EXOTHERMIC FLUX FORGE WELDING

OF STEEL TUBULARS

by

Jeremy Joseph Iten
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Golden, Colorado
Date __________________________

Signed: __________________________
Jeremy Joseph Iten

Golden, Colorado
Date __________________________

Signed: __________________________
Dr. Michael Kaufman
Thesis Advisor

Golden, Colorado
Date __________________________

Signed: __________________________
Dr. Eric Toberer
Professor and Program Director
Materials Science
ABSTRACT

Welding processes inevitably alter the local microstructure and in turn affect the properties. For many grades of steels that require high strength, ductility, and toughness, it is difficult to maintain this combination of properties after welding. While full part heat treatments can sometimes be used to recover the microstructure and properties, this approach is impractical for welding of tubular strings in service. Therefore, advanced welding and localized post weld heat treatment methods are needed that can economically produce high integrity welds in tubular strings while maintaining strength, ductility, and toughness property requirements. A novel exothermic flux forge welding method is introduced for solid-state welding of steel tubulars and aspects of the development are discussed including constituent and heating rate effects on self-propagating high-temperature synthesis of metal and oxide products. The exothermic flux forge welded process was investigated for solid-state welding of a high strength low alloy (HSLA) steel and American Petroleum Institute (API) Q125 grade high-strength casing with a 14-inch (355.6 mm) outer diameter and 0.866-inch (22 mm) wall thickness. Post weld heat treatment approaches, including a multi-step heat treatment that included an intercritical heating stage, were investigated on the welded steel for their effects on microstructure and properties. Welded steel performance was characterized by methods including tensile, bend, impact energy absorption, and strain life fatigue testing. Corrosion response was investigated by salt spray and by submersion in NACE Solution A. Heat affected zone microstructure and hardness were also examined along with bond plane fracture using the nick break method. The results include achievement of (1) material specified strength, ductility, and toughness requirements in welded Q125 steel and (2) demonstration of strain life fatigue mean reversals to failure in welded HSLA steel of 2.5 times higher than gas tungsten arc welded specimens.
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CHAPTER 1
INTRODUCTION

Investigation of the relationship between composition, processing, microstructure, and properties is an important ongoing focus of materials science. This relationship is of critical importance for welding operations where the welding process results in microstructural changes that alter the material properties in the affected regions. Aspects of a novel exothermic flux forge welding process are investigated and discussed including investigation of processing methods and the resultant microstructures and properties.

1.1 Background of the Problem

The global welding market is predicted to reach $48 billion USD by 2026 and there are growing needs for automated welding methods capable of producing high integrity welds for the oil and gas sector [1]. Failures in oil country tubular goods (OCTG) and pipelines commonly occur at the joints and result in high repair costs, lost production and transportation, and potential environmental disaster. Existing joining methods include threaded connections and arc welding. Threaded connections must maintain compression to maintain a seal and joint integrity can be compromised when the string is deformed during service. Traditional pin and box threaded connections also increase the profile of the tubular and can result in decreased production capacity for a given bore diameter while flush threaded connections are often an area of mechanical weakness. Field arc welded connections are limited in the grades of steel they can address and have low throughput for large diameters and wall thicknesses. Therefore, high integrity joining of steel tubulars is an important industrial problem and a suitable automated welding method is desirable. To be economically viable, the welding method must also be able
to provide comparable or better throughput to currently used joining technologies. For such a welding method to gain industry adoption, the weld microstructure, mechanical properties and representative service performance must be investigated and understood.

The exothermic flux forge welding (EFFW) method has been developed for this task. Exothermic flux forge welding is a solid-state forge welding process that can rapidly produce high quality welds and the equipment is amenable to providing in situ post weld heat treatment when required. The process can be used in a variety of environmental conditions and is therefore suitable for on-site welding.

The EFFW method utilizes a prefabricated exothermically reactive (‘green’) welding flux ring that is placed between the ends of two tubulars which are to be welded. The tubular ends have been machined to produce an end profile designed to facilitate extrusion of the molten welding flux and form the desired weld cap shape upon deformation. The two pipes are first aligned with each other end-to-end with a fixed gap distance. The flux ring is then placed in the gap between the pipes to be in contact with both pipe ends. The pipe ends are then heated by a suitable method such as induction heating or electrode based electro-resistive heating. The heated pipe ends conduct heat to the flux ring which initiates a runaway exothermic reaction forming molten products that serve as a welding flux. The molten welding flux provides additional heat directly to the faying surfaces, protects them from further oxidation, and facilitates removal of existing oxides through dissolution and reduction of the oxides into the molten flux. The molten flux product is comprised primarily of oxides and fluorides.

This study includes new research in a number of areas including self-propagating high-temperature synthesis of crystalline and amorphous oxide based materials, use of these reactive
compositions as exothermic fluxes for forge welding, and evaluation of the effects of forge welding and post weld heat treatment on weld and heat affected zone microstructure and properties.

Welding of steel will unavoidably alter the local microstructure and properties. Defects including inclusions and pores and cracking may occur in fusion or interface regions. The heating and cooling thermal history of the weld and nearby region making up the heat affected zone can produce grain growth, grain refinement, and phase changes that determine how the weld region will perform in service. The weld and heat affected zone must therefore be characterized and the relationship between composition, processing, microstructure, and properties investigated. These relationships are not yet well studied for the novel exothermic flux forge welding process with high strength steel tubulars.

1.2 Research Questions and Hypotheses

The purpose of this study is to investigate and document relationships between steel composition and condition, exothermic flux forge weld and post weld heat treatment processing variables, and post process microstructure and properties. Variables effecting self-propagating high-temperature synthesis reactions are also investigated towards the development of exothermic fluxes. The research attempts to address aspects of the following research questions:

- What are the effects of reactant particle size, hyper-stoichiometric reductant concentration, and heating rate on ignition temperature, combustion temperature, and reaction propagation rate for self-propagating high-temperature synthesis reactions forming metal and oxide products?
- What is the relationship between welding method and properties for gas tungsten arc welded and exothermic flux forge welded high strength low alloy steel tubing?
What are the effects of localized induction-based heat treatment on heat affected zone microstructure and properties of exothermic flux forge welded steel?

Hypotheses based on these questions include:

- Smaller reactant particle size will lower ignition temperature and increase reaction propagation rate due to increased reactant surface and contact area and reduced diffusion requirements. Hyper-stoichiometric reductant (aluminum) concentration for a system keeping a constant adiabatic combustion temperature will increase reaction propagation rate due to increased reactant surface area, contact, reduced diffusion requirements, and increased mass transport through additional low melting temperature phase. Increased heating rate will facilitate lower ignition temperature by increasing the rate of heat input relative to the time available for heat loss to the environment.

- A solid-state welding method like exothermic flux forge welding will show improved properties compared to a fusion welding process such as gas tungsten arc welding.

- Localized induction-based heat treatment can be utilized to improve heat affected zone properties and rapid processing approaches will result in improved properties due to better control of the intercritical and softened HAZ regions.

These questions relate to relevant engineering needs for determining if the exothermic flux forge welding method can be utilized together with an in-situ post weld heat treatment process in a practical manner to meet challenging performance requirement targets. Specific engineering questions related to these research questions include:

- Can the EFW method facilitate metallurgical bonding for API grade steel tubulars through diffusion and plastic flow to produce an interface sufficient for achieving
material strength, ductility, and toughness targets with use of post weld heat treatment when required?

- Is there a localized induction post weld heat treatment method that can be used with exothermic flux forge welding to produce weld heat affected zone microstructures suitable for overcoming penetration depth challenges with thick walled (22mm) and high strength (862 MPa) ferromagnetic steels and meet strength, ductility, and impact energy requirements?

### 1.3 Importance of the Study

An economical method of producing high integrity welded steel tubing connections is important for oil and gas exploration and production as well as chemical transport and processing. The oil country tubular goods (OCTG) market consists primarily of drill pipe, casing, and tubing. The global OCTG market was approximately $49 billion in 2017 and has been predicted to grow to $100 billion by 2026 according to a 2018 Research and Markets report [2]. This research is also applicable to pipeline markets including subsea pipelines and the gas pipeline infrastructure market has been valued at over $1 trillion USD in 2018 [3].

Currently, joining of OCTG is done almost exclusively by threaded connections and connection failures account for up to 90% of all tubular failures [4]. Connection failures can result in loss of well integrity and lead to consequences ranging from reduced production to environmental disasters and loss of life. Threaded connections also limit the weight and torque that can be applied to a tubing string. High-quality welded connections have the potential to reduce or even eliminate these problems. This work will primarily focus on the tubing and casing markets and use this terminology; however, the process and findings are generally also applicable to pipeline and other markets.
This study investigates a novel exothermic flux forge welding (EFFW) method and the effects of the critical process variables on the microstructure and mechanical properties of the welded connections. In addition, approximately one-thousand exothermic flux compositions have been characterized for reactivity and product characteristics. Very little literature is available on solid and liquid phase self-propagating reactions that produce molten products comprised fully of oxides or oxides and fluorides. This study examines self-propagating reaction systems to produce molten oxide compositions that solidify to glasses and oxide-based ceramics without containing significant amounts of reduced metals, intermetallics, carbides, or borides. The results of this work may therefore also be used as a foundation for further study of self-propagating high-temperature synthesis (SHS) of glasses and oxide-based ceramics.

This study also researches use of localized induction heating at the weld site to perform post weld heat treatments on investigated steel grades. The post weld heat treatment (PWHT) study includes non-standard techniques including intercritical heat treatments for dual phase microstructures. The effects of heating rate, temperature, time, and cooling rate on the heat affected zone (HAZ) are also investigated.

1.4 Summary

This study continues the materials science overarching goal of understanding the relationships between composition, processing, microstructure, and properties. High strength low alloy steel and API Q125 grade steel alloys welded by the exothermic flux forge welding process are investigated to characterize the effects of the welding process and investigated post weld heat treatments on microstructure and properties.
CHAPTER 2
BACKGROUND AND REVIEW OF THE LITERATURE

This investigation builds on the knowledge published by researchers in a number of areas of study. Research areas of particular importance to this work include studies on welding fluxes, self-propagating high-temperature synthesis, and welding methods and theory. In addition, background information is presented on oil country tubular goods and the novel exothermic flux forge welding method utilized for the investigated research is discussed.

2.1 Welding Flux Development

The importance, history, and fundamentals of welding fluxes and slags are discussed to better understand the exothermic flux forge welding method and the path to development of an exothermic flux.

2.1.1 Introduction

Welding fluxes are used extensively in a variety of welding processes and can have a significant impact on welding productivity and weld properties. The welding consumables market which includes welding fluxes and electrodes and wires with integrated fluxes was approximately $13.8 billion USD in 2018 and expected to grow to over $23 billion by 2026 [5]. Many researchers including Jackson, Olson, Liu, Chai, Eager, and others have contributed to a knowledge base in welding flux development and effects on steel weld properties [6-11].

2.1.2 Definition

The word flux is derived from the Latin *fluxus* meaning flow. The word therefore also has many other uses including within materials science for the flow of heat or diffusion such as in
Fick’s Law. The first usage relating to welding fluxes was for smelting to make the slag more fluid. Jackson and the AWS have described welding flux as “Material used to prevent, dissolve, or facilitate removal of oxides and other undesirable surface substances” [6, 12]. The terms flux and slag are often used interchangeably, however Jackson clarifies that “In flux-metal reactions, a slag is the product formed after the reaction of a fused liquid flux with molten weld metal” [6].

2.1.3 Background

Fluxes and slags have been used in steel making and blacksmithing for hundreds of years and their use has transitioned to modern steelmaking and welding techniques. The first patent for a welding electrode using an early form of a mineral based flux coating was by Kjellberg in 1907 [13]. Jackson published a comprehensive summary of welding fluxes and slags in 1972 that discusses many critical areas of flux development including binders, viscosity, surface tension, fluxing and deoxidizing of weld metal, alloying of weld metal, and control of hydrogen in weld metal [6]. Fluxes may also intentionally produce gaseous protection through cellulose or carbonate type materials although these fluxes may limit production rate and introduce hydrogen.

Flux covered metal consumable electrodes typically use a binder comprised of a sodium or potassium silicate dissolved in water with a composition of the form shown in equation (2-1) where the ratio of $x$ to $y$ is typically between 2 and 3.75 with the pH between 10 and 13 and the value of $n$ is sufficient to ensure that full dissolution occurs and the viscosity is suitable for the application [6]. After application, the binder is dehydrated to solidify.

$$x \text{SiO}_2 + y \text{Na}_2\text{O} + n \text{H}_2\text{O} \quad (2-1)$$

Submerged arc welding (SAW) and electroslag welding (ESW) fluxes have some similarities to the forge welding fluxes investigated in this work although the SAW fluxes are typically
compositionally designed for working viscosity ranges at higher temperatures than the steel forge welding temperatures. Authors including Jackson, Olson, Indacochea, and Liu have published useful composition, temperature, and viscosity relationships and binary and ternary phase diagrams on MnO-SiO$_2$ and CaO-SiO$_2$ based systems with additions such as Al$_2$O$_3$, ZrO, and TiO$_2$ [6, 14, 15].

Surface active components are often added to welding fluxes to modify surface tension. Surface active compounds can invert the relationship between temperature and surface tension and reverse the Marangoni convective flow in the weld pool [6, 16-18]. Figure 2-1 shows top-view and cross-sectional schematics of the melt pool with outward and inward Marangoni flows. The inward Marangoni flow occurs when surface active elements invert the temperature and surface tension relationship and results in deeper weld penetration.

![Diagram of Marangoni flows](image)

Figure 2-1. Conventional Marangoni flow (left) results in decreased penetration. Surface active element additions such as sulfur, potassium, phosphorus, and selenium can reverse the Marangoni convection (right) and results in deeper weld penetration [19].
Slag viscosity is an important characteristic of the molten welding flux. Generally, the slag should be fluid enough to flow across the weld region, but viscous enough to stay together and in place at the working temperature. A lower viscosity will promote faster flux action including surface interactions and dissolution and diffusion of surface oxides however may result in more spatter. Vertical or inverted surfaces will generally require higher flux viscosity than a horizontal upright surface. Attributes that have a direct relationship with viscosity include slag solidus and liquidus temperatures and the amount of compositional network formers, while viscosity has an indirect relationship with process temperature and compositional network modifiers. Jackson presents figures on the viscosity and temperature relationship for several useful welding flux compositional systems [6].

Welding slags often share attributes with glass formers while in the molten state and many relevant compositions will solidify amorphously with sufficiently rapid cooling conditions. Therefore, glass theory is generally applicable to welding slags and the foundational network model of glass forming by Zachariasen provides useful insight into slag viscosity modification [20]. Other valuable literature related to glass formation and modification include publications by Warren, Sun, Stanworth, and Angell [21-24]. Fluegel has developed useful glass property modeling approaches as well as (open source) published a number of spreadsheet based models for glass property development that are also useful for welding flux and slag development [25]. For simple ionic melts, the viscosity follows an Arrhenius type temperature relationship as shown in equation (2-2) where $\eta$ is the viscosity, $\eta_0$ is a system constant, $E_\eta$ is the activation energy for viscous movement while $e$ is Euler’s number, $R$ is the universal gas constant, and $T$ is the absolute temperature [26].
\[
\eta = \eta_0 e^{\left(\frac{E_0}{RT}\right)}
\] (2-2)

The flux basicity is another important consideration. The flux basicity inversely correlates to weld metal oxygen and sulfur content and generally directly correlates to improved weld metal properties; however, the basic components are also hygroscopic and lead to increased flux moisture with environmental exposure. Oxide constituents listed in order of increasing basicity are \(\text{SiO}_2, \text{P}_2\text{O}_5, \text{Al}_2\text{O}_3, \text{TiO}_2, \text{ZrO}_2, \text{FeO}, \text{MgO}, \text{MnO}, \text{CaO}, \text{Na}_2\text{O}, \text{K}_2\text{O}\) [6]. Several indices have been developed to empirically quantify the basicity of slags for steelmaking and welding with the basicity index (BI) selected by Olson, Liu, et al. for the ASM Metals Handbook shown in equation (2-3) [26]. Weld metal oxygen has been found to decrease with an increasing BI up to around 1.2 with BI values from 1.0 to 1.2 considered neutral and values greater than 1.2 considered basic [27].

\[
BI = \frac{\text{CaO} + \text{CaF}_2 + \text{MgO} + K_2O + Na_2O + \frac{1}{2}(MnO + FeO)}{\text{SiO}_2 + \frac{1}{2}(\text{Al}_2\text{O}_3 + TiO_2 + ZrO_2)}
\] (2-3)

Weld metal oxygen can be introduced either by the surrounding air or decomposition of oxide constituents in the slag [28]. Weld metal oxygen is surface active and reduces surface tension but can also promotes inclusions, porosity, reduces hardenability, and generally reduces toughness except when it promotes acicular ferrite [14, 15]. Deoxidation of the weld metal can be facilitated by the welding flux in ways including by dissolution and reduction by deoxidizing agents such as aluminum, titanium, and silicon [14]. Welding slags can be used to deoxidize weld metal to target levels based on compositional control of deoxidizing additions using deoxidation equilibria calculations. Welding slags can reduce weld oxygen content to a few hundred ppm where it is usually not very detrimental and up to 300 ppm of oxygen can even be
considered beneficial. Oxygen inclusions can restrict austenite grain growth and provide nucleation sites for acicular ferrite. Allotriomorphic ferrite at the grain boundaries can suppress bainite and Widmanstätten ferrite to allow acicular ferrite to nucleate at the oxide inclusion sites [15]. Weld metal hydrogen and oxygen content also tend to be inversely related and so a moderate oxygen content can reduce diffusible hydrogen [26]. Slag containing fluorides, particularly potassium fluoride and manganese (II) fluoride, can also greatly reduce weld metal hydrogen [10].

Carbon content of slags must be controlled to avoid over carburizing the weld metal leading to problems including brittleness and excessive hardness, but carbon additions can be used to avoid undesirable decarburization of the weld metal. Alloying elements can also be added to the weld metal through flux additions, but thermodynamic stability must be considered in the component design to prevent the flux oxides from oxidizing the alloying additions. Slag release is also an important aspect including for forge welding and researchers have investigated methods to improve release through modification of thermal expansion and solidification and lattice similarity to the steel [29].

2.2 Self-Propagating High-Temperature Synthesis (SHS)

The self-propagating high-temperature synthesis technique, also known as reaction synthesis and combustion synthesis, provides the scientific basis for the development of exothermic flux used in the exothermic flux forge welding process. Selected literature and background information is discussed to provide insight into the exothermic flux used in this work.
2.2.1 Introduction

Self-propagating high-temperature synthesis as a field of scientific study in solid state reactions has origins with Russian researchers Borovinskaya and Shkiro which they termed ‘solid flame phenomenon’ in their 1967 publication [30]. The fully solid-state reactions are a subset of other types of self-propagating reaction synthesis that include solid and liquid phase reactions, solid gas phase reactions, liquid gas phase reactions, fully gas phase reactions, and other combinations of these. Similarly, self-propagating reactions are a subset of an even broader group of synthesis reactions that include non-propagating exothermic reactions and endothermic reactions. The background presented here focuses on exothermic reactions involving primarily powder-based reactants that form products of solid, liquid, and mixed phase without the need for gas phase reactants and the SHS terminology will be considered inclusive of these reactions.

2.2.2 Background

Self-propagating high-temperature synthesis (SHS) is typically performed using powder metallurgy techniques where the reactant composition is batched, mixed, and then pressed into a compacted form such as a pellet. The compacted form is then ignited by an external heat source initiating the exothermic reaction that then propagates through the reactant materials forming the product phases at high temperature. A schematic of the reaction process is shown in Figure 2-2 where the reactant powders are represented by the green portion of the pellet, the reaction front by the yellow region, and the product material shown in orange graded from light to dark to represent cooling after the reaction.
Figure 2-2. Self-propagating high-temperature synthesis (SHS) reaction progression. The reaction is initiated by an ignition source in with the reaction front (yellow) then propagating through the unreacted (green) material. The material having passed through the reaction front has been converted to the product phases and begins to cool.

Self-propagating high-temperature synthesis has been used to produce a large number of product materials including metals, oxides, carbides, nitrides, silicides, aluminides, hydrides, intermetallics, carbonitrides, chalcogenides, cemented carbides and borides, and composites including metal matrix composites. Classification of the applications of these materials include abrasives, cutting tools, resistive heating elements, shape memory alloys, high-temperature intermetallic compounds, electrodes, corrosion resistant parts and coatings, materials additives, functionally graded materials, and other high-performance materials [31, 32].

2.2.3 Reaction Thermodynamics

A typical reaction synthesis process involves design of the reaction system composition, mixing reactant powders, pressing them into a green part or placing them in a mold, and applying a heat source to initiate an exothermic propagating reaction that converts the reactants to the product phases at high temperature. The local reaction releases enough heat to initiate the reaction in the adjacent regions which in turn release enough heat to continue the reaction
propagation. Thermodynamic equations utilizing enthalpy of formation and heat capacity data can be used to calculate adiabatic peak temperature, or adiabatic combustion temperature, of the reaction system. The combustion temperature can be optimized through the design of the reaction system with many SHS reactions having adiabatic combustion temperatures over 2000°C. Diluents can be added to the system to lower the combustion temperature and reduce or prevent unwanted propagation of the reaction.

By using thermodynamic principles, the energy balance of a reaction system can be examined. The adiabatic combustion temperature, \( T_{ad}(298) \), can be calculated with an iterative approach using tabulated thermodynamic data from the relation shown in equation (2-4) [31]:

\[
\Delta H(298) + \int_{298}^{T_{ad}(298)} \sum n_j C_p(P_j)\,dT + \sum_{298-T_{ad}(298)} n_j L(P_j) = 0
\]  

(2-4)

where \( \Delta H(298) \) is the reaction enthalpy at 298 K, \( n_j \) is the number of moles of species \( j \), \( C_p(P_j) \) is the constant pressure heat capacity of the product species, and \( L(P_j) \) is the transformation enthalpy of the products if they undergo a phase change.

The enthalpy-temperature relation for a reaction system with no phase changes is shown schematically in Figure 2-3. The enthalpy-temperature diagram shows schematically how the adiabatic temperature of the products is determined by enthalpy balance and the heat capacities of the reactants and products. For a reaction occurring in self propagating mode, the heat released by the reaction will heat the adjacent material to the ignition temperature \( T_{ig} \) which will in-turn react and again heat the adjacent material to \( T_{ig} \) with the propagation typically reaching steady state conditions.
Figure 2-3. Illustration of the enthalpy temperature relationship for reactants and products plot for reactants and products for a system with no reactant or product phase changes [31].

For an adiabatic propagating reaction with initial material temperature of $T_0$, the adiabatic combustion temperature, $T_{ad}$, can be obtained by following an isoenthalpic line from the reactant at $T_0$ to the product line which gives $T_{ad}(T_0)$ which is the adiabatic combustion temperature for an initial temperature of $T_0$. Real world SHS reactions are rarely adiabatic and will have some amount of heat loss during propagation. This enthalpy loss is illustrated by the downward sloped dashed line from the reactants at $T_0$ to the products at $T_c$ which represents the real combustion temperature. For a reaction initiating in a preheated material, an initial temperature to the right of $T_0$ would be used and the same process would result in a higher $T_{ad}$ and $T_c$. If the entire material is simultaneously heated to the ignition temperature, $T_{ig}$, then a simultaneous reaction will occur, often termed thermal explosion, with the adiabatic combustion temperature represented by $T_{ad}(T_{ig})$. The enthalpy temperature relationship for the reactant and product species is not truly linear as depicted in Figure 2-3, but for non-cryogenic temperature ranges without phase changes
the linear approximation works well and the ratio of the reported standard heat of formation and
the constant pressure heat capacity of the product at 298 K, \( \Delta H_f^{\text{298}}/C_p^{\text{298}} \), can be simply used as
a good estimate of \( T_{ad} \) for many solid state systems [33].

The predicted adiabatic combustion temperature, \( T_{ad}(298) \), can be calculated for each
system of interest using thermodynamic data such as from NIST-JANAF [34] with the energy
balance previously shown in equation (2-4) using an iterative technique to solve for the upper
integral limit. The enthalpy required to heat the reactants up to the ignition temperature, \( T_{ig} \),
where the exothermic reaction will initiate is given by equation (2-5) [31],

\[
H(R) = \int_{T_0}^{T_{ig}} \sum n_i C_p(R_i) dT + \sum_{T_0-T_{ig}} n_i L(R_i) \quad (2-5)
\]

where \( C_p(R_i) \) is the heat capacity of the reactants and \( L(R_i) \) represents the phase transformation
enthalpy of the reactants that undergo phase transformations. This equation can be used as a
guiding model for the minimum required energy input to initiate the reaction for an exothermic
flux forge welding ring.

2.2.4 Reaction Kinetics

The kinetics of self-propagating high-temperature synthesis reactions are influenced by
many process variables. For a reaction that proceeds to completion, as is typically the case for
SHS reactions, for a simple single product combination reaction involving two reactant species,
the instantaneous change in product concentration with respect to time, \( \frac{d[P]}{dt} \), can be expressed in
the form of equation (2-6). The concentration dependent activities of the reactant species are
indicated by \([A]\) and \([B]\) with the exponents \( m \) and \( n \) representing the reaction orders based on
reaction mechanism. The rate coefficient, \( k \) is a function of temperature, \( T \), based on the
Arrhenius relationship shown in (2-7) where $A$ is a pre-exponential frequency factor, $e$, is Euler’s number, $E_a$ is the activation energy, and $R$ is the universal gas constant [35]. This relationship shows that the reaction rate is heavily temperature dependent and the exothermic nature of the reaction results in an increasing temperature and increasing reaction rate feedback loop once the reaction enthalpy release exceeds the rate of local heat loss.

$$\frac{d[p]}{dt} = k(T)[A]^m[B]^n$$  \hspace{1cm} (2-6)

$$k = Ae^{-\frac{E_a}{RT}}$$  \hspace{1cm} (2-7)

The SHS reaction kinetics are also influenced by factors including the pellet size and geometry, green density, thermal conductivity, reactant powder sizes and surface areas, degree of intimate contact from mixing or milling, ratio of reactants, diffusion and flow rates of the reactants at a given temperature, intermediate reactions including catalytic reactions, and environmental interactions including thermal exchange or reactions with air. Thermal diluents can reduce combustion temperature by adding heat capacity to the system while kinetic diluents can slow reaction rates by reducing activity and mass transport of the reactants.

### 2.2.5 Reaction synthesis related to fluxes and welding

Oxide products are a well-known byproduct of thermite style reduction reactions. Oxide based reaction products including glass products have also been reported by researchers including Munir and Yi [33, 36]. A generalized thermite type oxidation and reduction equation is given by (2-8) where $M_pO_q$ represents metal oxides that will be reduced (often transition metal oxides), $F$ represents the fuel that will be oxidized, and $D$ represents diluent additives that may be of metal or oxide form. The reaction heat released $Q$ is typically negative by convention and...
\(a, b, c, p,\) and \(q\) are coefficient ratios. Adjustment of the reactant and diluent constituents will determine the product compositions including the amount of metals and oxides.

\[
\sum a(M_p O_q) + \sum bF + \sum cD^{\text{ignition}} \rightarrow \sum F_b O_{a+q} + \sum (a*p)M + \sum cD + Q
\]  

(2-8)

A common example of a reaction of this type is the thermite reaction between iron oxide and aluminum shown in equation (2-9) where aluminum oxide and iron metal are formed with approximately 850 kJ/mol of heat released bringing the adiabatic combustion temperature for this reaction to the boiling point of iron at around 2862 °C.

\[
Fe_2O_3 + 2Al \xrightarrow{\Delta H^o = -852 \text{kJ/mol}} Al_2O_3 + 2Fe
\]  

(2-9)

Powder metallurgy-based reaction synthesis methods have been successfully applied to commercial welding applications including railway welding and copper electrical connection welding using thermite-based reaction systems to produce molten metal products. Exothermic additions have been researched for welding fluxes and consumables by Allen, Olson, and Frost and by Malene, Park, and Olson [37-39]. The work by Olson et al. successfully demonstrated use of exothermic reactions for lowering electrical energy input requirements for arc welding. Nuechterlein and Iten have utilized exothermic reactions in situ in laser welding based reactive additive manufacturing processes to produce metal matrix composites and for in situ nucleant formation with an XRD plot shown in Figure 2-4, indicating good conversion to the target product phases with a laser powder bed fusion based process [40].
Figure 2-4. An XRD plot of a reactive additive manufacturing produced metal matrix composite. The plot peaks matching well with the target reference peaks indicating good in situ conversion to the intended product phases.

2.3 Established Welding Processes and Selected Theory

Welding process and metallurgical modeling theory are useful for understanding and predicting the effects of processes and variables on the weld microstructure and performance. Many researchers and editors have published works with useful weld modeling approaches including Grong, Cerjak, Easterling, and Rykalin [41-43]. Many welding processes are known in the literature with each process having application specific advantages and disadvantages. Welding methods can be broadly categorized as either fusion welding or solid-state welding. Fusion welding creates a liquid phase of similar composition to the base materials at the surfaces to be joined. Upon cooling, the liquid solidifies and forms a weld joining the parts. Solid-state welding processes create a bond between parts at temperatures below the base material melting points without the addition of lower melting temperature filler metal [26]. Brief overviews of established welding techniques with potential relevance to welding of steel tubulars are presented in APPENDIX A.
Arc welding processes are suitable for reliable automation with many commercially available orbital welding machines. However, they require multiple passes to weld thick walled tubulars. The fusion welding processes are susceptible to segregation of alloy constituents, solidification cracking (hot cracking), gas inclusions, and large grain sizes. These issues can reduce the weld performance compared to solid-state welding techniques. Of the fusion welding techniques, flash welding is of interest due to short welding time and moderate equipment cost. The flash welding process produces a high thermal gradient which can result in rapid cooling and formation of martensite. Flashing is generated during the process and must be removed using additional equipment and process time. Laser beam welding is also a promising approach for steels that do not require post weld heat treatment. The equipment cost and challenges welding thick-walled tubulars are potential drawbacks.

Solid-state high frequency welding and solid-state upset welding are both promising approaches for automated welding of steel tubulars. The two processes are similar in that they both heat the ends to be joined and apply a force to push the ends together. The primary difference between the two processes is the heating method. Upset welding (UW) uses resistive heating by flowing current between the two parts while high frequency welding (HFW) uses a high frequency alternating current to heat each part. The HFW process may be more suitable for PWHT ability and for repeatability and reliability while the UW process may have reduced equipment cost.

2.3.1 Weld Microstructure

Understanding weld microstructure formation allows for control through materials and process modifications. Mechanisms explaining formation of allotriomorphic, Widmanstatten, and acicular ferrite have been suggested by researchers [44]. Heating of the steel during welding
creates a heat-affected zone (HAZ). The HAZ can be divided into regions corresponding to the region of the steel phase diagram reached at the peak temperature. The typical HAZ regions found in a fusion weld are shown on the left in Figure 2-5 with the corresponding regions on a metastable iron-carbon phase diagram on the right.

![Heat-affected zone (HAZ) schematic for a hypoeutectoid steel with regions correlated to temperature-phase ranges on an iron-carbon phase diagram](image)

**Figure 2-5.** Heat-affected zone (HAZ) schematic for a hypoeutectoid steel with regions correlated to temperature-phase ranges on an iron-carbon phase diagram [26].

Low alloy steel phase diagrams typically have a similar form to the iron-carbon diagram shown, but small alloying additions can have significant effects on the boundary positions for the regions and so the transformation temperatures for the specific steel alloy used should be considered. For solid-state welding, the solidified weld and solid-liquid transition zone regions
shown in Figure 2-5 are not present, but the other regions are typically observed. The HAZ region widths and microstructures are determined by the peak temperatures, heating time, and cooling rates.

Grain growth is generally undesirable for API steel tubulars because large grain sizes negatively impact strength and toughness. Yield strength, $\sigma_y$, is related to grain size, $d$, by the Hall-Petch relation shown in equation (2-10) where $\sigma_0$ and $k_y$ are constants for the material. A fine-grained microstructure is therefore preferable for API tubulars and any coarse-grained region may need PWHT to refine the grain size.

$$\sigma_y = \sigma_0 + k_y d^{-\frac{1}{2}} \quad (2-10)$$

Grain growth is driven by the Gibbs-Thomson effect and results from movement of grain boundaries by atomic diffusion to minimize free energy. Grain boundaries have a higher energy than the grain crystal lattice and therefore there is a thermodynamic driving force to reduce the grain boundary area. The velocity of the grain boundary movement is proportional to the curvature of the grain boundary. From a two-dimensional perspective, triple junctions are most stable with angles of 120° as found in a hexagon. Polygons with more than six sides have angles larger than 120° and polygons with less than six sides have angles less than 120°. For a grain with more than six sides, the angles tend to bend inward to approach the stable 120° angle. This bending results in concave curvature for the grain and outward movement of the grain boundary towards the center of curvature in the adjacent grain as illustrated in Figure 2-6.
Above the $A_3$ critical temperature, austenite (fcc) is the stable microstructure, while below the $A_1$ critical temperature, ferrite (bcc) and pearlite are stable for hypoeutectic steels on the timescales of interest. Between the $A_1$ and $A_3$ temperatures, or the inter-critical region, a mixture of ferrite and austenite are stable [45]. Rapid cooling from austenite can produce non-equilibrium microstructures such as martensite and upper and lower bainite.

The austenite-ferrite/pearlite phase transformations occur by nucleation and growth with heterogeneous nucleation typically dominating. Formation of the more stable phase results in a negative volume free energy change, $\Delta G_v$, but also a positive volume strain energy change $\Delta G_\varepsilon$ and a positive surface free energy change, $\gamma$. The net free energy change, $\Delta G$, for the formation of an embryo or nucleus with radius, $r$, is shown in equation (2-11) and illustrated in Figure 2-7. Volume of a sphere is proportional to the radius cubed while surface area is proportional to the radius squared so at small radii, the surface energy term will dominate, while at larger radii the volume energy term will dominate. Therefore there is a critical nucleus radius size, $r^*$, that must be reached for the nucleus to be stable given in equation (2-12) and illustrated in Figure 2-7. The activation free energy, $\Delta G^*$, is given by equation (2-13) for homogeneous nucleation. It must be noted that the value of $\Delta G_v$ depends heavily on the degree of undercooling or overheating from the phase transition boundary.
Figure 2-7. Volume free energy change (red dashed line) and surface free energy change (blue dashed line) contributions to the net free energy change (black solid line) for homogeneous formation of a spherical embryo and nucleus [46].

\[
\Delta G = -\frac{4}{3} \pi r^3 (\Delta G_v - \Delta G_e) + 4\pi r^2 \gamma \quad (2-11)
\]

\[
r^* = -\frac{2\gamma}{\Delta G_v - \Delta G_e} \quad (2-12)
\]

\[
\Delta G^* = \frac{16\pi \gamma^3}{3(\Delta G_v - \Delta G_e)^2} \quad (2-13)
\]

For solid-state heterogeneous nucleation, the schematic shown in Figure 2-8 can be used to produce a surface tension balance between the parent solid (P), nucleating solid (N), and interface (I) as shown in equation (2-14). This surface tension balance can be used to derive equations for \( r^* \) and \( \Delta G^* \) for heterogeneous nucleation as shown in equations (2-15) and (2-16). The interfacial energy between the transforming phases, \( \gamma_{NP} \), is used along with a function with a value between zero and one, \( S(\theta) \), of the angle between the interface and nucleating phase. For
heterogeneous nucleation, the critical radius is the same as for homogeneous nucleation, but the
activation energy barrier is smaller corresponding to the value of $S(\theta)$. The volume change of
the solid-state transformation between austenite and ferrite/pearlite results in lattice strain and
this must also be accounted for by addition of a volume strain energy term like for homogeneous
nucleation.

![Surface energy vectors for the nucleating solid-interface, interface-parent solid, and nucleating solid-parent solid interfaces for solid-state heterogeneous nucleation [46].](image)

$$\gamma_{IP} = \gamma_{NI} + \gamma_{NP} \cos \theta$$  \hspace{1cm} (2-14)

$$r^* = - \frac{2\gamma_{NP}}{\Delta G_v - \Delta G_e}$$  \hspace{1cm} (2-15)

$$\Delta G^* = \left( \frac{16\pi \gamma_{NP}^3}{3(\Delta G_v - \Delta G_e)^2} \right) S(\theta)$$  \hspace{1cm} (2-16)

The austenite-ferrite/pearlite phase transformation results in the recrystallized region of
the HAZ shown in Figure 2-5 and allows for grain refinement and quench hardening post weld
heat treatment processes. The partially transformed (inter-critical) region of the HAZ has
undergone partial recrystallization with the untransformed ferrite undergoing tempering. The
tempered region has been tempered and therefore softened. The tempered and inter-critical
regions are at risk of inadequate strength while the grain growth and recrystallized regions are at
risk of developing brittle microstructures upon cooling.
Due to the rapid heating and cooling rates, non-equilibrium microstructures may be present on both heating and cooling. Time temperature transformation (TTT) diagrams can be used to estimate the amount of isothermal phase transformation over time. Continuous cooling transformation (CCT) diagrams are often more suitable for weld cooling situations as they can be used to predict the microstructures formed by cooling at a constant rate. Continuous heating transformation (CHT) diagrams are similar to CCT diagrams only predict the microstructures found for constant heating rates over time and are also useful for welding processes. For example, CHT diagrams can be used to determine the peak temperature needed for a given heating rate to achieve homogeneous austenite or the austenite grain size produced by a given heating rate and time. From a typical steel CCT diagram, it can be seen what cooling rate is required to form martensite, bainite, ferrite and pearlite, or combinations of these. From a typical CHT diagram, it can be observed that with high heating rates, higher temperatures must be reached to form homogeneous austenite than would be required with lower heating rates or as predicted by an equilibrium or quasi equilibrium phase diagram. Likewise, high heating rates can limit grain growth even with relatively high peak temperatures.

Post weld heat treatment can be beneficial to refine the HAZ grain size and to control the cooling rate to produce the desired microstructure. Tempering can be used to relieve weld stresses and to improve ductility and toughness such as in the case of tempered martensite. The induction coil used for the exothermic flux forge weld heating is also suitable for localized PWHT. Although it can be possible to heat treat the full pipe length with a continuous or scanning heating process, full length heat treatment is not practical to perform on site. Therefore, localized PWHT must be used and will leave a HAZ similar to weld heating. It is important to minimize the width of the tempered zone where the material can become over softened. As long
as the width of this material is small relative to the pipe wall thickness, then the constraint of the adjacent areas will minimize any strength loss. Water cooling nozzles can be added to the welding system to spray a controlled flow of water at the weld to produce a controlled rapid cooling rate to form martensite without cracking problems. This martensite can be subsequently tempered with a rapid tempering process at a temperature just below the $A_1$ temperature of the steel.

### 2.4 Oil Country Tubular Goods (OCTG) Overview

Well casing is categorized as an oil country tubular good (OCTG) and is used in a number of grades and sizes based on American Petroleum Institute API 5CT [47] specifications. The four major OCTG markets are North America, China, Russia, and the Middle East and North Africa (MENA), and account for approximately 85 percent of global demand. The largest manufacturers include Tenaris (Luxembourg), Vallourec (France), TMK group (Russia), United States Steel Corporation (U.S.), Nippon Steel and Sumitomo Metal Corporation (Japan), National Oilwell Varco (NOV) (U.S.), JFE Steel Corporation (Japan), Jindal Saw Limited (India), MRC Global (U.S.) and ArcelorMittal (Luxembourg) [48].

Well casing includes seamless and electric resistance welded (ERW) tubing. Casing is available in API grades H, J, K, N, R, C, L, M, T, P, and Q [47]. Within each grade, different yield strengths may be specified. The grades typically specify a composition range as well as performance requirements. Standard sizes for API tubing and well casing range from 26.67 to 508 mm (1 to 20 inches) outside diameter with wall thicknesses from 2.87 to 22.22 mm (0.113 to 7/8 inches). In addition to these standard sizes, non-standard sizes are commonly used.
2.4.1 Threaded Connections Background

Presently, casing is primarily joined by threaded connections. Many types of threaded connections are available for use with OCTGs. API threaded connections are openly available for use. API connections include round and square (buttress) thread types. They typically require application of a thread compound or “dope” prior to make-up to assist in lubrication and sealing. The thread compound typically consists of a petroleum-based lubricant with fine solid additives such as graphite and soft metals like lead, copper, or zinc. Some designs also use an elastomeric seal ring, often made of polytetrafluoroethylene (PTFE), to assist in sealing.

Premium connections are designed by companies including Tenaris, Vallourec, TMK, Sumitomo, and U. S. Steel. The designs are licensed for use to steel mills and threading facilities with royalty requirements per connection. Premium connections use a metal-to-metal seal and are designed to provide a strong and reliable connection. Premium connections may use thread compound or may be “dopeless”. Premium connections are preferred in the industry due to their increased reliability and strength, but the high royalty costs and long lead times can restrict use.

Threaded connection designs require compressive stresses from the connection make-up to maintain a seal. Down-hole, the pipe can be subjected to bending, twisting, and helical distortions. These deformations are generally within the elastic limits of the pipe but may also result in plastic deformation. If the compressive forces are lost due to down-hole deformation, then the seal will fail.

Connections may be either integral or coupled. Integral connections directly join two tubulars with one end having male threading and the other having female threading. Coupled connections use male threading on both ends and add a coupling, termed the “box”, with female
threading on both ends. Integral connections are often preferred due to their ability to achieve connections that are flush or near flush with the parent tubular, however they often have lower strength than coupled connections and so are not suitable for all applications.

2.4.2 Welded Connections Background

High integrity joining methods are especially important for the oil country tubular goods (OCTG) market which consists of drill pipe, casing, and tubing. Threaded connections are used almost exclusively for joining OCTG today and connection failures account for up to 90 percent of all casing failures [4]. Connection failures can result in loss of well integrity and lead to consequences ranging from reduced production to environmental disasters or loss of life. Threaded connections also limit the weight and torque that can be applied to a tubing string. High-quality welded connections have the potential to reduce or even eliminate these problems.

Welded connections offer the potential for higher strengths and improved reliability and well integrity. Welded connections can offer a lower profile than coupled connections and improved strength over integral connections. The lower connection profile can allow for increased well flow through use of larger diameter casing for the same well bore diameter. Improved connection strength can allow increased well depth and string length, improved deviated well capabilities, and increased torque on drill strings. Deviated wells are becoming increasingly common and use directional drilling capabilities to produce angled wellbores that may contain complex bends to place the borehole in the most productive formations. Welded connections also open the door to technologies that are currently limited by threaded connections such as the cold expansion of tubulars down-hole. These advantages can result in short term and long-term economic advantages for welded connections.
Welded connections are not currently commercially used for well casing primarily due to economic reasons but also due to limitations in reliably achieving property targets. Welds must be performed on the rig while the well casing is being run and therefore the welding process and inspection must be extremely rapid to be cost competitive with threaded connections. An automated welding method is desired for casing and tubing applications that can rapidly produce high quality welds with properties meeting specifications for the parent metals.

2.4.3 Governing Standards

Oil and gas casing and tubing specifications are covered by API 5CT [47]. It is preferred that welded connections meet the specifications of the parent tubulars when possible. There is no welding specification for API casing and tubing, but API 1104 [49] covers the specifications for welding of pipelines and related facilities. These specifications also cover testing methods and may be adopted for use welding casing and tubing. Qualification standards for welding of boiler and pressure vessels are covered by ASME IX [50] and are applicable to casing and tubing.

2.5 Introduction to Exothermic Flux Forge Welding (EFFW)

Exothermic flux forge welding is a newly investigated forge welding process that makes use of an exothermic welding flux to clean and protect the pipe ends prior to forging. Patent WO 2013124447 Al titled, “Method and machine for forge welding of tubular articles and exothermic flux mixture and method of manufacturing an exothermic flux mixture”, was issued to Yi, Iten, and Rudd in 2013 covering this method [51]. Exothermic flux forge welding can be used in conjunction with various heating methods, with high-frequency current preferred for the ability to heat the pipe ends rapidly and uniformly. High-frequency current may be applied either with an induction coil or by electrodes in contact with the pipes. In this study, an induction coil is used to provide the high-frequency current since electrodes can wear due the process heat.
contact pressure, electrical arcing, and forging deformation. In addition, electrode contact points can produce uneven heat distributions. The induction coil does not contact the parts being heated and therefore does not suffer from the life cycle problems associated with contacting electrodes.

An exothermic welding flux is utilized to protect the faying surfaces from oxidization and to dissolve and remove existing oxides and contamination. The exothermic flux enables rapid protection and oxide dissolution with successful testing of total forge heating times as low as 2.5 seconds for 1.5-inch diameter pipes. The pre-manufactured exothermic flux ring is placed into a gap between the aligned pipe ends prior to initiating the induction heating process. An exothermic reaction is initiated when the contacting pipe ends are heated by induction above the ignition point of the flux reactants. The reaction releases heat to rapidly form a molten welding flux and directly heat the steel faying surfaces. The molten flux provides a barrier between the heated steel and the surrounding atmosphere to prevent steel oxidation and dissolves or chemically reduces existing oxidation. The ability to protect from oxidation and remove existing oxidation allows for welding directly in air without the need for a controlled gas or vacuum environment and increases tolerance to pre-existing surface oxides and contamination. The exothermic reaction allows for increased process speed and potentially a higher quality bond compared to traditional welding or brazing flux. A schematic of the exothermic flux forge welding process used for these investigations is shown in Figure 2-9.

The steel pipe ends are machined with a rounded profile prior to use so that the molten flux will be extruded out of the weld during the forging process. The end profile is designed to produce complete flux extrusion, facilitate uniform and concentrated induction heating of the pipe ends, and produce a near flush weld. Generally, a flush inner wall with a small convex weld
cap on the outer wall is preferred. It is important that the formed weld cap not contain any convex regions with a small radius that could act as stress risers.

Figure 2-9. Exothermic flux forge welding process schematic showing cross-sectional view of upper and lower pipe walls with exothermic flux placed in the profiled end offset gap. Induction heating is used to heat the pipe ends and initiate the exothermic flux reaction followed by a forging movement that extrudes the flux and forms the solid-state weld.

The steel pipe ends are heated to the steel forging temperature by the induction heating and exothermic flux reaction. The forging temperature is specific to the steel composition but should typically be above the $A_3$ temperature for a fully austenite microstructure and below the temperature at which overheating will occur. Overheating results in a reduction in toughness and ductility from excessive grain growth and solution and reprecipitation of MnS on the austenite grain boundaries. Heating above this temperature can also lead to “burning” of the steel from melting and oxidation at the austenite grain boundaries. Burning results in significant intergranular weakness along the original austenite grain boundaries that cannot be corrected by
post weld heat treatment. Overheating damage is also undesirable but can be improved by a grain refinement PWHT stage. Reducing sulfur and manganese content in steel can reduce the susceptibility to overheating and burning, although reducing sulfur alone can reduce the temperature required for overheating because the resulting very fine MnS dispersions can rapidly dissolve and reprecipitate during forging [52]. Forging temperatures are therefore typically between 60 and 85 percent of the solidus point of the steel which is within the \( A_3 \) and \( A_4 \) temperatures for hypoeutectoid steels. The exothermic flux forge welding process was typically performed at temperatures between 1100 and 1220 °C to produce the desired forging deformation profile and ensure a good weld interface.

At forging temperature, the pipes are pushed together by a hydraulic press or similar means. Although force or pressure control is possible, position control is preferred for increased repeatability in producing the desired weld cap shape. Position based forging control improves tolerance to variations in steel chemistry and forging temperature that lead to differences in yield strength and viscous flow in the steel. Following forging, the weld may be cooled in a manner appropriate for the steel target condition. For lower strength steels, air cooling may be acceptable. For higher strength steels, quenching may be necessary. A water quenching system can be used to spray a controlled flow of water onto the weld area around the circumference of the pipe. The induction coil may then be utilized to re-austenitize the steel for grain refinement or HAZ control purposes or to temper the weld.

2.5.1 Heating Examination

Electrical current can be generated in a conductor by placing the conductor in a magnetic field. Conversely, a magnetic field can be generated by electrical current flowing through a conductor. Therefore, by using a potential to move current through a conducting coil, magnetic
fields can be generated that will induce current into a conducting workpiece. This process allows for electro-resistive heating in a work piece without the need for electrodes to contact the part. The coil used to induce the current can be water cooled for a long service life.

For an alternating current flowing through a conductor, the current flow is concentrated near the surface of the conducting part. This surface conduction is called the skin effect and is an important consideration when using high frequency heating. Maxwell’s equations can be used to derive an equation to approximate the current density, $I$, at distance $x$ from the surface of the conductor as shown in equation (2-17) where $I_0$ is the current density at the workpiece surface, and $\delta$ is the penetration depth given by equation (2-18). In the equation for the penetration depth, $\rho$ is the electrical resistivity, $\mu_0$ is the magnetic permeability of free space, $\mu_r$ is the relative magnetic permeability, and $F$ is the frequency. The penetration depth is defined as the distance from the surface towards the core where the current density is $e^{-1}$ of the value at the surface. Because power density is proportional to current density squared, the power density at the penetration depth is $e^{-2}$ of the value at the surface [53].

\[
I = I_0 \exp \left( -\frac{x}{\delta} \right) \tag{2-17}
\]

\[
\delta = \sqrt{\frac{\rho}{\pi \mu_0 \mu_r F}} \approx 503m \sqrt{\frac{\rho}{\mu_r F}} \tag{2-18}
\]

The penetration depth is therefore proportional to $F^{-1/2}$ and an increase in the frequency will produce a decrease in the penetration depth. Increasing the frequency is useful for case hardening steel, but higher penetration, and therefore lower frequencies, is preferable for uniformly heating thick walled tubulars. A high magnetic permeability also results in a reduced
penetration depth. For this reason, the penetration depth greatly increases when magnetic steel is heated above the Curie temperature which results in the magnetic permeability dropping to 1.

The total energy input required to heat the steel can be estimated from the mass of the steel being heated and temperature dependent heat capacity data. A steel pipe with a 355.6 mm (14-inch) outer diameter and 311.6 mm (12.27-inch) inner diameter giving a weight of 181 kg/m (122 lbs/ft) and a heated length of 30 mm (15 mm for each pipe end) was selected for calculation purposes. These steel dimensions result in a weight of 5.437 kg but the machined end profile removes approximately one-third of the steel from this region and therefore a weight of 3.625 kg is used for the mass of the heated region of the two pipe ends. To estimate the required heat input, polynomial form temperature dependent heat capacity data for iron was integrated over the range of 25 to 1100 °C. The total adiabatic energy required to heat the steel pipe ends was calculated by this method to be 3,080 kJ. In adiabatic conditions, 154 kW of power input over 20 seconds would be adequate to achieve this energy requirement, however in practice the power requirement will be higher due heat loss, and less than unity inductive coupling and other inefficiencies. The energy released by an exothermic flux ring with a typical composition and mass for this sized pipe is calculated to be 298 kJ.

Although the exothermic flux ring only contributes approximately ten pct. to the total adiabatic heating energy requirements, the contribution is localized at the location of the flux itself and the pipe-end faying surfaces. In adiabatic conditions for the exothermic flux ring alone, this energy is sufficient to heat the flux products to over 1800 °C thus rapidly producing a highly functional molten flux that also contributes heat to the pipe ends. A traditional flux would be heated only through contact with the pipe ends and this would result in a long heating time requirement for the flux to become fully molten and active. This long heating time requirement
for a traditional flux is exacerbated by the low thermal conductivity of pressed oxide-based powder flux compositions. A flux that took a longer time to become molten and active would delay protection of the pipe ends leading to increased oxidation during heating as well as reduced oxide dissolution activity. Additionally, any flux material that remained solid would risk becoming embedded in the pipe ends during forging. The exothermic flux therefore promotes rapid and effective end faying surface protection and cleaning to facilitate a low defect metallurgical bond while also enabling rapid forge heat application to minimize time at high temperature and provide a high temperature gradient to reduce the softened heat affected zone region widths.

The efficiency of the power transfer must be estimated to determine the power supply requirement. The efficiency of induction heating depends on the type of power supply used as well as the coil design and coupling with the part being heated. The part coupling is heavily dependent on the distance between the coil and the part. It is not unusual to have efficiencies of eighty percent or more with modern induction supplies and good coil design. More accurate heat input requirement calculations must also account for the heat transfer away from the region being heated. The heat transfer is primarily by conduction in these conditions and can be calculated from Fourier’s law by deriving a solution from the heat equation (2-19) with the system boundary conditions or using an already derived solution for compatible boundary conditions such as one presented by Carslaw and Jeager [54]. For the case with simultaneous induction heating and changing heating penetration depths with temperature and therefore time, a finite element modeling software capable of combining multiple processes such as COMSOL Multiphysics® is preferred and has been utilized for aspects of this study as shown in APPENDIX B.
\[
\frac{\partial u}{\partial t} = \alpha \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) \tag{2-19}
\]

Based on these approaches, a high-frequency induction power supply of 280kW is calculated to be adequate for heating tubulars as large as 80 kg/m to 1100 °C in twenty seconds. A 400-kW power supply is calculated to be adequate for heating steel tubulars as large as 186 kg/m to forging temperature in under 40 seconds time. These same power supplies would also be sufficient for post weld heat treatment the respective steel tubulars.

2.5.2 Forging Pressure

The flow strength of the material is the stress level required for plastic deformation. The flow strength of steel varies with temperature and strain rate with the strain rate sensitivity increasing with increasing temperature. At forging temperatures, the flow stress for plastic deformation of steel is highly strain rate dependent with increasing strain rates requiring increasing stress. Many viscoplastic models have been developed. Steinberg, Cochran, Guinan, and Lund [55] [56] developed a model that is applicable over a wide range of strain rates. This model can be used to predict the forging pressures required at various temperatures and strain rates when used with appropriate values for the material of interest and verified with experimental data.

Experimental data can also be readily be obtained for a steel type at a specific temperature and strain rate. This data can then be used to produce an estimated force required to forge weld a tubular of the specified weight per length or cross-sectional area. Experimental data was collected for API L80 grade steel casing pipe and used to produce Figure 2-10. Based on the experimental data used to generate Figure 2-10, a hydraulic press capable of supplying 200 metric tons-force should be enough to forge weld tubulars with a weight of 186 kg/m (125
pounds per foot). For steel with a density of 7.85 grams per cm³, this weight per foot is equivalent to a cross sectional area of 237 cm² (36.7 in²). These experimental results of 98 MPa forging force required at 1100 °C and strain rate of 0.8 s⁻¹ match well with the forging pressure data by Henning and presented in the ASM Handbook Forging of Carbon and Alloy Steels chapter which shows a forging pressure of approximately 95 MPa at a temperature of 1100 °C and strain rate of 0.7 s⁻¹ for both 1020 and 4340 steels [57, 58].

Figure 2-10. Estimated forging force in metric tons required to forge a low alloy steel tubular of a given weight per length at a forging temperature of 1100 °C and a strain rate of 0.8 s⁻¹.

2.5.3 Exothermic Flux

The fundamentals of exothermic flux are based on the principles of self-propagating high-temperature synthesis (SHS). Reactant powder mixtures are prepared with constituents that will undergo an exothermic chemical reaction to form the product materials. The mixture is stable at room temperature, but as the temperature increases, the reaction rate will also increase
according to the Arrhenius relation. Due to the exponential temperature dependence of the reaction rate and the heat releasing nature of the reaction, the positive feedback cycle can result in a thermal runaway reaction. The temperature at which this behavior occurs is known as the ignition temperature and is dependent on the reaction system composition, particle sizes, green density, heating rate, and rate of heat loss. If the reactant mixture is heated locally, then the local thermal runaway reaction can heat adjacent regions to also produce a thermal runaway reaction in these adjacent areas. Through this mechanism, the reaction can propagate throughout the reactant mixture.

The adiabatic combustion temperature of a reaction can be calculated from the standard enthalpies of formation, the enthalpies of transformation for any phase transitions of the products, and the temperature dependent heat capacities of the products. By the adiabatic energy balance equation shown in equation (2-20), the adiabatic combustion temperature, \( T_{ad} \), can be determined in an iterative manner \[31\]. The \( T_{ad} \) is the calculated temperature of the products with no heat lost to the environment. The standard net enthalpy of formation, \( \Delta H_{298} \), is negative for an exothermic reaction and is equal in magnitude to the sum of the product temperature dependent heat capacities, \( C_{p(prod)} \), with stoichiometric coefficients, \( n_j \), integrated from 298 K to \( T_{ad} \), and the sum of the enthalpy of transformations, \( \Delta H_{tr(prod)} \), for any phase transitions that occur in the products between 298 K and \( T_{ad} \). The temperature dependent heat capacities are commonly given in polynomial form which can be readily integrated over the temperature range of interest as shown in equation (2-21) which is used by HSC Chemistry data. The coefficients, \( A, B, C, \) and \( D \) are tabulated for various elements, molecules, and compounds. The antiderivative of this equation is given in equation (2-22) with the integration constant, \( E \), canceling out when
taking a definite integral. A versatile spreadsheet was designed to quickly compute adiabatic combustion temperatures from selected reactants and products.

\[ \Delta H_{298} + \int_{298}^{T_{ad}} n_j C_p(\text{prod}) dT + \sum_{298-T_{ad}} n_j \Delta H_{tr(\text{prod})} = 0 \]  

(2-20)

\[ C_p = A + B \times 10^{-3}T + C \times 10^5 T^{-2} + D \times 10^{-6} T^2 \]  

(2-21)

\[ \int C_p = A \times T + B \times \frac{T^2}{2 \times 10^3} - C \times \frac{10^5}{T} + D \times \frac{10^{-6} T^3}{3 \times 10^6} + E \]  

(2-22)

An example reaction showing the aluminothermic reduction of manganese (IV) oxide to manganese (II) oxide with \( x \) moles of boron oxide acting as a thermal diluent is shown in equation (2-23). Boron oxide has a low melting temperature, is a glass former, can dissolve basic oxides, and is useful as a forging flux. If \( x \) is chosen as 3, the procedure outlined above can be used to calculate an adiabatic combustion temperature of 2115 K (1842 °C) for the reaction. Choosing \( x \) as 5 results in a calculated adiabatic combustion temperature of 1629 K (1356 °C.) Similarly, other diluent species including the product species can be added to control the combustion temperature.

\[ 3MnO_2 + 2Al + xB_2O_3 \rightarrow Al_2O_3 + 3MnO + xB_2O_3 \]  

(2-23)

The reactant components and fractions are typically chosen both to achieve target combustion temperatures as well as produce slag compositions that have suitable molten temperature ranges and fluxing ability suitable for forge welding. To improve accuracy, thermodynamic equilibrium calculations should be performed at the calculated adiabatic combustion temperature to determine predicted product phases at temperature. Direct
minimization of Gibbs free energy is the most efficient method for complex systems and methods have been described by Rossi, Nichita, Teh and others [59-61]. The calculated equilibrium products can then be used to re-calculate a new adiabatic combustion temperature followed by new equilibrium product calculations in an iterative manner.

Batch calculations must also be performed to convert the molar equations into mass values for weighing and mixing. A simple stoichiometric equation like that shown in (2-23) can be readily converted to mass percent with the molecular weights of the components. Batching should consider both the desired product compositions and the desired adiabatic combustion temperature and can also account for multiple potential feedstock sources to form the desired product species.

Phase diagrams are also utilized for design of the welding flux product composition. The product phases should be liquid over the range of the welding temperatures. The vapor pressures of the product constituents should be sufficiently low at the combustion temperature to avoid significant gas generation during the reaction. Since a wide liquid range is desirable, eutectic systems are often preferred. Binary phase diagrams as well as liquidus projections for ternary and higher component phase diagrams are particularly useful in selection of product composition. Welding flux products are typically made up primarily of oxides and fluorides, but some metal additions may also be included.

Welding flux composition affects the ability of the flux to protect, deoxidize, and be extruded from the weld. The product viscosity is of particular importance to enable the flux to flow, fully cover and protect, and remove oxides from the faying surfaces while still having adequate viscosity to stay in place in the gap between the pipes without flowing away. The
thermodynamic stability of the oxides, as can be viewed from an Ellingham diagram or similar free energy diagram, is also an important factor in deoxidation of the weld. Equilibrium calculations should be performed to determine the concentrations of reactive species that may affect weld quality. Welding flux can also provide small alloying additions directly to the faying surfaces. The alloying additions can be used to assist in deoxidation or other purposes such as improving weld strength and toughness.

2.6 Summary

The exothermic flux forge welding process (EFFW) and the work performed for this dissertation build upon the work of researchers in many areas of study. The theories of welding flux development and usage as published by Jackson, Olson, Liu, Indacochea, Chai, and others are essential for the design of effective new flux compositions. The principles of self-propagating high-temperature synthesis as published by researchers including Merzhanov, Munir, Moore, Feng, Yi, Olson, and others serve as the foundation of exothermic mixture development.

Welding theory guides development of welding methods, heat treatments, and characterization of welded materials. Background information on oil country tubular goods and an introduction to the exothermic flux forge welding process is included to provide background information relevant to the weld characterization work in this study.
CHAPTER 3

RESEARCH METHODS

Research methods were selected based on applicability to the industrial exothermic flux forge welding (EFFW) process, identification of critical variables, and time and cost effectiveness. The research methods were designed to investigate a wide range of exothermic flux compositions, forming methods, and forge welding processing conditions. The methods employed are heavily based on experimental results and characterization with the broader goal of understanding the effects of variation of materials and processing conditions and the specific objective of identifying suitable process windows to achieve API qualification acceptance.

The physical experiments performed for this investigation include a number of methods that include characterization reactions, flux ring processing experiments, small-scale exothermic flux forge welding, full scale exothermic flux forge welding, post weld heat treatments, and weld testing and analysis. Analysis and evaluation techniques utilized for these experiments include differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), thermocouple and pyrometer temperature measurements, x-ray diffraction (XRD), optical and scanning electron microscopic (SEM) analysis, energy dispersive spectroscopy (EDS), phased array and x-ray radiography based non-destructive testing, Vickers and Rockwell hardness measurements, tensile testing, bend testing, Charpy V-notch impact testing, low cycle fatigue testing, and NACE Solution A corrosion testing, and videographic documentation and analysis.

3.1 Exothermic Investigations

The exothermic flux forge welding method utilizes an exothermic flux composed of reactant constituents designed to undergo an exothermic chemical reaction producing molten oxide and fluoride products once ignited. The product materials are designed to serve as forge
welding flux and protect the pipe faying surfaces from oxidation, reduce or dissolve existing surface oxides, and provide additional heat directly to the surfaces. The exothermic reaction also enables the flux to rapidly go from a solid to molten state so that the flux is fully functional in short time-scale induction heating processes. The flux can be formed in the shape of a ring in a manufacturing process prior to the exothermic flux forge welding process. The ring can be produced by uniaxial hot-pressing powdered constituents and can be profiled to compliment the beveled pipe ends. The flux ring profile can be designed to complement the rounded pipe end profile designed to facilitate extrusion of the molten flux during forging. The investigation methods relating to development and characterization of the exothermic flux are discussed.

Candidate exothermic flux reactant systems were prepared by powder metallurgy techniques including reaction system design, weighing and mixing the constituent materials in fine powder form, and pressing the mixed materials into unreacted, or ‘green’, pellets using a uniaxial die and a hydraulic press. The green pellets were then placed on top of an AISI 4130 steel sheet metal coupon held on the edge by a clamp attached to a ring stand post. The steel coupon was heated from below using an oxygen-acetylene torch to ignite the green pellet by contact with the heated plate to observe the ignitability, reaction propagation rate, product fluidity, and wetting and protection of the steel coupon. A simplified schematic of this setup is presented in Figure 3-1. The reactions were each digitally videographed and cataloged. The ignitability, or the temperature where the propagating reaction initiated, was either measured with a thermocouple, or estimated optically from digital video based on the color of the glow of the steel upon initiated on the reaction. The reaction propagation rate was determined by using two thermocouples in the pellet and recording the time of the peak temperature of each thermocouple or by the time required to fully react a pellet of known size based on digital video
of the reaction. Product fluidity was examined based on contact angle of the solidified product with the steel plate and maximum height of the solidified product after cooling. Wetting and protection of the steel plate was evaluated by the contact angle and the degree of oxidation observed on the plate after removal of the cooled flux. Other characteristics were also visually examined and noted during the live and digital video viewing of the reactions including the amount of smoke produced during the reaction (empirically classified as high, medium, or low) and the appearance of the solidified product including the amount of gas bubbles and opaqueness. The degree of crystallinity was evaluated for selected compositions using x-ray diffraction.

![Figure 3-1](image1.png)

Figure 3-1. Schematic of a reactive flux pellet on a steel sheet metal coupon heated by an oxygen-acetylene torch to ignite the pellet (left). A molten exothermic flux product immediately following reaction on a steel sheet metal coupon (right).

The primary objective of the steel coupon reactions was to provide an economical and time efficient method to provide initial characterizations of a large number of candidate reaction systems. This method allowed experimental examination of approximately 1400 reactant compositions to determine the most promising systems for forge welding experiments. Characterization of the compositional effects on the reactions and products allows for compositional modification to accommodate for the requirements specific to the forge welding
conditions for each tubular type and heating process. For example, a shorter heating time may require a more rapid flux reaction rate. Flux product viscosity may need to be increased if the flux is running off and not adequately covering the upper and lower pipes.

3.2 Exothermic Flux Ring Processing

A method is required to manufacture exothermic flux rings suitable for subsequent use and reaction during the welding of tubulars. The method must produce rings of sufficient strength to allow packaging, shipping, and handling during use. In addition, the rings must have a shelf life of one year or greater to provide adequate manufacturing, transportation, and usage scheduling allowances. Three manufacturing methods were experimentally examined in this study for suitability and can be classified as cold uniaxial pressing, cold pressing following sintering, and hot (or elevated temperature) uniaxial pressing.

**Cold (room temperature) press.** A uniaxial press die was designed consisting of an outer sleeve, an inner sleeve, and an upper and lower anvil that could slide between the sleeves. A pre-determined amount of mixed reactant powder was placed in the die on the lower anvil and the upper anvil was then placed on top of the reactant powder. A hydraulic press was used to apply forces to the anvils to compress the powder in the die. The compressed powder ring was then ejected from the die to form a compacted ring. The compacted rings produced by this method were found to be too fragile to be subsequently used for the EFFW process. Polyethylene glycol (PEG) was investigated as a binder to increase the ring strength. Quantities of one through ten weight percent PEG were investigated. The PEG was found to significantly improve the pressed flux ring form detail and strength. However, the PEG was found to interfere with the chemical reaction by causing the ring to expand and break apart prior to reaction and significantly
slowing the reaction rate. The flux ring strength was not maintained after baking out the PEG in a furnace.

**Cold press followed by sintering.** Use of a mixture component with a sintering temperature where the chemical reaction rate is sufficiently low allows for use of a secondary sintering step after cold pressing a flux ring while preserving the chemical reactivity. Boron oxide (B$_2$O$_3$) is suitable as a forge welding flux component and its low melting temperature of 450°C in anhydrous form is suitable for sintering. Boron oxide reacts with moisture to form metaborates and boric acid with an even lower melting temperature, however excessive water quantities can interfere with the reactivity and result in undesirable vapor generation and potential hydrogen embrittlement concerns in the weld.

**Hot (elevated temperature) press.** Experiments were performed using dies heated to temperatures between 120 to 320 °C to uniaxially press pellets and rings from exothermically reactive flux mixtures. The pressing temperatures were evaluated for their effects on pellet relative density, defects, die release, and susceptibility to environmental moisture. A fourteen inch diameter uniaxial ring press system with the die fitted with an inner and outer band heater is shown in Figure 3-2. Thermocouples were placed at two locations within the die for programmable logic controller temperature control. The hot press method was found to be suitable for producing exothermic flux rings with relative densities of approximately ninety pct. of the theoretical maximum density of the components with good strength and environmental stability.
3.3 Exothermic Flux Forge Welding Investigations

Exothermic flux forge welding (EFFW) investigations were conducted to determine the effects of process variables including exothermic flux composition, induction heating, pipe end profiles, and post weld heat treatment on the bond quality, heat affected zone microstructure, and properties. The exothermic flux forge welding method uses two tube lengths with each having one end machined to a rounded profile designed to deform to a low angle convex weld cap when forge welded together. The pipes are positioned end-to-end with an offset gap between the pipe ends. An exothermic flux ring is placed within the offset between the pipe ends. The exothermic flux ring can be produced by uniaxial hot-pressing powdered constituents and can be profiled to compliment the beveled pipe ends. The flux ring was composed of reactant constituents designed to undergo an exothermic chemical reaction producing molten oxide and fluoride products once ignited. The product materials are designed to serve as forge welding flux and protect the pipe
faying surfaces from oxidation, reduce or dissolve existing surface oxides, and provide additional heat directly to the surfaces. The exothermic reaction also enables the flux to rapidly go from a solid to molten state so that the flux is fully functional in short time-scale induction heating processes. The forge welding process included application of induction heating to heat the profiled pipe ends and initiate the exothermic chemical reaction to produce the molten flux. A forging movement is then applied with the flux being extruded by the rounded end contact and deformation while the pipe ends form a solid-state bond through diffusion and plastic flow to produce the weld.

3.3.1 Small-scale exothermic flux forge welding systems

A small-scale forge welding system was designed for proof-of-concept and development use for steel tubes with an outer diameter of up to 57 mm (2.25 inches.) The system utilized a hydraulic cylinder on the bottom and a stationary anvil on the top. The tubes were held in place end-to-end by an alignment system with locking bolts that adequately resisted gravitational and inadvertent movement of the pipes but allowed for sliding under force applied by the hydraulic cylinder with the alignment assembly shown in Figure 3-3. An induction coil was positioned to provide heating directly to the pipe ends and attached to a current controlled Sinac model induction power supply manufactured by EFD Induction. The system utilized a chamber that allowed for atmospheric control if desired and was fitted with a water quenching system. A prefabricated green exothermic flux ring was positioned between the ends of the two tubes to be welded. The ring had a complimentary profile to the pipe end profiles so that the placement and contact with the pipe ends would be consistent for each forge weld experiment. The small-scale EFFW system assembly is shown in Figure 3-3 with the upper anvil not yet in place. The systems allowed for the use of thermocouples to monitor and record temperatures around the
tube ends to evaluate heating uniformity, thermal gradients, and peak temperatures. The system was also fitted with a water quench capability. A polished and etched macrograph of two exothermic flux forge welded steel wall cross-sections from a weld produced in this system is shown in the image on the right of this same figure revealing the heat affected zone (HAZ) following an austenization, quench, and temper heat treatment.

![Figure 3-3. Chambered small-scale exothermic flux forge welding machine for initial development work (left). The exothermic flux ring is visible between the pipe ends. The pipes and alignment brackets are fixed on a lower hydraulic cylinder anvil while the upper anvil is not yet in place. The induction heating coil and thermocouple wires are also visible. Macrograph showing polished and etched cross-sections showing the heat affected zone on a post-weld heat treated steel specimen (right).](image)

The small-scale system was designed to allow proof of concept demonstration and affordable development work for the exothermic flux forge welding process. In particular, the small-scale system was utilized for examination of the following variables: flux ring composition, flux ring manufacturing method, flux ring mass and height, tube end profiles, induction heating rate, induction heating peak temperature, forging distance, steel composition and grade, post weld quenching and heat treatments.

A system was designed to exothermic flux forge weld sets of two four-foot lengths of coiled tubing to allow for low cycle fatigue testing of eight-foot long welded tubing. The system
was designed to allow for welding in both vertical and horizontal configurations and is shown in Figure 3-4 in the horizontal configuration. The system is designed for open air welds and is equipped with a water quench system.

![Figure 3-4](image)

Figure 3-4. Coiled tubing exothermic flux forge welding development machine in horizontal weld configuration. The machine is equipped with two hydraulic cylinders, an induction coil, and a water quench system.

In addition to allowing welding of eight-foot segments for low cycle fatigue testing, this system replaced the chambered small-scale EFFW machine as the small-scale development platform for testing new exothermic flux compositions and developing welding and post weld heat treatment processes for different grades and sizes of coiled tubing. In the horizontal configuration, the molten flux must be viscous enough to stay in the gap between pipes while also being fluid enough to allow flow and wetting for protection of the tube ends. Flux systems were designed with increased network forming components and reduced network modifiers for the horizontal welding configuration. The small diameter tubing is particularly sensitive to alignment, end bevel design, and forging conditions due to the low wall thickness and high rate of curvature of the tubes resulting in an outward translation of the forging force at the weld.
3.3.2 Full-scale exothermic flux forge welding

Following successful proof-of-concept development of the exothermic flux forge welding method on the chambered small-scale EFFW machine, a machine suitable for full-scale testing was constructed. This machine was initially designed for 9-5/8-inch casing diameters and later modified for welding of 14-inch diameter casing. A separate machine was also constructed for welding of 5-1/2-inch diameter casing.

9-5/8-inch diameter weld development. The full-scale EFFW machine pictured in Figure 3-5 on the left is fitted with a clamshell welding chamber and uses slips for gripping full forty-foot length pipes. A platform frame is also shown around the welding machine taking the place of a rig platform to provide operational access to the machine for development work. A close-up of a weld in progress is shown in Figure 3-5 on the right with the reacted molten flux shown radiating in the visible spectrum. An induction heating coil can be seen surrounding this area. This machine was used for development work on several steel tubular grades including J55, K55, L80, P110, and VM50.

14-inch diameter weld development. The full-scale EFFW machine shown in Figure 3-5 (left) was modified with a larger pipe gripping slips, and a larger weld chamber, induction coil, and quench system to allow for use with 14-inch diameter casing. Development work was carried out on Q125 grade steel pipe with a 14-inch outer diameter and a specified weight of 115 lbs/ft (22mm measured wall thickness.) Because of the high 125 ksi yield strength requirement for this grade as well as ductility and toughness requirements, Q125 grade steel casing is designated as unweldable by traditional means. This grade is of high commercial interest for offshore deep-water well casing where welding would offer significant benefits.
5.5-inch weld development. A machine was constructed for welding 5-1/2-inch diameter casing and designed to be suitable for field use on land-based oil platforms and is shown in Figure 3-6 (left). Development work was performed on 5-1/2-inch diameter P110 grade steel casing requiring yield strength of 110 ksi as well as minimum ductility and impact specifications. Welded 5-1/2-inch diameter P110 steel casing is shown after in-system post weld heat treatment in Figure 3-6 (right).

3.3.3 Post weld heat treatment development

In order to achieve the combination of strength and ductility required to meet the specifications for various grades of steel, the weld and heat affected zone (HAZ) microstructures must be controlled. Lower strength steels may only require an acceptable cooling rate or post weld a normalization step to produce a fine-grained ferrite and pearlite microstructure. Higher strength casing steels may require a tempered martensite microstructure. The full HAZ
microstructures must be considered since localized heating will result in microstructure transitions based on the local peak temperatures and cooling rates. The effects of temperature, heating and cooling rates, and thermal history have been evaluated for several steel types and heat treatment processes.

Figure 3-6. Exothermic flux forge welding machine for 5-1/2-inch diameter steel pipe casing (left). Welded and post weld heat treated 5-1/2-inch diameter P110 steel casing showing a smooth weld cap and some residual flux residue below the weld (right).

3.3.4 Weld testing and analysis

Extensive weld testing and analysis was performed to evaluate the relationship between process variables, microstructure, and properties. Non-destructive testing (NDT) was performed by radiography and ultrasonic phased array to identify weld plane defects. Cross-sectional specimens were polished, etched, and macrographed to examine weld cap shape, bond interface, and the heat affected zone (HAZ). The cross-sectional specimens were micrographed using an optical microscope to evaluate the bond interface and the HAZ microstructure. Selected
specimens were also examined using scanning electron microscopy. Vickers hardness measurements were performed across the HAZ on the cross-sectional specimens.

Welded steel tensile specimens were tested to evaluate the strength and elongation across the weld plane based on API 1104 and ASME IX methods. Root, face, and side bend specimens were evaluated according to API 1104 and ASME IX to evaluate ductility and examine for visible cracking. Charpy V-notch impact testing was performed according to ASME IX and ASTM E23 at temperatures ranging from -40 to 25 °C. Nick-break specimens were prepared, fractured by pulling in tensile, and evaluated according to API 1104 specifications. Examples of typical test specimen photographs are shown in Figure 3-7 for a 5-1/2-inch diameter P110 steel casing weld.

Figure 3-7. Typical weld testing and analysis steel specimens shown for 5-1/2-inch diameter casing including: (a) transverse-weld tensile specimens, (b) Charpy V-notch specimens, (c) bend test specimens, (d) nick-break specimens, (e) cross-sectional macrographs with outer-wall and inner-wall hardness indents visible, (f) micrograph at 200x showing tempered martensite microstructure at the weld plane.
3.4 Summary

The investigations presented used a wide array of research methods for development of
exothermic flux compositions and processing into forms suitable for exothermic flux forge
welding application. The exothermic flux forge welding investigations comprised welding of
steel tubulars in custom built exothermic flux forge welding machines. Welding process
variables and post weld heat treatment variables were investigated for various grades of steel
tubulars. Four EFFW machines were used for the welding and post weld heat treatment research.
In addition to the investigated processing methods, a wide array of characterization methods
were used for this work. Characterization methods included differential scanning calorimetry
(DSC) and thermal gravimetric analysis (TGA), thermocouple and pyrometer temperature
measurements of reactions, x-ray diffraction (XRD), optical and scanning electron microscopic
(SEM) analysis, energy dispersive spectroscopy (EDS), phased array and x-ray radiography
based non-destructive testing, Vickers and Rockwell hardness measurements, tensile testing,
bend testing, Charpy V-notch impact testing, low cycle fatigue testing, and NACE Solution A
corrosion testing, and videographic documentation and analysis.
CHAPTER 4

SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS INVESTIGATIONS
TOWARDS AN EXOTHERMIC FORGE WELDING FLUX

4.1 Abstract

The effects of reactant particulate size for oxide and reductant components including passivation layer thickness for the aluminum reductant or fuel in aluminothermic reactions was investigated and discussed. With decreasing aluminum size, the passivation shell makes up a higher fraction of the particulate and should be accounted for in reaction stoichiometry. Using thermocouple based investigations of pressed reactant pellets and differential scanning calorimetry, the nano scale reactants were found to lower the temperature of ignition of the propagating exothermic reaction with the size of the aluminum having a more significant effect than the size of the oxide reactant component. This effect remained significant in reaction systems designed to produce constant volume fractions of product phases despite a decrease in the calculated adiabatic combustion temperature for systems using nano aluminum due to the increased oxide shell fraction. Adding additional (hyper-stoichiometric) aluminum was also found to significantly increase the reaction propagation rate when locally ignited and the primary exotherm magnitude when heated using differential scanning calorimetry. The reaction systems for the hyper-stoichiometric aluminum investigations were designed to products with constant volume fractions of metal and slag but due to the lower volumetric heat capacity of aluminum relative to the copper it replaced also resulted in slightly increased adiabatic combustion temperature with increasing aluminum content. The effect of heating rate on enthalpy flow was
also investigated using differential scanning calorimetry and found to have a significant effect on
the initiation of a runaway exothermic reaction.

4.2 Introduction

Self-propagating high-temperature synthesis (SHS) is a form of reaction synthesis where, upon ignition, reactant materials undergo a local exothermic reaction where the released heat is sufficient to ignite adjacent material resulting in a self-sustaining propagating reaction front. If the reactant material is simultaneously heated to the ignition temperature, the process can also proceed in rapid near simultaneous reaction sometimes referred to as a thermal explosion. The SHS method can be used to produce a wide range of products including carbides, borides, intermetallics, metals, oxides, and composites. Exothermic oxidation-reduction reactions such as aluminothermic, calciothermic, magnesiothermic, and silicothermic reactions use reactants comprised of an oxide and a fuel such as aluminum, calcium, magnesium, and silicon to oxidize the fuel while reducing the oxide and releasing energy. These reactions are commonly termed thermite reactions with aluminothermic reduction of iron oxide being the most widely known reaction of this type. The energy released by such reactions can be determined through use of Ellingham diagrams or tables listing enthalpies of formation and the reaction temperatures can be calculated with the addition of heat capacity information.

Thermite type reactions have been used for pyrometallurgical applications and for generating molten metals and alloys for welding and casting applications with the oxide byproduct serving as a slag to help protect the molten metal from oxidation. For some applications such as for an exothermic flux, the oxide product is the phase of primary interest with the metal phase a potentially undesirable byproduct. This work discusses findings related to thermite type reactions towards development of an exothermic flux. For an exothermic flux, the
ignition temperature and reaction rate are critical aspects and the effects of heating rate and reactant particle size, concentrations, and exothermicity were investigated along with localized and near simultaneous heating methods.

### 4.3 Materials and Methods

The studies presented included reactant system investigations comprising metals and metal oxide powders with nano and micron scale average particle sizes. The materials used for these investigations are summarized in Table 4-1.

Table 4-1. Summary of materials used in these investigations.

<table>
<thead>
<tr>
<th>Material Name</th>
<th>Supplier</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micron aluminum</td>
<td>Cerac/Materion (A-2002)</td>
<td>&gt;99% purity, &lt;5 µm average particle size</td>
</tr>
<tr>
<td>80 nm aluminum</td>
<td>NanoAmor</td>
<td>See results and discussion</td>
</tr>
<tr>
<td>18 nm aluminum</td>
<td>NanoAmor</td>
<td>See results and discussion</td>
</tr>
<tr>
<td>Micron copper (II) oxide</td>
<td>Alfa Aesar (12299)</td>
<td>&gt;97% purity, -325 mesh</td>
</tr>
<tr>
<td>Nano copper (II) oxide</td>
<td>NanoAmor</td>
<td>See results and discussion</td>
</tr>
<tr>
<td>Micron copper</td>
<td>Cerac/Materion (C-1133)</td>
<td>&gt;99.5% purity, -325 mesh, 10 µm typical.</td>
</tr>
<tr>
<td>Nano copper</td>
<td>NanoAmor</td>
<td>See results and discussion</td>
</tr>
</tbody>
</table>

Investigative methods included scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), Gleeble 1500 heating and reaction thermocouple measurements, uniaxially pressed pellet locally ignited reaction thermocouple measurements for combustion temperature and propagation velocity measurements, and differential scanning calorimetry. Additional method information is presented in the results and discussions section. The mixtures evaluated in these studies were dry mixed in a benchtop Resodyn ResonantAcoustic (RAM) mixer. Ball milling was not used on the mixtures due to risk of ignition during milling and liquid mixing was not used due to contamination and drying concerns.
4.4 Results and Discussions

When exposed to air, aluminum will rapidly form an oxide layer on the surface. Aluminum oxidization in air is a highly exothermic process which will increase the temperature of the material resulting in an increased oxidation rate. The oxidation rate is proportional to the surface area while the temperature increase is inversely proportional to the heat capacity and therefore volume of the particle. If, for a given powder size, passivation layer thickness, and environmental conditions, the oxidation rate is high enough that the temperature increase is sufficient to overcome the increased diffusion requirements due to the increasing passivation layer thickness, then the powder will undergo a runaway reaction and burn with the air. This autoignition hazard necessitates that sufficiently small sized powder is passivated to a minimum thickness for the powder to be handled in air.

For isothermal oxidation, the oxide layer grows logarithmically over time with the rate of growth dependent on environmental conditions. It has been shown that a two nanometer thick oxide layer will form within hours with three to five nanometers expected on time frames of a year [62]. For nano-scale aluminum powders, this passivation layer can make up a significant volume fraction of the power and therefore must be accounted for in the batching ratios and thermodynamic calculations. The volume percent of oxide for various shell thicknesses in a spherical powder is shown as a function of particle diameter in Figure 4-1. From this figure, it can be seen that for an oxide shell thickness of 2 nm, an 18 nm spherical particle would be only 47 volume pct. metallic aluminum while an 80 nm spherical particle would be comprised of 86 volume pct. metallic aluminum with this same 2 nm oxide shell thickness. It should be noted that batching of powder is typically performed on a mass or weight basis and since alumina has a higher density than metallic aluminum, the mass percent of the metallic aluminum content is
even lower than the volume percent. Using a density of 2.7 g/cm³ for aluminum and 3.95 g/cm³ for alumina for calculations results in 38 and 80 mass pct. of metallic aluminum respectively for the 18 and 80 nm aluminum powder.

Figure 4-1. The calculated relationship between oxide surface layer thickness, particle diameter, and metallic aluminum content for spherical particles. The dashed grey lines represent the mean particle size powders investigated in this study.

Reactant powders used in this study were investigated for size, morphology, and composition using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) techniques. Characterization of the 80 nm aluminum by TEM, shown in Figure 4-2, indicated that a distribution of particle sizes was present with an average particle size near 80 nm diameter as described by the supplier. The nano aluminum was observed to form agglomerates believed to be due to electrostatic and other surface interactions such as hydrogen bonding. If not fully broken up during the mixture formation process, the agglomerates would be expected to kinetically reduce reaction rates by increasing diffusion requirements during the reaction compared to a homogeneously distributed
mixture. The micron scale aluminum also used in these studies is shown in an SEM image in Figure 4-3. The micron scale aluminum showed smooth and relatively spherical particles with sizes ranging from approximately 1 to 10 microns.

Figure 4-2. Transmission electron microscope (TEM) images of nano aluminum with an 80 nm average particle size. The nano aluminum particles agglomerate due to electrostatic and other surface interactions including hydrogen bonding.

Figure 4-3. Scanning electron microscope (SEM) backscatter image of micro sized aluminum used in these studies.
Energy dispersive spectroscopy was performed on 18 and 80 nm average diameter aluminum using EDAX equipment in the SEM system with the spectrums shown in Figure 4-4 up to 5 kilo-electron volts. The characteristic x-ray emissions indicated high aluminum content for both materials, however oxygen peaks were also indicated for both specimens with the 18 nm sized material showing a significantly higher magnitude oxygen peak in line with calculated predictions. The presented spectrums also showed a small peak for silicon in the 18 nm material and a small magnesium peak in the 80 nm material but these other elemental peaks varied with analysis location and no significant overall compositional differences were identified beyond the oxygen content.

![Spectra](image)

Figure 4-4. Energy dispersive spectroscopy is shown up to 5 kilo-electron volts for 18 nm (left) and 80 nm (right) average particle size aluminum nano powders. The smaller particle sized aluminum shows a significantly larger oxygen peak in line with calculated expectations due to the higher surface area to volume ratio.

Nano and micron scale copper (II) oxides were evaluated by scanning electron microscopy with images of each shown in Figure 4-5. The nano CuO agglomerated into larger units and if these agglomerates were not broken up during the mixture preparation processes,
they would likely reduce reaction kinetics compared to well distributed nano scale copper oxide.

The micron copper oxide appeared to have particles approximately one to 15 microns with particles appearing as fused clusters of smaller particles.

Figure 4-5. Scanning electron microscope (SEM) backscatter image of nano copper (II) oxide agglomerates on left shown at the same scale as micron copper oxide on right.

Images and spectroscopy for the copper metal was collected by SEM and EDS and is shown in Figure 4-6. The morphologies of the copper metal used in these studies is often referred to as ‘sponge’ and the images show particles of interconnected elongated and curving structures. Some of the observed structures had shells of solid copper material while other material was entirely composed of the curled and elongated structures. The EDS results indicated strong copper peaks with small peaks for carbon and oxygen with the carbon believed to be due to the carbon-based backing tape used for the analysis. The oxygen peak was minimal and indicated that the majority of the material consisted of unoxidized copper metal. The spong-like morphology may reduce density of the bulk and pressed material compared to more spherical fully dense particles.
Reactions using stoichiometric ratios of copper oxide and aluminum with excess copper metal were performed using mixed powder constituents pressed into a pellet and placed inside a graphite tube with a one-half-inch inner diameter and one-inch outer diameter. The reactions were all of the form shown in equation (4-1). A thermocouple was placed in a hole drilled from the outer wall to a depth of 1 mm away from the inner die surface centered on the location of the pressed mixture. Graphite rods with a diameter of one-half-inch were placed in contact with the pellet on each side and in contact with electrodes in a Gleeble 1500 system. The assembly was then heated by resistive heating from the direct current across the assembly at a rate of 250 °C with the temperature recorded by the thermocouple in the die and used for heating control. Three mixture systems were investigated in this manner with the heating continuing until a spike was observed in the thermocouple reading indicating the mixture had reacted.
Two of the reacted mixtures contained nano copper oxide with 80 nm aluminum along with micron scale copper diluent while the third mixture contained micron scale for all three constituents. One of the nano reactant mixtures was designed to produce seventy volume percent copper metal and 30 volume percent alumina while the other nano scale reactant system had increased amounts of copper diluent to produce a product with 80 volume percent copper metal by varying the diluent copper \( y \) in equation (4-1). These mixtures using nano scale aluminum metal considered the passivated shell and used a mass fraction of 79 pct. aluminum metal and 21 pct. alumina for calculations. The micron scale reactant mixture was designed to produce a product ratio of 75 volume percent copper metal and 25 volume percent alumina. The thermocouple plots for these systems are shown in Figure 4-7 showing the ignition temperature and peak measured temperature for each mixture.

Each of the pressed mixtures containing the nano scale reactants ignited at a lower temperature than the micron scale reactants. The mixture containing less copper diluent and therefore having a higher adiabatic combustion temperature igniting at 249 °C and having a peak measured temperature of 1184 °C while the mixture containing more copper diluent ignited at 292 °C and had a peak recorded temperature of 784 °C. The micron scale reactant system had an intermediate amount of copper diluent and ignited at 392 °C and had a peak measured temperature of 1035 °C and it was also observed that this system had a slower cooling rate following the reaction than the other two systems. The slower cooling rate is believed to be primarily due to slower reaction rate leading to less material lost outside the tube during the reaction. This system also did not contain a significant amount of alumina in the reactants due to

\[
2Al + 3CuO + yCu \rightarrow Al_2O_3 + (3 + y)Cu + Q
\]  

(4-1)
the larger aluminum particle size which resulted in a calculated enthalpy release similar to the 70 volume pct. nano reactant system even with the extra copper diluent in the micron reactant system.

Figure 4-7. Reaction system thermocouple measurements for three reaction systems inside a graphite cylinder using a Gleeble 1500 to provide a constant 250 °C per minute heating rate. The 70Cu-30Al2O3 (vol%) product using nano aluminum and nano copper oxide shown by the blue peak had the lowest ignition temperature and the highest measured combustion temperature. The 80Cu-20Al2O3 (vol%) system, shown in red, using all nano reactants had the next lowest ignition temperature but had the lowest measured combustion temperature. This system had the most copper diluent added and therefore had the lowest calculated adiabatic combustion temperature. The 75Cu-25Al2O3 (vol%) shown in black, used all micron scale constituents and had the highest ignition temperature but the second highest combustion temperature. The combustion temperature rank order is in line with adiabatic combustion temperature calculations, but all values are lower than for adiabatic conditions due to the significant heat absorption by the graphite mold.

It must be noted that all of the measured peak temperatures are much less than the calculated adiabatic combustion temperatures for the mixtures because of the significant heat
capacity of the graphite tube and rods in contact with the pellet and because the thermocouple was located in the graphite tube wall and not directly in contact with the pellet. These results demonstrate that the reactant particle size has a significant effect on the ignition temperature and may also have a significant effect on the combustion temperature in non-adiabatic situations due to the increased reaction rate. The reactant concentration and exothermicity is also shown to affect the ignition temperature, however the less exothermic nano reactant containing system still had a significantly lower ignition temperature than the more exothermic micron scale reactant system.

Reaction velocity is expected to be affected by reactant activity and therefore the effects of increasing aluminum concentration on reaction velocity were investigated. Each reactant mixture used stoichiometric ratios of 80 nm aluminum and nano copper (II) oxide together with micro copper diluent and excess micro aluminum powders where indicated and was designed to produce constant volume fractions of metal and slag (82.5 vol. pct. metal) based on the reaction shown in equation (4-2). The metal product compositions were varied from zero to thirty weight percent aluminum with the balance copper by varying x and y and with \( n \) and \( \mu \) indicating nano and micro scale constituents.

\[
2nAl + 3nCuO + x\mu Al + y\mu Cu \rightarrow Al_2O_3 + (3 + y)Cu + xAl + Q \quad (4-2)
\]

The reactants were pressed into one-half-inch diameter cylinders and ignited by a resistively heated tungsten filament at the bottom of the pellet velocity was obtained from thermocouples placed in the side of the pellet with one near the bottom and one near the top. The results are plotted in Figure 4-8 and show that the reaction rate increased by more than a factor of twenty from stoichiometric aluminum content to 30 pct. excess measured on a product metals
mass basis. The increased reaction rate is believed to be due to increased aluminum reactant activity due to the increased content and also facilitated by the low melting point of aluminum resulting in increased overall reactant mobility. The calculated adiabatic combustion temperature also increased slightly with aluminum content due to the reduced volumetric heat capacity of aluminum compared to copper. The increase in reaction rate was less with higher aluminum contents. The reaction rate increased by more than a factor of five with only 5 weight pct. on a metals basis of hyper-stoichiometric aluminum.

Figure 4-8. Relationship between reaction propagation velocity and hyper-stoichiometric reductant (aluminum) content for a reaction system producing a constant 82.5 percent volume fraction of metal (copper or copper-aluminum) with the balance alumina. The reaction velocity increases with increasing aluminum content through the range investigated but effect was reduced at higher contents. Reaction rate increased by more than a factor of twenty from stoichiometric aluminum to 30% hyper-stoichiometric content.
Differential scanning calorimetry (DSC) was utilized to examine the exothermic and endothermic behaviors under argon gas at a heating rate of 40 K per minute from 25 to 1400 °C. The enthalpy flow results of four mixtures each producing fifty volume percent copper metal with the remainder alumina are shown in Figure 4-9. The two mixtures shown in red used 80 nm diameter aluminum combined with either nano (dashed line) or micro (solid line) scale copper (II) oxide (CuO). These nano aluminum containing mixtures accounted for the alumina shell of approximately 21 weight percent of the aluminum by using additional copper diluent to maintain the same product composition as the micro scale aluminum systems shown in black. Therefore, the nano aluminum systems had a reduced calculated exothermic energy release of -3.81 compared to -4.25 kJ/g for the micro aluminum systems. Despite this, the nano aluminum systems both showed deep exotherms with onset temperatures of around 550 °C while the micro aluminum systems only showed small exotherms with onsets just before the melting point of aluminum. The aluminum melting endotherms are clearly visible in both micro aluminum mixtures but not in the nano aluminum mixtures indicating that the aluminum metal has been consumed in the deep exothermic reaction.

The nano aluminum systems show strong endotherms around 1080 °C indicating the melting of copper metal. The nano aluminum mixture using nano copper oxide shows two additional endotherms with one just over 1200 and the other just over 1300 °C. These endotherms correspond with the melting points of copper (I) oxide (Cu2O) and copper (II) oxide (CuO) indicating that the copper oxide was not fully consumed in the deep endothermic reaction, likely due to a stoichiometric deficiency of aluminum. The fully micro sized reactants had an exotherm onset around 900 °C with a small endothermic indication around 950 °C before another exothermic onset at 975 °C. These exotherms are likely due to sufficient aluminum transport.
outside of the oxide shell to react with the copper oxide in this temperature range. The copper melting endotherm is visible but less pronounced than in the nano aluminum mixtures.

Figure 4-9. Differential scanning calorimetry information for four mixture systems all using a heating rate of forty degrees Kelvin per minute. The mixture systems were all composed of aluminum and copper oxide reactants with copper diluent designed to produce the same product compositions. The reactant constituent ratios were adjusted for the systems using nano-aluminum to accommodate the increased fraction of aluminum oxide and maintain equivalent product compositions. The two systems using nano-aluminum powder (red) had large exotherms with onset temperatures of around 550 °C with the system also using nano-copper oxide (dashed) showing a deeper exotherm and slightly earlier onset. The two systems using micron-aluminum (black) did not show the same large initial exotherms and exhibited exotherms at higher temperatures that were not seen in the systems comprised of nano-aluminum. The calculated adiabatic combustion temperature for all systems was the enthalpy plateau at boiling point of copper but the micron-aluminum systems were calculated to release -4.25 kJ/g while the nano-aluminum systems were calculated to release -3.81 kJ/g due to the increased fraction of aluminum oxide.
Also shown in Figure 4-9, a significant exotherm onsets around 1200 °C just prior to the melting point of the copper (I) oxide with this exotherm followed by an endotherm and another smaller exotherm. These final features are believed to be related to additional copper oxide melting and subsequently reacting with the remaining aluminum. The system using micro aluminum with nano copper oxide had an exotherm onset just before 1000 °C and continue until the copper melting endotherm. Subsequent endotherms associated with copper oxide melting are not clearly visible for this mixture indicating that the copper oxide was consumed by the reactions.

The effect of heating rate was investigated using rates of 5 and 40 K per minute for the same micron sized aluminum and micron sized copper oxide mixture producing 50 volume percent copper with the remainder alumina as was shown in the previous figure. The effects of heating rate on this mixture is shown in Figure 4-10. With the slower 5 K per minute heating rate, the small early exotherm that was present just before the melting point of aluminum is no longer apparent. Less pronounced exotherms onset around 900 and 1000 °C with the first of these also corresponding to a major exotherm on the 40 K per minute plot. The endotherm near the melting point of copper appears shifted to slightly over 1100 °C with no sharp subsequent endotherms corresponding to copper oxide melting for the slower heating rate. The significant differences shown for the same mixture with different heating rates demonstrates the importance of heating rate for ignition and for enabling runaway reaction conditions that can allow the reaction to rapidly proceed to completion. It is noted that these conditions are specific to the investigated system and factors including reactant amount, density, surface area in contact with the environment, and other variables will all effect this behavior.
Figure 4-10. Differential scanning calorimetry information for one mixture system using heating rates of five- and forty-Kelvin per minute. The mixture system was composed of stoichiometric ratios of micron sized aluminum and copper oxide reactants with copper diluent. The 5 K per minute heating rate showed small exotherm onsets around 840 and 980 °C. The 40 K per minute heating rate showed much larger exotherms with onsets of approximately 820 and 1200 °C indicating the importance of heating rate for initiation of thermal runaway reactions.

The effects of extra (hyper-stoichiometric) aluminum content was investigated by DSC and shown in Figure 4-11 for a reaction system producing 82.5 volume percent metal with the remainder alumina. This same reaction system was also characterized for pellet reaction velocity with the propagation velocity results previously shown in Figure 4-8. The mixtures system examines the effects of stoichiometric aluminum to copper oxide ratios of up to 30 percent excess aluminum on a product metals basis and is shown in Figure 4-11. All mixtures used stoichiometric ratios of 80 nm aluminum and nano copper oxide with micro sized excess aluminum as indicated and micro copper diluent apart from 825CuAl15B represented by the green dashed line. This mixture used 560 nm average particle sized aluminum for the excess
aluminum and also used nano copper diluent. This mixture exhibited the strongest primary exotherm and this is believed to be due in part to oxidation of the nano copper leading to additional exothermic reaction with the excess aluminum. The other mixtures all exhibited a primary exotherm depth corresponding to the amount of excess aluminum they contained with the mixture with no excess aluminum having the smallest exotherm and the mixture having the highest extra aluminum at 30 weight percent on a product metals basis having the largest exotherm. Mixtures with excess aluminum also showed secondary exotherms in the range from 800 to 1000 °C believed to be related to copper aluminum intermetallic compound formation.

Figure 4-11. Differential scanning calorimetry information for seven mixture systems using heating rates of 40 Kelvin per minute for all runs. The primary exotherm increased with increasing aluminum content and most significantly with reduced reactant size with the only system using sub-micron scale reactants showing the largest primary exotherm. Secondary exotherms are observed for the systems containing excess aluminum and are believed to be related to Cu-Al intermetallic formation.
4.5 Conclusions

The effects of reactant particulate size for oxide and reductant components including passivation layer thickness for the aluminum reductant or fuel in aluminothermic reactions was investigated and discussed. With decreasing aluminum size, the passivation shell makes up a higher fraction of the particulate and should be accounted for in reaction stoichiometry. Using thermocouple based investigations of pressed reactant pellets and differential scanning calorimetry, the nano scale reactants were found to lower the temperature of ignition of the propagating exothermic reaction with the size of the aluminum having a more significant effect than the size of the oxide reactant component. This effect remained significant in reaction systems designed to produce constant volume fractions of product phases despite a decrease in the calculated adiabatic combustion temperature for systems using nano aluminum due to the increased oxide shell fraction. Adding additional (hyper-stoichiometric) aluminum was also found to significantly increase the reaction propagation rate when locally ignited and the primary exotherm magnitude when heated using differential scanning calorimetry. The reaction systems for the hyper-stoichiometric aluminum investigations were designed to products with constant volume fractions of metal and slag but due to the lower volumetric heat capacity of aluminum relative to the copper it replaced also resulted in slightly increased adiabatic combustion temperature with increasing aluminum content. The effect of heating rate on enthalpy flow was also investigated using differential scanning calorimetry and found to have a significant influence on initiation of a runaway exothermic reaction. These investigations were useful first steps towards the development of fully oxide product systems for use as exothermic forge welding fluxes.
CHAPTER 5
INVESTIGATION OF EXOTHERMIC FLUX FORGE WELDING AND POST WELD HEAT TREATMENT ON THE MICROSTRUCTURE AND PROPERTIES OF HSLA STEEL

5.1 Abstract

High strength low alloy (HSLA) coiled tubing was butt welded by manual gas tungsten arc welding (GTAW) and a novel automated exothermic flux forge welding (EFFW) process. All welded specimens demonstrated good performance across most of the investigated testing. Tensile, bend, and Charpy results were comparable across both welding methods and met standard acceptance criteria with the exception of low yield strength for the GTAW specimens. The salt spray corrosion testing also showed expected corrosion levels and acceptable uniformity for all specimens. Submersion in deaerated 5 weight percent sodium chloride and 0.5 wt. pct. acetic acid at 75 °C (NACE Solution A) showed the GTAW specimens developed a step interface and some signs of galvanic or crevice corrosion at the toe interfaces of the more noble weld metal and the parent metal. The step interface developed because the parent steel corroded more than the more noble filler metal and the angled interface could act as a stress concentrator and potential initiation site for stress corrosion cracking or fatigue cracking. The EFFW specimens demonstrated uniform corrosion across the specimen with minimal difference between the weld region and the parent. Fatigue performance is generally the most important consideration for butt welded coiled tubing and was investigated for cut specimens and full tubing. The GTAW specimens had mean reversals to failure of 27 pct. of the parent material in the ASTM E606 strain life testing and are estimated at 30 pct. of the parent life for pressurized full tubes based on industry experience. The EFFW specimens demonstrated 68 pct. of the parent strain life fatigue in the ASTM E606 testing and 75 pct. of parent life in the 4 ksi pressurized full
tube bend cycle testing and 74 pct. of the parent in the 7 ksi pressurized testing. These results, including the significantly higher fatigue life, demonstrate the potential of the automated EFFW process to extend service life and reduce in-service failures for butt welded coiled tubing.

5.2 Introduction

Continuous steel tubing, generally known as coiled tubing, is widely used in oil and gas operations including for well interventions, fracturing operations, circulation and pumping, drilling, and even as depleted well production tubing. As the name implies, coiled tubing is spooled around a large diameter reel with typical tube diameters from ¾ to 5-inch (19.05 to 127 mm) with lengths depending on diameter and spool size but may exceed 15,000 feet (4,500 m) for smaller diameters. Butt welding of coiled tube is commonly used to replace damaged sections or extend the length of tubing and thus the performance and economics of welded tube are important industry considerations. Manual gas tungsten arc welding (GTAW) of tubing requires highly skilled welders, is subject to human inconsistencies, and can be time-consuming. An automated process that can consistently achieve manual GTAW or better weld performance is therefore of value for the oil and gas industry and other users of coiled tubing. Tensile, bend, impact, corrosion, and fatigue performance are all important evaluation criteria for coiled tubing weld performance and are investigated in this study for high strength low alloy steel tubing welded manually by GTAW and by an automated novel exothermic flux forge welding process.

5.3 Materials and Methods

Weld performance of gas tungsten arc welding (GTAW) and a novel exothermic flux forge welding (EFFW) method was investigated for joining of high-strength low-alloy (HSLA) steel coiled tubing suitable for work string applications. Both welding methods involved end-to-end butt welding of the steel tubes. The two-inch (50.8 mm) diameter tubing used in this
investigation had an analyzed chemical composition including 0.12 wt. pct. carbon as presented in Table 5-1. The tubing was produced according to ASTM A1011M [63] from strip with a welded seam ground on the external surface. The production process included an austenitizing heating step followed by quenching to form martensite and then a tempering heat treatment. The pipe outer diameter, wall thickness, 0.2 pct. offset yield strength, ultimate tensile strength, and percent elongation at break specifications are listed in Table 5-2.

Table 5-1. Analyzed chemical composition of the high-strength low-alloy steel tubing.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>Bal.</td>
<td>0.120</td>
<td>1.470</td>
<td>0.013</td>
<td>0.0004</td>
<td>0.380</td>
<td>0.600</td>
<td>0.240</td>
<td>0.080</td>
<td>0.063</td>
<td>0.047</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5-2. Specified steel tubing physical dimensions and minimum mechanical properties.

<table>
<thead>
<tr>
<th>Diameter (mm / in.)</th>
<th>Wall (mm / in.)</th>
<th>Yield Strength (0.2% offset) (MPa / ksi)</th>
<th>Ultimate Tensile Strength (MPa / ksi)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.8 / 2.00</td>
<td>5.16 / 0.203</td>
<td>689 / 100</td>
<td>758 / 110</td>
<td>24</td>
</tr>
</tbody>
</table>

The GTAW butt welds used in this study were produced manually by certified welders according to known best practices for welding this grade of tubing. The exothermic flux forge weld (EFFW) method used in this study were produced from two tube lengths with each having one end machined to a rounded profile designed to deform to a low angle convex weld cap when forge welded together. The pipes were positioned end-to-end in a forge welding machine with an offset gap of 0.11-inch (2.8 mm) between the pipe ends. An exothermic flux ring with a profile complimentary to the pipe end profiles was placed in-between the pipe ends and the upper pipe lowered to ensure good contact and flux ring alignment. The exothermic flux ring was prefabricated by uniaxial hot-pressing of powdered constituents. The flux ring was composed of
reactant constituents designed to undergo an exothermic chemical reaction producing molten oxide and fluoride products once ignited. The product materials are designed to serve as forge welding flux and protect the pipe faying surfaces from oxidation, reduce or dissolve existing surface oxides, and provide additional heat directly to the surfaces. The exothermic reaction also enables the flux to rapidly go from a solid to molten state so that the flux is fully functional in short time-scale induction heating processes. The rounded end profile on the pipes was designed to facilitate extrusion of the molten flux during forging. The forge welding process included application of induction heating to heat the profiled pipe ends and initiate the exothermic chemical reaction to produce the molten flux. The induction heating and molten flux heated the pipe ends to approximately 1200 °C within five seconds at which time a position-controlled forging movement was applied. Following the forging step, the welded pipes were water quenched.

Three post weld heat treatments were investigated and are summarized in Table 5-3. An ex situ furnace post weld heat treatment was performed by austenitizing at 920 °C for one hour and water quenching followed by tempering at 620 °C for two hours and has been designated as HT1 throughout this study. A second ex situ heat treatment, designated as HT2, utilized induction heating and was intended to replicate the capabilities of an in-situ heat treatment. This process was used only for one group of fatigue specimens and heated the weld region to a peak temperature of 1000 °C with a total heating time of ten seconds followed by a water quench and then applied a 15 second tempering process with a peak temperature of 700 °C. An in-situ process, designated HT3, was also tested that used two 16 second peak temperature 940 °C stages each followed by a water quench, followed by a 1000 °C step and water quench. This heat treatment process then applied cycle with a heating time of 28 seconds and a peak temperature of
680 °C. The intention with the multistep process was to produce a fine-grained tempered martensite microstructure without having the softened outer heat affected zones overlap with each other or with the weld softened heat affected zone.

Testing was conducted both on full tube sections and by cutting specimens for tensile, bend, Charpy V-notch, fatigue, and metallographic / hardness from the welded tubing. Wall section tensile and bend specimens were prepared according to ASME IX and Charpy quarter-sized specimens were prepared and testing according to ASTM E23 [49, 50, 64]. Tensile testing was performed in a Zwick/Roell Z1200 frame. Charpy V-notch specimens were tested in Zwick/Roell PSW750 pendulum impact tester. Hardness specimens were prepared by sectioning across the weld region, mounting, and polishing. Hardness measurements used an automated Struers Duramin A300 Vickers 10 kgf load. Hardness scans were taken with 1 mm indent spacing with lines 1 mm from the outer wall, mid wall, and 1 mm from the inner wall. Fatigue wall sections were tested using a Schenk 40 kN machine with a 50 kN load cell and hydraulic grips using a stress ratio of R = -1, frequency of 2 Hz, and strain amplitude of 0.003. Full tube fatigue testing used a Stewart & Stevenson fatigue tester to cyclically bend pressurized tubing over a 72-inch radius and back to straight with the seam at the zero-degree position.

Table 5-3. Summary of post weld heat treatments applied to exothermic flux forge welded tubes and specimens.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Method</th>
<th>Austenitization</th>
<th>Tempering</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT1</td>
<td>Ex situ – furnace heating</td>
<td>920 °C – 1 hour; water quench</td>
<td>620 °C – 2 hours</td>
</tr>
<tr>
<td>HT1b</td>
<td>Ex situ – Induction heating</td>
<td>10 seconds heating, peak 1000 °C; Water quench</td>
<td>15 seconds heating, peak 700 °C.</td>
</tr>
<tr>
<td>HT2</td>
<td>In situ – Induction heating</td>
<td>(Twice) 16 sec. heating, peak 940 °C; Water quench. 23 sec. heating, peak 1000 °C; water quench</td>
<td>28 seconds heating, peak 680 °C.</td>
</tr>
</tbody>
</table>
5.4 Results and Discussions

A test matrix of welded tubes and test specimens was designed based on a selection of application relevant testing and practical and time-based considerations including EFFW equipment readiness for application of in situ heat treatment. The test matrix is shown in Table 5-4 with the EFFW-HT1 specimens being produced and tested earlier than the HT2 specimens using the in situ induction heat treatment.

Table 5-4. Test matrix for parent, gas tungsten arc welded (GTAW), and exothermic flux forge welded (EFFW) HSLA steel specimens. Tests were performed on EFFW specimens with ex situ and in situ heat treatments (HT1 and HT2).

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Parent</th>
<th>GTAW</th>
<th>EFFW-HT1/b</th>
<th>EFFW-HT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Specimens</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Root Bends Specimens</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Face Bends Specimens</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Hardness Microstructure</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Charpy in weld metal</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Charpy at Fusion line</td>
<td>3</td>
<td>1</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Charpy +1 mm</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Charpy +2 mm</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>ASME IX Fatigue</td>
<td>2</td>
<td>5</td>
<td>5(^1)</td>
<td>3</td>
</tr>
<tr>
<td>NACE Sol A</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Salt Spray</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Internally pressurized full tube bending fatigue</td>
<td>10</td>
<td>Calculated only</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Full tube tensile</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^1\) The indicated ASME IX Fatigue specimens used heat treatment HT1\(b\) while all other specimens in this column used HT1.
5.4.1 Tensile Results

Welded HSLA steel specimens were evaluated for tension performance according to ASME IX using wall sections as well as by full steel tube tensile testing with the tensile results summarized in Table 5-5. The ASME IX standard testing was used for two GTAW specimens and for two EFFW-HT1 specimens that used the ex situ furnace heat treatment. All of the ASME IX tested specimens had comparable ultimate tensile strength with the GTAW specimens mean value of 839 MPa and the EFFW-HT1 specimens having a mean UTS of 841 MPa which are both in line with the parent measured value of 845 MPa. The GTAW HSLA steel specimens had a mean 0.2 pct. offset yield strength value 664 MPa which was below the material specified minimum yield strength of 689 MPa for both specimens. The EFFW-HT1 HSLA steel specimens had a mean yield strength value of 800 MPa which is in line with the measured parent yield strength of 793 MPa. The parent HSLA steel tubing had a measured elongation of 28 pct. while the GTAW had mean elongation of 13 pct. and the EFFW-HT1 specimens had mean elongation of 9.5 pct.

All welded HSLA steel specimens had a ductile fracture and had similar reduction of area values of approximately 55 pct. Two EFFW-HT2 welded steel tubes that used the in-situ induction post weld heat treatment were pulled to fracture as full tubes with these results also summarized in Table 5-5. These steel tubes had the external weld cap ground flush and were tested transverse weld as full tube sections. Ductile fracture was observed in the parent HSL steel of the EFFW-HT2 steel tubes at a mean ultimate tensile strength of 850 MPa which is in line with the unwelded parent measured value of 845 MPa.
Table 5-5. ASME IX standard and full tube tensile results for gas tungsten arc welded (GTAW) and exothermic flux forge welded (EFFW) HSLA steel tubes.

<table>
<thead>
<tr>
<th>ASME IX Tensile Results</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>Elongation (%)</th>
<th>RoA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent</td>
<td>793</td>
<td>845</td>
<td>28</td>
<td>N/A</td>
</tr>
<tr>
<td>GTAW</td>
<td>655</td>
<td>852</td>
<td>12</td>
<td>55</td>
</tr>
<tr>
<td>GTAW</td>
<td>673</td>
<td>826</td>
<td>14</td>
<td>55</td>
</tr>
<tr>
<td>EFFW-HT1</td>
<td>811</td>
<td>852</td>
<td>9</td>
<td>56</td>
</tr>
<tr>
<td>EFFW-HT1</td>
<td>789</td>
<td>831</td>
<td>10</td>
<td>55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Full Tube Tensile Results</th>
<th>YS not measured</th>
<th>UTS (MPa)</th>
<th>Fracture Location</th>
<th>Fracture Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFFW-HT2</td>
<td>845</td>
<td></td>
<td>Parent</td>
<td>Ductile</td>
</tr>
<tr>
<td>EFFW-HT2</td>
<td>856</td>
<td></td>
<td>Parent</td>
<td>Ductile</td>
</tr>
</tbody>
</table>

5.4.2 Bend Results

Face and root bends were performed according to ASME IX specifications for GTAW, EFFW-HT1, and EFFW-HT2 HSLA steel specimens. Two face bends and two root bends were performed for each weld type and the results are summarized in Table 5-6. All welded specimens passed the testing with no significant observable defects. The mean maximum force was recorded for the GTAW and EFFW-HT1 steel bend specimens with the GTAW having a mean value of 112 MPa and the EFFW-HT1 specimens having a mean value of 104 MPa. The slightly higher force required for the GTAW specimens is believed to be due to higher hardness in the weld metal region of these welded steel specimens.

Table 5-6. ASME IX face and root bend test results from bending gas tungsten arc welded (GTAW) and exothermic flux forge welded (EFFW) HSLA steel wall sections 180° around a 15 mm radius former.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>GTAW</th>
<th>EFFW-HT1</th>
<th>EFFW-HT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face Bend</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_{\text{max}}$ (MPa)</td>
<td>118</td>
<td>106</td>
<td>100</td>
</tr>
<tr>
<td>Result</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Root Bend</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_{\text{max}}$ (MPa)</td>
<td>105</td>
<td>119</td>
<td>118</td>
</tr>
<tr>
<td>Result</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
</tbody>
</table>
5.4.3 Impact Energy

Charpy V-notch impact testing was performed on GTAW and EFFW-HT1 sub-sized HSLA steel specimens with dimensions of 10 mm x 2.5 mm according to ASTM E23 [64]. Notch locations were placed in the weld metal (only applicable for GTAW), at the fusion line (FL), FL + 1 mm, and FL + 2 mm. Three specimens for each weld type were tested for each applicable notch location with the results summarized in Table 5-7. The GTAW specimens had mean location-based values between 26.2 and 31.7 joules with an overall range from 24.1 to 35.7 J, an overall mean of 29.2 J, and an overall population based standard deviation of 4.0 J. The EFFW-HT1 specimens had location-based mean values between 28.1 and 29.4 J with an overall range from 27.0 to 31.1 J, an overall mean of 28.8 J, and an overall population based standard deviation of 1.3 J. The lowest overall value was for a GTAW specimen in the weld metal while the highest overall value was for a GTAW specimen in the FL + 1 mm location. The mean values were similar between both weld types with the GTAW values having higher variation.

Table 5-7. Charpy V-notch sub sized specimen energy absorption for gas tungsten arc welded (GTAW) and exothermic flux forge welded (EFFW-HT1) HSLA steel specimens with the notch in the weld metal (GTAW only), at the fusion/forge line (FL), at the FL + 1 mm and at the FL + 2 mm.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Weld Metal</th>
<th>FL</th>
<th>FL + 1 mm</th>
<th>FL + 2 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GTAW</td>
<td>EFFW-HT1</td>
<td>GTAW</td>
<td>EFFW-HT1</td>
</tr>
<tr>
<td>1</td>
<td>24.1</td>
<td>N/A</td>
<td>33.2</td>
<td>28.7</td>
</tr>
<tr>
<td>2</td>
<td>25.8</td>
<td>25.9</td>
<td>30.4</td>
<td>35.7</td>
</tr>
<tr>
<td>3</td>
<td>28.8</td>
<td>24.8</td>
<td>29.2</td>
<td>29.2</td>
</tr>
<tr>
<td>Mean</td>
<td>26.2</td>
<td>28.0</td>
<td>29.4</td>
<td>30.9</td>
</tr>
<tr>
<td>StdP</td>
<td>2.0</td>
<td>3.7</td>
<td>0.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Charpy V-notch 10 x 2.5 mm sub sized specimens tested at 25 °C.
5.4.4 Corrosion Testing

Salt spray facilitated corrosion has been demonstrated to significantly affect the fatigue life of HSLA steels and is therefore of importance for coiled tubing work string applications [65]. Salt spray testing was performed in a 1000L C&W Salt Spray Cabinet according to ASTM B117 on four welded HSLA steel tubes [66]. The testing conditions included a solution salt concentration of 5 ± 1 wt. pct. and recorded specific gravity of 1.038 and pH of 6.5. The measured temperature was 35 ± 0.1 °C. Two of the tested HSLA steel tubes were welded by the exothermic flux forge welding (EFFW) process and two of the tubes were welded by the gas tungsten arc welding (GTAW) process. The EFFW steel tubes used heat treatment 1 (HT1) previously shown in Table 5-3. Images of the tubes after 24 hours and 96 hours of testing are presented in Figure 5-1.

The GTAW steel specimens exhibited a brighter reddish orange oxide after 24 hours than the EFFW steel specimens but with additional exposure all specimens developed a similar heavily oxidized deep orange appearance. The more noble weld filler metal in the GTAW specimens showed less oxidation than the surrounding areas and the outer softened heat affected zone regions in the EFFW specimens also showed slightly less oxidation than adjacent areas, but the corrosion otherwise appeared relatively uniform across the specimens. Weld region microstructures can often be more susceptible to corrosion with increased hardness correlating with increased corrosion rate. The observed uniform corrosion across the parent HSLA steel and the weld and HAZ regions in the EFFW specimens is a desirable outcome for the salt spray testing.
Figure 5-1. Salt spray testing of two exothermic flux forge welded (EFFW) and two gas tungsten arc welded (GTAW) HSLA steel tubes with images shown after 24 and 96 hours of exposure. The GTAW specimens had a brighter oxide after 24 hours exposure but with additional exposure all specimens continued to develop a more uniform reddish surface and had similar appearances after 96 hours.

The corrosion behavior of GTAW and EFFW welded HSLA steel tubes was investigated by submersion in aerated NACE Test Solution A. Test Solution A is an acidified and buffered hydrogen sulfide saturated aqueous brine solution containing 5.0 wt. pct. sodium chloride and 0.5 wt. pct. glacial acetic acid [67]. The test specimens are shown in Figure 5-2 before and after 96 hours of exposure in Test Solution A at 75 °C. The welded steel tubes had the external weld cap ground and were degreased prior to submersion. After submersion, the specimens were half-
sectioned lengthwise, and the outer and inner surfaces were photographed. The GTAW steel specimens used a more noble filler metal containing 2.5 wt. pct. nickel compared to the parent metal with 0.08 wt. pct. nickel. The more noble filler metal resulted in higher corrosion in the parent metal than the weld metal with the weld metal interface showing a step-like transition.

The weld metal also had a darkened appearance compared to the parent HSLA steel and is readily visible in the after exposure external images. The internal surface was not ground prior to the test and the GTAW fusion interface showed varying surface conditions with some areas presenting acute interface angles directed under the weld metal. The step-like and acute interface angles can act as stress concentrators and could act as crack initiation sites in stress corrosion cracking or fatigue situations. The EFFW-HT1 specimens exhibited relatively uniform corrosion across the weld, HAZ, and parent material. The external surfaces showed no obvious corrosion differences across the specimens. The internal surfaces showed slightly increased surface corrosion behavior near the internal weld cap and the axial production weld seam. These effects are believed to be related to rougher surfaces in these areas resulting in increased surface area exposure.

Cross-sections of the steel tube walls after Test Solution A exposure were polished and etched for metallographic investigation with selected images presented in Figure 5-3. The GTAW outer wall image shows the step-like interface between the weld metal and grain coarsened HAZ interface with the weld metal present on the left side of the image. The corroded GTAW inner wall had varying surface conditions with the presented metallograph showing protruding structures in the weld metal and relatively uniform corrosion of the HAZ. The varying surface conditions observed are believed to be related to the unground root weld bead.
Before exposure | After exposure (external) | After exposure (internal)
---|---|---
GTAW | ![GTAW before exposure](image1) ![GTAW after exposure (external)](image2) ![GTAW after exposure (internal)](image3)
EFFW-HT1 | ![EFFW-HT1 before exposure](image4) ![EFFW-HT1 after exposure (external)](image5) ![EFFW-HT1 after exposure (internal)](image6)

Figure 5-2. Corrosion testing of gas tungsten arc welded (GTAW) and exothermic flux forge welded (EFFW) heat treatment 1 (HT1) HSLA steel specimens. Left images are welded, ground, and degreased specimens before corrosive exposure, center column images are the sectioned outer surfaces and right images are the sectioned inner surfaces after immersion in deaerated NACE TM0177 Test Solution A for 96 hours at 75°C. The GTAW welded steel specimens used a more noble filler metal and exhibited more corrosion in the parent metal than the weld metal and exhibited signs of crevice corrosion at the interface. The weld metal displayed significant discoloration. The EFFW specimen had similar corrosion characteristics in the weld region and the parent metal.
Figure 5-3. Metallographic images of polished and etched cross-sections of exposed surfaces at the weld interfaces of HSLA steel specimens after 96 hours of exposure to NACE Test Solution A at 75 °C.

The EFFW steel weld showed relatively uniform corrosion between the weld location, heat affected zone and parent metal. The presented outer wall image shows some angled wave-like surface features in the grain coarsened heat affected zone believed to be related to the grain size and orientation. The improved post weld grain refinement performed in the in-situ heat treated EFFW-HT2 specimens may show improved smoothness and are proposed for future corrosion behavior investigation. The inner wall image is shown at the weld cap transition where increased surface oxide was observed macrographically.
5.4.5 Strain Life Fatigue Testing

High strain fatigue performance is important for work string grade coiled tubing and therefore fatigue testing was performed on parent and GTAW and EFFW HSLA steel specimens. Wall sections of HSLA steel tubing were subjected to strain life fatigue according to ASTM E606 for the parent, GTAW, and EFFW specimens that were heat treated ex situ by induction. Full section pressurized steel tube bend cycle fatigue testing was performed by cyclically bending pressurized tubes around a 72-inch (1829 mm) radius and back to straight for parent tubes and EFFW-HT2 tubes with calculated results for GTAW tubes presented. The ASTM E606 testing used a strain amplitude of 0.003, a stress ratio of $R = -1$, and a frequency of 2 Hz. Several strain amplitudes were tested on the parent HSLA steel to determine a suitable amplitude to produce reversals to failure representative of real usage. The welded steel specimens used for this testing had the inner wall (root) weld cap left intact to replicate typical use conditions for the tubing. The fatigue performance data is summarized in Table 5-8.

The ASTM E606 based testing found the mean reversals to failure ($2N_f$) for the parent HSLA steel tube was 3280 based on two specimens. The GTAW specimens had a mean $2N_f$ value of 871 based on five specimens and the EFFW-HT1a specimens had a mean $2N_f$ value of 2231. The mean GTAW value was 27 pct. of the parent mean value while the mean EFFW-HT1a value was 68 pct. of the parent. All GTAW specimens fractured at the root toe and all EFFW specimens fractured at the analogous root weld cap base. The failure locations suggest that stress concentration at the weld was the primary failure mechanism which matches with theory.
Table 5-8. Strain Life Fatigue Testing for parent HSLA steel tube, exothermic flux forge welded (EFFW) steel tube using heat treatments HT1b and HT2, and gas tungsten arc welded (GTAW) steel tube.

<table>
<thead>
<tr>
<th>Specimen #</th>
<th>Parent</th>
<th>GTAW</th>
<th>EFFW-HT1b</th>
<th>Parent</th>
<th>GTAW</th>
<th>EFFW-HT2</th>
<th>Parent</th>
<th>GTAW</th>
<th>EFFW-HT2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 ksi internal pressure</td>
<td>Cycles to failure (N)</td>
<td></td>
<td>7 ksi internal pressure</td>
<td>Cycles to failure (N)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3120</td>
<td>954</td>
<td>2413</td>
<td>487</td>
<td>391</td>
<td>408</td>
<td>280</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3440</td>
<td>1120</td>
<td>2640</td>
<td>370</td>
<td>338</td>
<td>336</td>
<td>310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>650</td>
<td>2260</td>
<td>539</td>
<td>401</td>
<td>312</td>
<td>397</td>
<td>288</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>710</td>
<td>1890</td>
<td>471</td>
<td>311</td>
<td>403</td>
<td>234</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>920</td>
<td>1950</td>
<td>471</td>
<td>136</td>
<td>341</td>
<td>373</td>
<td>112</td>
<td>275</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>3280</td>
<td>871</td>
<td>2231</td>
<td>454</td>
<td>341</td>
<td>373</td>
<td>112</td>
<td>275</td>
<td></td>
</tr>
<tr>
<td>Population Std. Dev.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
<td></td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% of Parent</td>
<td>27%</td>
<td>68%</td>
<td>30%</td>
<td>75%</td>
<td>30%</td>
<td>74%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Increased internal pressure affects bend fatigue life and so full steel tube bend cycle fatigue was carried out with internal pressures of 4 and 7 ksi (27.6 and 48.3 MPa). The 4 ksi pressurized bend cycle testing found 454 mean cycles-to-failure for the parent HSLA steel tubing. New bend cycle pressurized full tube fatigue testing was not able to be performed on GTAW tubing for this project and calculated data based on typical 30 pct. life of the parent for GTAW butt welds is presented for reference [68, 69]. With 4 ksi internal pressure, the EFFW-HT2 tubes had mean cycles-to-failure of 341 which is 75 pct. of the parent mean. At 7 ksi internal pressure the parent tubing achieved a mean of 373 cycles and the EFFW-HT2 tubing achieved a mean of 275 cycles which is 74 pct. of the parent. No EFFW tubes failed catastrophically during bend cycle testing and all remained in one piece. These results suggest that EFFW welds have the potential to significantly increase fatigue life for butt welded coiled tubing compared to GTAW butt welds.
The microstructure of the inner heat affected zone region near or at the bond interface for the exothermic flux forge welded HSLA steel is shown after in-situ post weld heat treatment (EFFW-HT2) in Figure 5-4. The shown microstructure is a fine-grained tempered martensite which is the preferred microstructure for this type of steel product. The post weld heat treatment utilized three short (approximately 20 second) grain refinement steps to reduce the prior austenite grain size while managing the location of the softened outer heat affected zone regions by using a longer and slightly higher temperature third grain refinement step to produce a larger austenitized region prior to the water quenching. Martensite was formed during the water quench and followed by a temper cycle to reduce hardness and improve ductility and toughness.

Figure 5-4. Exothermic flux forge welded inner heat affected zone region microstructure of the high strength low alloy steel after in situ post weld heat treatment (EFFW-HT2). The heat-treated microstructure shows a fine-grained tempered martensite which is desirable for this type of steel product.
5.5 Conclusions

The GTAW and EFFW HSLA steel specimens both demonstrated good performance across most of the investigated testing. Tensile, bend, and Charpy results were comparable across both welding methods and met standard acceptance criteria with the exception of low yield strength for the GTAW specimens. The salt spray corrosion testing also showed expected corrosion levels and acceptable uniformity for all specimens. Submersion in NACE Solution A showed the GTAW steel specimens developed a step interface and some signs of galvanic or crevice corrosion at the toe interfaces of the more noble weld metal and the parent metal. The step interface can act as a stress concentrator and potential initiation site for stress corrosion cracking or fatigue cracking. The EFFW steel specimens demonstrated uniform corrosion across the specimen with minimal difference between the weld region and the parent. Fatigue performance is generally the most important consideration for butt welded coiled tubing. The GTAW specimens had mean reversals to failure of 27 pct. of the parent material in the ASTM E606 strain life testing and are estimated at 30 pct. of the parent life for pressurized full tubes based on industry experience. The EFFW steel specimens demonstrated 68 pct. of the parent strain life fatigue in the ASTM E606 testing and 75 pct. and 74 pct. respectively of parent life in the 4 and 7 ksi pressurized HSLA steel full tube bend cycle testing. These results, including the significant fatigue life improvements, demonstrate the potential of the automated EFFW process to extend service life and reduce in-service failures for butt welded coiled tubing.
CHAPTER 6

THE EFFECTS OF TEMPERING TEMPERATURE, GRADIENT, TIME, AND METHOD ON MECHANICAL PROPERTIES OF FORGE WELDED API Q125 STEEL CASING

6.1 Abstract

The effects of furnace tempering on welded API Q125 steel casing specimens at temperatures of 600, 625, 650, 675, and 700 °C on hardness, tensile response, and impact energy were characterized. Hardness showed a greater than linear decrease with increasing tempering temperature with maximum hardness exhibiting a larger decrease than minimum hardness. An Arrhenius style plot with the maximum natural logarithm of the hardness difference plotted as a function of inverse tempering temperature was found to have a relatively good linear fit. Impact energy, measured by Charpy V-notch at -20 °C, was found to increase with increasing tempering temperature. Specimens tempered at 600 to 625 °C exhibited primarily brittle fracture with average absorbed energies (24 and 31 joules) below material specifications while specimens tempered at 650 to 700 °C exhibited mixed to primarily ductile fracture and average energies (69.7, 78, and 92.7 J) above the material specified minimums.

Furnace tempering of welded tensile specimens at temperatures from 600 to 700 °C found that yield strength decreased from 885 to 701 megapascals, ultimate tensile strength decreased from 964 MPa to 789 MPa, and elongation increased from 12.5 to 20 percent with increasing tempering temperature. Tensile fractures occurred in the weld softened heat affected zone which was further softened during the uniform furnace tempering. In situ induction tempering investigations found a high temperature gradient across the wall thickness due to the skin effect but demonstrated the potential to locally temper the hardened weld region without
over softening the soft HAZ region. With a tempering temperature just below the A1 critical temperature, specimens were able to meet Q125 tensile and Charpy specifications while lower tempering temperatures resulted in too low Charpy energies and too high temperatures resulted in too low tensile strengths and inconsistent Charpy fracture surfaces.

6.2 Introduction

The ability to weld high strength steels including API Q125 grade steel casing is of growing importance to the energy sector. As the accessibility of known oil reserves decreases, deep well technology including improved joining of high strength well casing is needed for continued economical oil recovery. Additionally, high integrity joining solutions are needed to minimize project risk including risk of environmental disaster in deep water oil fields. Welded high strength casing grades typically cannot meet the high strength requirements as measured by tensile strength while simultaneously meeting the ductility and toughness requirements as measure by bend and Charpy impact testing. To be economically viable for mass adoption for casing applications, a joining method must also be fast whereas traditional arc welding methods are too slow to be economical. This study investigates the effects of post weld tempering temperature on the mechanical properties of exothermic flux forge welded (EFFW) Q125 steel casing to determine if the method can be a viable approach to meet the needs for high integrity joining of high strength casing. The study investigates the effects of ex situ post weld tempering temperature on hardness, strength, and impact toughness while also investigating the effects of in situ induction tempering.

6.3 Materials and Methods

Welded specimens were prepared by exothermic flux forge welding for investigation of post weld heat treatment. The welded specimens for this study were produced from 14-inch
(355.6 mm) diameter API Q125 grade seamless casing with a weight of 115 lbs/ft (171.1 kg/m) [47]. The chemical composition specifications and measured product certificate values are shown in Table 6-1. The tensile strength specifications are shown in Table 6-2 with the yield strength measured at 0.65 pct. extension under load (EUL). The wall minimum thickness of the pipe is specified as 0.812-inch (20.62 mm) but was measured at 0.866-inch (22.0 mm).

Table 6-1. API Q125 steel casing chemical composition maximum specifications and product measured values in weight percent.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>0.350</td>
<td>1.35</td>
<td>0.020</td>
<td>0.010</td>
<td>0.99</td>
<td>1.50</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>0.240</td>
<td>0.55</td>
<td>0.008</td>
<td>0.003</td>
<td>0.01</td>
<td>0.94</td>
<td>0.58</td>
<td>0.049</td>
<td>0.029</td>
</tr>
</tbody>
</table>

Table 6-2. API Q125 steel casing yield strength and tensile strength specifications.

<table>
<thead>
<tr>
<th>Strength Specifications</th>
<th>Minimum (MPa / ksi)</th>
<th>Maximum (MPa / ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Strength at 0.65% EUL</td>
<td>861.8 / 125</td>
<td>1034 / 150</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>930.8 / 135</td>
<td></td>
</tr>
</tbody>
</table>

To produce the welds in this study, the exothermic flux forge weld (EFFW) method was used. Two steel pipe lengths each had one end beveled to a rounded profile designed to deform to a low angle convex weld cap with a near flush (less than 2.5 mm convex) inner wall when forge welded together. The steel pipes were positioned end-to-end in a forge welding machine with an offset gap of 0.11-inch (2.8 mm) between the pipe ends. An exothermic flux ring was placed in-between the pipe ends and the upper pipe lowered to be in contact with the ring. The exothermic flux ring was produced by uniaxial hot-pressing powdered constituents and was profiled to compliment the beveled pipe ends and enable good end contact and reproducible positioning. The flux ring was composed of reactant constituents designed to undergo an
exothermic chemical reaction producing molten oxide and fluoride products once ignited. The product materials are designed to serve as forge welding flux and protect the pipe faying surfaces from oxidation, reduce or dissolve existing surface oxides, and provide additional heat directly to the surfaces. The exothermic reaction also enables the flux to rapidly go from a solid to molten state so that the flux is fully functional in short time-scale induction heating processes. The rounded end profile on the pipes was designed to facilitate extrusion of the molten flux during forging. The forge welding process included application of induction heating to heat the profiled pipe ends and initiate the exothermic chemical reaction to produce the molten flux. The induction heating and molten flux heated the pipe ends to approximately 1200 °C at which time a position-controlled forging movement was applied. Following the forging step, the welded pipes were water quenched and then underwent an in-situ grain refinement step by reheating with induction to approximately 900 °C followed by a water quench.

Tempering temperature effects were investigated by cutting sections for tensile, Charpy V-notch, and hardness specimens from the EFFW casing. The specimens were furnace tempering for one hour at temperatures of 600, 625, 650, 675, and 700 °C and air cooled. In situ post weld heat treatment was also investigated using the weld system induction coil and powder supply. Tensile specimens were prepared according to API 1104 and Charpy specimens were prepared and testing according to ASTM E23 [49, 64]. Tensile testing was performed in a Zwick/Roell Z1200 frame. Charpy V-notch specimens were tested in Zwick/Roell PSW750 pendulum impact tester. Hardness specimens were prepared by sectioning across the weld region, mounting, and polishing. Hardness measurements used an automated Struers Duramin A300 Vickers 10 kgf load. Hardness scans were taken with 1 mm indent spacing with lines 1 mm from the outer wall, mid wall, and 1 mm from the inner wall.
6.4 Results and Discussions

The effects of tempering temperature on hardness, tensile properties, and impact energy was investigated using an ex-situ furnace tempering process on EFW Q125 steel specimens. The furnace tempering allows for a controlled uniform temperature application across the entire welded specimen including the full heat affected zone and parent material. An in-situ localized induction tempering process was also investigated to characterize the effects of the localized heat source and resultant temperature gradients on the hardness, tensile properties, and impact energy of EFW specimens. The induction heating was centered at the outer wall weld cap and with the temperature reducing with distance both across the wall thickness and axially above and below the weld cap region.

6.4.1 Effects of Tempering Temperature (Uniform)

Welded API Q125 steel casing specimens were produced by the exothermic flux forge welding method including in situ grain refinement and water quench for investigation of tempering temperature effects. A furnace tempering study was then performed on forge welded steel specimens cut from the welded Q125 steel pipe to evaluate five tempering temperatures each held for one hour. Following tempering, the specimens were evaluated for hardness, tensile response, and impact energy with the results summarized in Table 6-3. The maximum and minimum hardness values were obtained by performing incremented hardness measurements across the heat affected zone in lines near the outer wall, the inner wall, and the mid wall. The data indicates that there is an inverse relationship between the investigated tempering temperatures hardness and strength a direct relationship between tempering temperature and elongation and Charpy energy.
Table 6-3. Measured values on forge welded API Q125 steel casing specimens with varied tempering temperatures.

<table>
<thead>
<tr>
<th>Tempering Temperature (°C)</th>
<th>Hardness (Max) (HV10)</th>
<th>Hardness (Min) (HV10)</th>
<th>Yield Strength (MPa)</th>
<th>U.T.S. (MPa)</th>
<th>Elongation (%)</th>
<th>Charpy V-Notch, -20 ºC (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>382</td>
<td>261</td>
<td>885</td>
<td>964</td>
<td>12.5</td>
<td>20, 22, 30</td>
</tr>
<tr>
<td>625</td>
<td>364</td>
<td>260</td>
<td>866</td>
<td>934</td>
<td>13.0</td>
<td>25, 35, 33</td>
</tr>
<tr>
<td>650</td>
<td>340</td>
<td>252</td>
<td>825</td>
<td>900</td>
<td>15.0</td>
<td>68, 78, 63</td>
</tr>
<tr>
<td>675</td>
<td>315</td>
<td>240</td>
<td>769</td>
<td>848</td>
<td>17.5</td>
<td>71, 73, 90</td>
</tr>
<tr>
<td>700</td>
<td>275</td>
<td>221</td>
<td>701</td>
<td>789</td>
<td>20</td>
<td>100, 76, 102</td>
</tr>
</tbody>
</table>

Notes: Tempering temperature was held for 1 hour. Hardness value measured with Vickers 10 kgf load. Yield Strength value based on 0.5% offset method. Elongation measured by fit-back method. Yield strength specified minimum 862 MPa and UTS specification minimum 931 MPa.

With increasing tempering temperature, the maximum and minimum hardness values measured by Vickers 10 kg force exhibited a greater than linear decrease in values as plotted in Figure 6-1 with the 600 ºC temper minimum and maximum hardness values used as the origins.

Figure 6-1. Hardness changes with tempering temperature from baseline values from API Q125 steel casing specimen tempered at 600 ºC. All specimens were held at temperature for one hour. The maximum and minimum hardness values measured across the heat affected zone are shown for each tempering temperature.
The maximum hardness values had the greatest change with increasing temperature with
the minimum values showing less decrease in hardness with increasing temperature. The
maximum hardness values were typically obtained near the weld line and near the outer wall as
this position is central for the heat input and water quench. The minimum hardness values were
typically obtained in the softened heat affected zone which experienced tempering during the
weld and grain refinement cycles prior to the furnace tempering.

Tempering of martensite can be viewed as a thermally activated phase transformation
reaction towards an equilibrium state and hardness can be viewed as a measure of the
transformation progress or the transformation rate when divided by time. Based on this approach,
it may be useful to examine the tempering transformation kinetics based on the form of
Arrhenius equation (6-1) where \(k(T)\) is the rate constant as a function of temperature, \(A\) is the
pre-exponential frequency factor, \(e\) is Euler’s number, \(E_a\) is the activation energy, \(R\) is the
universal gas constant, and \(T\) is the absolute temperature. The reaction rate is related to the rate
constant through reactant concentrations and reaction order. For a suitably high concentration of
martensite and a suitable time period, for the purposes of this examination, it may be sufficient to
approximate the temperature dependent rate constant as the hardness drop from the untempered
state (590 HV10) for the time period (one hour) at the temperature.

Caution is needed when taking this approach because the transformation rate is expected
to vary with time with an early lag period and the rate slowing near completion with an S-shaped
form as described by the Johnson-Mehl-Avrami-Kolmogorov (HMAK) equation [70]. The effect
of the reaction slowing near completion can explain the reduced change in hardness with
tempering observed in the minimum hardness values found in the soft heat affected zone region.
Using the described rate constant approximation for the maximum hardness regions, and taking the natural logarithm of both sites, the Arrhenius equation takes a linear slope intercept form as shown in equation (6-2).

\[ k(T) = Ae^{-\frac{E_a}{RT}} \]  \hspace{1cm} (6-1)

\[ \ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \]  \hspace{1cm} (6-2)

The values for the pseudo activation energy and pre-exponential factor can be estimated by plotting the natural logarithm of the reaction rate constant against \( T^{-1} \) will give a straight line with the y-intercept equal to \( \ln A \) and the slope equal to \( \frac{-E_a}{R} \). An Arrhenius style plot is presented in Figure 6-2 and shows relatively good linear fit with a coefficient of determination (R\(^2\)) of 0.986 with values of 9.301 for \( \ln A \) and -3.476 for \( \frac{-E_a}{1000+R} \).

Figure 6-2. Arrhenius style plot of the natural logarithm of the hardness difference between the as-quenched specimen and each specimen tempered at temperatures, T, plotted as 1000/T. The semi-log plot is relatively linear over the examined range.
The plot appears to minorly deviate from linearity at temperatures corresponding to 600 and 700 °C with a possible explanation that the lower rates at the early and late stages of the S-curve are more significant for these temperatures over the time period examined. Substituting values into the Arrhenius equation we obtain, equation (6-3) which provides a good estimate for the Vickers hardness drop per hour at a temperature between 873 and 973 K and time period of one hour starting from an untampered hardness of 590 HV10.

\[ k(T) = 10949e^{-\frac{3476}{T}} \]  

(6-3)

The effect of tempering temperature on the tensile response of the forge welded specimens with the summarized results plotted in Figure 6-3. With increasing tempering temperature, the yield and ultimate tensile strength exhibited a greater than linear decrease while elongation at break increased. Necking and fracture occurred in the softened HAZ resulting from the weld or grain refinement cycle. The reduction in tensile strength and hardness with increasing tempering temperature indicates that tempering resulted in further softening of this region. The increase in elongation is believed to be related to the reduced decrease in the minimum hardness values compared to the maximum hardness values. The higher tempering temperatures continue provide greater reduction to the maximum hardness values to produce a more uniform hardness and strength across the specimen. This more uniform strength results in more uniform strain distribution across the entire specimen during the tensile test resulting in delayed necking and better ability for strain hardening to result in additional deformation outside of the necking area.
Figure 6-3. Tensile response variation for exothermic flux forge welded API Q125 steel casing with tempering temperature. All specimens were held at temperature for one hour. With increasing temperature, the 0.5% offset yield strength and ultimate tensile strength decrease while the elongation increases.

Impact energy absorption was measured by Charpy V-notch using ASTM E23 standard V-notch specimens cooled to -20 °C. The 2 mm deep notch was placed at the weld line on each of the tested specimens. The results presented in Figure 6-4 showed increased energy absorbed with increased tempering temperature with a significant increase in energy absorbed for specimens tempered at 650 to 700 °C compared to specimens tempered at the lower temperatures. This behavior indicates that the specimens tempered at 650 °C or above had a ductile-brittle temperature transition (DBTT) below the -20 °C test temperature while the specimens tempered at 625 and 600 °C and had a DBTT above the test temperature.
Figure 6-4. Charpy V-notch impact energy at the weld line tested at -20 °C for API Q125 exothermic flux forge welded steel casing specimens tempered at the indicated temperatures for one hour. The impact energy increases with increasing tempering temperature between 600 and 700 °C. Tempering at 650 °C or above appears to lower the ductile to brittle temperature transition to below -20 °C.

To meet the material specification minimum requirements, the tempering process must retain adequate material strength while also meeting the requirements for toughness measured by Charpy V-notch impact energy. The material specifications require a minimum average impact energy of 38 J (28 ft-lb) and a minimum specimen value of 26 J (19 ft-lb) which only the specimens tempered at 650 °C or above achieve. The material strength specifications require a minimum yield strength of 862 MPa (125 ksi) and ultimate tensile strength of 931 MPa (135 ksi) which conversely, only the specimens tempered at 625 °C or below achieve. This dichotomy suggests that the uniform furnace temper is unlikely to produce the specified combination of strength and toughness; however, it should be noted that the impact energy was measured at the weld line while the tensile measurements were across the entire heat affected zone with necking.
and fracture occurring in the softened HAZ away from the weld line. This fracture location information indicates that an approach that sufficiently tempers the hardened HAZ region without over-tempering the softened HAZ might be able to achieve the specified results.

### 6.4.2 Effects of a Graded Tempering Temperature Profile

In situ tempering using an external induction heating coil was investigated on the welded specimen after re-austenitizing for grain refinement and water quenching. The induction heating penetration depth, $\delta$, is defined as the depth the current density decreases to $1/e$ (approximately 37 pct.) of the surface density. The penetration depth is proportional to the square root of the resistivity, $\rho$, and the inverse square root of the magnetic permeability, $\mu$, the induction frequency, $f$, and $\pi$ as shown in equation (6-4). Below the Curie temperature and especially below the $A_1$ eutectoid transformation temperature, the magnetic permeability is high and therefore the penetration depth is low. For the conditions of this tempering study, the penetration depth is estimated to be around 3 mm which results in difficulty uniformly heating the full wall thickness of 20.62 mm.

$$\delta = \sqrt{\frac{\rho}{\pi\mu f}}$$

(6-4)

Thermocouples were welded to the outer and inner walls at the weld location to measure the temperatures and examine the gradient during a ten-minute tempering process. The measured temperatures and the induction power input are plotted over time in Figure 6-5. The thermocouple data shows that when holding the outer wall near 700 °C, the temperature difference with the inner wall approaches a steady state with the inner wall approximately 95 °C cooler.
Figure 6-5. Temperature evolution of the API Q125 exothermic flux forge welded pipe outer wall and inner wall heated in situ by an external circumferential induction coil with corresponding induction power input. With a target outer wall temperature of 700 °C, the inner wall approaches a steady state approximately 95 °C cooler.

The effects of the temperature gradient across the wall thickness was examined using transverse weld hardness scans with a scan positioned 1 mm from the outer wall, another mid-wall, and another 1 mm from the inner wall. Four specimens were profiled with the peak exposure temperature varied for each specimen and the hardness scan results presented in order of increasing peak temperature in Figure 6-6. Plot shows the weld region of the outer wall having been tempered to a minimum hardness around 340 HV10 which is lower than the mid wall hardness for that position but still mostly above the inner wall hardness. With increased tempering heat, plot B shows a further hardness reduction near the outer wall to around 315 HV10 with the mid wall position reduced to around 335 HV10 and the inner wall region now having the highest hardness near the weld center. In plot C, the peak tempering temperature experienced at the outer wall was slightly over the A₁ critical temperature for a small region and
the high temperatures resulted in significant hardness reduction near the outer wall centered near the weld line. There is also a reduction in hardness of both the mid wall and near inner wall regions compared to plot B. Further increase in tempering heat, resulted in a larger region exceeding the $A_1$ temperature with most of this region remaining in the intercritical temperature range with these hardness scans presented in plot D. The outer wall central region that exceeded the $A_1$ critical temperature is shown to have a higher hardness than the surrounding regions that experienced the highest softening with a spike in hardness near the weld line indicating increased hardenability at this location.

![Hardness Scans](image)

**Figure 6-6.** Across weld hardness scans on four API Q125 exothermic flux forge welded specimens in situ induction tempered for 12 minutes. Captions A through D are presented in order of increasing induction heat applied to the outer diameter (O.D.) during tempering. The O.D. hardness is most affected with increasing heat followed by the center (mid wall) hardness. Caption D shows the centered region of the O.D. has been heated above the austenite transformation temperature.
Micrographs are shown in Figure 6-7 from a region of the exothermic flux forge welded API Q125 steel casing with hardness around 320 HV following the austenization, water quench, and tempering cycle. The microstructure consists of primarily tempered martensite and may also contain some bainite. Tensile specimens were cut from the EFW API Q125 steel casing at regions near the hardness specimens used for the scans shown in Figure 6-6 plots A and D. One tensile specimen experienced a peak outer diameter weld cap temperature of approximately 670 °C while the other experienced a peak temperature of approximately 820 °C which is near the $A_3$ critical temperature. The inner wall peak temperature was approximately 100 °C less than the peak outer wall temperature.

![Figure 6-7. Light micrographs of etched API Q125 steel casing after in situ grain refinement, quench and temper. Both micrographs show a primarily tempered martensite microstructure with the left micrograph taken at 200x and the right at 1000x.](image)

Photographs of the Q125 steel casing tensile specimens after testing and the strength and elongation results are shown in Figure 6-8. Tensile testing found that the specimen subjected to the lower tempering temperature fractured in the outer softened heat affected zone with a 0.5 pct. offset yield strength value of 904 MPa, an ultimate tensile strength of 967 MPa and a fit-back
method measured elongation of 11 pct. The fracture location showed significant necking and was observed to be ductile.

Tensile testing of the Q125 steel casing specimen subjected to the higher tempering temperature resulted in a mixed type fracture with brittle fracture at the weld line along the outer wall and a ductile fracture towards the inner wall angling away from the weld plane at approximately 60 degrees. The brittle failure at the weld line can be explained by the austenitic transformation in this region followed by a moderately high rate of cooling as heat flowed to cooler areas of the pipe and air resulting in a high hardness and low ductility in this region. The hardenability appears increased at the weld line, potentially due in part to a larger effective grain size than the adjacent areas.

<table>
<thead>
<tr>
<th>Peak O.D. Temp</th>
<th>~660 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y.S. (0.5% Off)</td>
<td>904 MPa</td>
</tr>
<tr>
<td>U.T.S</td>
<td>967 MPa</td>
</tr>
<tr>
<td>Elongation</td>
<td>11%</td>
</tr>
<tr>
<td>Peak O.D. Temp</td>
<td>~820 °C</td>
</tr>
<tr>
<td>Y.S. (0.5% Off)</td>
<td>867 MPa</td>
</tr>
<tr>
<td>U.T.S</td>
<td>943 MPa</td>
</tr>
<tr>
<td>Elongation</td>
<td>8%</td>
</tr>
</tbody>
</table>

Figure 6-8. Exothermic flux forge welded API Q125 steel casing tensile specimens exposed to differing induction tempering heats. The upper specimen was exposed to a peak outer diameter temperature of approximately 670 °C while the lower specimen was exposed to a peak outer diameter temperature of approximately 820 °C which is near the A₃ critical temperature. Each specimen experienced a temperature gradient across the wall thickness and for the lower specimen this resulted in a combination of brittle and ductile fracture. The upper specimen had a ductile fracture in the softened outer HAZ.

Three standard Charpy V-notch specimens were cut from a region of the exothermic flux forge welded API Q125 steel casing subjected to similar tempering heat as the region in Figure
6-6 C. The outer diameter of this region experienced a peak temperature just over the A<sub>1</sub> critical point, but this small surface area was machined away in fabrication of the Charpy specimens. The specimens were cooled to -20 °C and found to absorb energies of 93, 112, and 116 joules at the weld line. Specimens taken from a region with a peak outer diameter temperature around the A<sub>3</sub> critical point like the specimens used for the hardness profile in Figure 6-6 D, absorbed energies of 112, 64, and 68 J. The fracture surfaces, shown in Figure 6-9 A, were found to contain a mixture of ductile and brittle regions with the brittle regions corresponding to the area heated above the critical temperature. Specimens with a temper producing a hardness profile near Figure 6-6 A were found to absorb energies of 22, 22, and 36 J and exhibited a primarily brittle fracture surface with a shear lip around the edges and are shown in Figure 6-9 B.

Figure 6-9. Fracture surfaces and impact energies of standard size Charpy V-notch specimens cut from exothermic flux forge welded API Q125 steel casing with the notch at the weld plane and tested at -20 °C. The three specimens shown in A were subjected to induction heating with a peak temperature around the A<sub>3</sub> temperature. The orientation of the peak temperature region was rotated for each specimen resulting in position based mixed ductile and brittle fracture. The specimens shown in B were induction tempered with a peak temperature near 660 °C with mid wall hardness of around 360 HV10 and exhibited primarily brittle fracture with a shear lip around the sides.

These results indicate in situ induction tempering can achieve the required tensile and impact properties, however a high degree of control is required to achieve the desired
temperature profile to adequately soften the thick walled casing weld region without over
softening the outer heat affected zone regions and without exceeding the $A_1$ critical temperature.

6.5 Conclusions

Exothermic flux forge welding can be used to join 14-inch diameter, 115 lb/ft API Q125 grade steel casing, but post weld heat treatment must be applied to meet the required combination of strength, ductility, and toughness. The effects of furnace tempering of welded specimens at 600, 625, 650, 675, and 700 °C on hardness, tensile response, and impact energy were characterized. Hardness decreased superlinearly with increasing tempering temperature with maximum hardness exhibiting a larger decrease than minimum hardness. An Arrhenius style plot with the maximum natural logarithm of the hardness difference plotted as a function of inverse tempering temperature was found to have a relatively good linear fit. Impact energy, measured by Charpy V-notch at -20 °C, was found to increase with increasing tempering temperature. Specimens tempered at 600 to 625 °C exhibited primarily brittle fracture with average absorbed energies (24 and 31 J) below material specifications while specimens tempered at 650 to 700 °C exhibited mixed to primarily ductile fracture and average energies (69.7, 78, and 92.7 J) above the material specified minimums. Furnace tempering of welded tensile specimens at temperatures from 600 to 700 °C found that yield strength decreased from 885 to 701 MPa, ultimate tensile strength decreased from 964 to 789 MPa, and elongation increased from 12.5 to 20 pct. with increasing tempering temperature. Tensile fractures occurred in the weld softened heat affected zone which was further softened during the uniform furnace tempering.

In situ induction tempering investigations on the exothermic flux forge welded API Q125 steel casing found a high temperature gradient across the 22 mm wall thickness due to the skin
effect but demonstrated the potential to locally temper the hardened weld region without over
softening the soft HAZ region. With a tempering temperature just below the $A_1$ critical
temperature, specimens were able to meet Q125 grade tensile and Charpy specifications while
lower tempering temperatures resulted in too low Charpy energies and too high temperatures
resulted in too low tensile strengths and inconsistent Charpy fracture surfaces.
CHAPTER 7
INTERCRITICAL IN SITU HEAT TREATMENT EFFECTS ON THE MICROSTRUCTURE AND PROPERTIES OF EXOTHERMIC FLUX FORGE WELDED API Q125 STEEL CASING

7.1 Abstract

A multi-stage in situ induction post weld heat treatment that includes use of an intercritical heat treatment step is investigated as an approach for achieving API 1104 and ASME IX strength, bend, and toughness requirements for exothermic flux forge welded (EFFW) 14-inch (355.6 mm) diameter and 0.866” (22 mm) wall thickness 125 ksi (862 MPa) yield strength steel casing. The temperature dependent heat affected zone regions produced in each heating stage were investigated and positionally mapped. Use of an intercritical heat treatment step was found advantageous for producing a through-wall microstructure with sufficient strength to meet the material tensile strength requirements while also being able to pass bend tests and impact energy requirements. Five consecutive EFFW Q125 casing welds were produced using this post weld heat treatment approach with the tensile strength, bend, nick break, and Charpy results presented. By taking advantage of the unavoidable temperature gradients when induction heating thick walled ferromagnetic steel below the curie temperature, this PWHT approach enables relatively short PWHT cycle times compared with a traditional induction tempering approach.

7.2 Introduction

The ability to weld high strength steels including API Q125 grade steel casing is of growing importance to the energy sector. As the accessibility of known oil reserves decreases, deep well technology including improved joining of high strength well casing is needed for continued economical oil recovery. Additionally, high integrity joining solutions are needed to
minimize project risk including risk of environmental disaster in deep water oil fields. Welded high strength steel casing grades typically cannot meet the high strength requirements as measured by tensile strength while simultaneously meeting the ductility and toughness requirements as measure by bend and Charpy impact testing. To be economically viable for mass adoption for casing applications, a joining method must also be fast whereas traditional arc welding methods are too slow to be economical. The exothermic flux forge welding (EFFW) process is an automated high-throughput solid state welding process with in-situ induction post weld heat treatment capabilities. This study investigates the effects of a multi-step post weld heat treatment on the microstructure and mechanical properties of exothermic flux forge welding on API Q125 steel casing to determine if the method may be a viable approach to meet the needs for high integrity joining of high strength casing.

Uniform through-wall induction tempering is difficult on thick walled steel with high magnetic permeability. Without adequate tempering across the casing wall, a Q125 steel casing weld is unlikely to be able to achieve ASME IX impact absorption requirements. A multi-step heat treatment approach may be able to overcome these difficulties by including an intercritical heat treatment step where a significant portion of the weld region is intentionally exposed to peak temperatures between the $A_1$ and $A_3$ critical temperatures. This intercritical heat treatment step would produce a large intercritical microstructure region mid wall with the inner wall having been highly tempered and the outer wall having been fully reaustenitized. This approach, followed by a water quench and a temper cycle, is investigated in this study with the heat affected zone regions positionally determined and specimens characterized by API 1104 and ASME IX mechanical testing methods including tensile, bend, Nick-break, Charpy V-notch, and hardness.
7.3 Materials and Methods

Welded specimens were prepared by exothermic flux forge welding (EFFW) for investigation of post weld heat treatments. The welded specimens for this study were produced from 14-inch (355.6 mm) diameter American Petroleum Institute (API) Q125 grade pipes with a weight of 115 lbs/ft (171.1 kg/m) with the composition specifications and measured product certificate values shown in Table 6-1. The tensile strength specifications are shown in Table 6-2 with the yield strength measured at 0.65 pct. extension under load (EUL). The wall thickness of the pipe is specified as 0.812-inch (20.62 mm) but was measured at 0.866-inch (22.0 mm).

Table 7-1. API Grade Q125 steel casing chemical composition maximum specifications and product measured values.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>0.350</td>
<td>1.35</td>
<td>0.020</td>
<td>0.010</td>
<td>0.99</td>
<td>1.50</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>0.240</td>
<td>0.55</td>
<td>0.008</td>
<td>0.003</td>
<td>0.01</td>
<td>0.94</td>
<td>0.58</td>
<td>0.049</td>
<td>0.029</td>
</tr>
</tbody>
</table>

Table 7-2. API grade Q125 steel casing yield strength and tensile strength specifications.

<table>
<thead>
<tr>
<th></th>
<th>Minimum (MPa / ksi)</th>
<th>Maximum (MPa / ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Strength at 0.65% EUL</td>
<td>861.8 / 125</td>
<td>1034 / 150</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>930.8 / 135</td>
<td></td>
</tr>
</tbody>
</table>

The EFFW method includes using two pipe lengths with each having one end beveled to a rounded profile designed to deform to a low angle convex weld cap with a near flush inner wall when forge welded together. The steel pipes were positioned end-to-end in a forge welding machine with an offset gap of 0.11-inch (2.8 mm) between the pipe ends. An exothermic flux
ring was placed in-between the pipe ends. The exothermic flux ring was produced by uniaxial hot-pressing powdered constituents and was profiled to compliment the beveled pipe ends. The flux ring was composed of reactant constituents designed to undergo an exothermic chemical reaction producing molten oxide and fluoride products once ignited. The product materials are designed to serve as forge welding flux and protect the pipe faying surfaces from oxidation, reduce or dissolve existing surface oxides, and provide additional heat directly to the surfaces. The exothermic reaction also enables the flux to rapidly go from a solid to molten state so that the flux is fully functional in short time-scale induction heating processes. The rounded end profile on the pipes was designed to facilitate extrusion of the molten flux during forging.

The forge welding process involved application of induction heating to heat the profiled steel pipe ends and initiate the exothermic chemical reaction to produce the molten flux. The induction heating and molten flux heated the pipe ends to approximately 1200 °C at which time a position-controlled forging movement was applied. Following the forging step, the welded steel pipes were water quenched and then underwent in-situ post weld heat treatments by reheating with induction and utilizing in system water quench capabilities.

Testing methods used for this investigation are based on API 1104 and ASME IX standards as well as the ASTM impact testing standard [49, 50, 64]. In situ post weld heat treatment effects were investigated by cutting sections for tensile, bend, nick-break, Charpy V-notch, and metallographic/hardness specimens from the EFFW steel casing. Tensile, nick break, and bend testing was performed in a Zwick/Roell Z1200 frame. Charpy V-notch specimens were tested in Zwick/Roell PSW750 pendulum impact tester. Metallographic and hardness specimens were prepared by sectioning across the weld region, mounting, and polishing. Hardness measurements used an automated Struers Duramin A300 Vickers 10 kgf load. Hardness scans
were taken with 1 mm indent spacing with lines 1 mm from the outer wall, mid wall, and 1 mm from the inner wall. Metallographic specimens were etched using 2.0 pct. nital solution.

### 7.4 Results and Discussions

The effect of heating and cooling cycles on the heat affected zone (HAZ) microstructure was investigated. The forge weld heating cycle subjected two profiled pipe ends to a peak temperature of approximately 1200 °C with a heating time of 42.5 seconds. Upon reaching the peak temperature, the pipes were forged together to produce a welded connection and water quenched. An etched HAZ produced by the weld cycle is shown in Figure 7-1. The HAZ shown in Figure 7-1 was air cooled following the forge instead of water quenched to produce a lower hardness microstructure to facilitate sectioning of the weld region for analysis. The HAZ regions are shown with corresponding peak temperatures and position from the forge line.

The coarse grain region shown in Figure 7-1 results from austenitic grain growth during exposure to forging temperatures above approximately 1100 °C. Precipitates can anchor or pin grain boundaries and limit grain growth [71]. The chromium, vanadium, niobium and molybdenum additions can form $M_{23}C_6$ carbide and MX carbo-nitride precipitates that pin grain boundaries and limit grain growth below about 1100 °C. Around 1000 °C, the $M_{23}C_6$ type precipitates begin to dissolve with complete dissolution around 1100 °C but the MX type precipitates continue to limit grain growth until they begin to dissolve at 1100 °C with dissolution complete by about 1200 °C [72]. The region has an acentric hourglass shape due to a combination of the heating profile and material flow during forging. The bulk of the heat input was from an externally positioned induction coil that produced increased heat in the outer portion of the pipe wall shown at the top of the macrograph. The steel pipe end profile was designed
with a convex curvature with the highest amount of plastic flow occurring at the apex of the convex region where the two pipe ends first contact.

Figure 7-1. API Q125 steel exothermic flux forge weld heat affected zone showing the grain coarsened, fine grained, intercritical, and over-tempered regions along with the corresponding peak temperatures experienced. The specimen was produced by subjecting two steel casing ends to induction heating, forging them together, and then air cooling.

The fine-grained region in the steel HAZ is adjacent to the coarse-grained region and is formed by heat sufficient for austenite transformation, but below the grain coarsening temperature of around 1100 °C. Outside of the fine-grained HAZ is a relatively small intercritical HAZ. The intercritical region was exposed to temperatures between the $A_1$ and $A_3$ critical temperatures and was partially transformed to austenite. The untransformed ferrite will have softened from the high temperature exposure. Adjacent to the intercritical region, the steel was exposed to temperatures below the $A_1$ critical temperature, but sufficiently high to temper the
region and reduce the hardness below the base metal values. Outside of this region, the steel is largely unaffected.

Following the forge cycle, a grain refinement heat treatment cycle was applied by heating the welded region to approximately 950 °C and holding for about 2 minutes and 40 seconds. This provided enough heat to austenitize the weld region including the prior coarse-grained, fine-grained, and intercritical regions, with the new intercritical region extending past the previous overtempered region from the forging thermal cycle. Following the heat input, the region was water quenched. The HAZ produced by the grain refinement cycle is shown after polishing and etching in Figure 7-2 along with the temperature range and positions of the HAZ regions. The shown macrograph specimen was also subjected to a tempering cycle soften the region and facilitate sectioning for analysis. The macrograph shows that the previous coarse-grained region has now been refined and the inner region is now fine-grained steel.

The intercritical region in the steel specimen shown in Figure 7-2 after the grain refinement step is wider than the forge cycle intercritical HAZ due to the longer heating time resulting in a less steep temperature gradient than in the more rapid forge heating cycle. Outside of the intercritical region is the overtempered region with unaffected parent steel outside of that region. It is preferred that the overtempered regions from the previous heat treatment cycle are fully re-austenitized and hardened in the subsequent water quench to fully overwrite the previous HAZ and prevent overlapping softened regions. Therefore, the widening of the heat affected zone in this step is intentional to produce a grain refined inner region with a single outer transition and softened region.
Following the grain refinement and water quench cycle, the primarily martensitic and grain refined region was heated to produce a large intercritical region within the hardened area. A fully heat-treated specimen is shown in Figure 7-3 revealing the intercritically heat treated region within the previously grain refined region. The newly heated region had a graded temperature with the hottest area, representing about 5.5 mm in each direction from the weld line at the outer wall having been fully re-austenitized. The fully re-austenitized region only penetrated about 8 mm into the total wall thickness of about 25 mm in this weld capped region. The intercritical region extends about another 5.5 mm along the pipe wall axial direction and extends about 12 mm past the fully re-austenitized region to a total depth of about 20 mm across the wall thickness.
Outside of this intercritical region, the region that had been hardened in the prior heat treatment cycle has been tempered to improve ductility and toughness. The intercritical region from the previous heat treatment cycle is also visible near the outer edges of the macrograph and is unaffected by the new heat treatment cycle. A water quench was performed following heat input to harden the re-austenitized and partially re-austenitized material. The specimen was then exposed to an additional thermal cycle at approximately 700 °C to temper the newly martensitic material. Because the regions near the inner wall have already been tempered by the intercritical heat treatment step, the final tempering cycle only needs to adequately temper the newly formed martensitic material.

Figure 7-3. Exothermic flux forge welded API Q125 steel heat affected zone is shown after an intercritical heat treatment following the grain refinement heat treatment cycle. The fine grained, intercritical, and tempered regions are shown with the corresponding peak temperatures experienced.
The full four step heating and cooling profiles used for the weld and post weld cycles are shown in Figure 7-4. The thermocouple data shows that the peak temperatures are experienced in the forge central (0 mm) outer diameter position. At the high forging temperatures before the pipes have been forged together, the temperature is next highest on the inner diameter central position.

Figure 7-4. Full thermal exposure of the API Q125 steel casing showing forging heat, grain refinement, intercritical heat treatment, and tempering cycles. Each cycle was followed by a water quench.

In the post weld heat treatment cycles, the outer diameter ± 18 mm position has the next highest temperature highlighting the increased temperature gradient across the wall thickness at the lower temperatures due to the reduced induction penetration depth below the Curie temperature when the steel loses its ferromagnetic properties. The inner diameter ± 28 mm
positions are the coolest for all heating cycles as expected as this is the combined axially and radially furthest position from the induction heating coil. The inner diameter ± 18 mm positions notably have higher peak temperatures than the outer diameter ± 28 mm positions due to the induction heat input concentration near the induction coil and the primary heat transfer mode being axial conduction along the pipe walls.

During the water quench, the outer diameter positions show significantly higher cooling rates than the inner diameter positions owing to the water application to the outer diameter surface. The critical cooling times from 800 °C to 500 °C, abbreviated as $t_{8-5}$, are 3 to 4 seconds for the outer diameter positions but approximately 25 seconds for the inner diameter positions. The uneven peak temperature region on the second heating cycle is due to use of axial ‘scanning’ movement of the induction coil during this stage of the heating in an effort to better control the placement and the width of the softened heat affected zone regions. Due to this scanning movement, the coil position was not symmetrically distributed so the indicated plus and minus positions may deviate in temperature for this scanning cycle which is not represented in Figure 7-5.

Vickers 10 kgf hardness scans were performed on polished weld sections with spacing of 1 mm between points along axial lines. Hardness scan lines were taken at approximately 1 mm from the outer diameter, along the middle of the wall, and 1 mm from the inner diameter. Weld sections were evaluated around the circumference at positions 50, 142, 230, and 322 degrees from the front of the weld chamber. The etched macrographs, hardness can plots, and macrograph specimens with a hardness color mask applied are shown in Figure 7-5. The positions show relatively good uniformity with variation due primarily to imperfect induction coil centralization.
Figure 7-5. Exothermic flux forge welded API Q125 steel casing etched macrographs (on left) reveal heat affected zone regions from multiple heating cycles. Vickers hardness scans (center) show the corresponding hardness values 1 mm from the outer diameter, across the mid-wall, and 1 mm from the inner diameter. Hardness maps are overlaid onto the macrographs (right) with the hardest regions colored red and the softest regions green.

The hardness scans reveal that the fully re-austenitized region at the outer diameter produced in the third (intercritical) heat cycle and tempered in the fourth (tempering) heat cycle is harder than the surrounding areas. The regions just outside the intercritical region show low relative hardness measurements. Further away from the intercritical region but still within the region austenitized and quenched in heat cycle 2 (grain refinement) show the hardness is increased where the martensite has been more moderately tempered. Outside of this region, the hardness is again reduced at the intercritical and over-tempered zones from heat cycle 2 (grain
refinement). The right side of Figure 7-5 shows the same macrograph specimens on the left with the measured hardness values mapped to the specimens as colors with red as the hardest and green as the softest regions. The hardness overlay map shows the same region-based features visible in the HAZ macrographs. A micrograph of the intercritically heat treated region is shown in Figure 7-6 after intercritical temperature exposure, water quench, and tempering stage. The micrograph shows the mixed ferritic and lightly tempered martensite/pearlite microstructure with the martensite/pearlite appearing dark.

Figure 7-6. Light micrograph of API Q125 steel region heated between the $A_1$ and $A_2$ intercritical temperatures, water quenched, and then tempered. The light phase is primarily ferrite while the darker regions are primarily lightly tempered martensite/pearlite.
Five consecutive welds were produced using the exothermic flux forge weld method followed by in situ post weld heat treatments using induction heating. Each weld and post weld heat treatment utilized the same process variables including a post weld stage exposing the weld region to temperatures between the $A_1$ and $A_3$ critical temperatures. The heating and cooling sequences correspond to this shown in Figure 7-4. The welded and post-weld-heat-treated casing tubulars were sectioned and characterized by microstructural investigation, hardness scans, side bend, nick break, tensile, and Charpy V-notch. For welded Q125 steel, it is challenging to achieve both the specified tensile strength and the impact energy so this investigation in part was to examine the feasibility of the exothermic flux forge welds to consistently meet both of these specifications using the outlined thermal processing. The test results from these five welds are presented in Table 7-3.

The test results from the five welds exhibited relatively consistent results for ultimate tensile strength and yield strength meeting the material specifications. The U.T.S. range across all specimens was 953 to 969 MPa showing a sample standard deviation of only 5.9 MPa or 0.6 pct. of the mean value. The yield strength range across all specimens was 861 to 899 MPa showing a sample standard deviation of 10.5 MPa or 1.2 pct. of the mean. More variation was found in the elongation at break with a range across all specimens of 6.5 to 13.5 pct. and a sample standard deviation of 2.1 pct. which is 27 pct. of the mean. The Charpy V-notch energy absorption at -20 °C also had larger variation than the strength values with a range across all specimens of 52 to 92 J with a sample standard deviation of 16.3 J which is 23% of the mean value.
Table 7-3. Weld test results for five consecutive exothermic flux forge welds of API Q125 steel casing using the same four-stage heating cycles.

<table>
<thead>
<tr>
<th>Weld</th>
<th>Tensile U.T.S. (MPa)</th>
<th>Y.S. (MPa)</th>
<th>Elongation (%)</th>
<th>Charpy V-notch -20 °C (J)</th>
<th>Side bends (Location - Result)</th>
<th>Nick Breaks (Location - Result)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>955</td>
<td>886</td>
<td>7</td>
<td>76</td>
<td>40 deg. - Pass</td>
<td>0 deg - Pass</td>
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<tr>
<td></td>
<td>953</td>
<td>873</td>
<td>6.5</td>
<td>92</td>
<td>220 deg. - Pass</td>
<td>90 deg. - Pass</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>86</td>
<td></td>
<td>180 deg. - Pass</td>
</tr>
<tr>
<td>2</td>
<td>958</td>
<td>899</td>
<td>6</td>
<td>60</td>
<td>40 deg. - Pass</td>
<td>0 deg - Pass</td>
</tr>
<tr>
<td></td>
<td>968</td>
<td>888</td>
<td>8</td>
<td>76</td>
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<td>90 deg. - Pass</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<td>78</td>
<td></td>
<td>180 deg. - Pass</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>270 deg. - Pass</td>
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<tr>
<td>3</td>
<td>969</td>
<td>890</td>
<td>8</td>
<td>67</td>
<td>40 deg. - Pass</td>
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<tr>
<td></td>
<td>955</td>
<td>881</td>
<td>7.5</td>
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<td>46</td>
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<tr>
<td>4</td>
<td>966</td>
<td>877</td>
<td>13.5</td>
<td>70</td>
<td>40 deg. - Pass</td>
<td>0 deg - Pass</td>
</tr>
<tr>
<td></td>
<td>955</td>
<td>876</td>
<td>7</td>
<td>88</td>
<td>220 deg. - Pass</td>
<td>90 deg. - Pass</td>
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<tr>
<td></td>
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<td>88</td>
<td></td>
<td>180 deg. - Pass</td>
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<td></td>
<td>270 deg. - Pass</td>
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<tr>
<td>5</td>
<td>961</td>
<td>884</td>
<td>9</td>
<td>52</td>
<td>40 deg. - Pass</td>
<td>0 deg - Pass</td>
</tr>
<tr>
<td></td>
<td>960</td>
<td>861</td>
<td>7</td>
<td>92</td>
<td>220 deg. - Pass</td>
<td>90 deg. - Pass</td>
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<tr>
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<td></td>
<td>52</td>
<td></td>
<td>180 deg. - Pass</td>
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<td></td>
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<td>270 deg. - Pass</td>
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</tbody>
</table>

The mean values and sample standard deviations for tensile ultimate and yield strength and Charpy impact energy for each weld and for all five welds are shown in Figure 7-7. There is some indication of an inverse relationship between the yield strength and Charpy impact energy values that can be inferred from the plot. The ultimate tensile strength was relatively consistent across all welds and specimens while the Charpy impact energy values showed the largest standard deviations.

The side bend and nick-break tests are specified by API 1104 and are qualitative pass/fail tests [49]. The side bend specimens were produced according to API 1104 at 230 mm (9 in.) long, 13 mm (½ in.) wide, with smooth, parallel, and edge rounded sides, and the cover and root
weld caps ground flush. The welded steel specimens were then bent into a “U” shape using a 60 mm (2 5/16 in.) radius die and a 45 mm (1 3/4 in.) radius plunger.

![Graph showing Ultimate Tensile Strength (U.T.S) and Yield Strength (Y.S) measured at room temperature and Charpy V-notch impact energy at -20 °C for all five API Q125 steel casing exothermic flux forge welds. The error bars represent one standard deviation.](image)

Figure 7-7. Ultimate tensile strength (U.T.S) and yield strength (Y.S.) measured at room temperature and Charpy V-notch impact energy at -20 °C for all five API Q125 steel casing exothermic flux forge welds. The error bars represent one standard deviation.

All ten of the bend tested welded steel specimens (two per weld) met the passing criteria with no cracks exceeding 3 mm (1/8 in.) in any direction. Four nick-break specimens per steel weld (twenty total) were prepared from positions 90 degrees from each other by cutting specimens 230 mm (9 in.) long, 25 mm (1 in.) wide, and notching on all sides with a hack-saw approximately 3 mm (1/8 in.) deep. The specimens were pulled to fracture in a tensile frame. The exposed fracture surfaces were examined, and all showed complete bonding with no visible inclusions exceeding 0.8 mm (1/32 in.) or gas pockets exceeding 1.6 mm (1/16 in.) as specified in API 1104. Images of one of the welded sections of Q125 steel casing, etched metallographic
specimens, and the tested nick break, Charpy V-notch, tensile, and side bend specimens taken from the weld are shown in Figure 7-8.

Figure 7-8. Full array of specimens tested for each API Q125 steel casing weld. A) Exothermic flux forge welded casing, B) Etched metallographic specimens, C) Nick break specimens, D) Charpy V-notch specimens, E) Tensile specimens, F) Side bend specimens.
7.5 Conclusions

A multi-stage in situ induction post weld heat treatment that includes use of an intercritical heat treatment step is shown to be a viable approach for achieving API 1104 and ASME IX strength, bend, and toughness requirements for exothermic flux forge welded API Q125 steel casing. The temperature dependent heat affected zone regions produced in each heating stage were investigated and positionally mapped. Use of an intercritical heat treatment step was found advantageous for producing a through-wall microstructure with sufficient strength to meet the material tensile strength requirements while also being able to pass bend tests and impact energy requirements. Five consecutive exothermic flux forge welded 14-inch outer diameter and 22 mm wall thickness Q125 steel casing welds were produced using this post weld heat treatment approach with the tensile strength, bend, nick break, and Charpy results meeting the material requirements. By taking advantage of the unavoidable temperature gradients when induction heating thick walled ferromagnetic steel below the curie temperature, this post weld heat treatment approach enables relatively short cycle times compared with a traditional induction tempering approach.
CHAPTER 8
SUMMARY AND CONCLUSIONS

8.1 Summary

Welding processes inevitably alter the local microstructure and in turn affect the properties. For many grades of steels that require high strength, ductility, and toughness, it is difficult to maintain this combination of properties after welding. While full part heat treatments can sometimes be used to recover the microstructure and properties, this approach is impractical for welding of tubular strings in service. Therefore, advanced welding and localized post weld heat treatment methods are needed that can economically produce high integrity welds in tubular strings while maintaining strength, ductility, and toughness property requirements.

A novel exothermic flux forge welding method was investigated for welding of steel tubulars including a high strength low alloy (HSLA) steel and API Q125 grade steel casing with a 22 mm wall thickness. Post weld heat treatment approaches, including a multi-step post weld heat treatment that included an intercritical heating stage, were investigated on the welded tubulars for their effects on microstructure and properties. Performance characterization methods included tensile, bend, impact energy absorption, and strain life fatigue testing. Corrosion response was investigated by salt spray and submersion in NACE Solution A. Heat affected zone microstructure and hardness were also examined along with bond plane fracture using the nick break method. The investigated results include welded Q125 steel achievement of material specified strength, ductility, and toughness requirements and welded HSLA steel strain life fatigue mean reversals to failure 2.5 times higher than gas tungsten arc welded specimens.
8.2 Conclusions

Self-propagating high-temperature synthesis results were presented examining the effects of particle size, reductant (fuel) amounts in excess of reaction stoichiometry, and heating rate on ignition temperature, combustion temperature, and propagation rate. Findings included:

- With decreasing aluminum size, the passivation shell makes up a higher fraction of the particulate and should be accounted for in reaction stoichiometry.
- Nano scale reactants were found to lower the temperature of ignition of the propagating exothermic reaction with the size of the aluminum having a more significant effect than the size of the oxide reactant component. This effect remained significant in reaction systems designed to produce constant volume fractions of product phases despite a decrease in the calculated adiabatic combustion temperature for systems using nano aluminum due to the increased oxide shell fraction.
- Adding additional (hyper-stoichiometric) aluminum was also found to significantly increase the reaction propagation rate when locally ignited and the primary exotherm magnitude when heated using differential scanning calorimetry. The reaction systems for the hyper-stoichiometric aluminum investigations were designed to products with constant volume fractions of metal and slag but due to the lower volumetric heat capacity of aluminum relative to the copper it replaced also resulted in slightly increased adiabatic combustion temperature with increasing aluminum content.
- The effect of heating rate on enthalpy flow was also investigated using differential scanning calorimetry and found to affect the initiation and extent of completion of exothermic reactions.
The relationship between welding method and properties was investigated for gas tungsten arc welded (GTAW) and exothermic flux forge welded high strength low alloy (HSLA) steel. The experimental results included:

- Both GTAW and EFFW HSLA steel specimens demonstrated good performance across most of the investigated testing with ultimate tensile strength, face, root, and side bend tests, and Charpy V-notch results all meeting specifications. Salt spray corrosion testing of HSLA steel welded by both methods showed expected corrosion levels and acceptable uniformity.

- The GTAW HSLA steel specimens were found to have below specified yield strength while the EFFW specimens met the specified yield strength.

- Submersion in NACE Solution A showed the GTAW HSLA steel specimens developed a step interface and some signs of galvanic or crevice corrosion at the toe interfaces of the more noble weld metal and the parent metal. The step interface could act as a stress concentrator and potential initiation site for stress corrosion cracking or fatigue cracking.

- The EFFW HSLA steel specimens demonstrated uniform corrosion across the specimen with minimal difference between the weld region and the parent.

- The GTAW HSLA steel specimens had mean reversals to failure of 27 percent of the parent material in the ASTM E606 strain life testing and are estimated at 30 percent of the parent life for pressurized full tubes based on industry experience.

- The EFFW HSLA steel specimens demonstrated 68 percent of the parent strain life fatigue in the ASTM E606 testing and 75 and 74 percent respectively of parent life in 4 and 7 ksi pressurized full tube bend cycle testing.
These results including the significant fatigue life improvements demonstrate the potential of the automated EFFW process to extend service life and reduce in-service failures for butt welded HSLA steel coiled tubing. These results support the hypothesis that the solid-state exothermic flux forge welding method will show improved properties compared to a fusion welding process such as gas tungsten arc welding.

The effects of full-specimen furnace-based and localized induction-based heat treatment on heat affected zone microstructure and properties of exothermic flux forge welded 14-inch (355.6 mm) outer diameter and 0.866-inch (22 mm) wall thickness API Q125 steel casing were investigated. The experimental results for furnace tempered specimens included:

- Hardness of the exothermic flux forge welded API Q125 steel decreased with increasing tempering temperature over the 600 to 700 °C range with a greater than linear response. The maximum measured hardness values exhibited a larger decrease with tempering than the minimum measured hardness values.

- Impact energy of the EFFW API Q125 steel, measured by Charpy V-notch at -20 °C, was found to increase with increasing tempering temperature between 600 to 700 °C. Steel specimens tempered at 600 to 625 °C exhibited primarily brittle fracture with average absorbed energies (24 and 31 J respectively) below material specifications while specimens tempered at 650, 675, and 700 °C exhibited mixed to primarily ductile fracture and average energies (69.7, 78, and 92.7 J respectively) above the material specified minimums.

- Tensile response of the furnace tempered EFFW API Q125 steel tensile specimens found that yield strength decreased from 885 to 701 MPa, ultimate tensile strength decreased
from 964 to 789 MPa, and elongation increased from 12.5 to 20 pct. with increasing tempering temperature from 600 to 700 °C. Tensile fractures occurred in the weld softened heat affected zone which was further softened during the uniform furnace tempering.

• The furnace tempered EFFW API Q125 steel specimens that met the yield and ultimate tensile strength material specification requirements did not meet the Charpy energy requirements and vice versa.

In situ induction heat treated exothermic flux forge welded 14-inch (355.6 mm) outer diameter 0.866-inch (22 mm) wall thickness API Q125 steel casing results included:

• In situ induction tempering investigations of the API Q125 steel casing found a temperature gradient of 95 °C across the 22mm (0.866-inch) wall thickness due to the high frequency current skin effect but demonstrated the potential to locally temper the hardened weld region without over softening the soft HAZ region. With a peak tempering temperature just below the A1 critical temperature, API Q125 steel tensile and Charpy specifications were met. Lower tempering temperatures resulted in too low Charpy energies and increased tempering temperatures resulted in too low tensile strengths.

• A multi-stage in situ induction post weld heat treatment approach including an intercritical heat treatment stage was investigated for 22 mm wall thickness API Q125 steel casing and the temperature dependent heat affected zone regions for each stage were positionally mapped with corresponding hardness values.

• Five consecutive EFFW 14-inch outer diameter and 22 mm wall thickness API Q125 steel casing welds were produced using multi-stage post weld heat treatment approach
including an intercritical temperature stage with the measured tensile strength, bend, nick break, and Charpy results meeting material requirements.

- By taking advantage of the unavoidable temperature gradients when induction heating thick walled ferromagnetic steel below the Curie temperature, an in situ multi-stage induction heat treatment including an intercritical temperature stage enabled meeting EFW API Q125 steel casing ASME IX and API 1104 performance targets with relatively short PWHT cycle times compared with a traditional induction tempering approach.

The investigated results demonstrate that exothermic flux forge welding can be used to join 14-inch diameter, 115 lb/ft Q125 grade steel tubing, and in situ post weld heat treatment can be used to meet the required combination of strength, ductility, and toughness. These results support the hypothesis that localized induction-based heat treatment can be utilized to improve heat affected zone properties and rapid processing approaches will result in improved properties due to better control of the intercritical and softened HAZ regions.

### 8.3 Recommendations for Future Research

Continued investigations are recommended for characterization of the effects of exothermic flux forge welding process variables on the microstructure and properties of additional steel tubulars of commercial interest. It is also recommended to further evaluate scanning post weld heat treatment approaches that may be able to reduce the width of softened heat affected zone regions. Statistical reproducibility studies across large numbers of welds are also recommended along with correlation to in system non-destructive evaluation methods. Additional research on exothermic flux reactant and product compositional effects on steel and other metal forge weld interfaces should be investigated. Additional applications for exothermic fluxes slags, and glasses should also be investigated.
REFERENCES CITED


[69] "Coiled Tubing Fatigue Model," in "DEA-67, Phase II project to develop and evaluate coiled-tubing and slim-hole technology.," Maurer Engineering Inc., Houston, TX, 1996.


APPENDIX A

OVERVIEW OF ESTABLISHED WELDING METHODS

Table A-1. Overview of established welding methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc Welding (AW)</td>
<td>Arc welding processes include shielded metal (SMAW), gas-metal (GMAW), flux-cored (FCAW), gas-tungsten (GTAW), plasma (PAW), carbon (CAW), and submerged arc welding (SAW). Arc welding processes use an electrical arc between an electrode and the workpiece to generate molten filler metal which fuses with the base material in a fusion welding process. The SMAW process is not preferred for automation and is not considered further. The processes of GMAW, FCAW, GTAW, PAW, and SAW are all suitable for automated welding processes. However, SAW is best used in the horizontal downward position and the slag must be removed between passes, so this method is not further considered for the vertical configuration welding of tubulars. High quality welds can be produced with the GTAW process, but multiple passes are required for the wall thicknesses of interest. The PAW process can produce similar weld quality to GTAW but can weld thicker parts in a single pass when used in keyhole plasma mode. Keyhole plasma welding is suited to weld up to 6 mm thick steel in a single pass and can be used for the root pass on wall thicknesses above 6 mm. Keyhole mode allows welding of square butt joints without the use of filler metal although some filler may be required to prevent undercut. Subsequent passes can be completed with melt mode PAW, GTAW, GMAW, or SAW. Larger wall thicknesses require edge beveling to form a single-V butt to achieve full root penetration. When using keyhole mode to circumferentially weld a tubular, the keyhole must be closed with filler metal. Keyhole closure without porosity can be difficult but automated controls for reducing the gas flow and current slope-out have increased the closure repeatability.</td>
</tr>
<tr>
<td>Electroslag Welding (ESW)</td>
<td>Electroslag (ESW) and Electrogas welding (EGW) are related processes that use electric current to melt a large amount of filler metal under either molten slag or a shield gas. In ESW, an electric arc only occurs at the beginning of the process and subsequent heating is achieved by electro-resistance through the molten slag. The processes are attractive because of their high deposition rates for welding thick plates in the vertical position with the use of confining cooling shoes. This configuration is not well suited to joining well casing on a rig. Additionally, weld properties and toughness in particular are generally inferior to other processes. Energy inputs are typically hundreds of kilojoules per mm compared to 10 to 40 kJ/mm for most arc welding processes. The high energy input results in large amounts of molten metal and a relatively large HAZ. Due to the large amounts of molten metal, the process can be viewed as an in-situ casting process. The slow cooling rate results a course primary solidification structure with comparably poor mechanical properties.</td>
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Table A-1. Overview of established welding methods. Continued.

<table>
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<tr>
<th>Method</th>
<th>Description</th>
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<tbody>
<tr>
<td><strong>Laser Beam Welding (LBW)</strong></td>
<td>Laser beam welding uses a coherent high-power density focused beam of light to melt a thin layer of metal and produce a weld. With high powered continuous wave (CW) lasers, deep penetration welds can be produced. A 25 kW CO&lt;sub&gt;2&lt;/sub&gt; laser can weld steel plates up to 25 mm thick in a single pass. Typically, no filler metal is required which simplifies the process. The high-power concentration results in a narrow HAZ, but also results in high cooling rates. Laser welds in steels containing more than 0.25 percent carbon typically exhibit high hardness due to martensite formation resulting from the rapid cooling. Such welds may require a post weld heat treatment to reduce the weld hardness and provide the required ductility and toughness. Cooling rates can be somewhat reduced by using slower welding speeds or making a second pass adjacent to the initial pass. Hybrid processes that incorporate GMAW can also improve the weld properties for higher strength steels. High powered laser welders have a high capital cost but prices are expected to drop as technology continues to improve. Advances in high-powered solid-state fiber lasers allow for improved automation with a smaller footprint.</td>
</tr>
<tr>
<td><strong>Electron Beam Welding (EBW)</strong></td>
<td>Electron beam welding uses a focused beam of high velocity electrons to achieve high power densities of up to 10&lt;sup&gt;8&lt;/sup&gt; W/cm&lt;sup&gt;2&lt;/sup&gt; on the workpiece. These high-power densities enable deep weld penetration and high welding speeds. The high-power densities make joint preparation and positioning more critical than with lower power density processes. Generally, EBW is performed in a vacuum chamber which adds to the equipment cost and reduces the practicality for applications such as joining of well casing onsite on a rig.</td>
</tr>
<tr>
<td><strong>Thermite Welding (TW)</strong></td>
<td>Thermite welding is a fusion welding process based on in situ casting of molten filler metal generated by an exothermic reaction. Thermite welding of steels is usually accomplished by aluminothermic reduction of iron oxide to release heat and form aluminum oxide and molten iron. Alloying additions can be included to produce a chosen steel composition. The process typically utilizes a crucible where the reaction takes place and a mold where the molten steel solidifies and fuses with the parts being joined. Thermite welding suffers from course primary solidification and may have a high concentration of inclusions. Safety may be a concern since the rapid exothermic reaction may eject molten slag and metals or steam. The welds may also require post weld processing including grinding and post weld heat treatment to refine the grain size and produce the target microstructure.</td>
</tr>
<tr>
<td><strong>Flash Welding (FW)</strong></td>
<td>Flash welding uses electric resistance followed by application of pressure to join components of similar cross sections. The parts are typically placed in a butt-joint configuration with a small fixed gap between them. As the current flows across the part boundary, molten metal is formed and partially expelled by the rapid expansion. The arcing and expelled material creates a flash that cleans the surface of oxide and debris to facilitate coalescence. The process is fast and can be used to weld parts with cross sections of up to 130 cm&lt;sup&gt;2&lt;/sup&gt;. Welding of tubular geometries may result in non-uniform current flow and produce regions with poor weld quality. Flash welds typically require post weld grinding or machining to remove the “flashing” that is produced by the expelled metal.</td>
</tr>
</tbody>
</table>
Table A-1. Overview of established welding methods. Continued.

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
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<tbody>
<tr>
<td>Diffusion Welding (DW)</td>
<td>Diffusion welding is a solid-state welding process that utilizes heat and pressure in a suitable atmosphere to facilitate metallic bonding between parts. The surfaces to be joined must be carefully prepared to prevent voids and inclusions. Diffusion bonding can take place at temperatures between fifty to seventy percent of the melting temperature. Diffusion bonding is a relatively slow process and must usually be performed in an inert, reducing, or vacuum atmosphere adding to the process cost. Recrystallization, grain growth, and diffusion results in grains that extend beyond the original surfaces being joined and produces a high-quality homogeneous weld. The diffusion welding process alone cannot meet the speed requirements for on-site welding of well casing, but the principles of diffusion welding are applicable to other solid-state welding processes.</td>
</tr>
<tr>
<td>Forge Welding (FW)</td>
<td>Forge welding is a solid-state welding process that joins metal parts by heating them followed by application of a pressure to upset the surface. Forge welding has been used since ancient times by blacksmiths to hammer together hot steel. Automated processes can make use of hydraulic presses and microprocessors to control the application of pressure and heating. Forge welding in this manner is similar to upset welding and solid state high-frequency welding but is applicable to any heat source capable of heating the parts to temperatures around eighty to ninety percent of the melting temperature. Forge welding often makes use of a welding flux to protect the parts from oxidation and dissolve existing surface oxides. Due to the lack of specified forge welding heat source, upset welding and high frequency welding are presented separately.</td>
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<tr>
<td>Upset Welding (UW)</td>
<td>Upset welding is a solid-state forge welding process using electrical resistive heating with application of pressure that plastically deforms the ends to be joined. The solid-state nature of this process results in fewer weld defects than found in fusion welding processes. In addition, the weld metal does not undergo solidification and therefore has a superior microstructure. The process allows for welding of alloys with less concern for minor alloying additions and allows welding of many alloys that are considered unweldable by other processes. The process is fast and can rapidly weld large parts although the process may produce non-uniform current flow and heating with tubular geometries.</td>
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<tr>
<td>High-Frequency (HFW)</td>
<td>High-frequency welding uses a high frequency alternating current to resistively heat the parts to be joined. The high frequency results in a skin effect where the bulk of the current flows along the surface of the part. Current can be introduced into the work pieces by contacting electrodes or induced by an induction coil. High frequency welding can be used for both fusion and solid-state welding processes. The process is frequently used for continuous seam welding of tubes but could also be applied to butt joining of tubular ends.</td>
</tr>
<tr>
<td>Explosion Welding (EW)</td>
<td>Explosion welding uses an explosive charge to join metals by creating a rapid pressure wave. The explosive charge does not substantially heat the component metals due to the limited time for heat transfer. This low heat input results in maintaining the wrought parent microstructure and mechanical and corrosion properties that are equivalent to the parent metals. The process requires overlapping parts to form a lap joint and can be used on tubulars in this configuration. Although the welding process is extremely rapid, set-up can be time consuming. The use of explosives above grade on a rig presents safety concerns although explosive charges are used to create perforations below grade for well completions.</td>
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<td>Method</td>
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<tr>
<td>Friction Welding (FRW)</td>
<td>Friction welding utilizes friction created by contact between parts with one or both being rotated to produce heat and break up surface oxides and contamination. The rotational friction is combined with an axial pressure to upset the parts at the abutting surfaces and create a solid-state weld. Tubular parts are ideally suited for the friction welding process. For well casing and other long tubulars, an intermediary ring is rotated to avoid difficulties in the rotation of the long tubular parts. The intermediary ring bonds with the both the upper and lower tubular and thus creates two welds per joint. The kinetic energy can be provided either by a direct drive motor or by an inertial flywheel. Flashing is produced on both the outer and inner walls which may need to be mechanically removed following the weld. A related process, radial friction welding, uses “V” groove beveled pipe ends with a rotating ring with a slightly lower beveled angle. The ring can be rotated under compression outside of the joined parts or by expansion from the inside of tubular parts. The beveled design assists in alignment and can reduce or eliminate the need to mechanically remove flashing after welding.</td>
</tr>
<tr>
<td>Friction Stir Welding (FSW)</td>
<td>Friction-stir welding is a solid-state welding process that uses friction from a rotating tool to generate heat and mechanically intermix the parts being joined. The process can produce exceptional weld properties and was patented by The Welding Institute in 1991 [73]. The stirring tool first generates friction in one spot until it is heated enough for penetration of the tool into the parts to be joined. The tool then travels along the material interfaces until the weld is complete. For joining of tubulars end to end, the tool will need to pull out of the material after completing the weld. The tool pull-out will typically leave behind an exit hole which must be prevented or repaired for the process to be suitable for joining of tubulars. Some advances have been made with minimizing or preventing the exit hole by the addition of a consumable metal part placed over the exit location. The process is primarily used for welding aluminum alloys and problems with tool life limit the application to steels. Polycrystalline cubic boron nitride-based tools can be used to successfully FSW steel, but these tools are expensive and must be frequently replaced. Tools made of tungsten and molybdenum alloys have also been investigated with some success [74]. The travel speed in steel is relatively low compared to other welding methods.</td>
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Figure B-1. Equilibrium phases of an example flux composition over a temperature range of 0 to 2000 °C as predicted by direct minimization of Gibbs free energy using HSC 5.1 software.
Figure B-2. Calculated induction heating power density with depth in low alloy steel at an induction frequency of 1 kHz with each line representing the time when the steel has been fully austenitized to a depth indicated by the numerical subscript. Initially at $t_0$, the penetration depth is low due to the high magnetic permeability of the ferritic steel. At $t_1$, the first mm of steel is above the Curie temperature and has a higher penetration depth, but the steel transitions to ferritic and has a lower depth of penetration resulting in power concentrating in this area. At times with more steel over the Curie temperature such as $t_{15}$, the same effect is observed, but the power reaching this depth is reduced.
Figure B-3. Two-dimensional simulation of induction heating applied to cross-section of upper and lower profiled low alloy steel pipe ends. A two-turn rectangular profile induction coil is shown on the right. The upper left image is after 5 seconds of heating with a peak temperature near the coil of 801 K, the upper right image is after 10 seconds and has a peak temperature of 1160 K, the lower left image is at a time of 20 seconds and a peak temperature of 1219 K, and the lower right image is at a time of 40 seconds and peak temperature of 1458 K and ready for forging. As more of the steel is heated above the Curie temperature, the high-frequency induction heat has a deeper penetration depth and the heating becomes more uniform across the wall thickness. The simulation was created in COMSOL Multiphysics software.
Figure B-4. Three-dimensional simulation of induction heating applied to upper and lower profiled low alloy steel pipe ends shown in a cross-sectional view. A two-turn rectangular profile induction coil is shown around the outer wall at the ends of the pipes. The upper left image is after 5 seconds of heating with a peak temperature near the coil of 836 K, the upper right image is after 10 seconds and has a peak temperature of 1187 K, the lower left image is at a time of 20 seconds and a peak temperature of 1263 K, and the lower right image is at a time of 40 seconds and peak temperature of 1463 K and ready for forging. As more of the steel is heated above the Curie temperature, the high-frequency induction heat has a deeper penetration depth and the heating becomes more uniform across the wall thickness. The three-dimensional simulation has slightly increased temperatures from the two-dimensional simulation due to the three-dimensional curvature reducing the material on the inner wall compared to the two-dimensional case. The simulation was created in COMSOL Multiphysics software.
Figure B-5. Two-dimensional simulation of von Mises stress and deformation upon application of forging force to profiled pipe ends. The initial state is shown in the upper left with additional forging movement applied each step from upper right, to lower left, to lower right. The initial profile is shown in a black outline on each image with the deformed state and von Mises stresses represented by the colored body. The simulation was not able to continue deformation beyond the final state shown. The simulation as performed in COMSOL Multiphysics software.