NICKEL ALLOY WELD OVERLAYS IMPROVE THE LIFE OF POWER GENERATION BOILER TUBING

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1. Abstract

Nickel base weld overlays are commonly used in the Power Industry to extend the life of equipment subjected to aggressive corrosion environments. Weld overlay via the Pulsed Gas Metal Arc process is the most common form of protection. Good bond integrity and thermal conductivity are desirable characteristics of such overlays in the interest of providing optimal life for overlaid components on waterwalls as well as superheaters and reheaters. As boiler conditions have become more aggressive over the years, nickel base alloy overlays have become more commonly used, not just for repair and maintenance purposes, but also as a cost effective solution for new boiler installations. New nickel base products for use as overlays in advanced power applications will be discussed.

Keywords: Fossil boiler, waste-to-energy, waterwall, superheater, reheater, alloy 72, alloy 686

2. Introduction

Power Boilers that make significant contributions to the electrical grid are fired with various grades of coal (fossil fuels) and a variety of waste materials. Both types of boilers suffer from fireside corrosion, but the types of corrosion encountered in each are different and require different solutions. For waste-to-energy Boilers (WTE), waterwall overlays of alloy 625 (ERNiCrMo-3) provide best combination of corrosion resistance, protection and economy while WTE superheaters require INCO-WELD 686CPT (ERNiCrMo-14) for best service life. On the other hand, fossil fired boiler waterwalls are best protected with alloy 622 (ERNiCrMo-10) and superheaters and reheaters are well protected with INCONEL FM72 (ERNiCr-4). The two types of boilers will be addressed separately with historical commentary offered on how the optimum alloy choices have been made. Failure mechanisms are discussed and the attributes of the successful alloy choices are defined.

3. Fossil-fired Boilers

The clean air act of 1990 has provoked significant changes in how electrical power is generated by fossil fired boilers. Many units have been forced to add flue gas desulfurizers (FGD's) to control SO_2 effluent and many have added low NOx burners and other devices to reduce NOx emissions. With the advent of low NOx burners came the change in the boiler environment from SO_2 to H_2S which prompted the need for protective fireside waterwall overlays. Before the advent of low-NOx burners, ferritic steels maintained a corrosion rate of less than 5 mils per year, while corrosion rates of over 100 mils per year have been reported under the most severe low-NOx conditions. Due to the myriad of boiler designs, firing conditions, and creative solutions, there has been a progression of material selections for weld overlay that would claim to be best practice. The earlier stages of competition would seem to have eliminated chromized tubes and stainless steel 312 weld overlay, while relegating 309 overlays to subcritical boilers. This leaves the domain of supercritical boilers to the nickel-base alloys such as 625, 622, 52, 72 and the newcomer, 72M. Of these, alloy 625 has shown itself to be more effective in waste to energy boilers (WTE) than in fossil fired boilers. Circumferential cracking, also referred to as a corrosion fatigue mechanism, brought on by coal ash corrosion attack of segregated dendrite cores accompanied by oxide wedging to drive crack propagation, was found to be a short-coming for alloy 625 in fossil fired applications [1]. The addition of Nb in alloy 625 assists in creation of terminal liquid phase which backfills small microfissures that may form during welding. The same element which elicits such a positive response also exerts a negative effect upon the distribution of molybdenum in the weld deposit, leaving the dendrite cores poor in molybdenum, and susceptible to coal ash corrosion attack. Filler metal 622, with no niobium and fortification in molybdenum and tungsten, has offered significantly improved performance over that of alloy 625 primarily due to its lower tendency to segregate during solidification. The watershed 1000 square foot test panels of 622 versus 625 in the PP&L system over one decade ago established the preeminence of alloy 622 over 625 for fossil waterwall overlays. Therefore, the remaining best practice alloy selections for waterwall overlay are 622, 52, 72 and perhaps 72M. While there is a great deal of experience with 622 overlays, there are sparse data for waterwall weld overlays with 52 and 72. The current examination of 5000 square feet of FM52 at AEP's Muskingum River #5 is arguably the most substantial application in terms of both square feet of coverage and time of exposure to have been evaluated to date.

In addition to waterwall overlays, a second application that requires protection is the upper boiler tubing, namely superheater and reheater tubing. These tubular structures often suffer from accelerated erosion-corrosion damage that prompts the use of largely ineffective "shields". Thus, superheater and reheater overlays will also be addressed in this paper.

The chemical compositions of the alloys discussed in this paper are given in Table 1, along with their American Welding Society classifications.

3.1 FM 52 Overlay Experience

Inspection of the aforementioned 5000 square foot installation of FM52 overlay was performed in a 600 MW supercritical B&W boiler operating with 1005°F (566°C) steam

and burning “Eastern” coal containing 1% sulfur. The boiler operated without a

Table 1. Chemical Composition (Wt. %) for Materials Evaluated

Material	C	Ni	Cr	Fe	Mo	Nb	W	Al	Ti	Others	AWS Class
FM52	0.015	60.0	29.0	9.0	0.02	0.01	0.02	0.6	0.5		ERNiCrFe-7
FM72M	0.020	58.0	38.0	0.2	0.3	1	0.01	1	0.6		ERNiCr-7
FM72	0.015	56.0	43.0	0.2	0.01	0.01	0.01	0.15	0.6		ERNiCr-4
625	0.020	60.4	21.6	4.4	9.1	3.60	0.1	0.14	0.24		ERNiCrMo-3
622	0.004	59.3	20.4	2.3	14.1	0.04	3.1	0.25	0.06		ERNiCrMo-10
686CPT	0.01	58.5	20.4	0.4	16.2	-	3.9	0.32	0.08		ERNiCrMo-14
Carbon Steel	0.19	-		Bal.						0.3 Cu, 0.5 Mn	---

scrubber in nearly continuous service for 7-1/2 years. Neither circumferential nor longitudinal cracking of the waterwall tube overlay was observed. Fig. 1 shows grit blasted exposures of one location of three elevations including areas at each of the end walls where highest corrosion rates have been encountered. Even in highest corrosion rate areas, no beads were observed without original solidification ripples. Some were quite smooth yet faint indications of ripples were present. On the other hand, most of the overlays exhibited well defined ripples with only slight corrosion/erosion loss with no cracking observed at any location within the 5000 square feet of overlay.

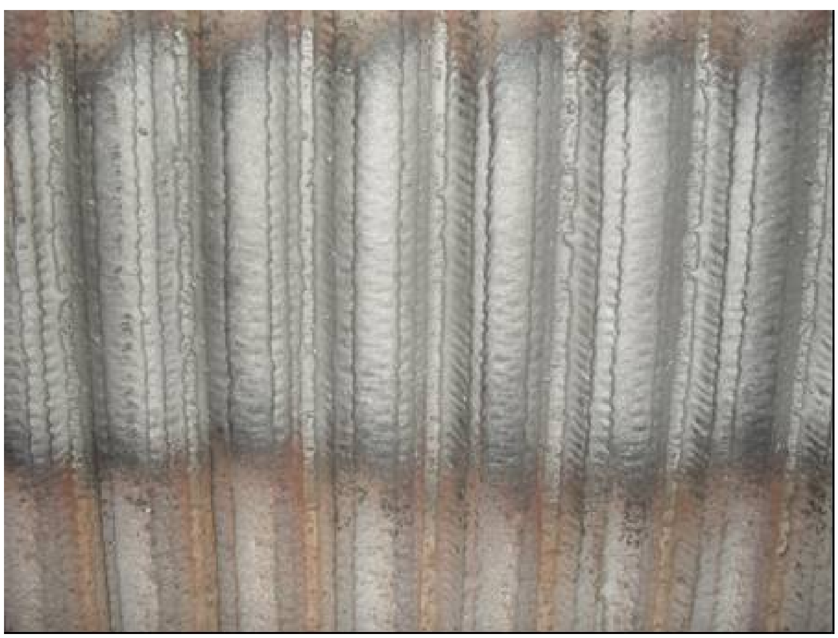

Fig. 1. Grit blasted section of waterwall section weld overlaid with FM 52 from AEP Muskingum River #5.

A second installation of filler metal 52 waterwall overlay has been investigated with contrary results. A major Northeastern utility has had a somewhat smaller overlaid area within one of their Combustion Engineering supercritical boilers that operated with

1020°F steam temperature while burning coal having 1.5 to 2.5 pounds of sulfur per MBtu. It was characterized as serving in base load service. After 5.5 years of this service, metallographic examination has revealed deep oxide notches within the surfaces (Fig. 2). These are often referred to as oxide wedges and are initially formed as cracks which are

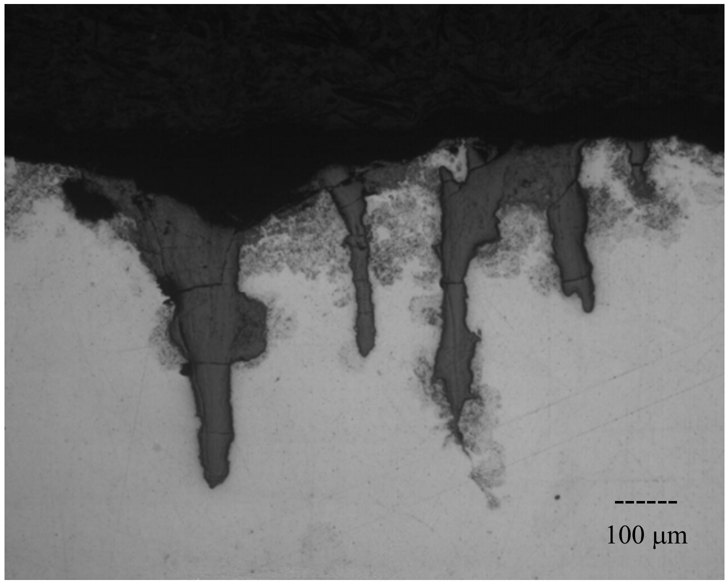

Fig. 2 Longitudinal section through FM52 overlay on waterwall tubes exposed to high heat flux for 5.5 years in base load service in a Northeastern supercritical utility boiler having 1020°F steam and burning coal having 1.5-2.5 pounds of sulfur per MBtu.

opened further with successive thermal cycles and the opened cracks then fill with sulfides and oxides to form the wedges. Of course, the wedges are circumferentially disposed such that they would appear macroscopically as circumferential cracking when longitudinal sections are investigated. The major driving forces behind the differences in performance between these two discussed filler metal 52 installations are the percent sulfur in the coal, the severity and frequency of thermal and mechanical cycles, and variations in heat flux experienced by particular locations within the boilers. The sample shown in Fig.2 was taken from a high heat flux area of the boiler.

3.2 Laboratory Results

Results obtained in Special Metals laboratories compared the corrosion performance of several nickel-base alloys and overlays in a simulated low-NOx corrosion environment. The test environment consisted of the following gas mixtures at 1000°F (538°C):

Reducing Cycle: N_2-16%CO_2-10%H_2O-5%CO-2%H_2S (flow rate 500 sccm).
Oxidizing Cycle: N_2-17.2%CO_2-10.75%H_2O (CO and H_2S turned off).

Table 2 shows calculated equilibrium compositions for both gas mixtures. The test consisted of alternating cycles consisting of 4 days sulfidizing-oxidizing and 3 days oxidizing. Samples were cycled at 500h, 1000h and 4940h. Testing methods and results are described in greater entirety in other publications [2].

Table 2. Inlet and Calculated Equilibrium Compositions of Simulated Low-NOx Boiler Environment

	Oxidizing-Sulfidizing		Oxidizing	
	Inlet	Outlet	Inlet	Outlet
N_2	67	67.2	72	72
CO_2	16	19.4	17.2	17.2
H_2O	10	6.8	10.75	10.75
CO	5	1.45		
H_2S	2	1.97		
SO_2				
H_2		3		
pS_2		2.07E-08		
pO_2		1.64E-28		3.10E-10

Fig. 3 shows the depth of attack values of different alloys after exposure in simulated low-NOx corrosion test at 1000°F (538°C) for 4940 hours. Carbon steel, included as a control sample, exhibits an attack rate, which is an order of magnitude greater than that of the nearest nickel-base sample tested. Alloys 625 and 622 are next in the order of decreasing attack rate. These two alloys exhibit very similar behavior after 4940 hours, despite the much higher initial attack rate of alloy 622. Short-term test results for alloy 622 would have greatly underestimated the material's ultimate performance in this test. The depth of attack values provide an accurate assessment of material performance in this test.

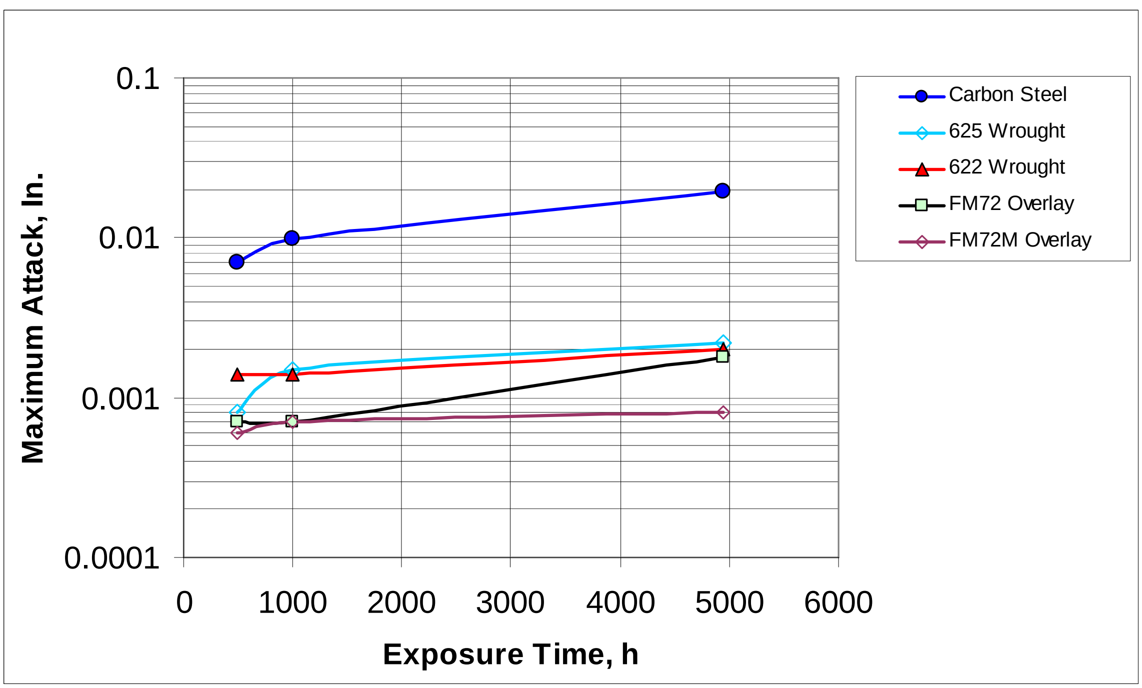

Fig. 3. Depth of attack results after exposure in simulated low-NOx corrosion test at 1000°F (538°C) for 4940 hours.

Fig. 4 and 5 show the microstructure of cross sections from the alloy 622 and 625 samples, respectively, after 4940 hours of exposure. The outer corrosion layers were found to be rich in nickel and sulfur, via SEM-EDS, with chromium increasing moving toward the scale-metal interface. The sulfide scale on the alloy 625 sample was much more friable in appearance and less adherent than that of the alloy 622 which seems to be a reasonable explanation for the actual in-service experience where 622 outperforms 625 by a substantial margin.

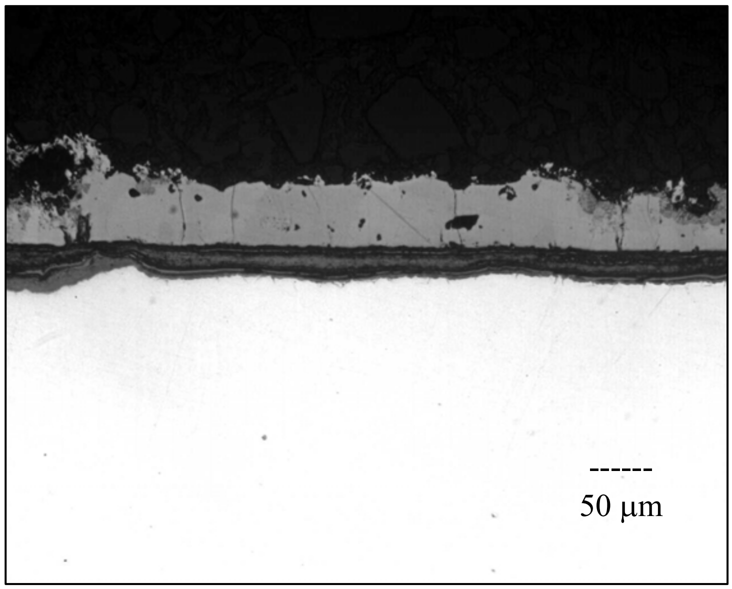

Fig.4. Photomicrograph showing alloy 622 wrought sample after exposure for 4940 hours in simulated low-NOx boiler environment at 1000°F (538°C).

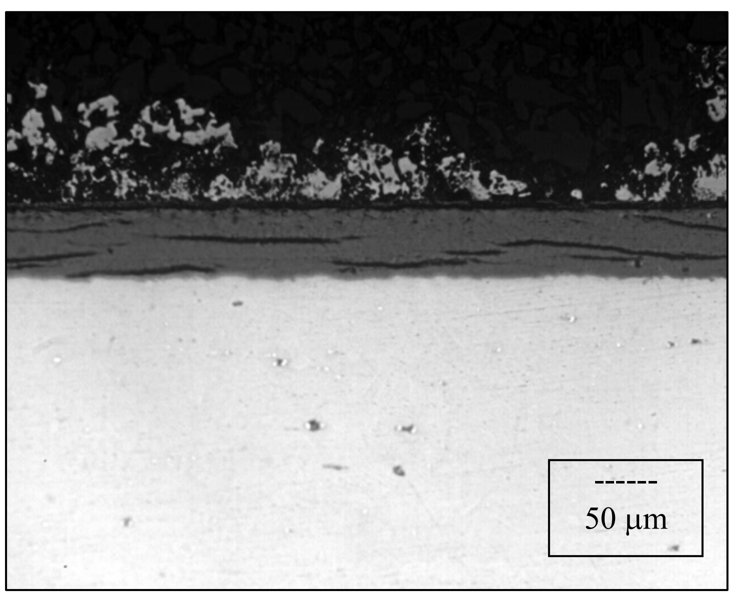

Fig. 5. Photomicrograph showing alloy 625 wrought sample after exposure for 4940 hours in simulated low-NOx boiler environment at 1000°F (538°C).

Depth of attack results for the filler metal 72 overlay sample are shown to be slightly less than those for alloy 622. Filler metal 72M, a modification of filler metal 72 with additions of aluminum and niobium, exhibited superior performance. Fig. 6 and 7 show photomicrographs of filler metals 72 and 72M after 4940 hours of testing. The sulfide surface scales are less extensive for the filler metal 72M product than the corrosion product observed on the filler metal 72 overlay sample and internal oxide layers are also much more compact. Also note the pronounced flatter slope exhibited by the filler metal 72M maximum attack rate. Fig.8 shows the estimated performance of each alloy in one year with a half-cycle extrapolation.

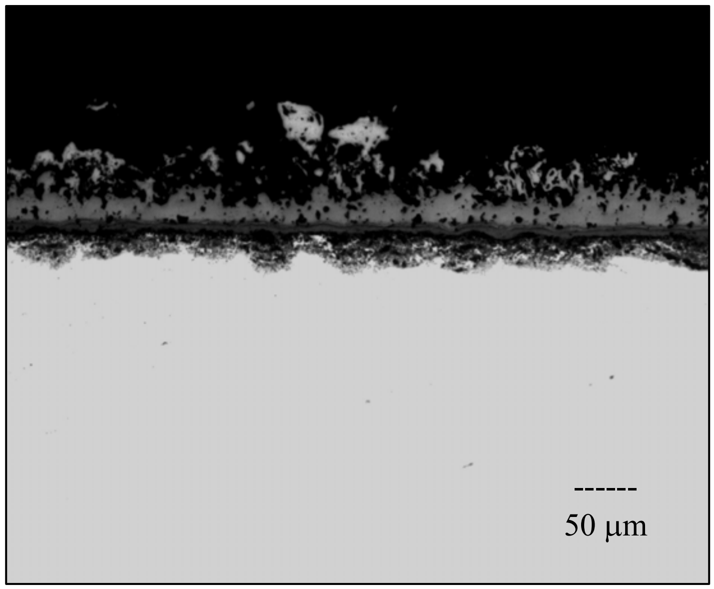

Fig. 6. Photomicrograph showing filler metal 72 sample after exposure for 4940 hours in simulated low-NOx boiler environment at 1000°F (538°C).

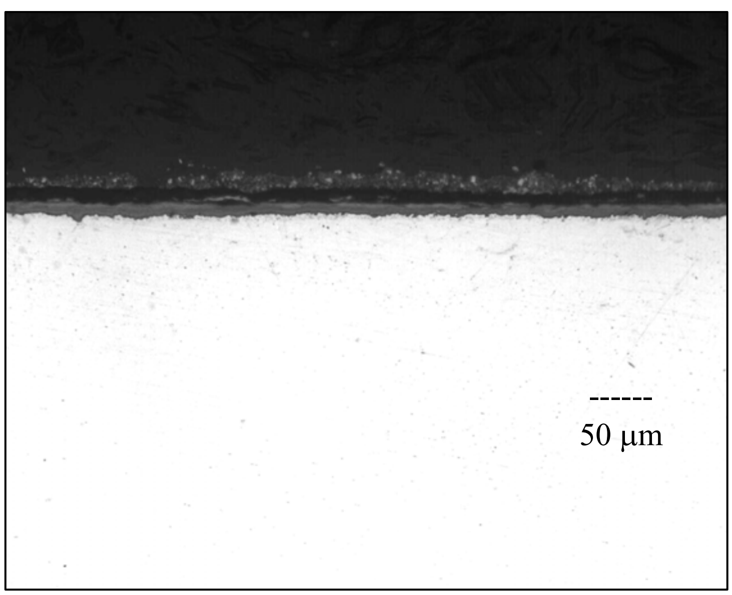

Fig. 7. Photomicrograph showing filler metal 72M sample after exposure for 4940 hours in simulated low-NOx boiler environment at 1000°F (538°C).

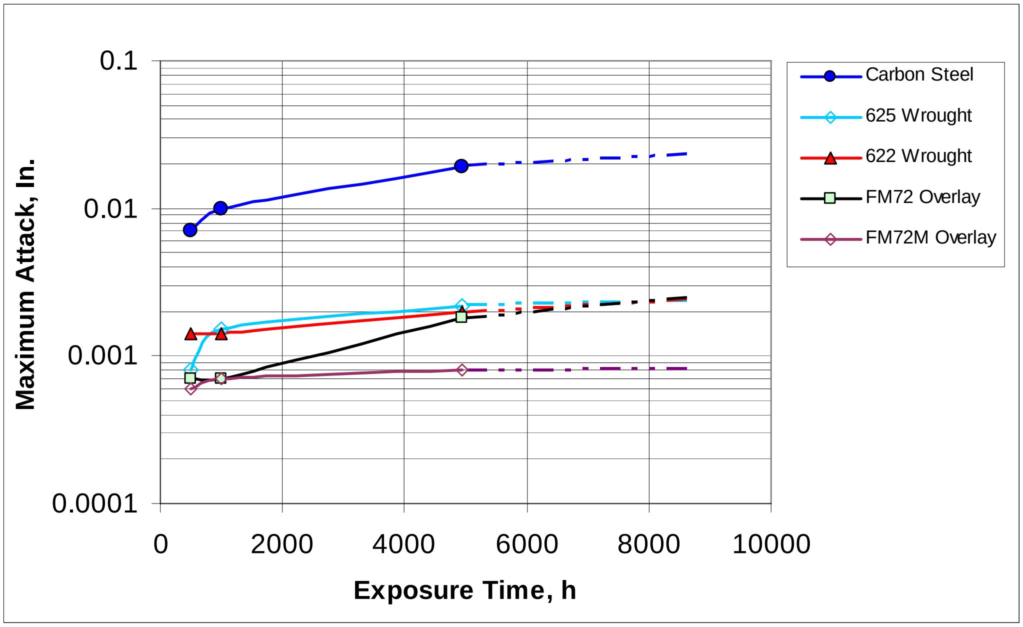

Fig. 8. Depth of attack results after exposure in simulated low-NOx corrosion test at 1000°F (538°C) for 4940 hours, showing extrapolation to one year (8760 hours).

3.3 Experience with Filler Metals 72 and 72M

While there are test patches of INCONEL Filler Metal 72 and INCONEL Filler Metal 72M on waterwalls with very good reports to date, there are no large deposits with extended service from which to draw conclusions regarding performance. A ten tube by 40 foot long test panel has been installed in Gibson Station Unit Number 1 of the Duke Energy System (650 MW supercritical plant operating with 3500psi and 1005°F steam). Fig. 9 shows the qualification weld overlaid sample that represents the test panel that has been installed. While evaluation of waterwall installations incorporating Filler Metals 72 and 72M are on-going, there is an extensive body of data which reports robust performance of FM 72 (AWS ERNiCr-4) when used in superheater and reheater overlays. Fig. 10, 11, and 12 show sections of these upper boiler overlaid tubes after 28 months, 2+ years, and 6 years of service respectively. Fig. 11 shows a tube bend section which was given a simulated weld repair via SMAW using WE117 electrode; dye penetrant testing revealed no cracking in the repaired area. Fig. 12 shows the thickness profile and hardness level of a reheater tube which was in service for 6 years in a low-NOx boiler with an estimated metal temperature at 1200-1250°F. The hardness ranged from Rockwell C 46-52. This increased hardness served to enhance erosion resistance. There is a wealth of additional data for FM 72 overlaid INCOLOY 800H that is reported in the B&W- OCDO-DOE study reported by McDonald and Robitz [3]. These data were generated by exposing the overlays to approximately 1200F. for 1, 2, and 3 years into a boiler environment generated by burning 3.5% S Ohio coal. Overall, the corrosion rates experienced by superheater and reheater overlays of FM72 is about 1-2mils/year with no cracking of the FM 72 overlays. By comparison, FM 52 overlays exposed to the same environment perform well, but not enough to serve for 10 to 20 years as would be desired for upper boiler tubulars.

Fig 9. Waterwall panel section overlaid using INCONEL Filler Metal 72M via the automatic GTAW process. The membrane weld was performed using the SAW.

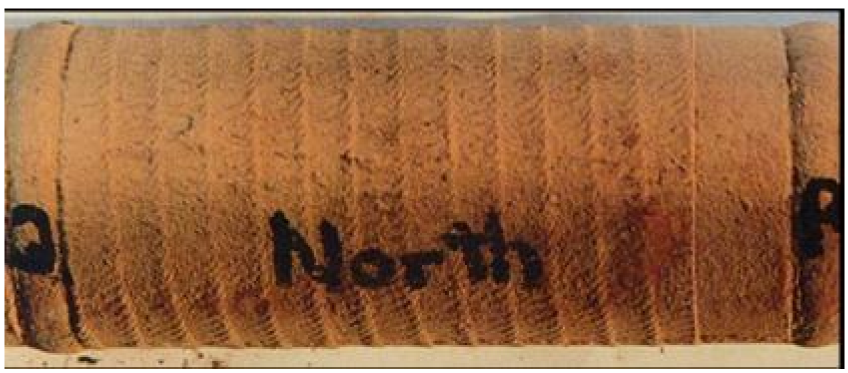

Fig. 10. Filler metal 72 overlaid superheater section exposed in B&W/OCDO/DOE study at Niles, Ohio plant for 28 months of at-temperature service [3].

Fig. 11. Reheater tube overlaid with filler metal 72 after 2+ years in low-NOx boiler service, showing a simulated repair via SMAW using WE117. Dye penetrant testing shows no cracking.

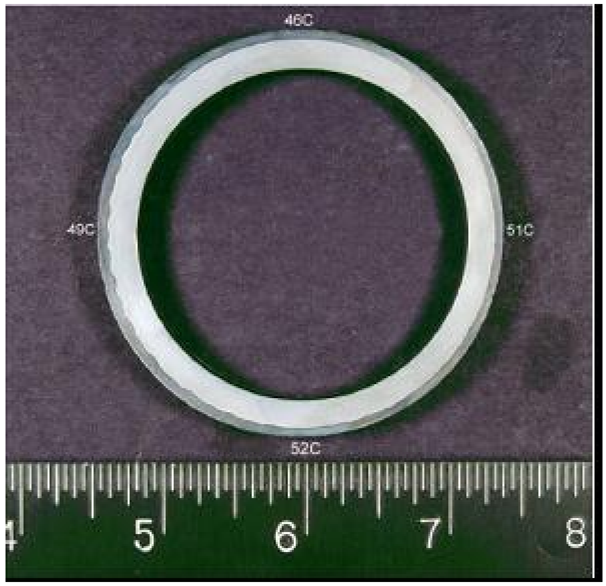

Fig. 12. Reheater tube overlaid with filler metal 72, removed from low-NOx boiler service after 6 years of service. Note overlay integrity and erosion-enhancing hardness levels.

The Reliant Energy consortium in southwestern Pennsylvania have several boilers with extensive FM 72 overlaid upper boiler tubes in their Conemaugh and Keystone facilities. These overlays have been performing exceptionally well for over 9 years. The Conemaugh superheater tubes have their "J-legs" overlaid while the Keystone facility has FM 72 overlaid reheaters.

The INCO-CLAD 671/800H previously mentioned was a co-extruded product of INCONEL alloy 671 powder surrounding an INCOLOY 800H billet. This product produced an approximately 46% Cr nickel alloy cladding that is characterized in the B&W-OCDO-DOE study.

The final information to report on superheater tubes is the outstanding performance of FM 72 overlaid superheater tubes at AEP's supercritical Rockport #1 Station (operating at 1010°F (543°C) at 26.5 MPa) that were used as soot blower lane superheater tubing. Fig. 13 and 14 show overlaid tubes that have been in service (at the time of photograph, about 7 years), but now about 9 years. Note the strong appearance of ripples still existing after years of harsh service from soot blowing.

Fig.13. SA213-T2 superheater tubes overlaid with filler metal 72, after 7 years of service in AEP's Rockport #1 plant.

Fig. 14. SA213-T2 superheater tubes overlaid with filler metal 72, after 7 years of service in AEP's Rockport #1 plant.

3.4 Conductivity and Erosion Considerations

After extended service at typical operating temperatures, changes in the properties of filler metal 72 and 72M products have been observed. Fig. 12 has already shown the hardness increase that can be observed in filler metal 72 after extended exposure. The atomic nickel-chromium ratios in filler metal 72 and 72M are nominally 1.22:1 and 1.14:1 respectively. This would imply that both materials would be subject to long-range ordering. A study by Marucco showed that long-range ordering in Ni_2Cr occurs in 100-1000h below 977°F (525°C), and at 30,000h in Ni_3Cr, accompanied by a significant decrease in electrical resistivity [4]. Filler metals 72 and 72M, at $Ni_{1.14}Cr$ and $Ni_{1.22}Cr$, respectively, would yield different responses still. Fig 15 and 16 illustrate the measured drop in electrical resistivity (at room temperature) observed in Filler Metals 72 and 72M, respectively, after exposure under various conditions. Figure 17 illustrates the correlation between electrical resistivity and thermal conductivity (room temperature data are shown) for a variety of materials.

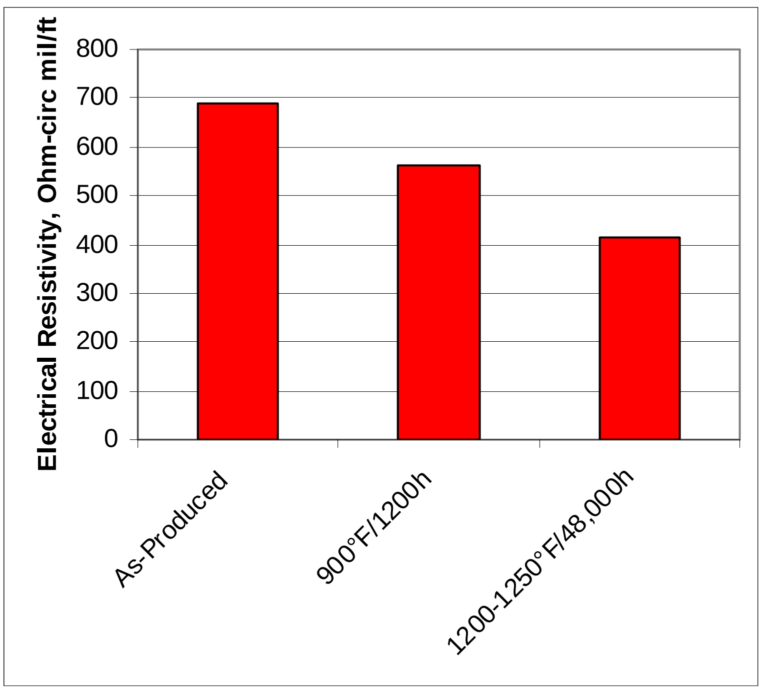

Fig. 15. Electrical resistivity measurements for wrought Filler Metal 72 samples before and after exposure under the indicated conditions.

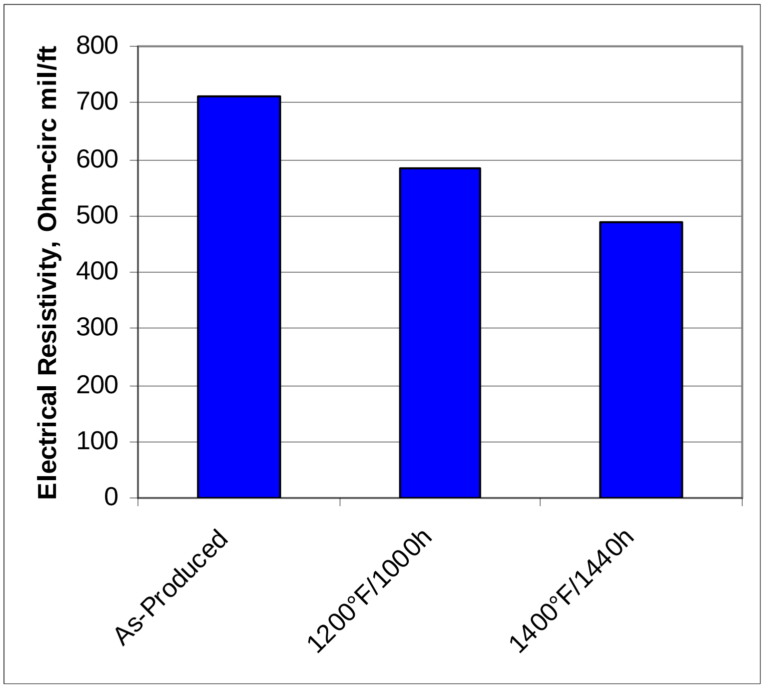

Fig. 16. Electrical resistivity measurements for wrought Filler Metal 72M samples before and after exposure under the indicated conditions.

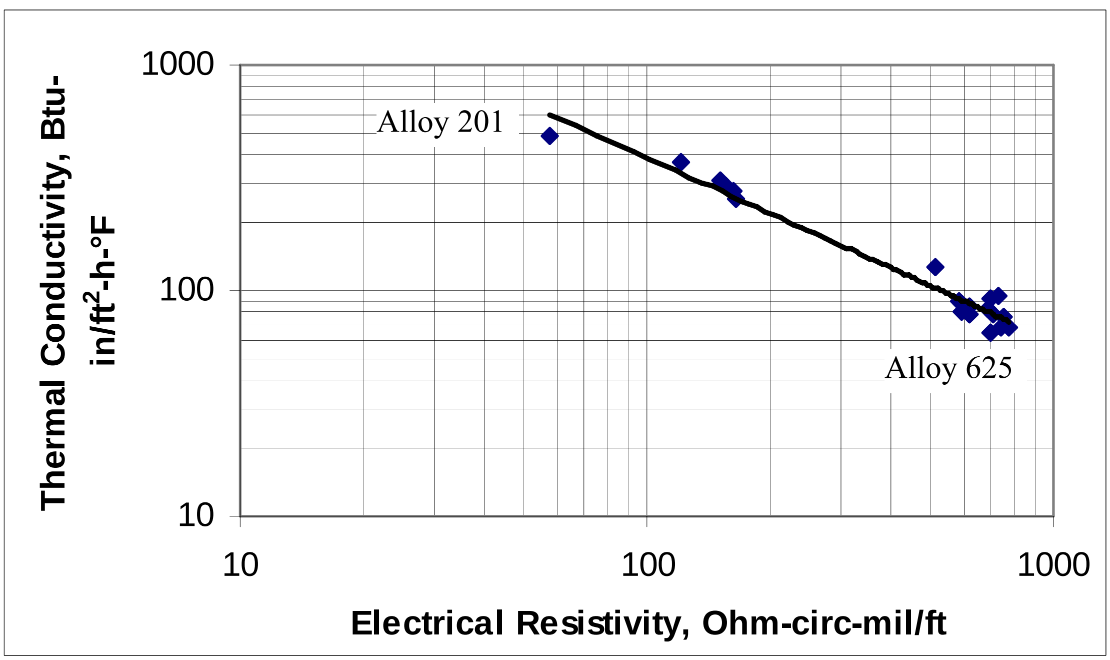

Fig. 17. Thermal conductivity versus electrical resistivity for a variety of materials ranging from Nickel alloy 201 at the low end of resistivity to alloy 625 at the high end.

4. Waste-to-energy Boilers

The principle corrosive agents in WTE boilers are chlorine compounds 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 [5], making WTE boiler corrosion an even greater concern. In WTE boilers the relative concentration of sulfur 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 localized environment. Various researchers have proposed a number of chemical reactions that may govern the corrosion processes [6]. 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.

4.1 Materials and method

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 [7]. The GMAW welding process is widely used due to its high productivity, ability to weld in all positions and application of the process for on-site use within the boiler. Alloy 625 (AWS A5.14 ERNiCrMo-3) is used extensively for this application. While 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 a variety of high nickel Ni-Cr-Mo-W/Nb alloys, including INCO-WELD 686CPT (A5.14ERNiCrMo-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 behavior in aggressive acidic chloride environments [8, 9]. Additionally, laboratory corrosion assessments, using the alloy 686CPT exhibited improved corrosion resistance compared to other alloys [10]. 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 1.9 inches (48.3 mm) diameter and 0.18 inches (4.5mm) wall thickness in Cr-Mo low alloy steel with an overlay thickness of 0.09 inches (2.3mm). These superheater tubes were installed in a WTE boiler located in Europe for which the design operating temperature was 930°F (500°C).

After an operating period of 8000 hours, the tubes were removed from the boiler and examined to determine the respective corrosion rates and to investigate the corrosion

mechanisms operating within 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.

4.2 Results and discussions

The design operating steam temperature of the boiler was 930°F (500°C) with a flue gas temperature of 1160°F (630°C). Examination of the internal bore of the tubes indicated an internal metal temperature of 1020-1040°F (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 1160°F (630°C). On the basis of this information the estimated surface temperature at the weld overlay surface was 1080-1110°F (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 with the exception of the tube overlaid with alloy 686CPT. This corrosion attack resulted in complete penetration and dissolution of large areas of the overlays of all compositions except for the overlay made with alloy 686CPT. While there was a range of high nickel Ni-Cr-Mo alloys included in the test program, the comparative corrosion characteristics of the alloy 686CPT 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 for waterwall tube overlays (Fig. 18a and Fig. 19a)

Chemical analysis of the weld overlays was conducted using EDS analysis at 10 different points on the nickel alloy overlay remaining 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 686CPT deposit. This level of dilution resulted in elevated levels of iron and consequently reduced levels of the other main alloying constituents of chromium, molybdenum and tungsten which is detrimental to the corrosion resistance of the weld alloy overlay. Yet corrosion-resisting performance of alloy 686CPT was excellent in spite of the higher than normal dilution.

Table 1. Chemical analysis of welding wires and weld overlays (ND- not determined)

	C	Mn	Si	Ni	Cr	Mo	Fe	Nb	W
625 Wire	0.008	0.02	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	3.50	0.2
686CPT Wire	<0.01	0.22	0.02	58.52	20.41	16.26	0.36	-	3.94
686CPT Deposit	ND	0.3	ND	53.9	18.4	14.7	8.6	0.2	3.6

Large areas of penetrating corrosion of alloy 625 overlaid tubes were experienced (Fig. 18) with areas of overlay completely corroded away leaving the carbon steel tube beneath the overlay exposed and available for rapid corrosion and consequent penetration of the tube wall. Pitting of the surface was observed with a morphology 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.

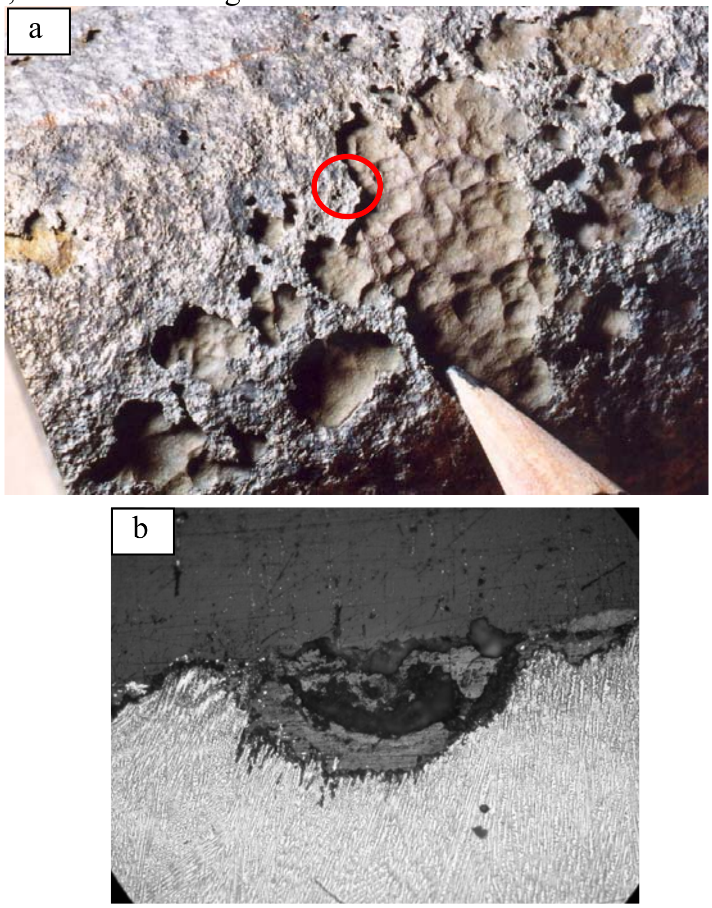

Fig 18. Alloy 625 overlaid tube removed from WTE boiler after 8,000 hours of operation. The microstructure picture of Figure b was taken from the circled area shown in Figure a.

While the alloy 686CPT overlaid tube suffered from extensive general corrosion, the overlay remained intact without any penetration to the substrate tube (Fig. 19). There is limited evidence of pitting of the surface from chloride salt melt attack. The metal interface showed leaching of the dendrite cores through gaseous chlorine attack.

Electron microprobe analyses of the overlaid surface (Fig. 20) and adjacent salt deposits clearly demonstrate 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 oxidized in the upper regions of the salt deposit leading to regeneration of the chlorine, which is free to return to the corrosion interface.

For the alloy 686CPT overlay, the elements molybdenum and tungsten remain in the corrosion zone (Fig. 21) while 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. Sulfur 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. For example, it would appear that chlorine leads the corrosion attack and as the alloy chlorides are formed, the metallic ions become oxidized/sulfidized. This oxidation/sulfidation of the metallic ions releases the chlorine for further penetration into the alloy.

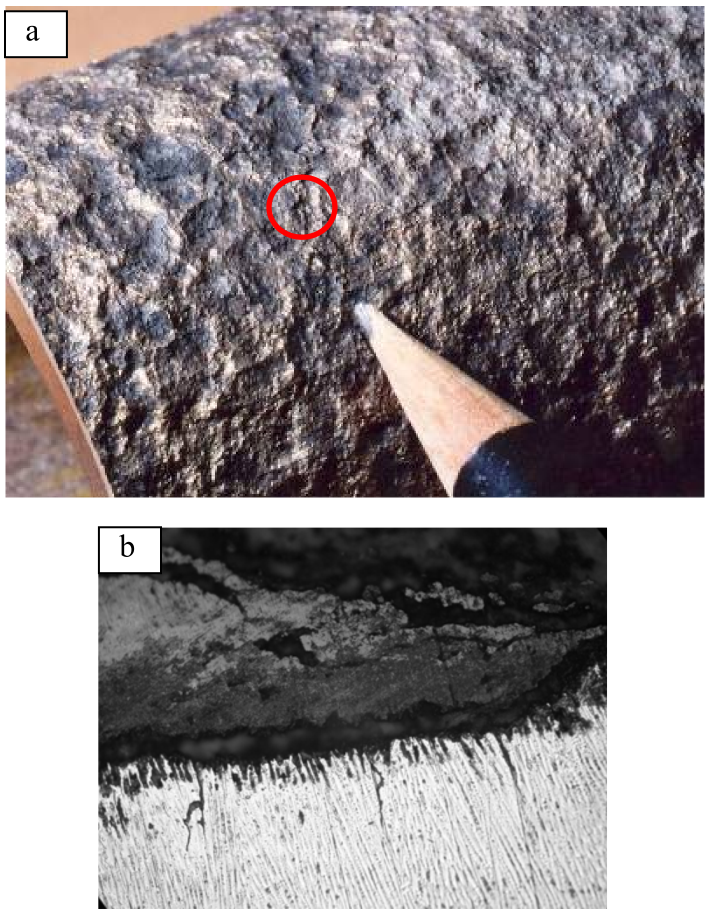

Fig 19. Alloy 686CPT overlaid tube removed from WTE boiler after 8,000 hours of operation. The microstructure picture of Figure b was taken from the circled area shown in Figure a.

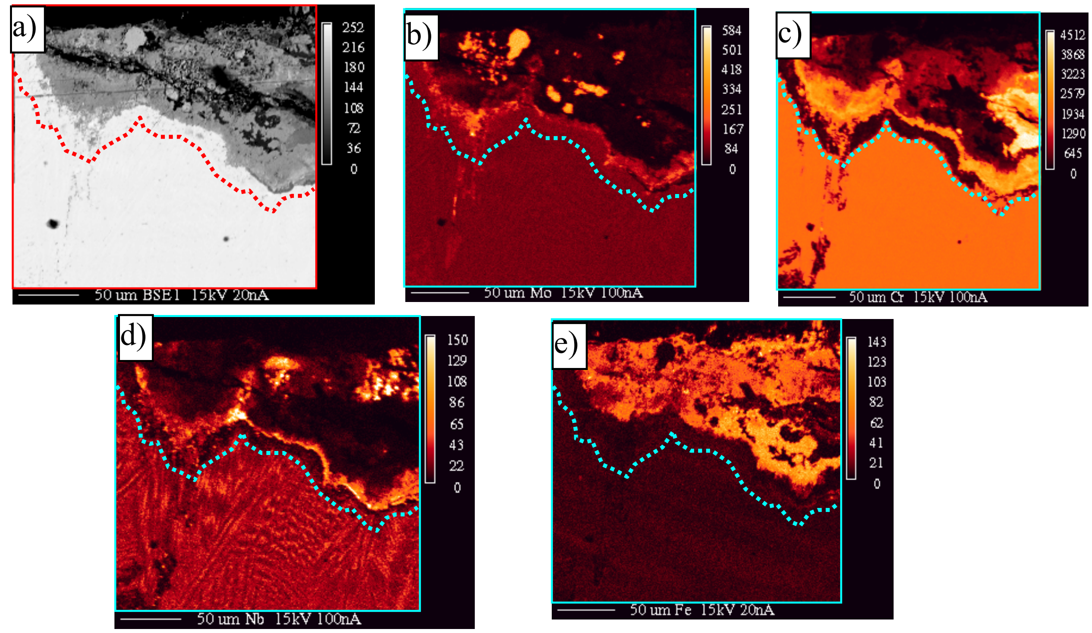

Fig.20. Element microprobe analysis of alloy 625 overlay after removal from the WTE boiler. Bright areas indicate regions of maximum element concentration; blue line indicates corrosion interface. Figure a): Optical microstructure, Figure b): Molybdenum distribution, Figure c): Chromium distribution, Figure d): Niobium distribution, and Figure e) Iron distribution.

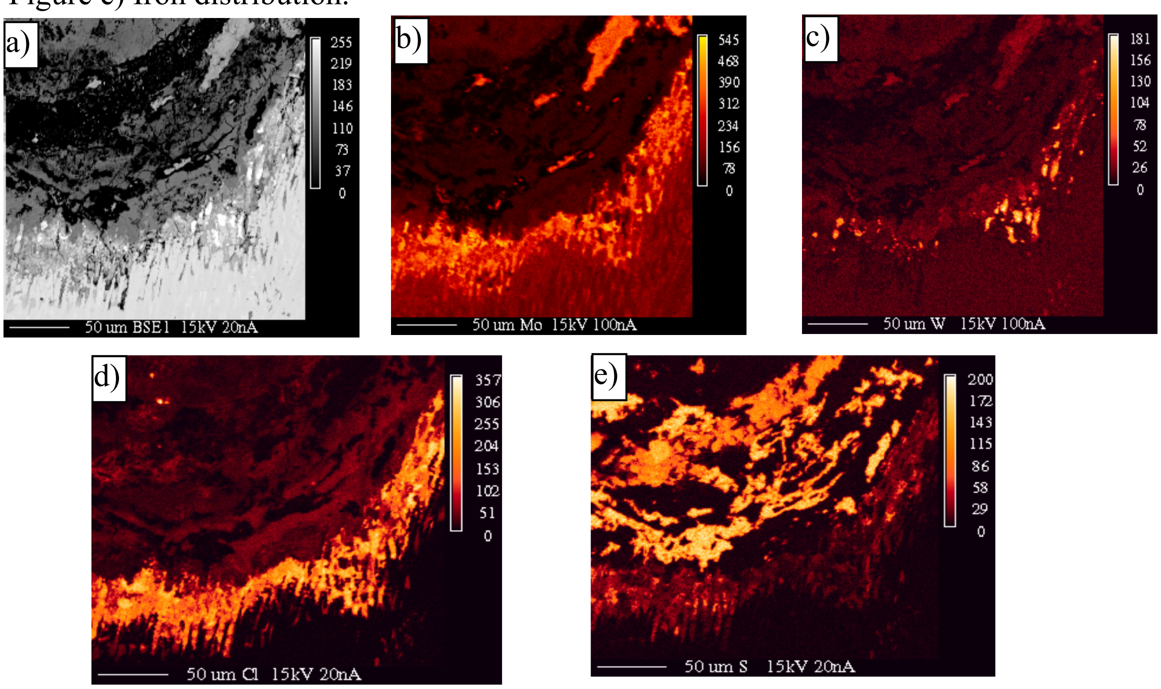

Fig. 21. Element microprobe analysis of alloy 686CPT overlay after removal from the WTE boiler. Bright areas indicate regions of maximum element concentration. Figure a): Optical microstructure, Figure b): Molybdenum distribution, Figure c): Tungsten distribution, Figure d): Chlorine distribution, and Figure e) Sulfur distribution.

In this investigation of the corrosion behavior of superheater tubes overlaid with a number of Ni-Cr-Mo-Nb/W alloys, it has been observed that the improved corrosion behavior exhibited by alloy 686CPT is due to the formation of a protective film at the corrosion interface which is rich in the elements molybdenum and tungsten. The observation of the beneficial effect of increased levels of molybdenum, when operating at increased temperatures 1020°F (550°C), has also been observed in other studies of corrosion in WTE boilers [11, 12]. The weld overlays completed with alloy 686CPT 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, while tungsten segregates in the dendritic cores. As such, the dendrite cores of 625 overlays corrode preferentially due to the lower alloy content in these regions, but the alloy 686CPT overlay suffers less attack of dendrite cores due to the beneficial effect of the W content of alloy 686CPT.

5. Conclusions

Weld overlay technology for protection of boiler tubing and superheaters/reheaters in coal-fired supercritical plants is a dynamic endeavor. Service exposure of Filler Metal 52 overlays has resulted in varied results, dependent upon the characteristics of the coal being utilized as well as heat flux and the cyclic nature of boiler operation. Filler metal 72 has distinguished itself in superheater and reheater service for many years now. The new modification thereof, Filler Metal 72M, shows promise as an improvement over Filler Metal 72. These materials are now being evaluated as waterwall overlay materials as well. Initial results for Filler Metal 72 are encouraging, while trials with Filler Metal 72M are just beginning. Filler Metals 72 and 72M offer intriguing characteristics of outstanding corrosion resistance coupled with apparent long range ordering effects. The benefits of these characteristics are clearly demonstrated in remarkably good performances of FM72 and 671/800H in upper boiler tubes. Future benefits expected as a result of long-range ordering by both are continuing erosion-corrosion resistance and greatly enhanced thermal conductivity through the tube wall overlay. This increased thermal conductivity provides improved overall boiler efficiency as well as decreased ΔT across the overlay and tube wall to the steam or water on the inside. The decreased ΔT results in lower thermally-induced strain, particularly in high heat flux areas which should offer a reduced tendency for circumferential cracking. Operating performance data will be accumulated and reported over the next two to five years, as outages permit. Superior performance is expected due to excellent corrosion resistance and improved thermal conductivity of overlays.

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 686CPT 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, demonstrated by the lack of perforation of the alloy 686CPT 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. While alloy 686CPT 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 686CPT provides tolerance to variations in weld deposit quality while still providing excellent corrosion behavior.

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

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