Welding and Corrosion Performance of INCO-WELD 686CPT Filler Metal In Waste-To-Energy Power Plants

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ABSTRACT

The increasing amounts of PVC plastic contained in refuse, together with higher steam temperatures have shown that corrosion in refuse incineration boilers remains a concern. Nickel alloy welding consumables are used to provide protection against the highly corrosive environments found inside these boilers. The superheater tubes and water walls in waste incineration boilers are often overlaid with high nickel chromium molybdenum (Ni-Cr-Mo) alloys to provide improved corrosion resistance compared to carbon manganese and low alloy steels. For this application, alloy 625 (AWS A5.14 ERNiCrMo-3) is usually the alloy of choice. Whilst alloy 625 has performed well in many applications, there have been instances where it has exhibited accelerated rates of corrosion.

In recent trials, a number of different Ni-Cr-Mo alloys, including INCO-WELD 686 CPT filler metal (AWS A5.14 ERNiCrMo-14), have been used to weld overlay superheater boiler tubes. Following a period of use in a waste incineration boiler, it was observed that the tubes that had been overlaid with the 686 alloy exhibited both the lowest and most uniform rates of corrosion. The comparative corrosion performance of these tubes are presented together with metallographic and chemical analysis work which shows the beneficial effects within the nickel alloy weld overlay of the alloying elements molybdenum and tungsten on segregation and corrosion performance.

KEYWORDS

INCO-WELD 686CPT, waste-to-energy, corrosion, nickel alloys, weld overlay, cladding, alloy 625

1. INTRODUCTION

Corrosion, which arises from the burning of municipal solid waste in waste-to-energy boilers (WTE), has been the subject of extensive studies, as has that of corrosion in coal-fired boilers used for electricity generation. Domestic and commercial waste contains a variety of materials that on combustion form compounds that are carried in the flue gas leading to fireside corrosion. The principle corrosive agents in WTE boilers are compounds of chlorine for which the main sources are polyvinyl chloride (PVC) and alkali metal chlorides (Na + K). Other chlorides may be present, especially those of the heavy metals such as Pb, Zn and Sn.

The amount of chlorides derived from PVC has steadily increased since the 1960's and is forecast to further increase in the 21st century(1), making WTE boiler corrosion an even greater concern. In WTE boilers the relative concentration of sulphur compounds is lower than in coal-fired boilers, where corrosion from these compounds is the primary concern.

Corrosion in the chloride containing combustion environment is governed by competing oxidation-chloridation reactions that are also dependent on the alloy and localised environment.

Various researchers have proposed a number of chemical reactions that may govern the corrosion processes [2]. Some of these chemical reactions lead to the generation of chlorine gas and these play a critical role in the corrosion mechanism. It has been proposed in various studies that two types of corrosion are taking place with attack by chlorine and also hot corrosion from molten salts. The fly ash condenses on the boiler tubes and at sufficiently high temperatures molten salts are formed at the metal interface. These molten chloride salts, which have low melting points due to the formation of eutectic mixtures of alkali and/or heavy metal chlorides, can act as aggressive corrosive agents.

2. MATERIALS AND METHODS

2.1 Weld Overlay

The upper portions of the low alloy steel water walls and superheater boiler tubes in WTE boilers are overlaid with nickel alloy welding consumables to provide protection against the corrosive environments experienced. A number of methods have been used to overlay these areas including metal spraying, plasma welding and GMAW welding[3]. The GMAW welding process is widely used due to its high productivity, ability to weld in all positions and application of the process for in-situ use within the boiler. The Ni-21Cr-9Mo-3.5Nb alloy 625 (AWS A5.14 ERNiCrMo-3) is used extensively for this application. Whilst this alloy has provided acceptable performance, changes in service conditions, including excessive sources of chlorides and increases in operating temperature and pressure, may compromise the performance of the alloy. In pursuit of improved alloy performance in these aggressive environments, a number of superheater boiler tubes were weld overlaid with different high nickel Ni-Cr-Mo-W/Nb alloys, including the Ni-21Cr-16Mo-4W alloy INCO-WELD 686CPT (A5.14 ERNiCrMo-14). INCO-WELD 686CPT filler metal was selected as one of these alloys as this welding consumable has been found to exhibit excellent aqueous corrosion behaviour in aggressive acidic chloride environments[4,5]. Additionally, laboratory corrosion assessments, using simulated WTE environments, of different Ni-Cr-Fe and Ni-Cr-Mo alloys had shown that the 686 alloy exhibited improved corrosion resistance compared to other alloys[6]. Welding was conducted using the GMAW process with the overlay being deposited as a single layer spirally along the length of the tube. The tubes were of 48.3mm diameter and 4.5mm wall thickness in 13CrMo45 low alloy steel with an overlay thickness of 2.3mm. These superheater tubes were installed in a WTE boiler located in Europe for which the design operating temperature was 500°C.

2.2 Examination of Superheater Tubes

After an operating period of 8000hours the tubes were removed from the boiler and examined to determine the respective corrosion rates and investigate the corrosion mechanisms operating with in the boiler. Sections of the tubes were cut and cleaned to reveal the surface of the weld overlay for optical examination. Sections were also cut from the tubes for optical microscopy and SEM examination, including EDS analysis of the corrosion products and metal interface. The samples for microscopy were dry prepared to preserve the corrosion products remaining at the metal surface.

3. RESULTS AND DISCUSSION

3.1 Examination Of Tubes

The design operating steam temperature of the boiler was 500°C with a flue gas temperature of 630°C. Examination of the internal bore of the tubes indicated an internal metal temperature of 550-560°C based on the thickness of the oxide on the internal tube surface. During operation the

flue gas temperature had been measured at 630°C. On the basis of this information the estimated surface temperature at the weld overlay surface was 580-600°C.
All the tubes, which had been overlaid with various Ni-Cr-Mo-Nb/W alloys, were found to have been severely corroded resulting in large areas of penetration of the overlaid surface in all instances with the exception of the tube overlaid with alloy 686. Whilst there was a range of high nickel Ni-Cr-Mo alloys included in the test program, the comparative corrosion characteristics of the alloy 686 overlay, as the only alloy to resist penetration of the weld overlay, were compared to those of alloy 625, which is widely used in this application.

3.2 Chemical Analysis
Chemical anlysis of the weld overlays was coducted using EDS analysis at 10 different points on the nickel alloy overlay remiainng on the tubes. The average weld deposit analysis is shown in Table 1 together with the reported chemical analysis of the welding wires. A dilution level of 4% had been achieved in the alloy 625 deposit compared to over 8% in the alloy 686 deposit. This level of dilution, resulted in elevated levels of iron and consequent reduced levels of the other main alloying constituents of chromium, molybdenum and tungsten which is prejuditial to the corrosion resistance of the weld alloy overlay.

Table 1. Chemical anaysis of welding wires and weld overlays (ND – not determined).

	C	Mn	Si	Ni	Cr	Mo	Fe	Nb	W
626 Wire	0.008	0.01	0.08	64.4	22.19	8.84	0.36	3.60	-
625 Deposit	ND	ND	0.1	62.4	21.1	8.4	4.0	3.5	0.2
686 Wire	<0.01	0.22	0.02	58.52	20.41	16.26	0.36	-	3.94
686 Deposit	ND	0.3	ND	53.9	18.4	14.7	8.6	0.2	3.6

3.2 Alloy 625 Overlaid Tube
Large areas of penetrating corrosion were experienced (Fig. 1) with areas of overlay completely removed such that the carbon steel tube beneath the overlay was exposed and available for rapid corrosion and consequent penetration of the tube wall. Pitting of the surface was observed with a morpholgy consistent with the predominant corrosion mechanism being by chloride rich salt melts. Examination of the metal interface within the pitted regions also showed some preferential corrosion within the dendrite cores, consistent with gaseous chlorine attack.

3.3 Alloy 686 Overlaid Tube
Whilst the tube suffered from extensive general corrosion, the overlay remained intact without any pentration to the substrate tube. There is limited evidence of pitting of the surface from chloride salt melt attack. The metal interface shows leaching of the dendrite cores through gaseous chlorine attack.

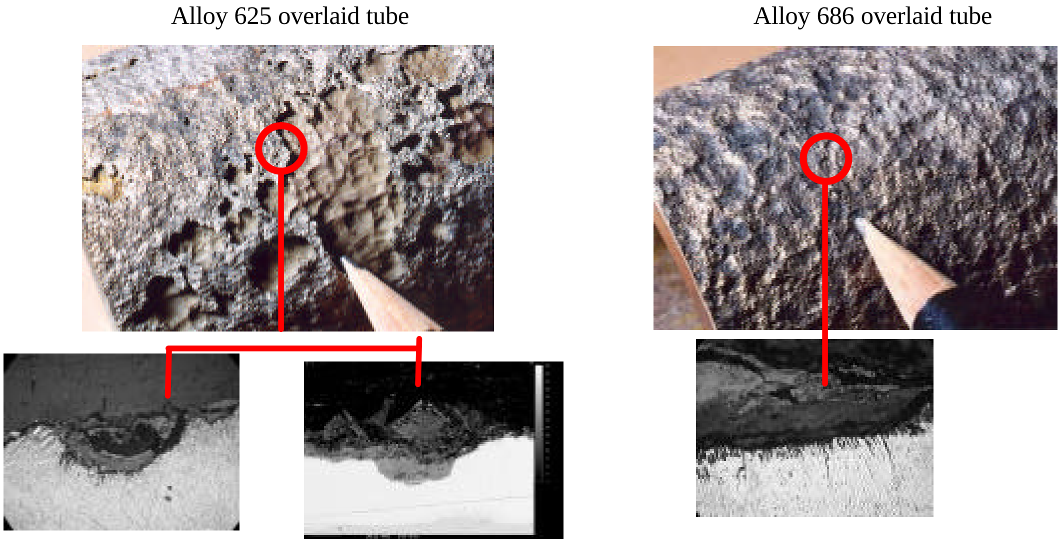

Figure 1 – Overlaid tubes removed from WTE boiler after 8,000hours of operation.

3.4 Corrosion Interface

Electron microprobe analysis of the overlaid surface (Fig. 2) and adjacent salt deposits clearly demonstrates that the elements iron, manganese, chromium and niobium are transported away from the corrosion interface thus offering little or no inhibiting resistance to corrosive attack. There is evidence that molybdenum, which has been leached from the alloy matrix, forms a partial boundary layer at the interface. The metal chlorides (of Fe, Cr, Mn etc), which are transported in the salt deposits away from the corrosion interface, become oxidised in the upper regions of the salt deposit leading to regeneration of the chlorine, which is free to return to the corrosion interface.

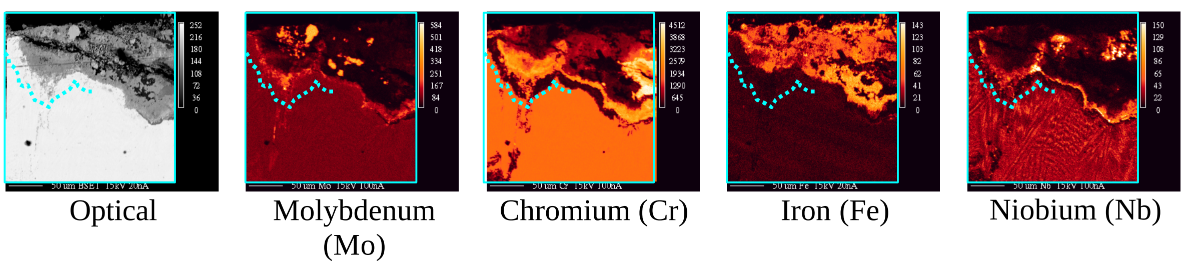

Figure 2. Element microprobe analysis of alloy 625 overlay after removal from the WTE boiler. *(Bright areas indicate regions of maximum element concentration; blue line indicates corrosion interface)*

For the alloy 686 overlay the elements molybdenum and tungsten remain in the corrosion zone (Fig. 3) whilst the other elements are leached out in the same manner as for alloy 625. Additionally, there is evidence of chlorine/chloride enrichment at the corrosion interface. It is postulated that a protective film, comprising primarily molybdenum but also tungsten oxy-chloride at the corrosion interface, protects the alloy from further attack by free chlorine or salt melt. Sulphur was found to be present in the salt melt in regions away from the corrosion interface, and although it is not directly involved in the metal salt reaction at the interface, it is strongly involved in the inter-slag reactions, supporting the corrosion mechanisms associated with chlorine.

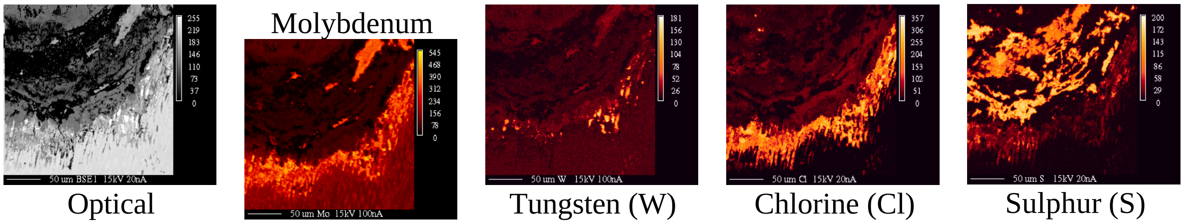

Figure 3. Element microprobe analysis of alloy 686 overlay after removal from the WTE boiler. *(Bright areas indicate regions of maximum element concentration)*

3.5 Discussion

In this investigation, of the corrosion behaviour of superheater tubes overlaid with a number of Ni-Cr-Mo-Nb/W alloys, it has been observed that the improved corrosion behaviour exhibited by alloy 686 is due to the formation of a protective film at the corrosion interface which is rich in the elements primarily molybdenum but also tungsten. The observation of the beneficial effect of increased levels of molybdenum, when operating at increased temperatures (550ºC), has also been observed in other studies of corrosion in WTE boilers[7,8]. The weld overlays completed with alloy 686 and alloy 625 exhibited preferential attack at the dendrite cores at the corrosion interface. This is due to the segregation of the main alloying elements during solidification of the weld deposit. In high nickel Ni-Cr-Mo alloys molybdenum segregates in the interdendritic regions, leaving the dendrite cores denuded in this element, whilst tungsten segregates in the dendritic cores. As such it is expected that the dendrite cores will corrode preferentially due to the lower alloy content in these regions and this has been observed in this investigation.

4. CONCLUSIONS

The industrial operating experience gained in a WTE boiler, using superheater tubes which had been overlaid with a number of high nickel Ni-Cr-Mo-Nb/W alloys, has shown that the only tube where the weld overlay has remained intact is that where INCO-WELD 686CPT wire was used for the overlay. The alloy 686 was found to have exhibited a more uniform rate of corrosion compared to that of all the other alloys, including alloy 625, which were evaluated in this program. This more uniform corrosion rate, demonsterated by the lack of perforation of the overlay, importantly provides increased availability of the WTE boiler to the operator of the WTE facility.

Alloy 686 exhibited resistance to corrosion by chloride rich salt melts with corrosion occurring primarily through chlorine attack. The high levels of molybdenum and tungsten in alloy 686 have been found to promote the formation of a protective film, which protects the alloy from chlorine/chloride attack. Whilst alloy 686 was the only alloy not to have experienced failure of the overlay, the weld deposit overlay exhibited a comparatively high level of dilution, demonstrating that alloy 686 provides tolerance to variations in weld deposit quality whilst still providing excellent corrosion behaviour.

Although alloy 686 is not immune to corrosion, it has provided the greatest operating life in this 8000hour exposure of the superheater tubes, which maximises the availability of the WTE boiler between planned shut-down periods.

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REFERENCES

(1) Wright I.G., Krause H.H., Nagarajan V., Boiler Tube Failures in MSW/RDF Incineration/Co-firing, EPRI Report TR-103658, Paola Alto, CA. 1994.

(2) Sorell G., J. Materials at High Temperatures, 13, 137-150, 1997.

(3) Takeuchi Y., Kawahara K., Hasoda T., Corrosion 2000, Proceedings 55th NACE Annual Conference, Paper No. 00261, Orlando, FL, USA. March 2000.

(4) Thornton C.E., Cooper C., Proc. Stainless Steel World 2004 Conf., Paper No. SSW2005-P0468, Houston, Tx, USA. 2004.

(5) Kiser S.D., Cooper C., Proc. Stainless Steel World 199 Conf., Paper No. SSW99-076, The Hague, Holland. 1999.

(6) Baker B.A., Smith G.D., Shoemaker L.E., Proceedings 56th NACE Annual Conference, Paper No. 01183, Houston, USA. March 2001.

(7) Kawahara Y., Kaihara Y., Corrosion 2001, Proceedings 56th NACE Annual Conference, Paper No. 01173, Houston, USA. March 2001.

(8) Kawahara Y., Nakamura M., Tsuboi H., Yukawa K., Corrosion 97, Proceedings 52nd NACE Annual Conference, Paper No. 165, New Orleans, USA. March 1997.