38				
L1 BACKGROUND AMPS	18		12						
LEVEL 2 AMPS	49		32		33				
L2 BACKGROUND AMPS	18		12						
LEVEL 3 AMPS	47		30		31				
L3 BACKGROUND AMPS	18		7						
LEVEL 4 AMPS	45		26		27				
L4 BACKGROUND AMPS	18		7						
TIME 1	6		3						
TIME 2	5		3						
TIME 3	5		3						
TIME 4	5		4						
DOWNSLOPE	6								
TOTAL REVLTN. less D5	1.04								
TOTAL REVLTN. incl. D5	1.36								
RPM	3.2		9.2						
PURGE PARAMETERS									
PREPURGE TIME (secs.)	300		120					300	
PURGE FLOW: HEAD (slpm)	35								
PURGE FLOW: ID (slpm)	4.41								
POST PURGE TIME (secs.)	30								
FLOWMETER: AIR (F4)	0.008					0.005	0		
FLOWMETER: AR MAIN (F3)	1.24	0.1		1.24		2	0		
AIR 1ST DILUTION RATE	155	50		155		400	0		
FLOWMETER: 1ST MIX (F2)	0.021	0.033	0.051	0.032		0.015	0		
FLOWMETER: AR 2ND (F1)	4.4		6.55	6.88					
AIR 2ND MIX DILUTION RATE	214	133		213		450	0		
O2 ANAL. READING (ppb)	475	2570				105	11		
CALC. O2 CONC. (ppm)	6.3	31.6		6.3		1.2	0		
MAIN AIR	40						0		
MAIN AR	30					29	30		
BLEEDOFF FLOW (slpm)	2					8.5	0		
I.D. PRESSURE READING	1.5								
OBSERVATIONS									
COLOR (downstrm of weld)	ok fluor.	v. oxid.	v. oxid.	ok fluor.	ok fluor.		ok fluor.	ok fluor.	ok fluor.
IRREGULARITIES (bead ext.)	fail mag			fail mag	fail mag		fail mag	ok mag	ok mag
BEAD WIDTH	2.5 mm		1.5 mm	1 mm	1.5 mm		1.6 mm		
BEAD CONTOUR	flat			flat	flat		convex		

Notes from weld experimental data:

Any blank in the data can be assumed to be the same as first number on the left of the blank

Runs 1 - 7 were used to establish weld parameters for heat V20892. They were recorded manually

Runs 14 and 15 were the actual specimens based on run 8 parameters

Run 9 was skipped

Run 10 was used to establish weld parameters for heat B3040

Runs 12 and 13 were the actual specimens based on run 11 parameters

Runs 16 and 17 were trying to achieve oxidation (discoloration) at weld. Inadequate time allowed for mixing

Runs 21 and 22 were the actual specimens based on run 20 with heat V30110

Runs 25 and 26 were the actual specimens based on run 24 with heat V30112

Runs 29 and 32 were the actual specimens based on run 28 parameters

Runs 40 and 41 were specimens from run 39

Runs 43 and 44 were specimens from run 42

Runs 46 and 47 were specimens from run 45

Runs 49 and 50 were specimens from run 48

Run 52 was a specimen from run 51

Runs 55 and 56 were specimens from run 54

Runs 59 and 60 were specimens from run 58

Runs 62 and 63 were specimens from run 61

Runs 67 and 68 were specimens from run 66

Run 70 was a specimen from run 69

APPENDIX 3: X-RAY FLUORESCENCE AND TYPE 316L STAINLESS STEEL NIST CERTIFICATE OF ANALYSIS

X-Ray Fluorescence is an excellent elemental analysis technique for rapid, simultaneous, non-destructive identification of all elements with atomic numbers greater than oxygen ($Z > 8$). Detection limits are generally in the low ppm range for all elements with atomic numbers greater than neon ($Z > 10$). An X-ray beam is used to irradiate a specimen, and the emitted fluorescent X-rays are analyzed with a crystal spectrometer and scintillation or proportional counter. The sampling depth for stainless steel is typically greater than 10 μm , and so it is considered a bulk analysis technique.

The fluorescent radiation is diffracted by a crystal at different angles to separate the X-ray wavelengths and therefore identify the elements. Quantification is performed by measuring the relative peak intensities. For accurate quantification, standards of the material being analyzed are required.

For this analysis, an NIST certifiable standard of Type 316L stainless steel was used. For the supplied specimens, the major constituents were determined by XRF at SSL as limited by the reported composition of the NIST standard. A copy of the NIST standard certificate is shown on the next page.

Certificate of Analysis
STANDARD REFERENCE MATERIAL 1155
Stainless Steel
Cr 18-Ni 12-Mo 2 (AISI 316)

(This material also is available in chip form as SRM 160b, primarily for application in chemical methods of analysis)

Element	Percent by Weight
Carbon	0.046
Manganese	1.63
Phosphorus	0.020
Sulfur	.018
Silicon	.502
Copper	.169
Nickel	12.18
Chromium	18.45
Vanadium	0.047
Molybdenum	2.38
Cobalt	0.101
Lead	.001

SIZE AND METALLURGICAL CONDITION: Samples are 1¼ in (3.2 cm) in diameter and ¾ in (1.9 cm) thick, and are issued in the annealed condition.

ANALYTICAL CERTIFICATION: The value listed for an element is the present best estimate of the true value based on the use of methods at NBS of high reliability. To check for possible systematic errors, other SRM's were chemically analyzed concurrently. The value is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for values having subscripted numbers the deviation is not expected to be more than ± 5 in the subscripted numbers. Based on the results of homogeneity testing, maximum variations within and among samples are less than the estimated accuracy figures given above.

Washington, D. C. 20234
August 4, 1969

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

APPENDIX 4: AES DATA

APPENDIX 5: CORROSION DATA

APPENDIX 6: Heat flow in welding

During the welding process, many complex thermal cycles are produced that affect the physical, chemical, and metallurgical properties of the metal, resulting in three distinct metallurgical zones that are upon completion of the weld, namely: the weld-zone, the Heat Affected Zone (HAZ), and the base-metal zone. There are two thermal states associated with the welding process; the quasi-stationary start, and the non-stationary state. The quasi-stationary state represents a steady thermal response in respect to a moving heat source, and occurs close to the weld during long welding cycles. The non-stationary state occurs at the beginning and end of a weld. Mathematical analysis of the quasi-stationary state is easier as the problem can be considered as a steady heat-flow problem for a moving coordinate. To simplify the analysis in this study, the non-stationary state was not considered, and the effect of the argon flow across the HAZ was assumed to be negligible. For a full description of the mathematical derivation and literature review, the reader is referred to the references. ^(53 54, 55)

In this study, the thermal conditions near the weld zone were of interest, particularly the distribution of the peak temperature in the HAZ. The distribution of peak temperatures in the base metal adjacent to the weld for a semi-infinite plate of thickness t is given by: ⁽⁵⁵⁾

$$1/(T_p - T_o) = (4.13\rho C_p t Y/H_{net}) + 1/(T_m - T_o) \quad [A1]$$

where T_p is the peak temperature ($^{\circ}\text{C}$) at distance Y (mm) from the weld fusion boundary, T_o is the initial temperature ($^{\circ}\text{C}$), T_m is the melting temperature of the alloy ($^{\circ}\text{C}$), H_{net} is the net energy input (J/s.mm), ρ is the density of the material (g/mm^3), C_p is the specific heat of the solid metal ($\text{J/g.}^{\circ}\text{C}$), and t is the thickness of the base metal (mm).

The net energy input H_{net} , is given by:

$$H_{\text{net}} = \eta VI/v \quad [\text{A2}]$$

where V is the arc voltage (volts), I is the arc current (Amperes), v is the weld speed (mm/s), and η is the arc efficiency.

In tungsten-gas arc welding, a substantial part of the heat generated at the electrode tip dissipates into the electrode holder, and a wide range of arc efficiencies of between 36 to 46% for TIG welded steel have been reported.⁽⁵⁶⁾ For this analysis, an average value of 41%, or $\eta = 0.41$ was used (values of the peak temperature were also calculated for the 36 and 46% values, and the spread is shown by the error bars in the plot). Also for these specimens, the welding current was pulsed, and so the arc current (I) was taken as the average current over one cycle for the welding parameters for a typical specimen V30110.

The other values used for the calculation of the peak temperature of the metal as a function of distance from the boundary of the weld zone are shown in Table A1. These values are a first approximation, but provide for a reasonably accurate simulation of the determination of the temperature gradient from the weld zone. The results are shown in plotted form in Figure 38 in the discussion section.

Table A1: Values used for weld heat flow calculation

Parameter	Value	Reference
Density (ρ)	7.8 gm/cm ²	54, 57
Specific heat (C_p)	0.51 KJ/Kg.°C	54, 57, 58
Sample thickness (t)	0.089 cm	Appendix 2
Arc efficiency (η)	0.41	56
Arc voltage (V)	9 V	Appendix 2
Arc current (I)	20.9 A	Appendix 2
Melting point of 316L (T_m)	1387 °C	59
Initial temperature (T_o)	23 °C	Appendix 2

IMAGE EVALUATION TEST TARGET (QA-3)

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