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The Development of Low Cost GMAW Fe-Al-Cr Filler Metals for Corrosion Resistant Weld Overlay...

January 2007

The Development of Low Cost GMAW Fe-Al-Cr Filler Metals for Corrosion Resistant Weld Overlay Applications

by

Matthew R. Galler

Presented to the Graduate and Research Committee
of Lehigh University
in Candidacy for the Degree of
Masters of Science

in

Materials Science and Engineering

Lehigh University

This thesis is accepted and approved in partial fulfillment of the requirements for the Master of Science

10-16-06

Date

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Acknowledgements

I would like to acknowledge and thank my advisors, Professor Arnold Marder and Professor John DuPont, for providing me the opportunity to perform research with the Engineering Metallurgy Group. Your technical, professional, and personal advice has been key in my learning process here at Lehigh University over the last 2 years. Professor DuPont, thank you for your assistance in helping me pursue my dream to live and study in Austria. Your confidence in my abilities and support has been invaluable in my decision to continue my education in Materials Science. Dr. Marder, thank you for always being there for support and guidance. I always left your office with a smile on my face.

I would like to thank the members of the EMG and fellow graduate students: Jon Regina, Ryan Deacon, Tim Anderson, Rick Noecker, Ken Adams, Jeff Farren, Joe Murphy, Patrick Clasen, and Ram Chandra. Jon and Ryan: Thank you for your enthusiasm and mentorship; I truly learned so much about how to be a great leader from both of you. To EMG: I will miss all of the laughs but take with me the good times and the knowledge that I will never work with a group of people that are so willing and capable to solve any problem, both technical and personal. To Pat and Ram, thanks for your great friendship and for instilling the passion for success and for personal growth.

I would also like to thank Arlan Benscoter for his metallographic aid and for his passion to help and teach students. I would like to thank Dave Ackland for his help with the Probe, Mike Rex for his welding advice, and Bill Mushock for his electrical knowledge.

Special thanks go to my family and friends for listening with love and helping me make my decisions. To my Dad, thanks for keeping me on the right path to success and having such great confidence in my ability to finish my thesis. Thanks to my Mom, for always being there, for helping me follow my dreams, and for being a great role model in my life. Thanks to my brothers Mike and Jon, for all of the great times in the past. I look forward to all of the ski trips in Austria together. Thanks to Uncle Al, for the unforgettable days fly fishing on the Lehigh River, and for sharing all of your knowledge about fishing and life.

I would especially like to thank my girlfriend Iris. You have taught me so much about myself and you have been my motivation to succeed in everything that I do. I love you so much.

Table of Contents

Acknowledgements.....iii

Table of Contents.....iv

List of Tables.....v

List of Figures.....vi

Abstract.....1

1. Introduction.....2
   1.1 Corrosion of Fe-Al based alloys.....3
   1.2 Weldability of Fe-Al based alloys.....4
   1.3 Hydrogen Cracking.....7
   1.4 Dilution.....10
   1.5 GMAW Transfer Characteristic.....11
   1.6 Summary of Fe-Al-Cr Weld Overlay Requirements and Project Outlines.....12

2. Experimental Procedure.....13

3. Results and Discussion.....17

   3.1 Minimizing Globular-to-Spray Transition Current and Hydrogen Cracking.....17
   3.2 Summary of Weldability, Transition Current, and Hydrogen Cracking Results.....24
   3.2 Corrosion Behavior.....25

4. Conclusions and Recommendations.....27

5. Future Work.....28

List of Tables

Table I - Potential hydrogen trapping sites in ferritic steels and the associated binding energy for each trap site....29

Table II - Filler metal wire and base metal chemical compositions using ICP-AES....30

Table III - Table showing the optimal shielding gas and minimum spray arc current for each welding wire....30

List of Figures

Figure 1 – Kinetic data for Fe-Al-Cr weld overlays in a simulated low NOx environment at 500°C.[4] 31

Figure 2– Compositional welding boundary for binary Fe-Al weld deposits. Blue numbers indicate aluminum concentration in weight percent, red numbers indicate number of cracks (M represents more than 15 cracks).[3] 31

Figure 3 – Weldability curve showing the cracking susceptibility of Fe-Al-Cr weld overlay claddings and the cracking dependence on the aluminum and chromium concentrations of the claddings.[4] 32

Figure 4: Particle surface area as a function of the weld metal carbon concentration for Fe-Al-Cr weld overlays deposited on plain carbon substrates.[4] 32

Figure 5: Effect of Yttrium additions to Fe-filled cored wires on the amount of diffusible hydrogen content in the weld deposit. [16] 33

Figure 6: Diagram showing the effect of processing parameters on dilution with experimental date for the SAW process. Low melting power and high filler metal feed rates are desired for low dilution values.[17] 33

Figure 7: Electrode tip during welding displaying different modes of GMAW metal transfer. A) Spray transfer and B) globular transfer mode.[19] 34

Figure 8: Transition current between spray and globular transfer. Transition current is a function of electrode composition, wire diameter, and shielding gas. [19] 34

Figure 9: Hydrogen cracking in Fe-Al-Cr weld overlays from welding with the 0.045" cored wire. 35

Figure 10: Diagram showing the number of cracks versus the average welding current for a variety of shielding gases at 30 volts 35

Figure 11: Diagram of number of crack versus welding current for different shielding gases at 32 volts. The 90%Ar-7.5%He-2.5%CO_2 mixture produced crack free overlays at the lowest Welding Current 36

Figure 12: Crack measurements plotted against the welding current for different Ar/He mixtures of shielding gases. The 50%Ar-50%He mixture produced crack free results at the lowest 36

Figure 13: Diagram showing measured dilution as a function of melting power for the 0.045" filler metal with fluoride addition. 37

Figure 14: GTA weldability study with 0.062" cored wire electrode. Hydrogen cracking occurred at very low aluminum and chromium concentrations.............37

Figure 15: Diagram showing the effect of heat treatment of cored wire electrode. Crack free fusion zone compositions approach cracking boundary. 38

Figure 16: GMA weldability study using 0.062" cored wire electrode. Cracking behavior depends on type of shielding gas used during welding process. 38

Figure 17: GMA weldability study shows that heat treatment of the cored wire allows for crack-free aluminum composition up to 9 wt %. 39

Figure 18: GMA weldability study using 0.045" cored wire electrode with fluoride additions. Multi-pass overlays could not be deposited crack free due to hydrogen cracking. 39

Figure 19: GMA weldability study of 0.045" wire after heat treatment. 7.5wt% Al-3.5wt% Cr alloy from multi-pass weld overlay selected for corrosion tests in a simulated low NOx environment...40

Figure 20: GMA weldability study of Fe-Al-Cr solid wires containing solid Al core with chromium powder , solid aluminum core with TiC, and power cored wire with yttrium oxide...40

Figure 21: Microstructure of A) Solid aluminum core wire and B) cored wire containing yttrium oxide additions. 41

Figure 22: Microstructure of weld overlay from Fe-Al-Cr slid core wire containing TiC additions. 41

Figure 23: Long term corrosion results of alloy 7.5wt% Al 3.5 wt% Cr in low NOx conditions at 500°C. Critical concentrations of 10wt% Al and 5wt% Cr must be obtained for excellent corrosion resistance...42

Abstract

Fe-Al-Cr weld overlays are being considered for corrosion protection of boiler tubes operating under low NOx burner conditions. The weldability of these alloys using gas tungsten arc welding (GTAW) and gas metal arc welding (GMAW) was investigated and compositions have been identified for corrosion resistance in simulated low NOx environments. It is known that hydrogen cracking occurs in these claddings at elevated Al and Cr compositions and is strongly related to the microstructure in the weld fusion zone and the amount of diffusible hydrogen present in the weld overlay. This current study investigated the hydrogen cracking susceptibility and corrosion resistance of Fe-Al-Cr powder cored and solid core wires with hydrogen trapping and arc stabilizing additions. Five different Fe-Al-Cr filler metal wires were fabricated and weld overlays were produced using various shielding gases, voltages, filler metal feed rates, and travel speeds. Single-pass and multi-pass weld overlays were tested for metal transfer mode, hydrogen cracking susceptibility, dilution, and corrosion resistance. It was discovered that cracking of Fe-Al-Cr weld claddings made with GMAW occurred at much lower Al and Cr concentrations than the GTAW process. The weldability limit for crack-free weld overlays from various filler metals was around 8 wt% Al and 4 wt% Cr for single pass with the GMAW process. Heat treating the cored wires before welding improved the weldability with both GTAW and GMAW processes. The crack-free multi-pass weld overlay composition of 7.5 wt% Al and 3.5 wt% Cr was tested for long term corrosion in a simulated low NOx environment. It was determined that the corrosion behavior of

Fe-7.5 wt% Al-3.5 wt% Cr was very similar to IN-622, which is currently used for weld overlays on boiler tubes. Future work is needed to minimize the diffusible hydrogen level of these Fe-Al-Cr overlays in order to reduce cracking at higher Al and Cr levels.

1. Introduction

Corrosion on waterwall tubes has become a problem for fossil-fueled power companies. The Clean Air Act recently called for a reduction in the amount of harmful NOx compounds released into the air, prompting utilities to alter their burner conditions to reduce the amount of NOx compounds in the furnace exhaust. As a result, several power plant operators have moved toward a staged combustion process in order to reduce boiler emissions. By delaying the mixing of fuel and oxygen, the amount of nitrous oxides (NOx) that is released as a by product of combustion is reduced. The staged combustion process consists of starving the lower furnace zones of oxygen and adding oxygen at higher elevations in the furnace. This process creates a reducing atmosphere in the lower furnace zone due to lack of oxygen in the fuel rich atmosphere. As a result, sulfur compounds from the coal, such as SO_2 and SO_3, are transformed into highly corrosive gaseous H_2S. Since the implementation of staged combustion, high temperature corrosion has caused undesirable tube metal loss and has resulted in several shutdowns due to tube failure.[1]

Power companies have considered using alternate corrosion resistant materials to reduce the amount of corrosion that occurs on boiler tube walls. The favored solution to the problem of waterwall wastage has been to deposit a weld overlay cladding of a more corrosion resistant alloy on to the tube. Commercially available nickel based superalloys, such as Inconel 625 and 622, have been used for weld overlays. Although these alloys provided more protection in the reducing environment than standard steels, they are considered expensive and are susceptible to circumferential cracking due to microsegregation.[2] One alloy system that is less costly and has been known to provide a good corrosion resistant coating is the Fe-Al-Cr system. These alloys have advantages over commercially available alloys because they are cheaper and do not exhibit microsegregation.[3] One potential obstacle to the application of Fe-Al-Cr alloys is their susceptibility to hydrogen cracking at elevated Al concentrations. Although a comprehensive gas tungsten arc weldability study has been performed on these alloys investigating the hydrogen cracking phenomenon[2], the fossil-fueled power companies deposit these overlays using gas metal arc welding due to its high deposition rate and ease of operation. One of the major issues when welding with cored wire electrodes is the diffusible hydrogen potential. It is important to limit the diffusible hydrogen level in the overlay in order to avoid hydrogen cracking. Various studies have shown that diffusible hydrogen content in weld overlays is dependent on welding parameters, electrode type, and weld metal microstructure.[5-7]

1.1 Corrosion of Fe-Al based Alloys

Recent work at Lehigh University has focused on development of alloys specifically for weld overlays in low NOx boilers. Fe-Al based alloys have demonstrated superior corrosion behavior over commercial alloys such as austenitic stainless steel or nickel based super alloy coatings in sulfidizing environments. The superior behavior is attributed to the formation of a passive Al_2O_3 layer for corrosion protection rather than a Cr_2O_3 scale that forms on the Ni-based super alloy and the stainless steel alloy.[8] The addition of Cr to Fe-Al alloys can help improve the corrosion resistance of alumina forming alloys. Figure 1 shows the corrosion kinetics of Fe-Cr-Al alloy is significantly reduced compared to that of binary a Fe-Al alloy. Cr additions are beneficial because they decrease the critical Al concentration needed to form a uniform protective Al_2O_3 layer.[9] Fe-Al-Cr alloys have a critical Al content of approximately 10 wt % Al and require a Cr content of 5 wt% Cr to significantly reduce the amount of corrosion that occurs in simulated Low NOx environments.[4] Therefore, the critical composition of 10 wt % Al-5 wt % Cr will be targeted for the fusion zone of Fe-Al-Cr weld overlays using GMAW.

1.2 Weldability of Fe-Al Based Alloys

Optimization of the weld overlay processes for high temperature boiler tubes requires the ability to weld in spray transfer, to achieve low dilution levels, and to produce creak-free overlays at compositions that are corrosion resistant. The weldability of alloys for overlay applications is as crucial a factor as corrosion resistance for determining its overall performance. Welding defects, such as hydrogen cracking, provide easy paths for corrosive gases to attack base metal, rendering it unable to protect the waterwall tube.

Banovic et al[3] examined the weldability of binary Fe-Al alloys using gas metal arc welding and gas tungsten arc welding with solid Al core electrodes. Intergranular and transgranular cracking of the Fe-Al cladding occurred in deposits containing greater than 10 wt % Al in the fusion zone for both types of welding processes. Creak-free single pass overlays were deposited with the GMAW process at fusion zone compositions up to 8 wt% Al. Figure 2 shows a welding matrix of single pass welds prepared using GTAW. Each data point is labeled cracked or non-cracked and represents a different Al concentration in the weld overlay. It is shown that cracking occurs above 10 wt% Al, which is approximately the boundary between the disordered iron solid solution α and the ordered intermetallic phase Fe_3Al.[3] Alloys in the intermetallic composition range demonstrate low ductility values and are susceptible to environmental embrittlement, while alloys in the disordered α range are immune to environmental embrittlement and demonstrate good room temperature ductility.[10] The weld overlay susceptibility to cracking may be due to the presence of the intermetallic phase Fe_3Al.

Many intermetallic compounds have been reported to possess limited room temperature ductility. Intermetallic compounds such as Fe_3Al and FeAl are present in the Fe-Al system at Al contents of approximately 10-37 wt%. These compounds exhibit brittle behavior because of their crystal structures, low cleavage strength, insufficient number of deformation modes, and low boundary cohesion which promotes weak grain boundaries.[11] Fe_3Al intermetallic compounds have been shown to exhibit brittle behavior by demonstrating low room temperature ductility and transgranular fracture upon failure. These compounds are also very susceptible to hydrogen embrittlement, as hydrogen is thought to diffuse into the alloy lattice and decrease the cleavage strength. As a result, Fe-Al intermetallic compounds have demonstrated very low room temperature ductility when in the presence of hydrogen.[12,13]

Additions of Cr have been shown to have a beneficial effect on the room temperature ductility of intermetallic Fe_3Al alloys. Regina et al[4] determined the Fe-Al-Cr weld overlay cracking susceptibility was a function of the Al and Cr concentration of the weld claddings. Figure 3 shows a weldability curve revealing the critical Al and Cr concentrations that can be deposited crack-free using gas tungsten arc welding. Two independent wire feeders were used with a pure Al (1100) filler and a ferritic stainless steel (430SS) filler metal to vary the Al and Cr contents in the weld overlay. Each point represents a single pass weld overlay from the study, with blue circles representing crack-free deposits and red squares representing cracked deposits. The hydrogen cracking susceptibility of these weld overlays was found to be strongly dependent on the type, size, and distribution of hydrogen trapping particles present within the weld metal. The amount of particle surface area and the volume fraction of carbides that formed in welding these alloys, which is related to the carbon content in the weld metal, significantly affected the cracking behavior of Fe-Al-Cr welds. Figure 4 shows the effect of carbon concentration and the amount of $(Cr,Fe)_xC_y$ carbide particle surface area on the cracking behavior of Fe-Al-Cr welds. There exists a critical weld carbon concentration and particle surface area above which welds were immune to hydrogen cracking for the welding conditions used in these experiments. The carbides act as hydrogen trapping sites and decrease the amount of diffusible hydrogen available, thus aiding to prevent weld cracking.[4]

1.3 Hydrogen Cracking

Hydrogen assisted cracking is a problem welding Fe-Al-Cr alloys. Generally, the primary cause of hydrogen cracking is the buildup of hydrogen at regions of stress concentration in the weld as a result of hydrogen diffusion. Free hydrogen is initially introduced into the weld pool during the weld pass from the base metal, filler metal, shielding gas, and/or from the atmosphere. Understanding the interaction between hydrogen and the weld microstructure is important for mitigating the problem of hydrogen cracking during welding and to improve the quality of weld overlays.[14 15]

Hydrogen atoms have attractive interactions with microstructural features such as vacancies, solute atoms, dislocations, grain boundaries, and second phase particles. The hydrogen that is incorporated in a weld is classified as either residual hydrogen or diffusible hydrogen. Residual hydrogen is the hydrogen that becomes trapped at certain microstructural features in the weld overlay. Diffusible hydrogen is the mobile hydrogen that is available for diffusion to the triaxial stress sites and is considered to be potentially harmful for hydrogen cracking. During the weld cooling cycle some of the diffusible hydrogen atoms leave the steel matrix while others are transported through the lattice and accumulate at stress intensifiers or other hydrogen traps. Trapped sites can be regarded as competing hydrogen sinks to stress intensifiers. A weld microstructure with numerous hydrogen trapping sites will be more resistant to hydrogen cracking by limiting the amount of diffusible hydrogen present. A hydrogen trapping site has to possess an optimum combination of binding energy and hydrogen capturing kinetics to be effective at reducing the amount of hydrogen cracks[14].

Appropriate selection of hydrogen traps offers the potential to control the distribution of hydrogen in welds and to reduce the susceptibility to hydrogen cracking.

Hydrogen trapping sites are classified as reversible or irreversible sites depending on the magnitude of their binding energies, as seen in Table I. Reversible traps possess a binding energy less than 60 kJ/mol H and irreversible have binding energies higher than 60 kJ/mol H.[14] Reversible traps are characterized by a process in which the capturing and releasing of hydrogen occurs at the same rate. Due to their high binding energies, irreversible sites only capture hydrogen until they become saturated. It is very difficult to release hydrogen atoms from irreversible traps.[14]

Control of the diffusible hydrogen in steel weld metal reduces the susceptibility of the weld overlay to hydrogen cracking. Control of diffusible hydrogen in the weld metal can be achieved by the addition of rare earth metals, such as yttrium, or by forming strong hydrogen trapping sites in the microstructure such as carbides. The effectiveness of hydrogen trapping additions to filler metals depends on the ability of these particles to form irreversible hydrogen traps in the microstructure of the weld overlay. Thus, the amount of trapping particles added to the wire and the type of particles being used have a significant influence in hydrogen trapping. Introducing rare earth metals to the filler metal during the gas metals arc welding process can control the amount of diffusible hydrogen.[16] Yttrium reacts with oxygen in the arc to form two different irreversible hydrogen traps in the weld metal: yttrium oxide and yttrium oxysulfide inclusions. Figure 5 shows the effect of yttrium additions on the amount of diffusible hydrogen in the weld deposit for several steels. Two cored wires with no yttrium additions have the same diffusible hydrogen content at about 6.5 mL H_2 per 100 g weld deposit. The two wires with yttrium additions show a significant reduction in diffusible hydrogen content below 2 mL H_2 per 100g. The yttrium additions were in the form of ferroyttrium (Fe_2Y), with a particle size distribution between 200-600 microns. The yttrium oxide particles acted as irreversible hydrogen traps and limited the amount of diffusible hydrogen present in the weld overlay, improving the weldability of these alloys.[16]

The welding parameters in GMAW also have an influence on the amount of diffusible hydrogen incorporated into the weld deposit. There is a significant reduction in the amount of diffusible hydrogen content at very low voltage and an increase in the diffusible hydrogen content as the voltage increases. This trend is attributed to the arc length during welding. A larger arc length at high voltages results in a large amount of diffusible hydrogen in the weld deposit. The large arc lengths expose more of the welding arc to the atmosphere and allows for more moisture pickup during the process. The welding current has a similar effect on the amount of diffusible hydrogen content. The current effect can be attributed to the mode of metal transfer during arc welding. When yttrium is present in the filler metal, spray transfer mode is most effective in limiting the amount of diffusible hydrogen content in the weld deposit because it provides the most efficient transfer mode for the formation of yttrium oxide and yttrium oxysulfide inclusions. The high frequency and small droplet volume of metal droplets that transfer across the arc during spray transfer promotes a greater surface area for the yttrium in the arc to react with oxygen and thus enables the formation of more irreversible trapping sites in the weld deposit.[16]

1.4 Dilution in GMAW

Careful control of dilution level is required to maintain fusion zone compositions that are corrosion resistant and crack-free. Dilution is highly sensitive to the welding parameters and will depend on the volumetric filler metal feed rate and melting power. Figure 6 shows the effect of processing parameters on dilution in arc welding processes.[17] The filler metal feed rate is plotted as a function of the melting power, with the slopes corresponding to various calculated dilution levels. There exists a boundary between an operable range and an inoperable range at 0% dilution. At 0% dilution, there is no melting of the base metal and thus no fusion between the filler metal and the base metal. In this work, simple mass and energy balance expressions were used to model the dilution as a function of the welding parameters. Measured values of dilution are in reasonable agreement with the calculated dilution values. Dilution increases with increasing melting power if the filler metal feed rate is fixed. In this case, the increase in melting power cannot be absorbed by the filler metal and the substrate must absorb the extra melting power, resulting in an increase in the melting of the substrate and an increase in dilution. If the melting power is fixed, an increase in the filler metal feed rate will result in a decrease in dilution. The filler metal consumes a much larger portion of melting power and less energy is available to melt the substrate.[17] In the GMAW process, the filler metal feed rate and the melting power cannot be controlled independently. An increase in the feed rate will increase the current and thus the melting power of the process. Therefore it is difficult to achieve low dilution values by only adjusting the filler metal feed rate in the GMAW process.

In the GMA weldability study of Fe-Al-Cr weld overlays, it is important to weld the overlays at very low dilution values, typically around 10-20 percent. The low dilution value is important for many reasons. Low dilution levels will allow for high amounts of Al and Cr content in the weld, which results in corrosion resistant fusion zone compositions in the overlay. Welding at low dilution levels will also be most cost efficient as there will be minimum material wastage in the filler metal material. Finally, welding at low dilution values is essential to minimize the heat affected zone and the depth of penetration of the weld, as the thickness of the tube is only ¼ in. Low dilution welding requires careful control of the welding parameters that affect dilution in gas metal arc welding, specifically the arc power and the volumetric filler metal feed rate.

1.5 GMAW: Metal Transfer Characteristics

The shielding gas used in a welding process has a significant influence on the overall performance of the welding process, on the mode of metal transfer, and on arc stability. The primary purpose of the shielding gas in GMAW is to protect the molten weld metal from contamination by the surrounding atmosphere. The shielding gas can also influence the depth of penetration of the weld as well as the microstructure and resultant strength, toughness, and corrosion resistance. [15,18]

Metal transfer in GMAW is determined by welding current, electrode wire diameter, electrode composition, and shielding gas. Figure 7 shows high speed photographs of two different modes of metal transfer in GMAW: globular and spray transfer. Globular transfer is characterized by larger droplets of metal transferring across the welding arc due to gravity. Welding in globular transfer generally produces spatter and poor fusion of the overlay. Because the transfer is accomplished by gravity, it is difficult to weld out of position in this transfer mode. Spray transfer is an ideal form of metal transfer in GMAW. In spray transfer, the filler metal is accelerated across the arc in fine droplets and the weld is spatter-free with good fusion. Spray transfer mode is ideal for welding out of position. As the average welding current increases in GMAW, there is a distinct transition between globular and spray transfer, as shown in Figure 8.[19] At low welding currents, the droplet volume is high and the transfer rate is low, which is characteristic of globular transfer. At high welding currents, the transfer rate is high and the droplet volume is low, which is characteristic of spray transfer. It is important to weld at currents above this transition current to stay in spray transfer mode when producing weld overlays in GMAW.[15,19] The power plant industry generally welds in the vertical down position when welding overlays on waterwall tubes. Welding in this position is best accomplished by spray transfer. In spray transfer mode the droplets are accelerated across the arc, which allows for welding out of position, specifically in the vertical down position that is used in all low NOx boiler tube applications.

1.6 *Summary of Fe-Al-Cr Weld Overlay Requirements and Project Outlines*

This weld overlay application requires low transition currents for welding in spray transfer mode and crack-free welds with approximately 10 wt% Al and 5 wt% Cr for good corrosion resistance. The spray transition current is primarily controlled by wire diameter and composition, shielding gas, and welding parameters. The hydrogen cracking behavior is affected mainly by process type, process variables, shielding gas composition, filler metal type (solid wire, solid core wire, powder core wire), and the heat treatment condition of the wire. The corrosion resistance of Fe-Al-Cr weld overlays is dependent on the Al and Cr fusion zone concentrations. Thus, the objectives of this study are to develop Fe-Al-Cr filler metals and welding procedures to deposit corrosion resistant crack-free weld overlays using GMAW in spray transfer mode. This study will:

1) Optimize the filler metal composition, diameter, and shielding gas for achieving low transition currents

2) Identify the optimum processing condition for achieving crack-free deposits at the maximum possible Al and Cr concentration

3) Determine the corrosion resistance of this overlay compared to previously optimized Fe-Al-Cr overlays and currently used Ni based overlays.

2. Experimental Procedure

Single-pass and multi-pass Fe-Al-Cr weld overlay claddings were deposited using five different types of filler metal wires with an automated GMAW system onto plain carbon steel substrates (A-285 Grade C) at ¼ inch thickness. The mill scale of the plates was ground clean using a SiC grinding wheel in order to expose bare metal. Stoody Company in Bowling Green, Kentucky was used as the Fe-Al-Cr wire manufacturer for this study. The cored wire electrodes were fabricated from a low-carbon iron sheath which was contoured into a U-shaped cross section into which Al and Cr powder ingredients were deposited. The U-shape then was passed through closing rolls that formed the wire into a tube. The continuous tube then passed through a series of dies that tightly compressed the power additions and drew down the wire to its final diameter. The solid cored wires were manufactured in a similar manor, with an iron sheath wrapping around a solid Al wire and Cr powder. All filler metal wires were wound into 25 pound spools and packaged in air-tight plastic wrap before being shipped to Lehigh University.

The electrodes were produced at two diameters of 0.062" and 0.045". Chemical analysis of the electrodes and base metal was performed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and the results are shown in Table II. Fluoride additions were added to the 0.045" diameter wire and all of the 0.062" diameter solid core wires in very small amounts to act as arc stabilizers to achieve spray transfer at lower welding currents. Electrode compositions were specifically chosen to deposit weld overlays around 10-20 % dilution to achieve a target fusion zone composition of 10 wt % Al and 5 wt % Cr. All welds were produced in the flat position with a constant electrode tip-to-plate distance of 0.5 inches. Travel speeds varied between 25-35 inches per minute (IPM) and shielding gas flow rates were between 40-45 cubic feet per hour (CFH). The base metal was constrained by clamps at each end to simulate the external constraint encountered during welding. Welding was performed using both heat treated and non-heat treated wires to determine the effect of heat treatment on the hydrogen cracking susceptibility of these alloys. For the heat treated experiments, the filler metal was held in a furnace in air for 3 hours at 300° C and then for 48 hours at 200°C. Weld overlays approximately 10" in length were produced using GMAW and a variety of shielding gases, voltages, filler metal feed rates, and travel speeds in an effort to achieve a variety of fusion zone compositions, to reduce hydrogen cracking susceptibility, and to weld in spray transfer. Weld overlays were also produced using the GTAW process. A constant current of 225 amperes, a travel speed 2 mm/s, and an argon shielding gas were used during this experiment. Filler metal feed rates varied between 30-100 IPM to achieve different dilution levels and fusion zone compositions. The mode of metal transfer for GMAW was recorded for each weld overlay by visual inspection of the electrode tip during and after welding and by listening to the process during operation. All weld overlays were tested for cracks using a non-destructive dye-penetrant technique. Welds were allowed to cool and were left for at least 48 hours for sufficient time for cracking to occur. After this incubation period, the weld surfaces were cleaned with a wire brush and a red dye was sprayed on the surface of the overlay. The dye was removed with a cloth after five minutes and a crack indicator solution was sprayed over the cladding to reveal the presence of cracks.

Selected weld overlays were cross sectioned, mounted and etched in 5% Nital to reveal the fusion zone. Fusion zone weld metal was removed and sent to IMR test labs in Lansing, NY for chemical analysis by ICP-AES. Electron probe microanalysis (EPMA) was also performed on the weld specimens to determine the amount of Al and Cr in the fusion zone of the weld overlay.

Multi-pass weld overlays to be used for corrosion testing were prepared with the GMAW process on A-285 C steel substrates using the 90%He-7.5%Ar-2.5%CO_2 (He tri-mix) shielding gas and tested for cracking with the dye-penetrant crack technique as previously reported in the single-pass weld overlay experiments. Welding parameters were held constant for each multi-pass experiment and care was taken to ensure each pass was welded in spray transfer mode. Each weld overlay was wire brushed clean before the subsequent multi-pass weld was deposited. Rectangular corrosion coupons from the best performing (creak-free) multi-pass weld overlay were extracted from the cladding with a high speed saw with special care taken not to include any base metal. The coupons were ground to 600 grit, measured for dimensions, and weighed to the nearest 0.1 mg before exposure to the corrosive environment. Long-term corrosion experiments were conducted using Lindberg/Blue horizontal tube furnaces. A simulated Low NOx atmosphere was created by introducing a mixed oxidizing/sulfidizing gas (10%CO-5%CO_2-2%H_2O-0.12%H_2S-N_2) into the furnace. The samples were heated at a rate of 50°C/min and were held at 500°C for exposure times of 500, 1000, and 2000 hours. Capillary tubes attached to a syringe pump provided the water vapor present in the gas at a controlled rate. At the termination of the corrosion tests, coupons were weighed and compared to results from previous corrosion studies.

3. Results and Discussion

3.1 Minimizing Globular-to-Spray Transition Current and Hydrogen Cracking

Optimization of weld overlay processes for high temperature boiler tubes requires the ability to weld in spray transfer, to achieve low dilution levels, and to produce crack-free overlays. Typical microstructures of hydrogen cracking, both intergranular and transgranular, are given in Figure 9. In the development of a welding procedure for weld overlays it is important to select a proper shielding gas mixture which optimizes spray transfer and cracking resistance while still operating at low currents to obtain the target dilution level.

The shielding gas composition is a critical process variable that influences the behavior of the arc during welding and thus the operation of the GMAW system. Weld overlays were initially produced with the 0.062" diameter cored wire filler metal and the number of cracks was recorded for each shielding gas tested during this experiment. Figures 10-12 show the cracking behavior of the weld overlays as a function of arc current and shielding gas composition for the 0.062" diameter filler metal with no fluoride additions. Each figure represents a welding study at a constant voltage given above the plot. Each point on the figure represents a single pass weld overlay approximately 10" in length. The different shapes represent different shielding gases used in the process. The solid shapes represent globular transfer mode and the open shapes represent spray transfer mode. These results show that, as the average welding current decreases, the number of cracks increases. A decrease in the current will result in a decrease in the dilution during welding, causing an increase in the amount of Al and Cr in the fusion zone. Previous research has shown that elevated

Al concentration renders the weld overlay susceptible to hydrogen cracking. These plots also show the importance of limiting hydrogen incorporation during the welding process. The shielding gas rich in hydrogen (95%Ar-5%H_2) exhibited the highest degree of welding cracking. This is expected because of an increase in the amount of hydrogen in the shielding gas will increase the amount of diffusible hydrogen in the weld overlay and will cause an increase in the hydrogen cracking in the weld overlay. It is important to note that hydrogen incorporation during GMAW can also come from other sources such as the atmosphere and the welding consumables.

The addition of He to the Ar/CO_2 gas mixture produced creak-free overlays at the lowest welding currents, as evident from the results of the 90%Ar-7.5%He-2.5%CO_2 shielding gas seen in Figures 10 and 11. These results prompted further investigation into Ar/He shielding gas mixtures in an effort to identify an optimal shielding gas for this process. Figure 12 shows crack measurements for different Ar/He shielding gas mixtures. Creak-free overlays were produced at the lowest current using the 50% Ar-50% He mixture, although welding at such low currents occurred in globular transfer mode and it was very difficult to weld in spray transfer mode with the increased addition of He to the shielding gas. The difference in welding performance for each shielding gas can be attributed to the difference in physical properties of each shielding gas. Ar and He are inert gases, and unlike carbon dioxide and oxygen, will not oxidize the base material readily and thus provides a cleaner weld overlay surface. Ar has a low ionization potential and promotes easier arc starting and a more stable arc operation than He, which has a high ionization potential. It is generally easier to achieve spray transfer with a shielding gas rich in

Ar. He is lighter than air and has a lower density than argon. Density of the shielding gas is one of the main properties that influence the gas effectiveness. The combination of Ar and He in the shielding gas selection provides optimal transfer characteristics and cracking behavior in this GMAW study. However, note that the transition currents (i.e., the current required for spray transition) for this filler metal is on the order of 450 amperes, which is too high for practical applications. These high currents would restrict the use of the filler metal for out-of-position welding and would also result in unacceptably high levels of dilution. Thus, a smaller wire diameter was investigated with fluoride additions in order to decrease the transition current.

Careful control of dilution during GMAW is essential to obtain corrosion resistant fusion zone composition in weld overlays. Figure 13 shows the measured dilution as a function of arc current for the 0.045" diameter cored wire filler metal with fluoride addition for arc stability. In the GMAW process, there is a direct correlation between dilution and the arc current. An increase the current during GMAW results from an increase in the filler metal feed rate during welding, which increases the dilution. Dilution was calculated from the measured Al and Cr fusion zone concentrations measured using EPMA. The different shapes on Figure 13 represent different transfer modes. Globular transfer is denoted by pink squares and spray transfer is denoted by the blue diamonds. Spray transfer occurred in the wire at 160 amperes with the 50%Ar-50%He shielding gas. This shielding gas was used in an effort to combine the better cracking resistance associated with the 50%Ar-50%He mixture with a smaller diameter wire containing fluoride additions to induce spray transfer at lower welding current and lower dilution levels. Although this gas mixture provided the optimal cracking resistance for the 0.062" diameter wires, it resulted in excessive cracking with a new 0.045" diameter wire, as all of the welds made with this gas exhibited excessive hydrogen cracking. It was previously reported[8] that cracking during GMAW in solid Al core wires occurred at Al fusion zone concentrations above 10 wt%. In the current weldability study in Figure 13, cracking occurred as low as 8 wt% Al with cored wire electrodes, prompting further investigation into the hydrogen incorporation behavior of cored wires and solid core wires. Figure 13 also shows the beneficial effect of reducing the electrode wire diameter, as spray transfer mode was accessible at much lower welding currents. In order to achieve good corrosion resistant compositions there should be at least 10 wt % Al and 5 wt % Cr in the weld overlays. These compositions are obtained with the 0.045" diameter wire by welding at 20% dilution or lower and less than 160 amperes. However, the problem of cracking at these compositions must be eliminated to provide good candidate coatings for corrosion resistance in low NOx environments.

The previous gas tungsten arc weldability study determined that Fe-Al-Cr weld overlays were able to be deposited creak-free up to fusion zone concentrations of 12% Al and 5% Cr.[2] The important differences with the current weldability study that may affect the diffusible hydrogen incorporation during welding are the change in process from GTAW to GMAW and the change in electrode from a solid core wire to a powder cored wire. The different arc characteristics of GMAW and GTAW may allow for different amounts of hydrogen incorporation during welding. In the GMAW process the filler metal acts as the electrode and metal droplets from the filler metal that transfer across the arc are exposed to the atmosphere, allowing for a reaction with water vapor from the air. In the GTAW process, there is a non-consumable tungsten electrode creating the arc, and the filler metal is fed into and melted by the arc and weld pool. Also, the cored wires used in the GMAW process have a higher susceptibility for moisture pickup during fabrication and also during welding.[5-7] To determine the effect of the process and filler metal type (i.e., solid versus cored) on the hydrogen cracking susceptibility of these cored wires, GTAW experiments with a pure argon shielding gas were conducted on 0.062" diameter cored wires electrodes that were both heated and non-heated and the results are shown in Figures 14 and 15. The Al and Cr concentrations in the overlays were increased by increasing the filler metal feed rate while holding all other variables constant. The dotted line is the previous weldability boundary established from the GTAW process using a solid, commercially pure Al and a solid iron/Cr electrode.[4] Cracking with the cored wire electrode occurred at much lower Al and Cr concentrations than previously reported, as the highest amount of Al present before cracking was approximately 6 wt%. A heat treatment of the wire was performed to bake out the residual moisture in the wire from the fabrication process as shown in Figure 15. The cracking resistance greatly improved after the heat treatment, and cracking in these wires occurred very close to the previous weldability boundary derived from the solid wires. Hydrogen is present in the cored wires from the water-based lubricants that are used during the fabrication of the wire, and heating of the wires removes this hydrogen and limits the amount of hydrogen in the weld overlay, making the cladding less prone to cracking.

Single-pass weldability results from the GMAW process using the 0.062" diameter cored wire filler metal are shown in Figure 16. There is a significant difference in the cracking susceptibility of these wires depending on the type of shielding gas employed. Overlays were deposited creak-free with the 50%Ar-50%He mixture up to 8 wt% Al, but the He tri-mix shielding gas demonstrated poor resistance to hydrogen cracking with these filler metals. Heat treating the wires improved the weldability slightly and creak-free overlays were deposited up to approximately 9 wt% Al, as seen in Figure 17.

Power companies currently deposit weld overlays on boiler tubes using wire diameters between 0.035-0.045" diameters. It is important to use these smaller wire diameters in order to achieve overlays with low dilution values and to weld in spray transfer. Single-pass and multi-pass weld overlays were deposited using the 0.045" diameter cored wire with fluoride addition. Results from the wire in both the heated and as-received condition are given in Figures 18 and 19 respectively. Different shielding gases resulted in different weldability results, and the Helium tri-mix gas providing creak-free overlays at the highest fusion zone compositions. The optimal shielding gas for the 0.045" diameter cored wire was a different mixture than the optimal gas for the 0.062" diameter cored wire. The He tri-mix shielding gas also provided the best looking overlay with optimal wetting of the bead, which is very important when producing multi-pass weld overlays.

Figure 20 shows a weldability graph of three 0.062" diameter filler metals: a solid Al core wire with Cr power, a solid Al core wire with Cr powder and TiC additions, and a powder cored wire with yttrium oxide additions. The Helium Tri-mix shielding gas was used in the study because it gave optimal cracking and wetting conditions for Fe-Al-Cr weld overlays. 3000 ppm of yttrium oxide particles with a -

325 mesh size were added to the cored wire electrode in an effort to form yttrium oxide inclusions. There is some improvement in the weldability of the wires containing yttrium oxide, as creak-free single pass weld overlays were deposited up to 8 wt% Al. There is no significant increase in the weldability of the solid Al core wire when compared to powder cored wires previous examined in the study, as cracking occurs above 7 wt% Al with both wire types. There is also no improvement in the weldability behavior with wires containing TiC additions. Typical microstructures of weld overlays from these three wires are shown in figures 21 and 22. Although second phase particles have formed in the overlays, it does not appear that the addition of yttrium oxide or TiC resulted in significant formation of hydrogen trapping sites. The particle distribution and shape in each overlay must be more closely examined in future research to obtain a better understanding of the effectiveness of the particle additions in these wires.

Table III summarizes the GMA weldability study performed on single pass Fe-Al-Cr- wires. Each wire used in this experiment is given along with the Al and Cr compositional range between cracked and crack-free weld overlays. The optimal shielding gas for each wire is given along with the minimum current required for spray transfer. Spray transfer modes was most easily established with solid cored wires, with fluoride additions, and with smaller wire diameters.

3.2 Summary of Weldability, Transition Current, and Hydrogen Cracking Results

The weldability of Fe-Al-Cr wires is influenced by the welding process type (GTAW or GMAW), the shielding gas composition, the processing parameters, the filler metal type (solid wire, solid core wire, powder core wire), and the heat treatment condition of the wire. The shielding gas is a very important variable that affects the weldability of Fe-Al-Cr overlays. The 95% Ar-5% H_2 shielding gas, which contained the most hydrogen, resulted in the most extensive hydrogen cracking in the overlays welded with the 0.062" diameter cored wire. The gas mixture providing the optimal cracking resistance for the 0.062" diameter cored wire electrode was the 50% Ar-50% He shielding gas, while the mixture providing the optimal cracking resistance for the four remaining electrodes was the He tri-mix shielding gas.

The mode of metal transfer is influenced by the welding current, the shielding gas, and the electrode diameter and composition. Spray transfer with the 0.062" diameter cored wire occurred at high welding currents around 450 amperes. Shielding gases containing the highest amount of argon promoted spray transfer at the lowest welding currents. Reducing the electrode wire diameter to 0.045" and adding fluoride allowed for welding in spray transfer mode at much lower welding currents. The minimum current for spray transfer for the 0.045" diameter wire with fluoride additions was 160 amperes. The 0.062" diameter solid core wires with fluoride additions had a minimum spray arc current of 325 amperes.

The extent of hydrogen cracking in Fe-Al-Cr weld overlays is influenced by the welding process type, the wire type, and a pre-weld heat treatment of the welding wire. Crack-free weld overlays were previously[4] deposited up to 12 wt% Al and 5 wt% Cr with the GTAW process and up to 8 wt% Al and 4 wt% Cr with the GMAW process. There is a difference in the hydrogen incorporation with the two different welding processes, as more hydrogen is incorporated into the weld with the GMAW welding process. This is most likely due to the different arc characteristics between the two processes. The wire type also influences the weldability of Fe-Al-Cr filler metals. Fe-Al-Cr cored wires are susceptible to hydrogen cracking at lower Al concentrations than previously[4] reported with solid core wires. The GTA weldability study showed a significant increase in the performance of these wires after a heat treatment. The heat treatment of the cored wires removed much of the moisture present form the manufacturing process of these wires. Implementing a heat treatment on the 0.062" cored wire with the GTAW process allowed for creak-free weld overlays up to 11 wt% Al and 5 wt% Cr. There was no significant increase in the weldability of Fe-Al-Cr powder cored wires and Fe-Al-Cr solid core wires with the GMAW process. After a pre weld heat treatment, crack-free weld overlays were deposited up to 8 wt% Al and 4 wt% Cr. There was also no significant increase in the weldability with wires containing yttrium oxide and TiC. The type of particles formed in the microstructure by these additions should be more closely examined.

3.3 Corrosion Behavior

Multi-pass overlays were deposited using the He tri-mix shielding gas with the 0.045" diameter cored wire. This wire was chosen because it allowed for welding in spray transfer at the lowest dilution values. Subsequent passes were deposited with the electrode at the edge of the previous pass, providing a bead-to-bead overlap of approximately 50%. It is assumed that 50% of the previous weld pass re-melts and is incorporated into the following weld pass. Each subsequent pass is thus richer in Al and Cr than the previous pass until around the 5th pass, where compositional difference between subsequent multi-pass overlay are minimal. Cracking in multi-pass weld overlays occurred at slightly lower Al and Cr fusion zone concentrations than single-pass weld overlays. This may be due to excess diffusible hydrogen incorporated into the weld during multi-pass welding. The second pass of the multi-pass weld re-melts a portion of the previous pass. Diffusible hydrogen from the re-melted weld overlay may become incorporated into the current pass, resulting in an increase in hydrogen levels in a multi-pass weld overlay compared to a single pass. The best performing creak-free multi-pass overlay from the heat treatment experiments was a 7.5 wt% Al 3.5wt% Cr alloy. This alloy was selected for corrosion testing in simulated low NOx environments and was compared to IN 622, which is currently being used for corrosion protection in low NOx boilers. The results of the long term corrosion tests up to 2000 hrs can be seen in Figure 23, where the red triangles represent three different corrosion tests from alloy 7.5Al-3.5Cr at 500, 1000, and 2000 hrs. The corrosion rate of this overlay is slightly higher than that of IN 622 and significantly higher then the 10Al-5Cr weld overlay. The importance of achieving the critical Al and Cr compositions in the fusion zone is seen in the figure. Weld overlays must have at least 10 wt% Al and 5 wt% Cr to achieve excellent corrosion resistance in low NOx environments. Based on this observation, further research is needed to improve the hydrogen cracking resistance of these overlays so that higher and Al and Cr concentrations can be achieved for adequate corrosion performance.

4. Conclusions and Recommendations

The weldability of Fe-Cr-Al alloys was investigated in this study. The transition current from globular-to-spray transfer was investigated as a function of filler metal diameter and composition, while the hydrogen cracking susceptibility was investigated as a function of welding process type, process variables, shielding gas composition, the filler metal type, and filler metal heat treatment condition. The corrosion resistance of the overlay with the highest possible Al and Cr concentration was measured and compared to IN622 and a 10Al-5Cr weld overlay. The following conclusions can be drawn from this work:

1. The shielding gas that provided optimal cracking behavior in single pass Fe-Al-Cr weld overlays was the 90%He- 7.5%Ar-2.5%CO_2 mixture.
2. Spray transfer mode was most easily established with a smaller wire diameter and fluoride additions to the filler metal. The minimum spray arc current for the 0.045" diameter cored wire with fluoride was 160 amperes and the minimum spray arc current for the 0.062" diameter solid core wire was 325 amperes.
3. The welding process type greatly influenced the weldability of Fe-Al-Cr weld overlays. Crack-free weld overlays were deposited up to 11 wt% Al and 5 wt% Cr with the GTAW process and up to 8 wt% Al and 4 wt% Cr with the GMAW process.
4. Pre-weld heat treatment of the cored wires allowed for crack-free weld overlays at greater Al and Cr fusion zone concentrations for

both GMAW and GTAW processes. The heat treatment evaporated much of the hydrogen present in the wires from the manufacturing process and improved the weldability of these alloys.

5. The highest Al and Cr concentrations in the multi-pass weld overlay study was 7.5 wt% Al-3.5 wt% Cr. The corrosion rate of this overlay in a simulated Low NOx environment at 500°C was slightly higher than that of IN 622 and significantly higher then the 10wt% Al-5wt% Cr weld overlay.

5. Future Work

In order to achieve good corrosion resistance in Low NOx environments the weld overlay must contain at least 10 wt% Al and 5 wt% Cr in the fusion zone. To produce crack-free overlays at these compositions there must be adequate control of the diffusible hydrogen inside the microstructure by the addition of irreversible hydrogen trapping sites. The formation of irreversible hydrogen traps in the microstructure will reduce the amount of diffusible hydrogen in the weld to acceptable levels and allow for crack-free weld overlays at more corrosion resistant compositions. The size, type, and amount of particle additions must be studied further in order to form effective irreversible traps in the microstructure of the weld overlay.

Table I – Potential hydrogen trapping sites in ferritic steels and the associated binding energy for each trap site.

Trapping Site	Binding Energy (kJ mol)	Trap Type
Dislocation	0 – 30	Reversible
Grain Boundary	18 – 59	Reversible
AlN	65	Irreversible
MnS	72	Irreversible
Al_2O_3	79	Irreversible
Fe_3C	84	Irreversible
TiC	87 – 95	Irreversible

Table II - Filler metal wire and base metal chemical compositions using ICP-AES. *Represents wires with Fluoride additions.

Element	0.062" filler metal	0.045" filler metal	0.062" Solid Al core filler metal*	0.062" Solid Al Core with TiC *	0.062" Solid Al Core with Y_2O_3 *	Steel Base Metal (A285C)
Fe	Bal	Bal	Bal	Bal	Bal	Bal
Al	13.89	13.3	15.8	15.8	16.0	0.031
Cr	5.56	5.3	5.9	5.9	8.0	0.086
Ca	0.02	0.02	0.02	0.02	0.02	N/A
Cu	0.05	0.06	0.05	0.05	0.05	0.284
Mn	0.25	0.25	0.25	0.25	0.25	0.52
Mo	< 0.01	< 0.01	< 0.02	< 0.03	< 0.04	0.055
Ni	0.01	0.01	0.01	0.01	0.01	0.148
P	< 0.005	< 0.005	< 0.006	< 0.007	< 0.008	0.005
Si	0.01	0.01	0.01	0.01	0.01	0.043
S	0.015	0.015	0.015	0.015	0.015	0.001
C	0.09	0.09	0.09	0.09	0.09	0.16

Table III - Table showing the optimal shielding gas and minimum spray arc current for each welding wire. The weldable range of aluminum and chromium in the fusion zone is also given for each wire.

Filler Metal	Optimal Shielding Gas	Min spray arc current (Amps)	Al Weldability Range (wt%)	Cr weldability Range (wt%)
0.062 cored wire	50%He-50%Ar	450	8.8-9.2	3.1-3.8
0.045 cored wire with fluoride additions	90%He-7.5%Ar-2.5%CO_2	160	8-8.5	4-4.2
0.062 solid Al core wire with fluoride additions	90%He-7.5%Ar-2.5%CO_2	325	7.2-8.1	3-3.5
0.062 solid Al core wire with fluoride and TiC additions	90%He-7.5%Ar-2.5%CO_2	325	7-7.5	3-3.3
0.062 cored with with yttrium oxide and fluoride additions	90%He-7.5%Ar-2.5%CO_2	350	8-8.8	4-4.2

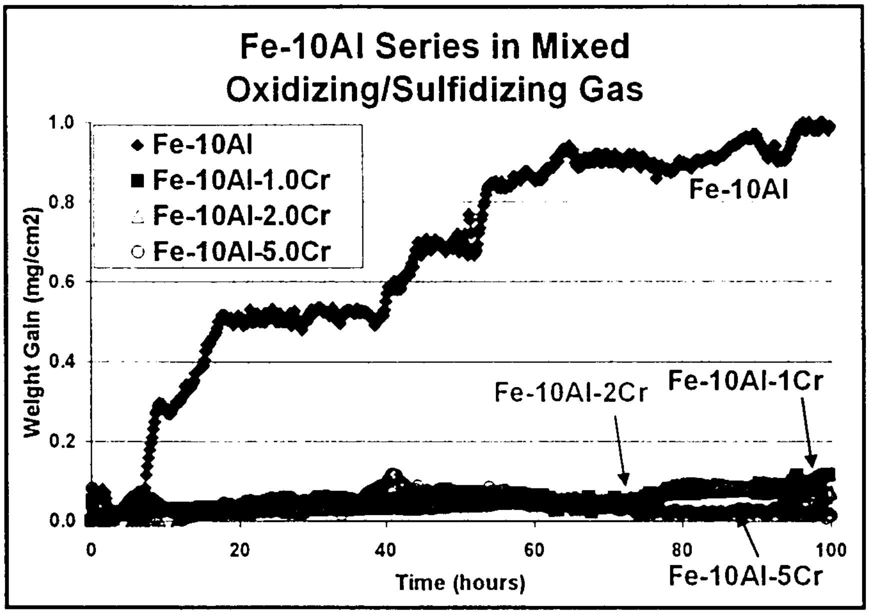


Figure 1 – Kinetic data for Fe-Al-Cr weld overlays in a simulated low NOx environment at 500°C.[4]

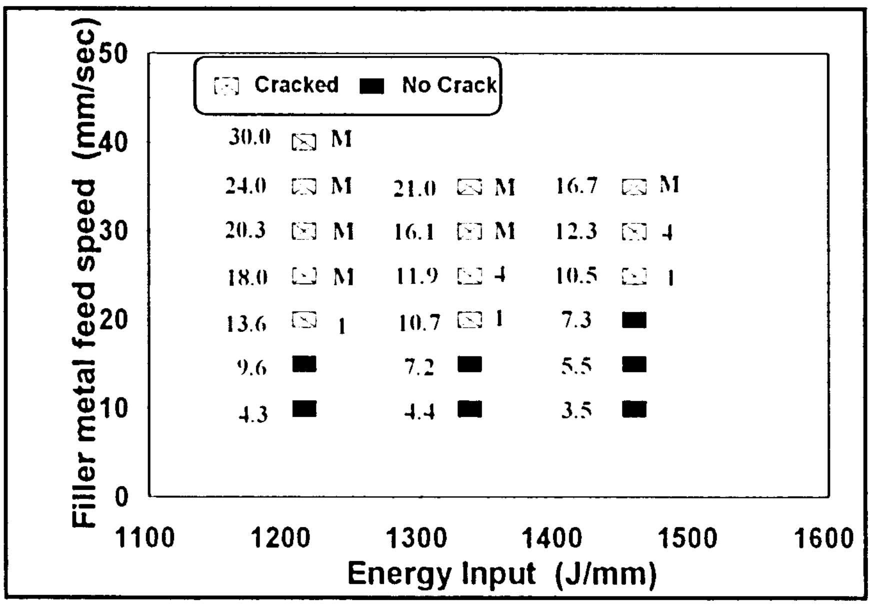


Figure 2– Compositional welding boundary for binary Fe-Al weld deposits. Blue numbers indicate aluminum concentration in weight percent, red numbers indicate number of cracks (M represents more than 15 cracks).[3]

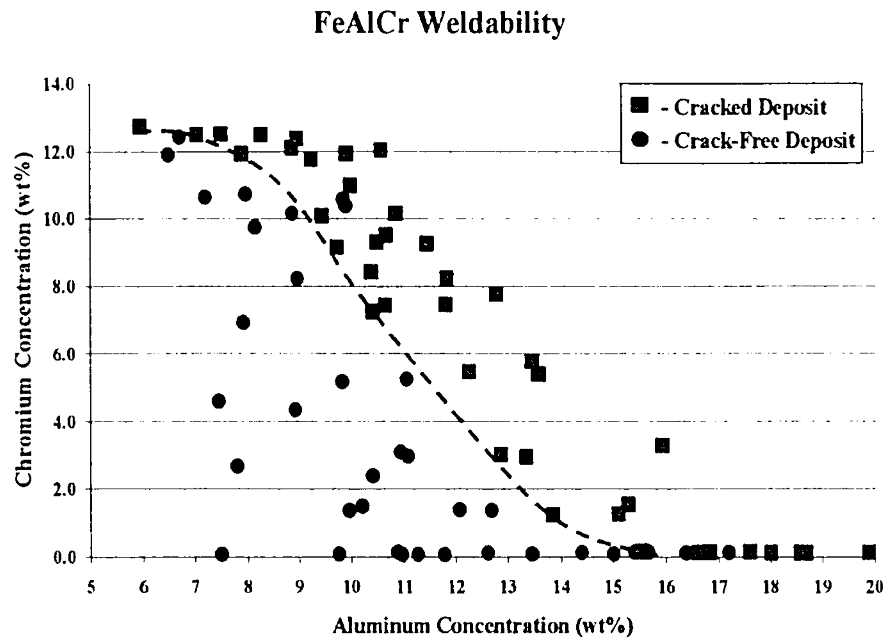


Figure 3 – Weldability curve showing the cracking susceptibility of Fe-Al-Cr weld overlay claddings and the cracking dependence on the aluminum and chromium concentrations of the claddings.[4]

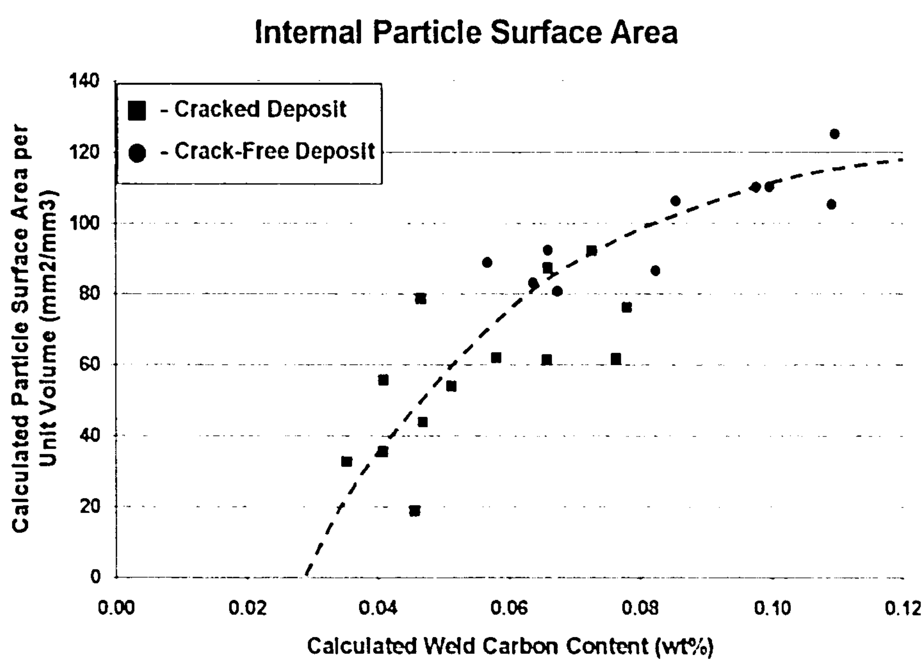


Figure 4: Particle surface area as a function of the weld metal carbon concentration for Fe-Al-Cr weld overlays deposited on plain carbon substrates.[4]

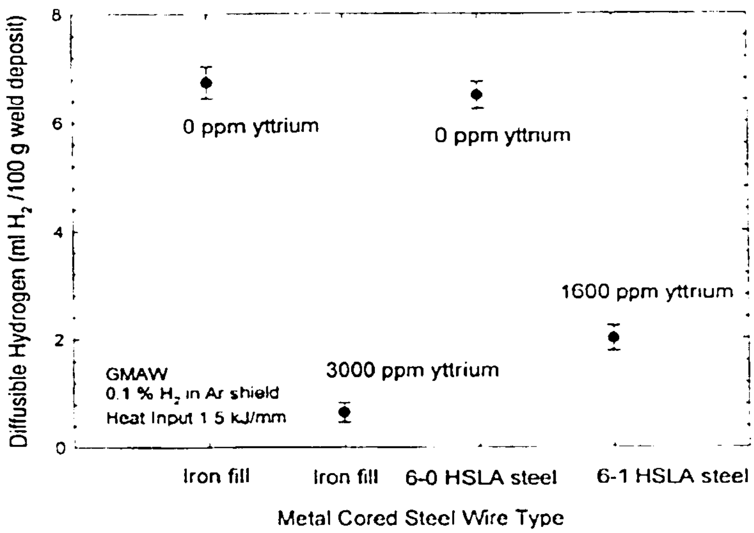


Figure 5: Effect of Yttrium additions to Fe-filled cored wires on the amount of diffusible hydrogen content in the weld deposit.[16]

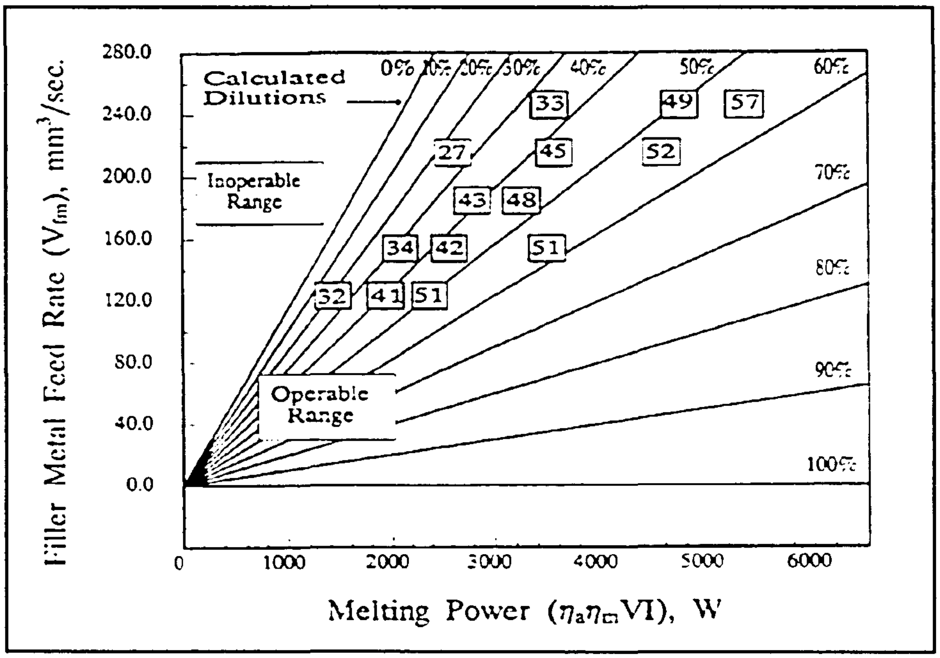


Figure 6: Diagram showing the effect of processing parameters on dilution with experimental date for the SAW process. Low melting power and high filler metal feed rates are desired for low dilution values.[17]

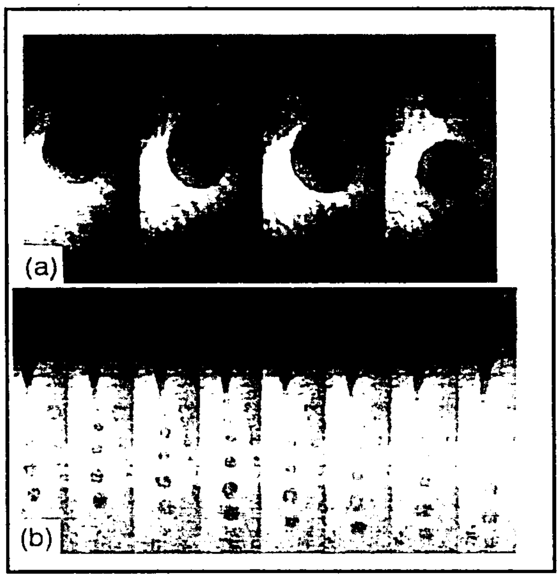


Figure 7: Electrode tip during welding displaying different modes of GMAW metal transfer. A) Spray transfer and B) globular transfer mode.[19]

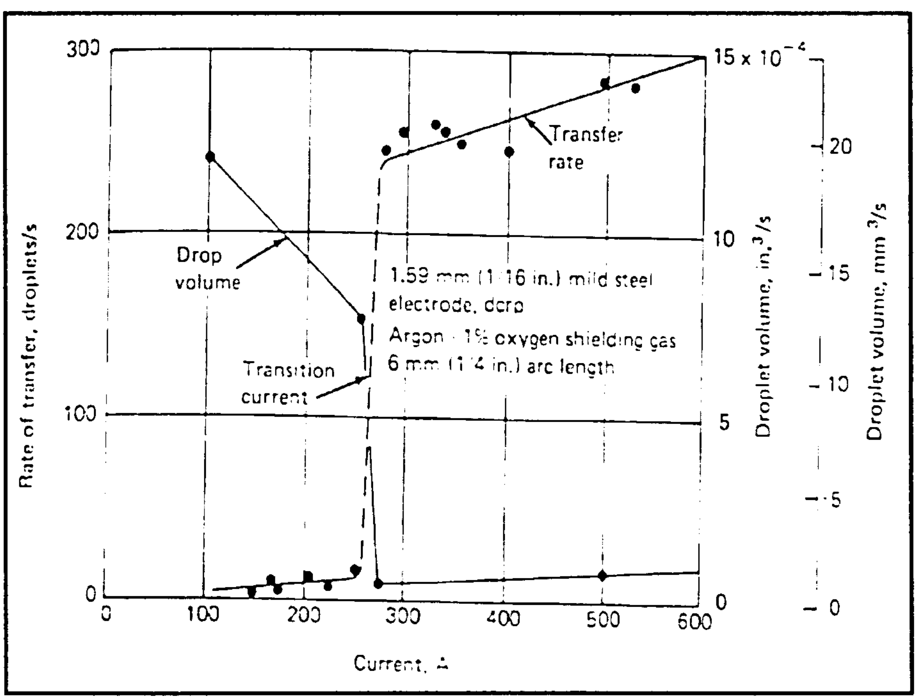


Figure 8: Transition current between spray and globular transfer. Transition current is a function of electrode composition, wire diameter, and shielding gas.[19]

INTENTIONAL SECOND EXPOSURE

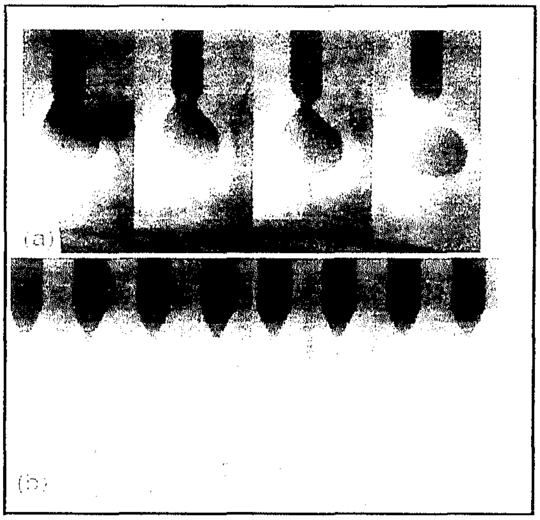
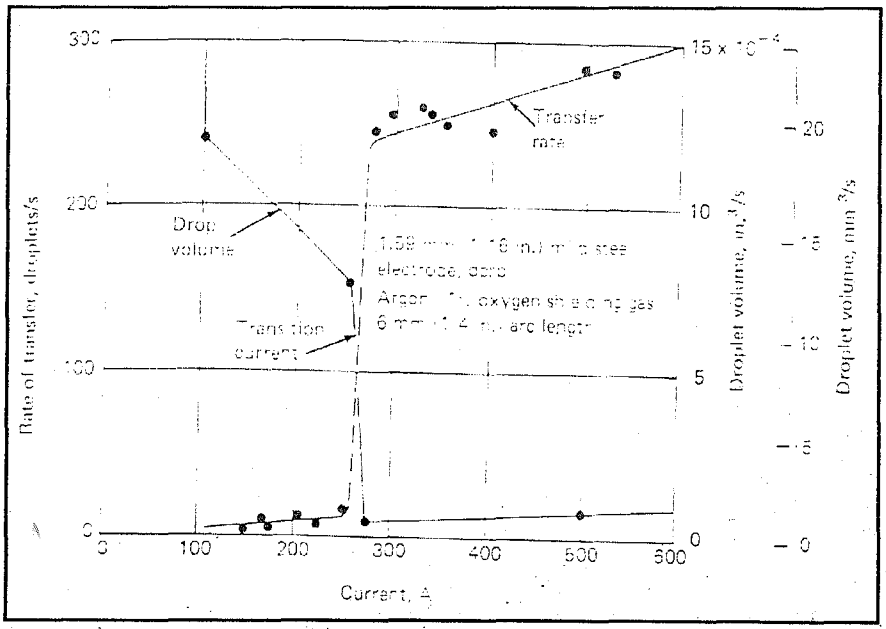


Figure 7: Electrode tip during welding displaying different modes of GMAW metal transfer. A) Spray transfer and B) globular transfer mode.[19]



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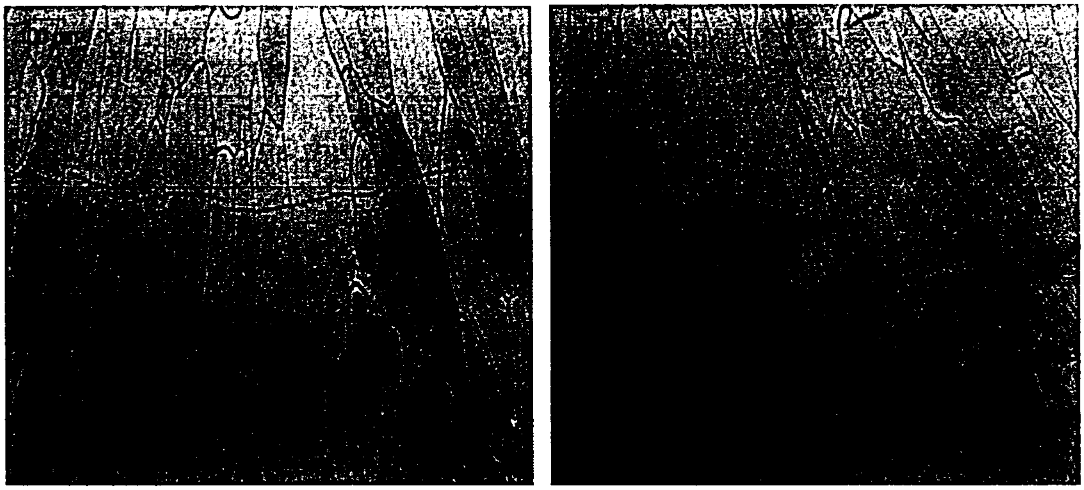


Figure 9: Hydrogen cracking in Fe-Al-Cr weld overlays from welding with the 0.045" cored wire.

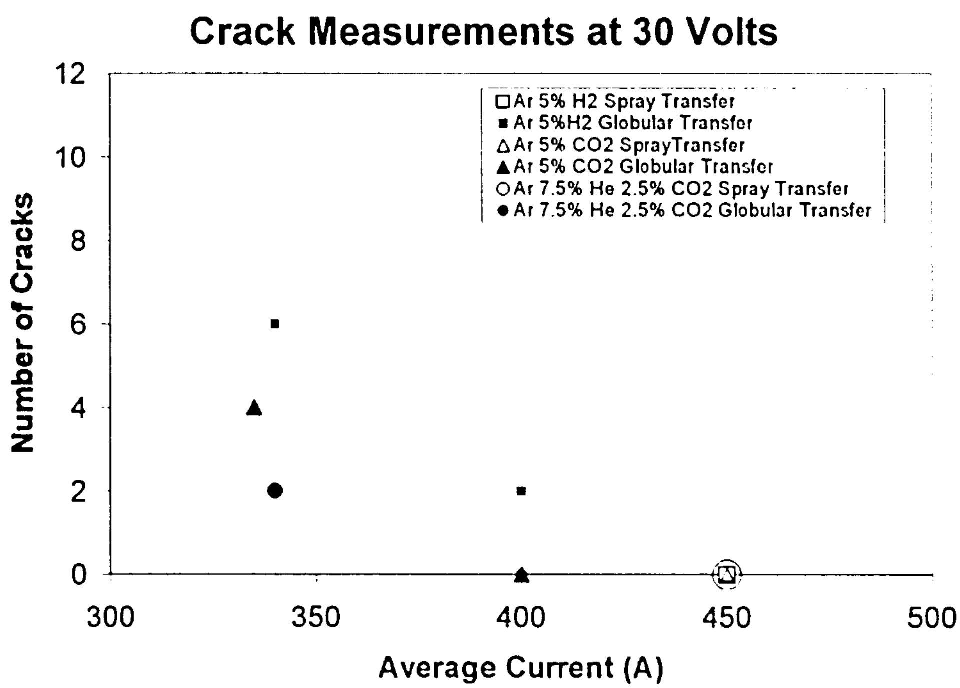
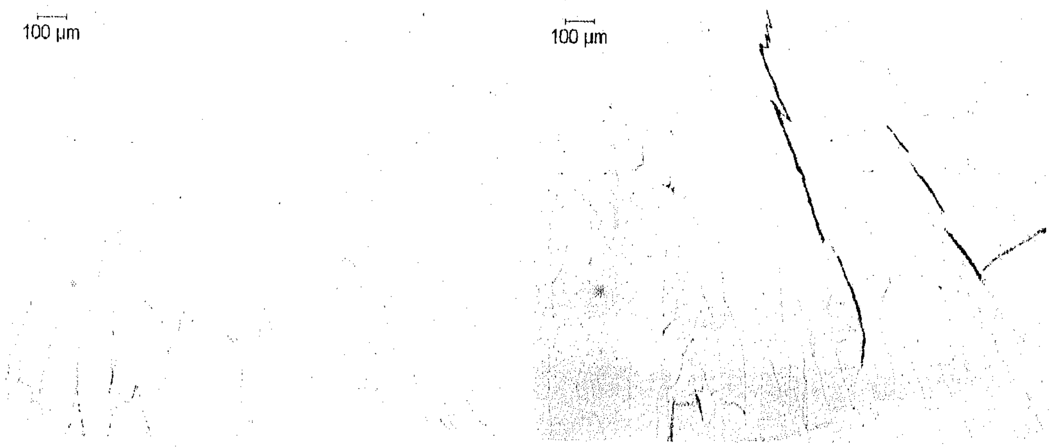


Figure 10: Diagram showing the number of cracks versus the average welding current for a variety of shielding gases at 30 volts.

INTENTIONAL SECOND EXPOSURE



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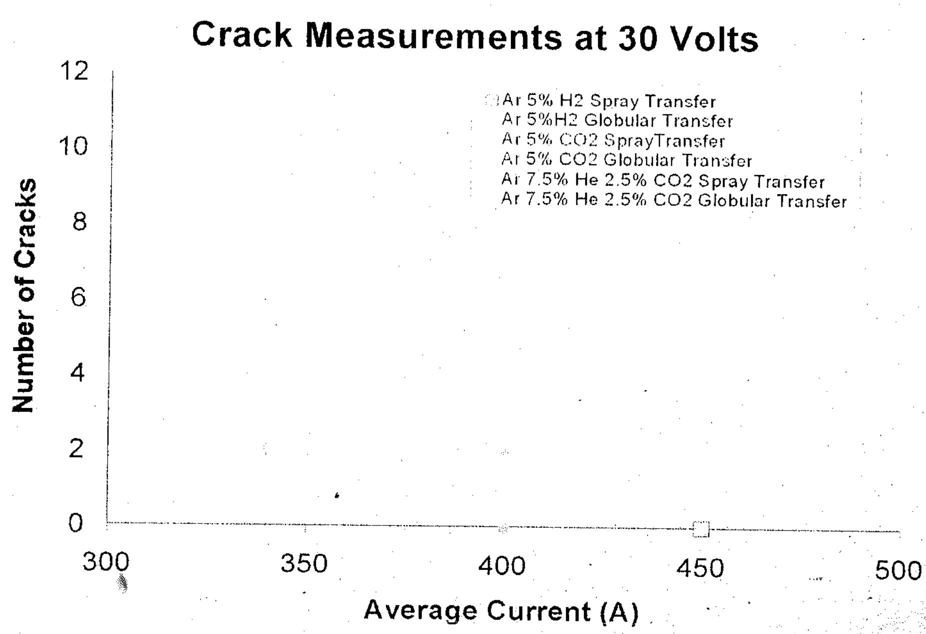

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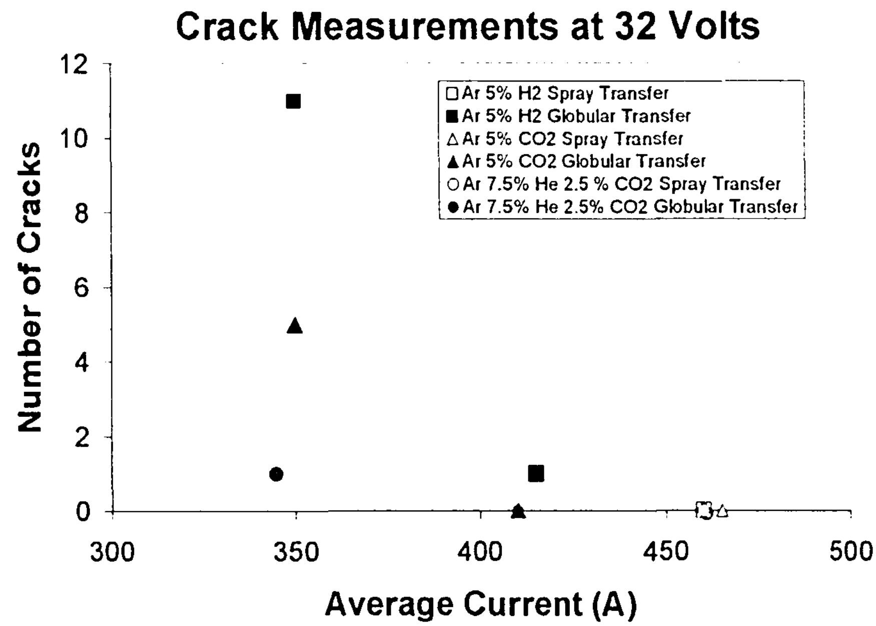

Figure 11: Diagram of number of crack versus welding current for different shielding gases at 32 volts. The 90%Ar-7.5%He-2.5%CO_2 mixture produced crack free overlays at the lowest Welding Current

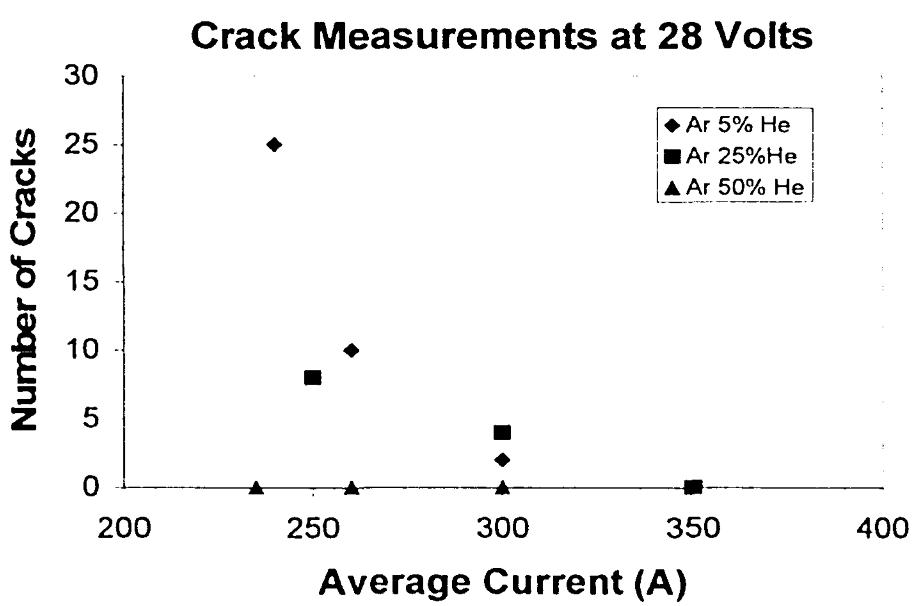

Figure 12: Crack measurements plotted against the welding current for different Ar/He mixtures of shielding gases. The 50%Ar-50%He mixture produced crack free results at the lowest

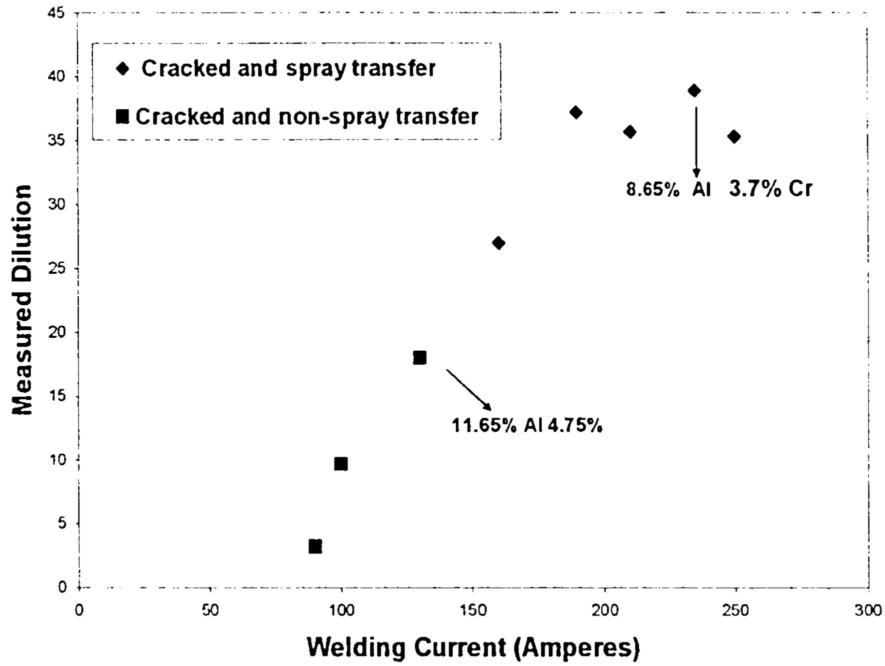

Figure 13: Diagram showing measured dilution as a function of melting power for the 0.045" filler metal with fluoride addition.

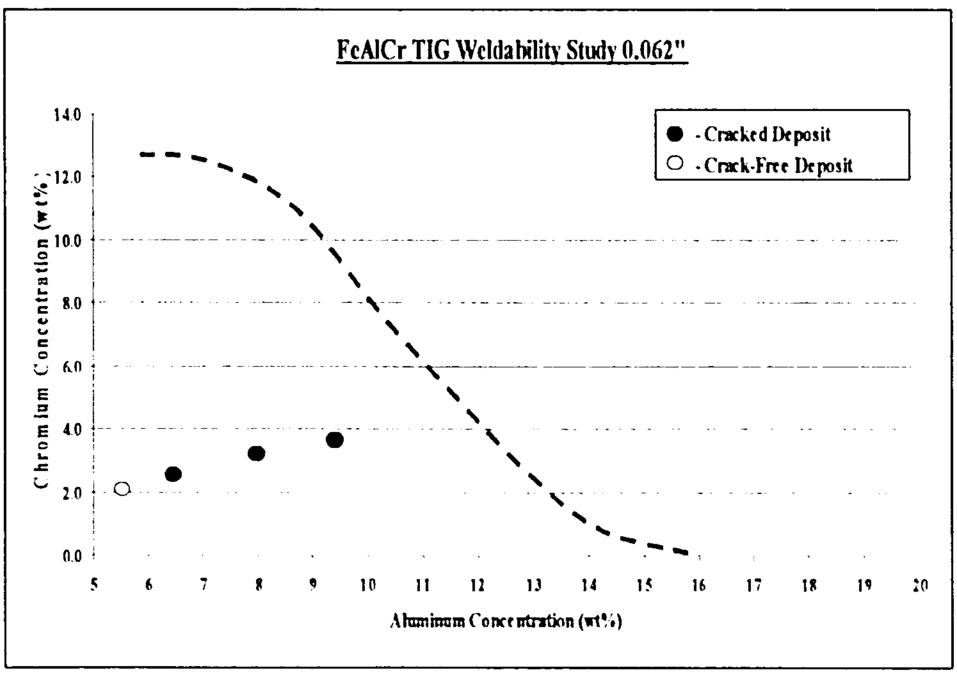

Figure 14: GTA weldability study with 0.062" cored wire electrode. Hydrogen cracking occurred at very low aluminum and chromium concentrations.

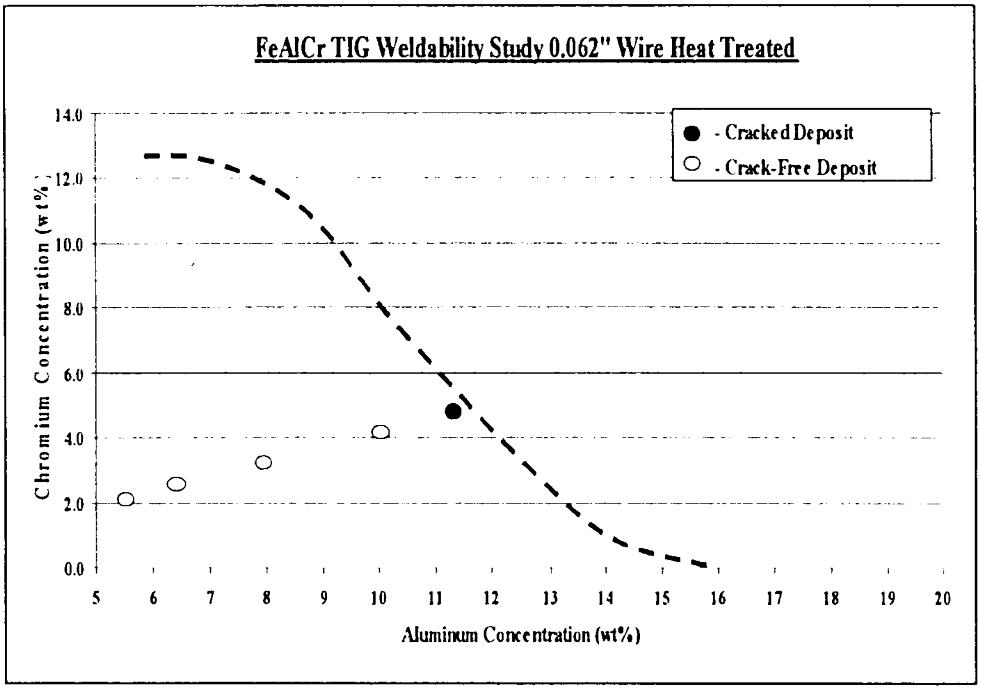

Figure 15: Diagram showing the effect of heat treatment of cored wire electrode. Crack free fusion zone compositions approach cracking boundary.

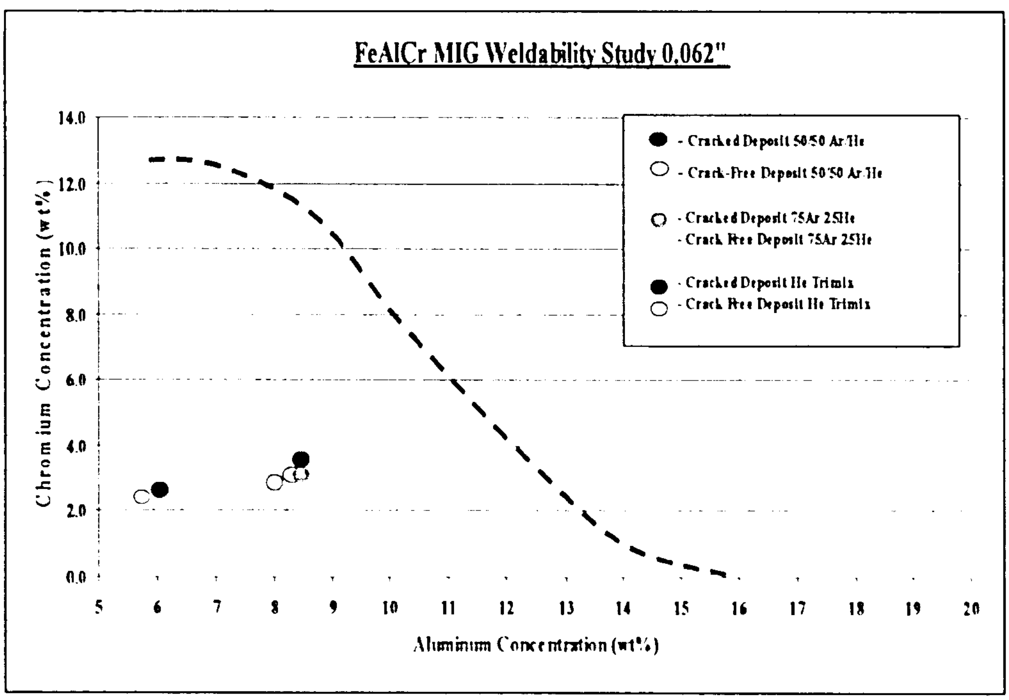

Figure 16: GMA weldability study using 0.062" cored wire electrode. Cracking behavior depends on type of shielding gas used during welding process.

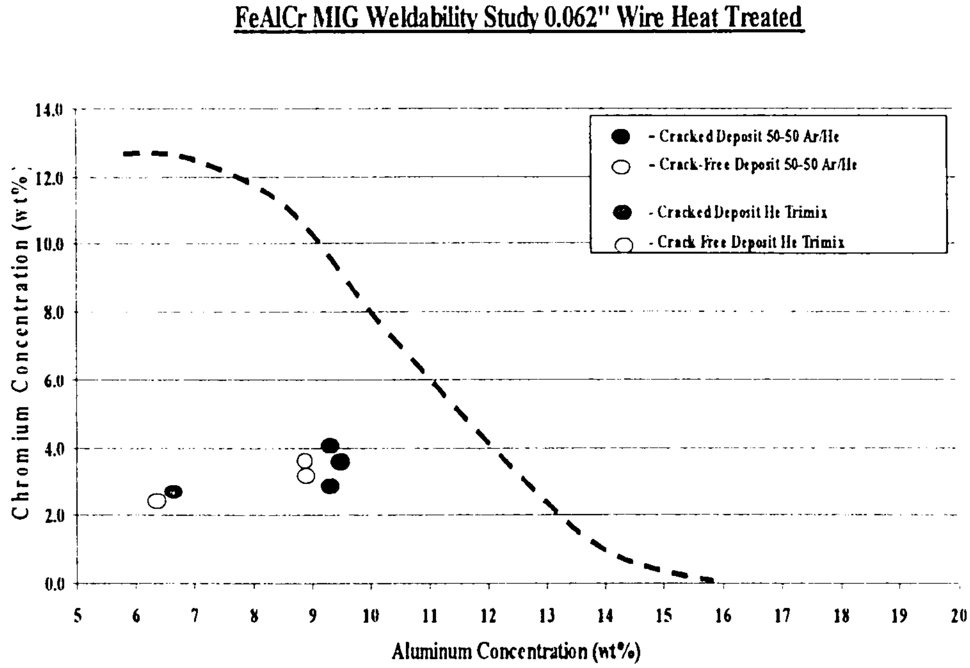

Figure 17: GMA weldability study shows that heat treatment of the cored wire allows for crack-free aluminum composition up to 9 wt %.

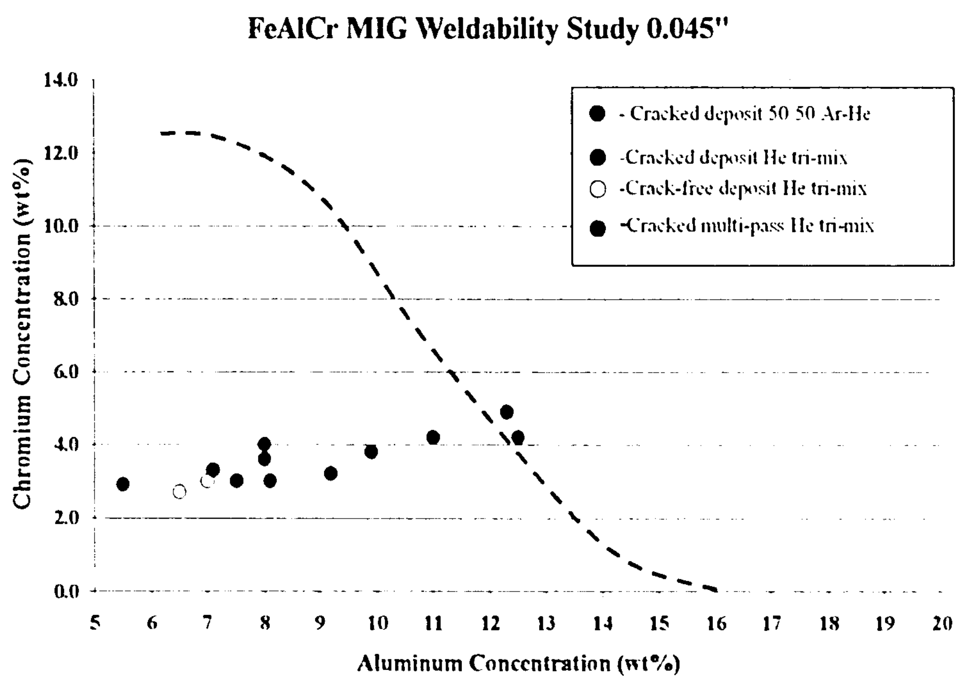

Figure 18: GMA weldability study using 0.045" cored wire electrode with fluoride additions.

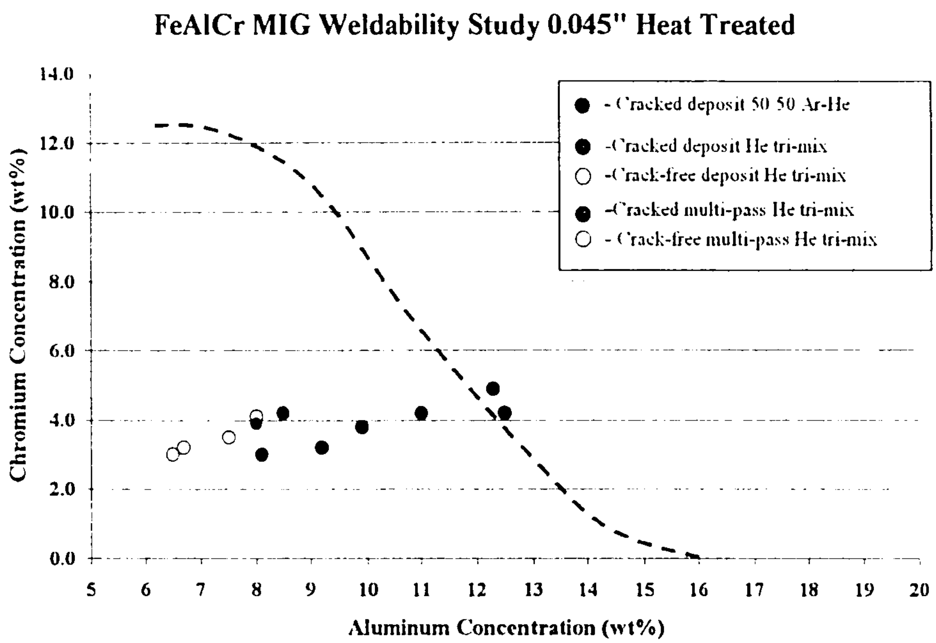

Figure 19: GMA weldability study of 0.045" wire after heat treatment. 7.5wt% Al-3.5wt% Cr alloy from multi-pass weld overlay selected for corrosion tests in a simulated low NOx environment.

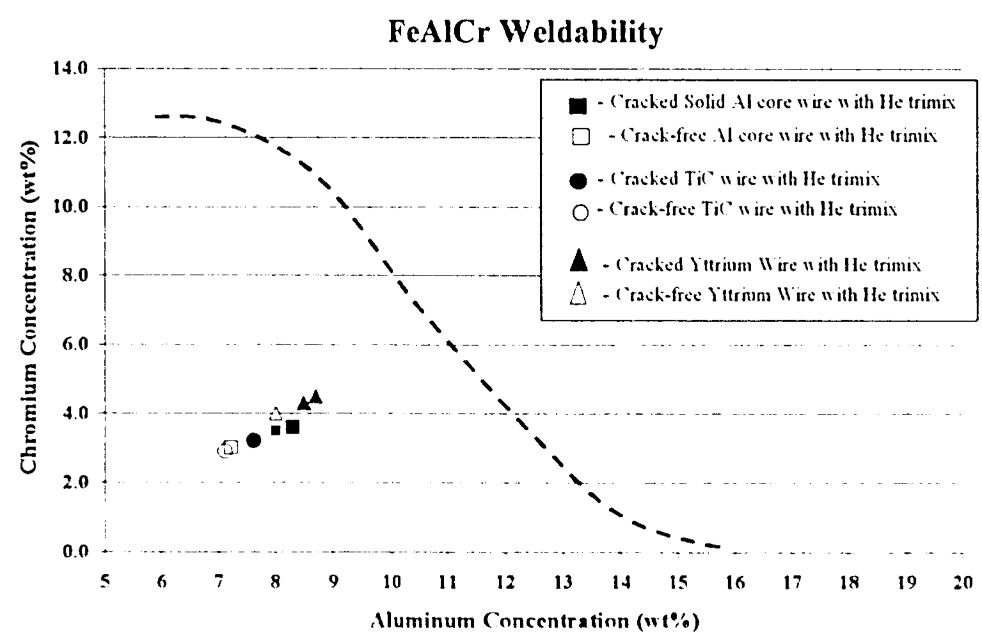

Figure 20: GMA weldability study of Fe-Al-Cr solid wires containing solid Al core with chromium powder, solid aluminum core with TiC, and power cored wire with yttrium oxide

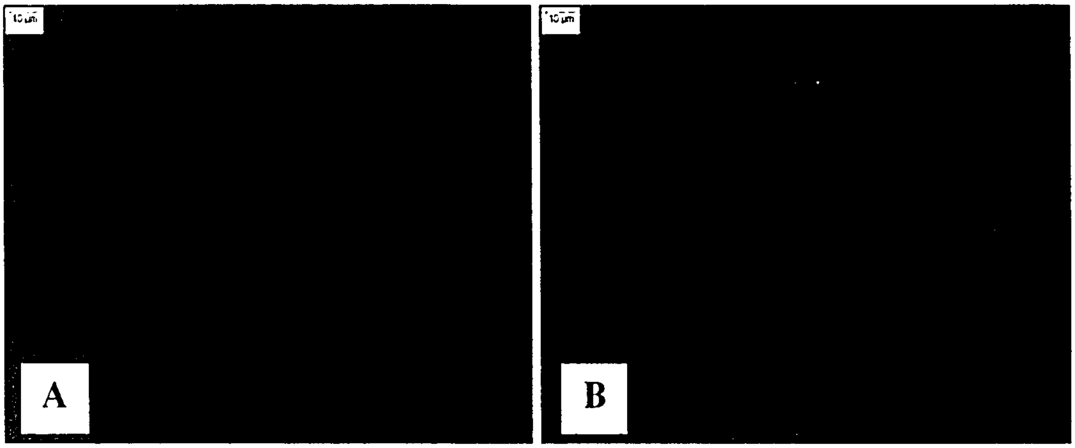

Figure 21: Microstructure of A) Solid aluminum core wire and B) cored wire containing yttrium oxide additions.

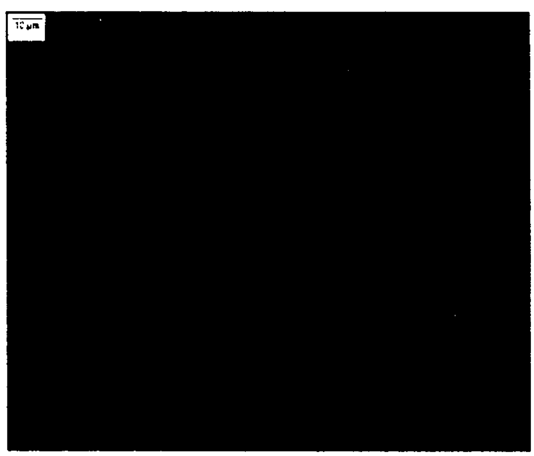

Figure 22: Microstructure of weld overlay from Fe-Al-Cr slid core wire containing TiC additions.

INTENTIONAL SECOND EXPOSURE

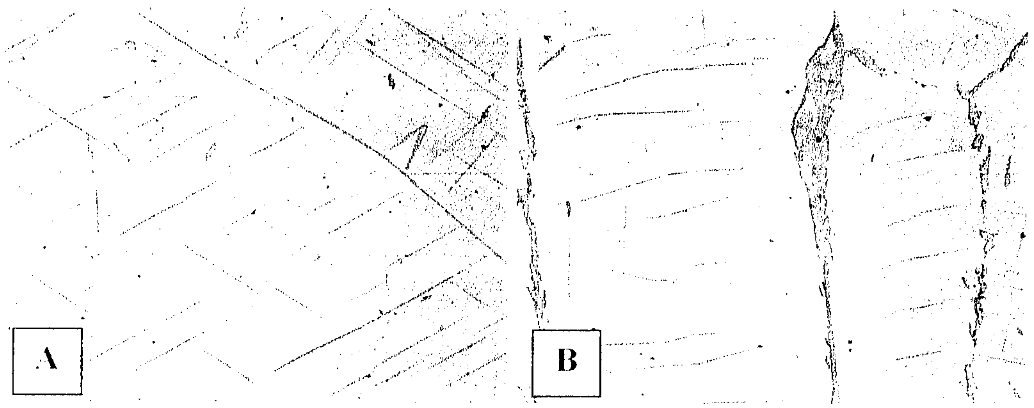

Figure 21: Microstructure of A) Solid aluminum core wire and B) cored wire containing yttrium oxide additions.

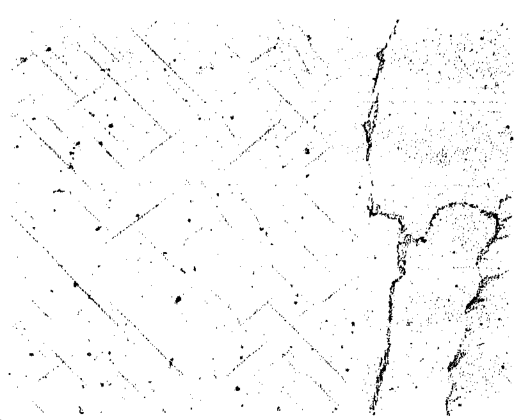

Figure 22: Microstructure of weld overlay from Fe-Al-Cr slid core wire containing TiC additions.

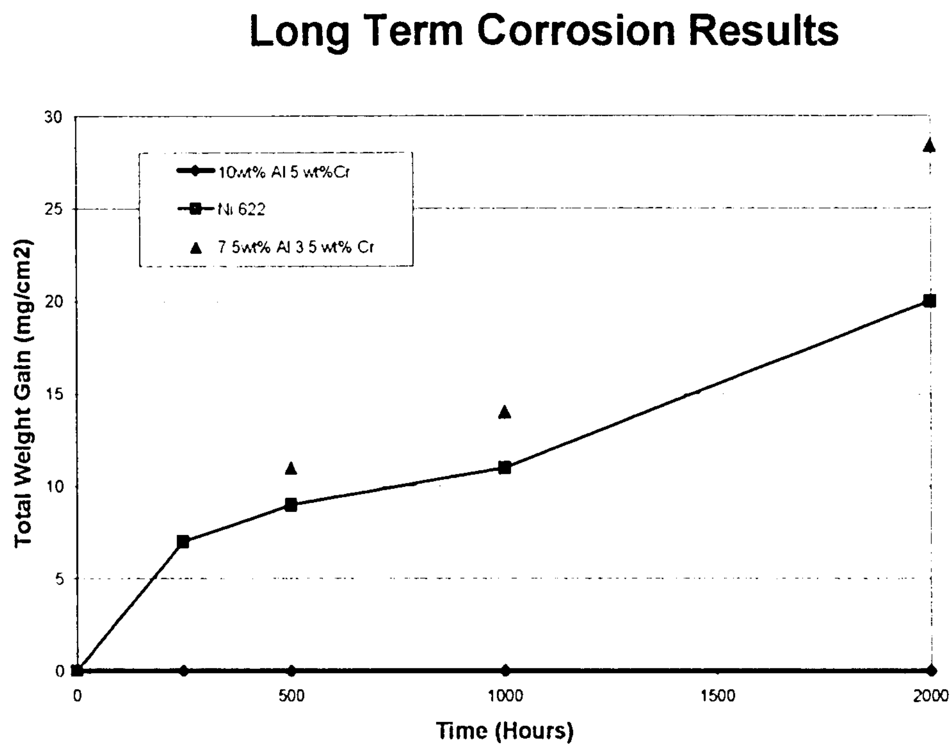

Figure 23: Long term corrosion results of alloy 7.5wt% Al 3.5 wt% Cr in low NOx conditions at 500°C. Critical concentrations of 10wt% Al and 5wt% Cr must be obtained for excellent corrosion resistance.

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6. Vita

Matthew Ryan Galler was born on October 12, 1982 in Westchester, Pa to parents Michael and Barbara Galler. He grew up on the Connecticut shoreline in Old Saybrook with older brother Mike and younger brother Jonathan. He graduated with honors from Xavier High School, where he was a member of the Soccer team and captain of the Tennis team. He attended Lehigh University in 2000 in the footsteps of his father and older brother. During his undergraduate career, Matthew was the President of Lehigh's Club Soccer team, an active Pi Kappa Alpha fraternity member, and a passionate fly fishing enthusiast. He graduated with his Bachelors in Materials Science and Engineering as a member of the Alpha Sigma Mu Honors Society in 2004.

END OF TITLE