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THE PYRO-METALLURGICAL, PHYSICAL AND MECHANICAL BEHAVIOR OF WELDMENTS

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The physical and chemical behavior of welding consumables were investigated in studies of the titanium and zirconium as grain refining nucleants in aluminum alloys, and studies of the influence of titanium, zirconium and boron additions on oxide inclusion formation and on the nucleation of acicular ferrite in microalloyed steel weld metal. The influence of electrochemical reactions during arc welding on weld metal composition was investigated for direct current welding processes including: covered electrode welding, gas-metal-arc welding, and gas-tungsten-arc welding. The influence of cover gas composition on the weld metal microstructural formation in gas-metal-arc welds was studied. Also the influence of underwater wet conditions on the weld metal metallurgy and the management of hydrogen in steel including its influence on weld pore formation have been studied.

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TABLE OF CONTENTS

ABSTRACT

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1.0 STATEMENT OF THE PROBLEMS RESEARCHED

Six different areas of research concerned with the pyrometallurgy and physical metallurgy of weld metal were addressed. These research areas included the following:

a. Titanium and zirconium grain refining additions were used to refine the microstructure and reduce hot cracking in aluminum alloy weld deposits. Microalloying additions to aluminum welding consumables were evaluated for their ability to improve weld metal properties.

b. Titanium, zirconium and boron additions were evaluated for their influence on the formation of oxide inclusions in steel weld metal and on the nucleation of acicular ferrite to enhance weld metal toughness. An experimental evaluation was made of models which suggest that lattice missmatch between the weld metal inclusion and ferrite is the primary factor in acicular ferrite formation.

c. Electrochemical experiments examined the influence of electrochemical reactions on weld metal composition in direct current arc welding processes. These experiments included the effects of polarity and of the high current density at the electrode tip on weld metal composition.

d. Gas-metal-arc welding experiments were used to study the influence of cover gas composition on the formation of oxide inclusions in steel weld metal. The objective was to evaluate the use of cover gas oxygen content as a welding parameter to achieve desired weld metal microstructure and properties.

e. Experiments were conducted to determine the influence of the wet underwater welding environment on steel welding metallurgy. An evaluation was made of the ability to predict weld metal microstructure and properties even in a severe wet environment with high cooling rates and excessive hydrogen pickup.

f. Methods to manage hydrogen in steel and steel weldments were studied to evaluate hydrogen pick up in steel and the formation of weld metal porosity as functions of moisture content in the cover gas.

2.0 SUMMARY OF RESULTS

2.1 Grain Refinement and Hot Cracking in Aluminum Alloy Weld Metal

Titanium and zirconium grain refining additions were made to aluminum alloy filler metals to investigate the mechanism for nucleation and grain refinement, and the influence of the refined solidification structure on weld metal hot cracking. This investigation used systematic variations in titanium and zirconium additions with cold wire feed gas tungsten arc welding to fully evaluate the nature of aluminum weld metal grain refinement. This investigation required special preparation of the experimental consumable at CSM (3.1-12).

Significant improvement in both weld metal grain refinement and hot cracking resistance was found with proper amounts of these additions (3.1-5,11,15,18). These results are consistent with our earlier finding using yttrium microadditions to the weld pool (3.1-3).

Experiments with titanium and zirconium additions to aluminum welding consumables showed that $TiAl_3$ and $ZrAl_3$ particles are effective nucleants, but that they are susceptible to dissolution in the weld pool environment, and that they must be present prior to welding in order to achieve nucleation and grain refinement. The grain refining response at a constant inoculant concentration was found to increase with increasing thermal undercooling of the weld metal (ratio of the thermal gradient to the solidification velocity). This effect is attributed to the decrease in dissolution times experienced by the particles and to an increased driving force for heterogeneous nucleation. The processing variables employed in the production of the welding consumable were found to have a strong influence on the morphology and size distribution of the intermetallic particles; and, thus on the grain refining. This work has resulted in a patent application for specially prepared aluminum welding consumables (3.2-1).

2.2 Steel Weld Metal Transformations

Acicular ferrite is known to have a major influence on the development of optimum strength and toughness in low carbon steel weld metal. The present research utilized titanium, zirconium and boron additions to evaluate several possible mechanisms for inclusions to influence the nucleation and growth of acicular ferrite. These mechanisms include: (1) Nucleation at inclusion surfaces with a low crystallographic mismatch, (2) Nucleation caused by an increase in strain energy due to differences in the coefficient of thermal expansion, and (3) Heterogeneous nucleation at intragranular inclusions promoted by a large undercooling caused by an increased prior austenite grain size. A fundamental understanding of the specific role of inclusions is necessary if new advanced welding consumables are to be developed and optimized based on sound metallurgical concepts.

Prior literature suggests that titanium and boron microalloying additions to the weld pool produce a microstructure with a high volume fraction of acicular ferrite, which enhances the weld metal toughness. Models suggest that boron hinders the formation of grain boundary ferrite which allows for a large undercooling that promotes the intragranular formation of fine acicular ferrite on TiO inclusions. These TiO inclusions have a very low lattice missmatch with ferrite, and this feature that has been suggested as a primary factor controlling acicular ferrite formation. This Ti-B model was investigated using zirconium, an element chemically very similar to titanium and aluminum which its chemically similar to boron. Even though zirconium and aluminum have chemical similarities with titanium and boron, they have distinct physical and structural characteristics which are different and allow for an interesting comparative analysis.

Zirconium was used as a surrogate for titanium additions to evaluate the various proposed mechanistic models for acicular ferrite formation. Zirconium additions of 0.02 to 0.05 wt. pct. with boron additions of 40 to 60 ppm were compared to titanium-boron additions to identify the structural role of zirconium relative to titanium (an element of the same periodic group). Zirconium oxide inclusions with a large oxide-ferrite crystallographic mismatch and titanium oxide inclusions with a small mismatch were compared to evaluate the suggested models. The difference in crystallographic mismatch allowed for evaluation of the leading model of Mori et al. which suggests that the lattice mismatch between TiO and ferrite is one of the primary factors in achieving acicular ferrite. The results showed that the crystallographic mismatch is not a major factor in the formation of acicular ferrite.

This work has also verified the role of boron in the suppression ferrite at the prior austenite grain boundaries and the promotion of intragranular acicular ferrite (3.1-6,17). Substitutions of 20 to 60 ppm. aluminum for boron in the titanium-boron system were used to study the influence of boron on blocking grain boundary ferrite nucleation. The results showed that the substitution of aluminum for boron (an element of the same periodic group) reduced the amount of acicular ferrite in the weld microstructure. Aluminum appears to act as a deoxidizer, and it did not segregate to the austenite grain boundaries. SEM analysis indicated the presence of both aluminum and titanium in the oxide inclusions. These experiments suggest that the ability of boron to block grain boundary ferrite depends on the fact that boron is a weak deoxidizer and that it needs to be protected by a strong deoxidizer such as titanium. This work has resulted in a patent disclosure for an optimal composition (3.2-2) for welding consumables for welding high strength - high toughness steels.

The results have shown that the lattice mismatch model does not explain the achievement of nearly 100 pct. weld metal acicular ferrite. The work reinforces the importance of boron as an agent to hinder the formation of grain boundary ferrite. This hinderance allows significant undercooling and increases the tendency to form intragranular ferrite. The concentration and size distribution of inclusions, rather than the type of inclusion, was found to be the major factor influencing intergranular nucleation of acicular ferrite.

2.3 Influence of Electrochemical Reactions on Weld Metal Composition in D.C. Arc Welding Processes

Previous research has shown that electrochemical reactions in the electroslag welding process has a significant influence on alloy element additions or losses and on the pickup or refining or tramp elements. The objective of the current research was to evaluate the influence of electrochemical reactions on submerged arc welding, gas-metal-arc welding and shielded metal arc (covered electrode) welding processes. Electrochemical perturbations to the weld pool chemistry suggest that current can alter the weld metal composition and thus microstructure. Experiments suggest that welding current modification can be used to adjust weld metal composition, microstructure and properties and maintain weld composition within the acceptable specification range (3.1-1, 13).

Research efforts on flux related processes have shown that composition changes can occur at four sites: the electrode tip, the detached droplet, the weld pool under the arc, and the weld pool after the arc has passed. Electrochemical changes are important at the electrode tip and in the weld pool under the arc. Electrochemical perturbations to the weld pool chemistry are also most likely to be important at the higher current densities. Thermochemical reactions predominate in the detached droplet and in the solidifying weld pool behind the arc.

In this investigation, welds were made with straight polarity (DCEN) and reverse polarity (DCEP) to alter the extent of electrochemical reactions. The experimental results show a significant influence of polarity. The straight polarity welds show the electrochemical pickup of alloying elements, and the reverse polarity welds show electrochemical losses. The behavior of molybdenum was found to be opposite to that of the other alloying elements. Molybdenum concentrations were higher for straight polarity welds than for reverse polarity welds. This behavior is the result of electrochemical iron losses at the anode and electrochemical iron pickup at the cathode. Iron is the major constituent in the alloy and it is more easily oxidized than molybdenum. The composition changes for manganese, silicon, and the other more easily oxidized alloy elements, along with the opposite behavior shown by molybdenum are strong evidence for the effect of electrochemical reactions during shielded metal arc welding (3.1-13).

The electrochemical behavior in gas shielded arc welding was also investigated. In this situation only positive ions can exist, and this limits the nature of the electrochemical perturbation to the pyrochemistry which occurs during welding. It was more difficult to find evidence of electrochemical influence in gas tungsten arc and gas metal arc welding process.

2.4 The Influence of Cover Gas Oxygen Content on Steel Weld Metal Microstructure and Properties

Some of the gas shielded arc welding processes have active gas components such as oxygen and CO_2. They are typically added to assist in arc stability and to maintain an acceptable weld bead morphology. In GMA welding it is common to introduce oxygen to the argon shielding gas. It is also common for some steel fabricators to use CO_2 additions to the Argon to reduce cost and increase productivity. These active gases introduce oxygen to the weld pool, and the increased oxygen influences the weld metal microstructure and properties. This investigation has correlated the variations in oxygen content with changes in the amount of a specific morphological type ferrite in the weld metal. The results of this research lead to the concept that the amount of active gas can be considered a welding parameter, which can be tuned to achieve optimum weld metal strength and toughness.

Variations in shielding has oxygen and CO_2 contents were investigated for three heat inputs and two different wires to quantify the weld metal microstructural variations. A plot of [O] + 1/4[Si] versus the content of hardenability elements provided a correlation between the composition and the weld microstructure (3.1-16). Much of this work was performed in an earlier ARO contract, but the final results were analyzed and reported in this contract period.

2.5 Underwater Wet Welding Metallurgy

Underwater wet welding causes major perturbations in the arc welding of steel. These perturbations involve the introduction of large amounts of hydrogen to the weld pool and an extremely large rate of cooling. These conditions cause porosity and the formation of unique weld metal microstructural features. This present investigation has extended our understanding of weld metal metallurgy and our ability to predict weld metal properties at these higher cooling rates.

Wet underwater welding consumable research, which used a pressure increase of one bar for each 10 meters increase in water depth, was able to identify the role of specific welding pyrochemical reactions and to demonstrate that metallurgical fundamentals can be used to develop new consumables which can achieve required properties in stringent environments. The CO reaction was found to be the controlling chemical reaction down to a depth of 100 feet, and this reaction was found to have a strong influence on the oxidation of alloying elements. Below this depth (below approximately 150 feet) the dissociation of water appears to be the dominant reaction which controls weld pool oxygen and the deoxidation process. The resulting changes in weld metal microstructure were directly correlated with these compositional modifications (3.1-10).

2.6 The Management of Hydrogen in Steel

Two projects have been completed which concern the management of hydrogen in steel. The first project developed a technique for the use of capacitance measurements to evaluate the moisture content of the flux coating in shielded metal arc electrodes (3.1-9).

The second investigation evaluated the hydrogen pickup during dry hydrogen annealing of high strength steels (3.1-20).

The use of capacitance to measure moisture in the flux coating of shielded metal arc electrodes was developed and evaluated during the last ARO contract period, but it was reported in this ARO contract period. The method offers an electronic method to nondestructively evaluate covered welding electrodes, and it has the potential to significantly reduce weld metal hydrogen pickup, especially in the fabrication of high strength steel structures.

It is known that reactions between water and molten steel can introduce significant amounts of hydrogen into the weld metal. The second project considered the influence of shielding gas dryness on the pickup of hydrogen by high strength steel at elevated temperatures. This investigation established accurate data for the hydrogen solubility and for the rate of hydrogen pickup by high strength steel in a dry hydrogen environment. These data will serve as the standard reference values for a future investigation which will determine the influence of moisture in the annealing or welding environment on hydrogen pick up in steel weld metal.

A systematic study was designed to quantify the presence of hydrogen in three high strength steels and evaluate any harmful effects. The solubility limits for hydrogen in AISI 4130, AISI 4340, and Laddish D-6ac steels were determined to be between two and three parts per million at 900°C and one atmosphere pressure. The equilibrium solubility is unique for each alloy composition and temperature. The equilibrium constant, K, has been determined for each alloy investigated and a value reported for future hydrogen solubility calculations.

The equilibrium solubility of hydrogen in the three high strength steels was found to be significantly less than the solubility in pure iron in the austenitic region. AISI 4130 steel, which contains the lowest total alloy content, showed the lowest solubility. AISI 4340 steel exhibited an equilibrium hydrogen solubility of 2.6 ppm at 900°C.

The change of standard free energy of solution of hydroger in three high strength steels was determined at austenitic temperatures. AISI 4130 steel showed the lowest entropy for hydrogen sites in the lattice. A comparison of pure iron with the three high strength steels showed pure iron to have the largest entropy for hydrogen solution in the lattice.

The ingress diffusivity of the three high strength steels was determined by the fractional saturation method. The activation energy for the three high strength steels is twice that reported by continuous permeation experiments which measured hydrogen mobility in pure iron. Alloy additions caused a reduction in the availability of sites for hydrogen in the lattice. The trap binding energy of hydrogen in the steel lattice becomes significant because it limits hydrogen transport.

The effusion of hydrogen from gaseous charged AISI 4340 steel was studied, and evolution rates were determined at various temperatures. Complete extraction of hydrogen was accomplished in one hour at 400°C. The diffusivity of hydrogen from gaseous charged AISI 4340 steel was determined for three different egress time periods. The activation energy and the frequency factor were in good agreement with similar studies. The comparison of egress and ingress diffusivities revealed the barrier effect of the oxide film formed when the samples were heated in air to expel hydrogen.

3.0 RESEARCH PUBLICATIONS AND PATENTS

3.1 Research Publications Resulting from ARO Support (1989-1992)

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12. Matthew J. Dvornak "A Consideration of the Processing Variables and Solidification Kinetics for Optimization of Titanium and Zirconium Additions in Relation to Weldability", Colorado School of Mines Ph.D. Thesis, T-3800, March (1990).

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3.2 Patent Applications and Patents Resulting from ARO Support (1989-1992)

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2. D.W. Oh, D.L. Olson and R.H. Frost, "Zirconium and Boron Microalloyed Filler Metals for Welding of Low Carbon Steel", Patent Applied for December, 1991.

3. R.H. Frost and D.L. Olson, "Exothermically Assisted Welding Consumables for Field Welding Application", patent disclosure, January, 1992.

4.0 PARTICIPATING SCIENTIFIC PERSONNEL

R.H. Frost - Co-Principal Investigator

D.L. Olson - Co-Principal Investigator

M.J. Dvornak - Graduate Research Assistant (completed PhD program in 1990)

W.J. Engelhard - Research Assistant (completed MS program in 1990)

J.H. Kim - Graduate Research Assistant (PHD program in progress)

D.W. Oh - Graduate Research Assistant (PhD program in progress)

J. Allen - Graduate Research Assistant (Ph.D. Program in Progress)

5.0 SIGNIFICANT ACCOMPLISHMENTS OF THIS CONTRACT

5.1 Improvement in both grain refinement and hot cracking resistance in aluminum weld metal can be achieved with proper amounts of zirconium, titanium, and yttrium microalloy additions.

5.2 $TiAl_3$ and $ZrAl_3$ particles were found to be effective nucleants and they must be present prior to welding in order to achieve nucleation and grain refinement. Aluminum welding consumables were developed (cast, annealed and drawn) which have these aluminides already present in the electrodes prior to use. A patent was awarded for this consumable development.

5.3 The role of titanium and boron microalloy additions in the promotion of acicular ferrite in steel weld metal was clarified. The concentration and size distribution of inclusions, not the type of inclusion, was found to be the major factor for achieving high acicular ferrite contents. Boron, which is protected from deoxidation by the presence of titanium, retards the formation of grain boundary ferrite, and causes a large undercooling which allows for intragranular formation of fine ferrite on inclusions.

5.4 Electrochemical reactions have been found to be an important consideration in understanding the pyrochemistry which occurs in direct current arc welding. The results suggests that welding current modifications can be used to modified weld metal composition.

5.5 The reactive gas content in the shielded gas can be used as an effective welding parameter to achieve the desired weld metal strength and toughness.

5.6 The nature of the pyrochemical reactions in wet underwater arc welding were characterized and modeled as a function of depth (pressure).

5.7 A nondestructive technique based on the measurement of electrical capacitance was developed for determination of the moisture content of shielded metal arc electrodes. The method offers a practical way to reduce hydrogen pickup during the welding of high strength steel.

5.8 The hydrogen solubility limits and rate of hydrogen pickup were determined for three high strength steels. This data serves as a standard reference for future investigations on the influence of moisture in the welding environment on hydrogen pickup in steel weld metal.