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CRADA Final Report
for
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SURFACE TREATMENT FOR IMPROVING SULFIDATION RESISTANCE OF FOSSIL POWER SYSTEMS

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Managed by
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Metals and Ceramics

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CONTENTS

Abstract

The purpose of the cooperative research and development agreement (CRADA) between ABB Combustion Engineering, Inc. and the Oak Ridge National Laboratory (ORNL) was to develop improved, longer life, and corrosion resistance surfaces for fossil power system components for use primarily in sulfidizing environments. Four surface protection techniques were to be explored. These included diffusion process, weld overlay, hot-isostatic processing, and various spraying methods. The work was to focus on Fe_3Al-based iron aluminide to increase the component life. The successful completion of the CRADA would have required the achievement of the following four goals: (1) fabrication development, (2) characterization and possibly modification of the alloy to optimize its manufacturability and environmental resistance, (3) testing and evaluation of the specimens, and (4) fabrication and testing of prototype parts. Because of lack of active participation from the participant, this CRADA did not achieve all of its goals and was terminated prematurely. Work carried out at ORNL on the CRADA is described in this report.

CRADA Benefits to DOE

Carbon and ferritic steels of 1.25 to 9 Cr-Mo are commonly used in a range of boiler applications. Important issues for performance of these materials are related to their corrosion, sulfidation, oxidation, and erosion resistance. Iron aluminides based on Fe_3Al are the potential alloys to improve all concerns with the current alloys. However, the most economical method of applying them is through the weld overlay process. This CRADA has dealt with a range of aspects related to making the weld overlays with Fe_3Al-based alloys and resulted in an approach of using pure aluminum as the weld wire with surface weld overlay compositions to improve corrosion and erosion resistance of steels in low NO_X boilers.

Technical Discussion

<u>Alloy Identification and Basic Properties</u>

The Fe_3Al-based compositions developed at ORNL are shown in Table 1. All of these compositions contain 28 at. % (15.9 wt %) Al and 2 to 5 at. % (2 to 5 wt %) Cr. The sulfidation resistance of Fe_3Al-based alloys with and without chromium has been published.[1,2] These data show that the Fe_3Al-based alloys have significantly better sulfidation resistance than type 310 stainless steel. The addition of chromium reduces the sulfidation resistance somewhat, but it is still significantly better than type 310 stainless steel.

The density and melting point data for Fe_3Al-based alloys are given in Table 2. These data are useful in processing and application of Fe_3Al-based alloys by weld overlay and other surface modification processes. The elastic modulus data for the Fe_3Al-based alloys are given in Table 3.

Table 1. Chemical composition of Fe_3Al-based alloys
and type 310 stainless steel

Element	Alloy, weight percent			
	FAS	FAL	FA-129	Type 310[a]
C	--	--	0.05	0.08[b]
Cr	2.2	5.5	5.5	25.0
Al	15.9	15.9	15.9	--
B	0.012	0.01	--	--
Zr	--	0.15	--	--
Nb	--	--	1.0	--
Mn	--	--	--	2.0[b]
Si	--	--	--	1.50[b]
Ni	--	--	--	20.0
Fe	*c*	c	c	c

[a]Wrought composition.
[b]Maximum.
[c]Balance.

Table 2. Density and melting point data for Fe_3Al-based alloys
and competitive type 310 stainless steel

Alloy	Density		Melting temperature	
	lb/cu-in.	g/cm^3	˚F	˚C
FAS	0.236	6.53	2606 to 2691	1430 to 1477
FAL	0.235	6.51	2606 to 2691	1430 to 1477
FA-129	0.236	6.54	2606 to 2691	1430 to 1477
310 SS	0.290	8.02	2550 to 2650	--

Table 3. Elastic modulus of Fe_3Al-based alloys and 310 stainless steel

Temperature (˚C)	Young's Modulus (GPa)			
	Alloy[a]			
	FAS	FAL	FA-129	310 SS
23	183.0	201.0	207.0	200.0
150	178.0	193.0	198.0	190.0
300	167.0	179.0	*b*	176.0
500	159.5	160.5	166.0	162.0
700	135.0	148.0	144.0	141.4
900	116.5	134.5	130.0	110.3
1100	100.0	108.5	108.0	62.1

[a]All data on sheet material.
[b]Not available.

The thermal expansion data, which is critical for any method of surface improvement, is given in Table 4.

Table 4. Thermal expansion and thermal conductivity of wrought FA-129 alloy and 310 stainless steel

Temp. (˚C)	**Alloy**			
	FA-129		**310 SS**	
	Mean coefficient of expansion (10-6/˚C)[a]	**Thermal conductivity (w/m k)**	**Mean coefficient of expansion (10-6/˚C)[a]**	**Thermal conductivity (w/m k)**
100	15.41	*b*	14.76	4.76
200	15.88	*b*	15.66	5.66
300	16.70	*b*	16.20	6.06
400	17.93	*b*	16.47	6.64
500	19.18	*b*	16.74	7.51
600	20.37	*b*	16.83	8.37
700	21.00	*b*	18.00	9.53
800	21.84	*b*	18.36	10.05
900	22.79	*b*	18.90	10.80
1000	23.38	*b*	19.08	--
1100	23.37	*b*	--	--
1200	23.46	*b*	--	--

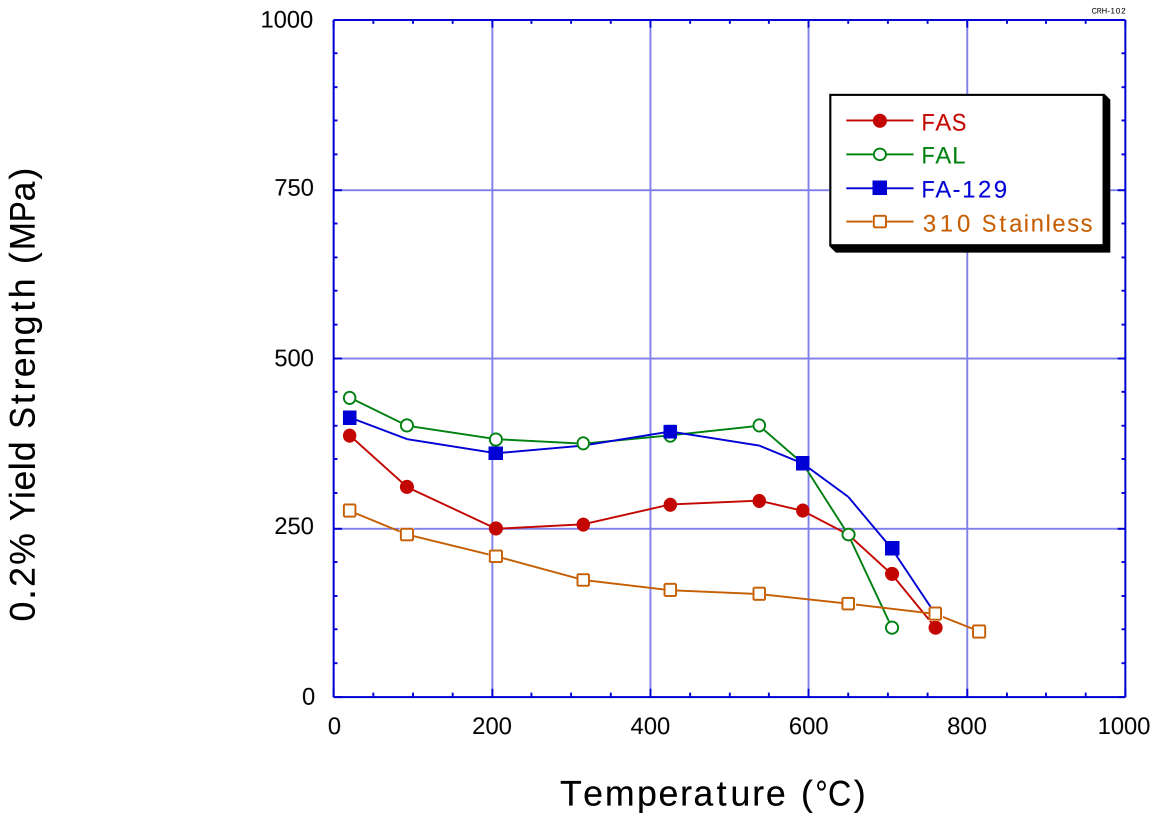
[a]Room temperature to specified temperature.
[b]Not available.

The strength and ductility data of Fe_3Al-based alloys are shown in Fig. 1.

The Fe_3Al-based alloys have limited ductility in the as-cast condition at room temperature. Typical processing of cast structure occurs at 1100˚C followed by subsequent processing at temperatures approaching 650 to 700˚C. The refinement of cast structure by processing and its heat treatment at 700˚C followed by oil (mineral) quench yields elongation values between 10 to 18% at room temperature. The cast structure will only have an elongation of 2 to 3%.

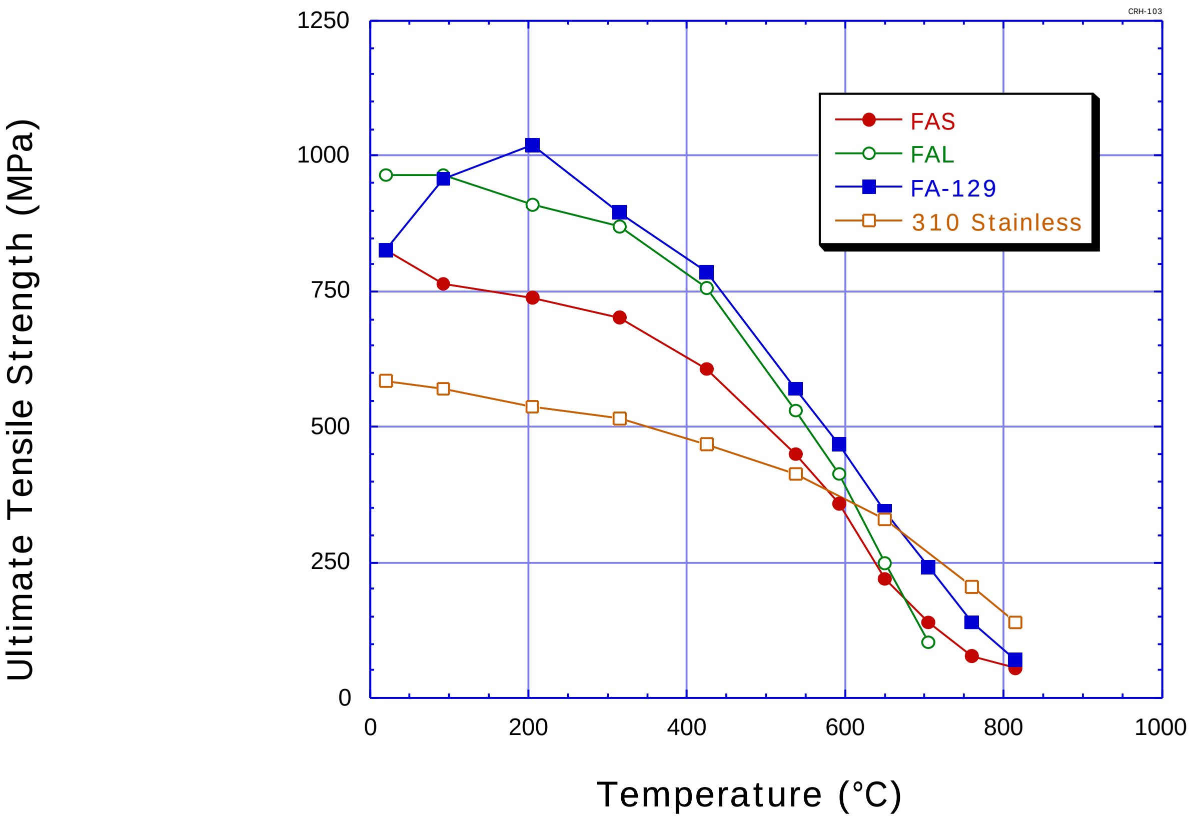
<u>Surface Enhancement of Boiler Steels with Iron Aluminide Alloy(s)</u>

Given the sulfidation properties, physical, and mechanical properties, the weld overlay was identified as the best method for surface enhancement of boiler steels (1.25Cr-0.5Mo alloy, commonly known as T-11). The weld wire for iron aluminide was prepared by three methods. These methods are described below.



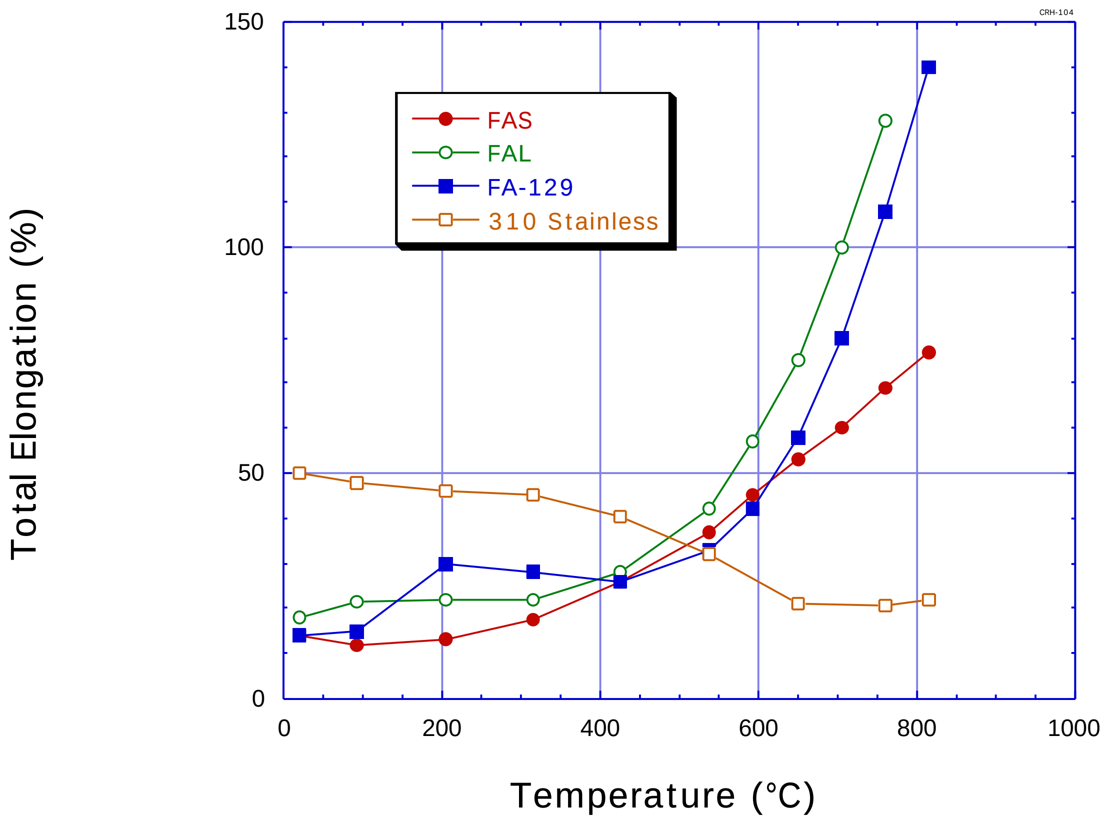
(*a*)

Fig. 1*a*. Comparison of average yield strength of wrought Fe_3Al-based alloys with that of 310 stainless steel.



(*b*)

Fig. 1*b*. Comparison of average ultimate tensile strength of wrought Fe_3Al-based alloys with that of 310 stainless steel.



(*c*)

Fig. 1*c*. Comparison of average total elongation of wrought Fe_3Al-based alloys with that of 310 stainless steel.

Short length trial wire by vacuum suction process: In this method, the desired alloy composition was air-induction melted and subsequently cast into weld wire by vacuum suction process using Pyrex™ glass tubes. The wires produced were 1/8-in. diam of typical length ranging from 12 to 18 in. This method permitted an inexpensive method for processing small batches of several different compositions.

Powder cored wire with elemental powders: In this method, elemental powders of the alloy composition are filled into a carbon steel strip formed progressively into a tube. The tube is subsequently sealed and powder consolidated by wire drawing process. This process was useful for producing continuous wire of different sizes ranging from 1/16- to 1/8-in diam. Vendors such as Stoody Company can run small batches of 50 to 100 lbs of wire by such a process. The process only requires steel strip and elemental powders. The weld process using the powder cored wire results in the desired alloy composition.

Solid core wire: In this method, a solid wire of aluminum is enclosed in a steel strip. Any of the alloying elements required is also added to the enclosure as elemental powder. This process also results in continuous wire of different sizes (1/16- to1/8-in. diam) and can be produced at a commercial vendor such as Stoody Company.

Weld Overlay Process

The weld overlay process on steels of different types (ferritic and austenitic) could be carried out using the filler wires produced by any of the methods described above. However, there were two issues noted.

1. The dilution effect in the first pass required using two weld overlay passes. The second pass generally resulted in some cracking because of low ductility in the as-cast condition.

2. The desired composition could be reached by compensating the weld wire for the dilution effect. However, it was noted that the aluminum loss occurred not only from dilution but also from the evaporation process.

In order to overcome the above issues, it was decided to check if pure aluminum wire, which is commercially available, could be used for the weld overlay process. The trial welds were made using the gas-tungsten arc (GTA) welding process with direct current and argon shielding gas. During the process, a molten weld pool is first established on the base metal, to which the aluminum wire is fed. The aluminum wire melts and reacts in the pool to form an alloy in situ with the base metal. The resulting weld deposit is an alloy of aluminum and the base metal. A cross-sectional view of a weld bead deposited on plain carbon steel plate is shown in Fig. 2. The weld bead was approximately 3 mm thick. There was no chemical segregation in the weld region shown in Fig. 2. Also, no indication of cracking or other weld defects were observed in Fig. 2. Examination of weld beads made under identical conditions by electron microprobe analysis determined that their concentration of aluminum was about 22.4 at. % (12.25 wt %). For any particular overlay deposit made by GTA welding, its aluminum content will depend

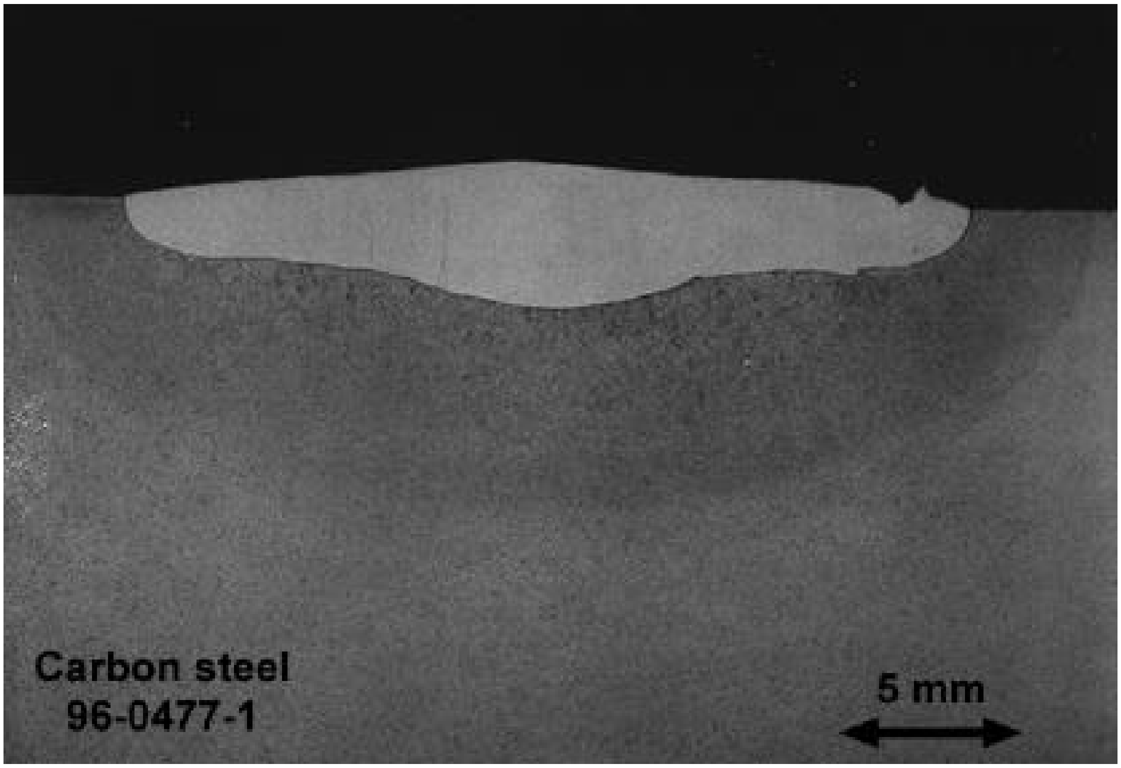


Fig. 2. Cross-sectional view of weld bead made by depositing aluminum wire on carbon steel using the gas-tungsten arc welding process.

substantially on the welding arc current, welding travel speed, and the aluminum wire feed rate into the molten weld puddle.

To further demonstrate this process, several sections of 75-mm-OD carbon steel tubing were aluminum weld overlaid by automatic GTA welding. The use of automatic welding allows for better reproducibility and uniformity of weld overlay thickness and chemical composition. A photograph of two aluminized tubing sections is shown in Fig. 3. For these welds the individual beads were deposited along the tube axes with slight overlapping. The chemical analysis results from specimens taken from several tubes are presented in Fig. 4. Each of these weld overlay deposits were made using identical welding conditions: arc current of 250A, voltage of 11V, arc travel speed of 10 ipm. However, each weld was made with a different aluminum wire feed rate, and Fig. 4 shows that as the wire feed rate increased from 10 in./min to 18 in./min the aluminum concentration in the weld deposit increased from 10.0 to 19.0 at. % (5.1 to 10.2 wt %). These data confirm that the aluminum concentration in the weld deposits can be controlled and varied.

Fig. 3. Sections of 75-mm-diam carbon steel tubing that were aluminized by automatic gas-tungsten arc welding.

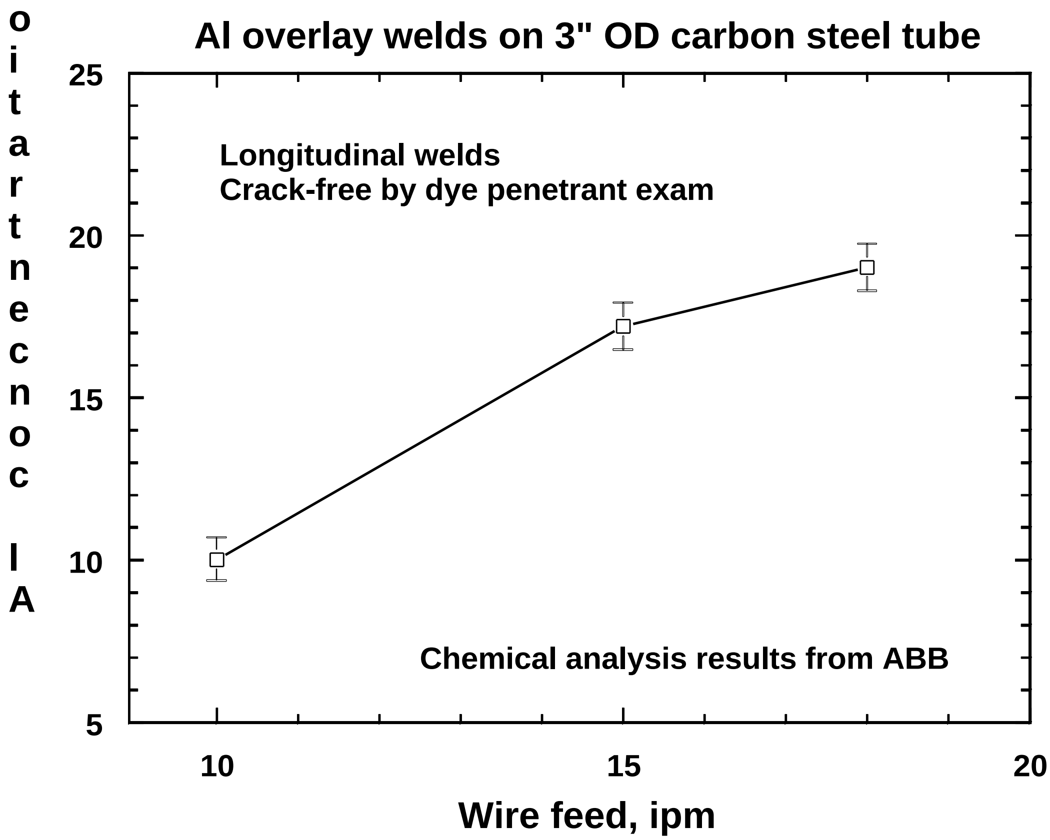


Fig. 4. Plot showing the variation of aluminum concentration in weld deposits on carbon steel with the rate of addition of aluminum wire into the weld puddle.

To assess whether the weld overlay aluminizing improved the environmental resistance of carbon steel, 0.5-in.-thick rings were cut from a tube like that shown in Fig. 3 and heated in air to temperatures of 500, 750, and 1000°C for 24 h. The oxidation of the carbon steel was dramatically improved by the weld overlay. For example, at 1000°C the thickness of the weld overlay was unchanged in 24 h, but the carbon steel's thickness was reduced by 0.040 in.

<u>Corrosion-Erosion Data</u>

An extensive corrosion-erosion study on weld overlaid composition of aluminum on steel with aluminum content of 10 wt % was carried out at Lehigh University.[3] This study showed excellent corrosion resistance of Fe-10 wt % weld overlays to aggressive low NO_X gas compositions and comparable erosion rates to commercially used alloys in the service temperature range (below 600˚C). The study further concluded that with the requirement of combination of weldability and corrosion resistance in moderately reducing environments, weld overlaid steels with aluminum are viable candidates for further evaluation for use as sulfidation-resistant weld overlays.

Inventions

The aluminum weld overlay process was invented (patent pending) through a separate work under way on weld overlay of FeAl (not Fe_3Al) compositions on steel. However, since resulting aluminum levels were of interest to the CRADA, some work was carried out on boiler tubes to demonstrate the applicability of the process.

Commercialization Possibilities

As additional corrosion and erosion data become available on steels weld overlaid with aluminum, there is strong potential for their commercial applications for boilers.

Plans for Future Collaboration

There are no plans for future collaboration in this area with ABB (now Alstom Power).

Conclusions

There was minimal interaction from ABB on this CRADA with ORNL. However, still it resulted in the evaluation of Fe_3Al-based iron aluminides as weld overlays of steels for improved corrosion and erosion resistance. Results of this CRADA demonstrated that while it was difficult to implement the weld overlays of Fe_3Al-based compositions, good results in producing corrosion- and erosion-resistant surfaces could be obtained through the use of weld overlays with pure aluminum wire. Testing of such coating at Lehigh University has confirmed the good combination of corrosion and erosion performance for low NO_X boiler environments.

Acknowledgments

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