

## INCONEL FILLER METAL 72M PROVIDES CORROSION AND WEAR RESISTANCE AND LOW “DELTA T” THROUGH WALLS OF TUBING IN FOSSIL-FIRED BOILERS

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### ABSTRACT

INCONEL Filler Metal 72, a 43% Cr nickel alloy welding wire, has been used in elevated temperature service to protect boiler tubing for over 20 years. Along with FM 72 overlays, INCOCLAD 671/800H co-extruded tubing has also been used to great advantage for resisting sulfidation, oxidation, carburization and wear in boiler environments. INCONEL Filler Metal 72M is an optimized alloy that offers improved weldability and the lowest corrosion rate of any of the alloys evaluated in our simulated low NO<sub>x</sub> boiler environment. Testing results are presented along with illustrations of applications for the above materials. New interest has been expressed in 72 and 72M for waterwall tubing overlays where the normal failure mode with other weld overlays has been circumferential cracking and corrosion fatigue. Filler Metal 72 overlays have shown outstanding resistance to abrasion and wear in soot blower lane tubing and resistance to corrosion-fatigue-cracking in severe waterwall service. 72M overlays have been chosen to replace erosion shields in the high wear “nose” areas of superheater and reheater tubing. 72M overlays provide protection against corrosive attack even under reducing conditions created by low NO<sub>x</sub> firing, and 72M is capable of performing well at the high temperatures experienced in advanced ultra-super critical (AUSC) boilers. In addition to outstanding corrosion resistance, both 72 and 72M weld deposits increase in hardness and thermal conductivity with exposure time at service temperatures. As thermal conductivity of weld overlays increase with service time, the “delta T” (temperature difference across the tube wall) is reduced and provides substantial increases in thermal efficiency for the boiler, while providing long life due to excellent corrosion and erosion resistance and reduced tendency for thermal fatigue (corrosion fatigue). Overall cost-savings are derived from lower maintenance costs as well as higher boiler thermal efficiency. Both waterwall and upper boiler tubing overlays will be addressed 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.

**Keywords:** Fossil boiler, water-wall, super-heater, re-heater, alloys 72, 72M 622, 625, and 33

### INTRODUCTION:

Investment in fossil-fired boilers in the USA has been stifled in recent years due to stringent pollution control requirements imposed by the environmental protection agency (EPA) and the emergence of inexpensive natural gas via “fracking.” The remaining countries of the world continue to have strong and growing desires for more electrical energy, and those with access to fossil fuels pursue conventional and advanced power boilers. It has been reported recently that some power suppliers in the Middle East have inquired for high efficiency boilers to be fired with high-impurity residual oil. These boilers would require overlay with alloy 72. In addition, the power industry in the USA has anticipated sharp increases in the cost of natural gas due to the coming expected surge in exports of LNG. These factors have prompted a renewed interest in

fossil-fired boilers. With this renewed scrutiny comes interest in the improved materials of construction needed to survive the ever increasing severity of operating conditions brought about by demands for greater efficiency and smaller carbon footprint.

Nickel-based 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 (PGMAW) process is a common form of protection, but more recently, the automatic gas tungsten arc welding (GTAW) process and the hot-wire laser (HWL) processes have been used. Good bond integrity, low corrosion rate and high thermal conductivity are desirable characteristics of such overlays. These characteristics provide optimal life for overlaid components on water-walls, super-heaters and re-heaters. As boiler conditions have become more aggressive over the years, nickel based 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. Filler Metal 72, a 43% Cr, balance nickel alloy welding wire has been used for over 20 years in elevated temperature service to protect boiler tubing where resistance to sulfidation, oxidation, and carburization is required. INCO-CLAD 671/800H clad tubing made using alloy 671 (46 Cr, balance Ni) co-extruded over alloy 800H tubing has been used for over 30 years for superheater tubing in the AEP system. Filler Metal 72M is an optimized alloy that offers improved weldability and the lowest corrosion rate of any of the alloys evaluated in our simulated low NO<sub>x</sub> boiler environment. Testing results are presented along with illustrations of applications for the above materials. New interest has been expressed in 72 and 72M for water-wall tubing overlays where the normal failure mode with other weld overlays has been circumferential cracking or corrosion fatigue.

Filler Metal 72 has shown outstanding resistance to corrosion fatigue in severe service in water-wall tubing and very long service life in upper boiler applications. A large new application for re-heater service is discussed along with a novel Hot-Wire Laser Beam Welding (HWLBW) process. This welding method using FM 72M allows a thinner weld deposit to be produced that increases the thermal conductivity thorough the tube wall. These thinner overlays and the fact that the thermal conductivities of 72 and 72M weld deposits increase with exposure time provide multiple advantages. These two accomplishments reduced the “delta T” (temperature difference) through the tube wall and allow substantial increases in thermal efficiency for the boiler at lower overall cost, while providing long life due to excellent corrosion and erosion resistance and reduced tendency for thermal fatigue.

Power Boilers that make significant contributions to the electrical grid are fired with various grades of coal (fossil fuels). These boilers suffer from fireside corrosion, but the types and severity of corrosion encountered vary with the grades of fuel used and operating conditions [1, 2]. Historically alloy 622 (ERNiCrMo-10) overlays have been chosen most often to protect water wall tubing, and alloy 72 (ERNiCr-4) has been the most popular overlay for super-heater and re-heater protection. However, Filler Metal 72 is beginning to show outstanding results in water-wall overlay, Filler Metal 72M is being evaluated for water wall overlay protection, and has just been chosen for two major re-heater applications, as well as in super-heater tubing in soot blower lane protection.

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

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

Material	C	Ni	Cr	Fe	Mo	Nb	W	Al	Ti	Others	AWS Class
309	0.20	12-15	22-24	Bal.	-	-	-	-	-	2.0 Mn, 1.0 Si	ER309
312	0.15	9.0	30.0	Bal.	-	-	-	-	-	2.0 Mn, 1.0 Si	ER312
33	0.015	31	33	32	1.6	-	-	-	-	0.6 Cu	ER33-31
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	---

### Fossil-fired Boiler Water-wall Applications

The clean air act of 1990 has provoked significant changes in how electric power is generated by fossil-fired boilers. Many units have been forced to add flue gas desulfurizers (FGD's) to control SO<sub>2</sub> effluent, and many have added low NO<sub>x</sub> burners and other devices to reduce NO<sub>x</sub> emissions [3, 4]. More recently, stringent controls have been added that include more restrictive limits on mercury, CO<sub>2</sub>, and other pollutants that result from the combustion of fossil fuels. As a result of the high cost of scrubbers and the recent surge in "fracking" to produce lower cost natural gas, the price of methane has become attractive as a firing alternative. However, many boilers in worldwide service today will continue with cost-effective fossil fuels due to the considerably higher heating value of coal and the lack of infrastructure to import and distribute LNG. Very recently, there are rising concerns that the export of LNG from the U.S. may result in price increases for natural gas, so many power providers continue to hedge their bets with fossil-fired boilers. With the advent of low NO<sub>x</sub> burners came the change in the boiler environment from SO<sub>2</sub> to H<sub>2</sub>S. This change in boiler environment prompted the need for protective fireside water-wall overlays. Before the advent of low-NO<sub>x</sub> 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 for ferritic steels under the most severe low-NO<sub>x</sub> 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 alloy overlays and most recent survey of overlay performance are given in Tables 2 and 3.

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 elimination of chromized tubes and 312 stainless steel leaves the domain of supercritical boilers to the nickel-base alloys such as 625, 622, 52, 72, 72M and the cheaper iron-based alloy 33. Recent results have shown alloy 52 to have been effective with no cracking after 7.5 years in a large supercritical application in the AEP system, but 52 did not perform well in the more stringent "acid tests" at PP&L's Montour and Brunner Island Stations. The earliest experience of note with alloy 33 was reportedly in a sub-critical drum boiler at Western Kentucky Electric.

Table 2. Survey Performance of Alloys used in Water-wall Overlays

309	24 Cr, 13 Ni	4-6 yrs. Some cracking	Not popular for supercriticals.
312	30 Cr, 9 Ni	Little data 3-6 yrs.	Solidification cracks?
33	33Cr, 31Ni, 32Fe	6 years	Removed after 6 years-cracking
625	64 Ni, 21 Cr, 9 Mo, 3.5 Nb	18 mths. To 6 years	5-15 mpy
622	59 Ni, 22.2 Cr, 14 Mo, 3 W	Greater than 7 years	No cracking, 2-3mpy
72	56 Ni, 43 Cr, 0.6 Ti	Greater than 7 years	No cracks after 7 years
72M	58Ni, 38Cr, 1nb, 1Al, 0.6Ti, 0.3Mo	Multiple tests to 2.5 yrs. Multiple new applications	lab corrosion results <1mpy
52	59 Ni, 30 Cr, 9 Fe	5.5years-7.5years	Removed after 6 years-cracking
53MD	60 Ni, 30 Cr, 5 Fe, 3 Al	No Data	No Data
Chromized Steel	Fe	2-4 years	Not effective in some low NOx
Steel	Fe	1 year	120 mpy

Table 3. Exposure Effects of Alloys used in Water-wall Overlays

Alloy	Temperature Limits	Exposure Effects
309,309L	900 deg F- ?	Carbides, sigma phase
33	800 deg F-?	Carbides
312	885 deg F-?	Carbides, sigma phase, alpha phase
625	800 – 1150 deg F.	Carbides, $\gamma$ double prime, BCT, Orthorhombic
622	800- 1100 deg F.	P, Mu phase
72	800- 1300 deg F.	Alpha chromium, Ni <sub>2</sub> Cr, Ni <sub>3</sub> Cr
72M	800- 1500 deg F.	Alpha chromium, Ni <sub>2</sub> Cr, Ni <sub>3</sub> Cr
52	800- 1300 deg. F.	Gamma Prime, carbides
53MD	800- 1300 deg F.	Gamma Prime, carbides

However, when exposed to the acid test of the PP&L system, like 52, another 30%Cr alloy, the alloy 33 failed. When installed in the Montour station of PP&L, the alloy 33 overlay began to show cracking after three years and was removed from service after six years when it exhibited major circumferential cracking. Although the supplier of alloy 33 has not reported on this service and a sample tube is not available for investigation, we expect that a cross-section of one of those tubes would appear to be similar to that shown in Figure 1. These failures in alloy 33 and 52 are not unexpected in view of the previous research done in Niles, Ohio. The failure results (due to low Ni of 33 and low Cr of both 33 and 52) serve to verify the conclusions of the B&W, OCDO, DOE, Niles, Ohio study[5] that Nickel + Chromium is the most effective alloy combination to withstand severe fossil-fired boiler environments as shown in Figure 2.

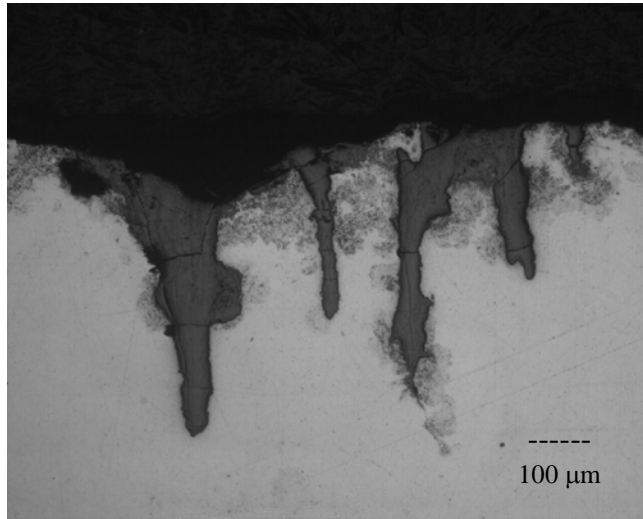


Figure 1. Longitudinal section through FM52 overlay on water-wall tubes exposed to high heat flux for 5.5 years in base load service in a Northeastern supercritical utility boiler having 1020°F steam and burning coal having 1.5-2.5 pounds of sulfur per MBtu. (This is likely indicative of the appearance of the sample of alloy 33 removed from the same system after 6 years with major circumferential cracking).

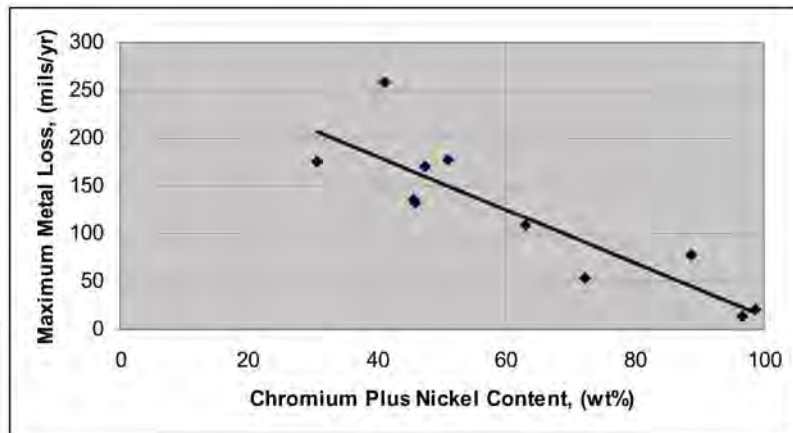


Figure 2. Chromium + Nickel Content Versus Metal Loss [5].

Generally, circumferential cracking, (which is 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[6]. The addition of Nb in alloy 625 assists in creation of terminal liquid phase which backfills small micro-fissures 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 [4]. The watershed 1000 square foot test panels of 622 versus 625 installed into the defining power plants in the PP&L system (that is considered to be the “acid test” for water-wall overlays) over one decade ago established the preeminence of alloy 622 over 625 for fossil water-wall overlays. Therefore, the remaining best practice alloy selections for water-wall overlay are 622, 72 and perhaps 72M. While there is a great deal of experience with 622 overlays, there are sparse data for water-wall weld overlays with 52 and 72. The recent examination of 5000 square feet of FM52 at AEP’s Muskingum River #5 is the most substantial application to have been evaluated to date, in terms of both square feet of coverage and time of exposure. The results were no cracking anywhere in the 5000 square feet after 7.5 years service (these results were reported previously and are available in the long version of this report). While alloys 52 and 33 have been disqualified at PP&L, a sample of alloy 72 installed in PP&L’s Brunner Island Station has passed its 2.5 year and 6 year inspections with no cracking. Thus there is hopeful expectation for good performance of alloys 72 and 72M in severe water-wall service applications. In addition to the sample of 72 overlaid water-wall panel just described in the PP&L system, there is another water-wall panel overlaid with 28 square feet of FM72 in the Duke Energy system (Gibson #2) that has 6 years of crack-free service. While there are test patches of Filler Metal 72 and Filler Metal 72M on water-walls with very good reports to date, there are no large weld overlay deposits with extended service from which to draw conclusions regarding performance. A ten tube by 40 foot long test panel made with FM 72M 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. 3 shows the qualification weld overlaid sample that represents the test panel that has been installed.



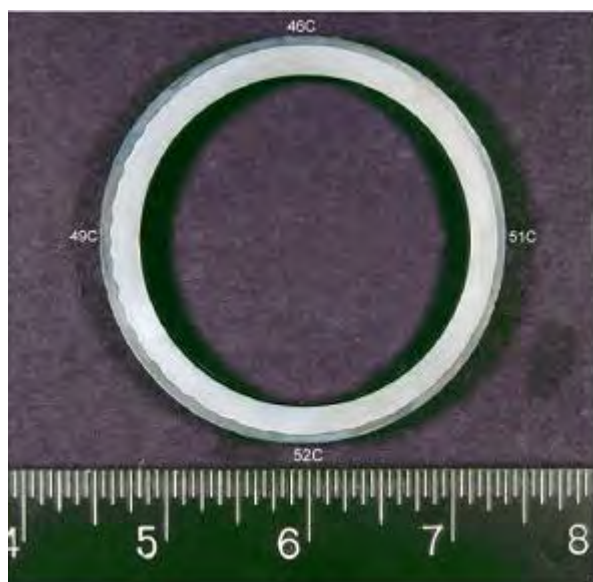
*Figure 3. Water-wall panel section overlaid using INCONEL Filler Metal 72M via the automatic GTAW process. The membrane weld was performed using the SAW process.*

### **Fossil-fired Boiler Superheater and Reheater Tubing Applications**

In addition to water-wall overlays, a second application that requires protection is the upper boiler tubing, namely super-heater and re-heater tubing. These tubular structures often suffer from accelerated erosion-corrosion damage that prompts the use of largely ineffective erosion “shields.” These shields often become unattached during service and fall to the bottom of the boiler. When attached, they offer poor erosion protection, but when they fall off, they offer no protection and become a major maintenance headache. A new design idea is to replace these attachments with integral alloy 72M weld overlays that do not fall off, offer much better protection, and offer greatly improved heat transfer.

In support of upper boiler tube overlays, there is an extensive body of data which reports robust performance of FM 72 (AWS ERNiCr-4) when used in superheater and reheater overlays. Figure

4 shows a section of an overlaid re-heater tube after 6 years of service. The cross section shows the thickness profile and hardness level of the reheater tube after service in a low- NOx boiler with an estimated metal temperature of 1200-1250F. . The hardness ranged from Rockwell C 46-52. This increased hardness served to enhance erosion resistance. The increase in hardness of 72 and 72M with extended service coupled with the excellent service exhibited in soot blower lane tubing would indicate these overlays can replace the troublesome “thermal shields” that are often used in the upper boiler of many units. There is a wealth of additional data for FM 72 overlaid INCOLOY 800H that is reported in the Babcock & Wilcox-Ohio Coal Development Organization-Department of Energy (B&W-OCDO-DOE) study reported by McDonald and Robitz [5]. These data were generated by exposing the overlays to approximately 1200F for 1, 2, and 3 years in a boiler environment generated by burning 3.5% S Ohio coal. Overall, the corrosion rates experienced by super-heater and re-heater overlays of FM72 are 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 well enough to serve for 10 to 20 years as would be desired for upper boiler tubulars.



*Figure 4. Re-heater 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 of 46 to 52 Rc.*

The Reliant Energy consortium in southwestern Pennsylvania has 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 super-heater tubes have their “J-legs” overlaid while the Keystone facility has FM 72 overlaid re-heaters.

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 a nickel-alloy cladding of about 46% Cr that is characterized in the B&W-OCDO-DOE study.

The final information to report on super-heater tubes is the outstanding performance of FM 72 overlaid super-heater 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 super-heater tubing. Figure 5 shows overlaid tubes that were in service (at the time of photograph, about 7 years), but now have



provided about 14 years of service. Note the strong appearance of ripples still existing after years of harsh service from soot blowing.



*Figure 5. SA213-T2 super-heater tubes overlaid with filler metal 72, after 7 years of service in AEP's Rockport #1 plant.*

### **Conductivity Hardness and Erosion Considerations**

After extended service at typical operating temperatures, changes in the properties of filler metal 72 and 72M overlays have been observed. Fig. 4 has already shown the hardness increase to 46-52Rc that can be observed in filler metal 72 deposits after extended exposure. The atomic nickel-chromium ratios in filler metal 72 and 72M are nominally 1.14:1 and 1.22:1 respectively. This would imply that both materials would be subject to long-range ordering. A study by Marucco showed that long-range ordering in  $\text{Ni}_2\text{Cr}$  occurs in 100-1000h below 977°F (525°C), and at 30,000h in  $\text{Ni}_3\text{Cr}$ , accompanied by a significant decrease in electrical resistivity [7]. Filler metals 72 and 72M, at  $\text{Ni}_{1.14}\text{Cr}$  and  $\text{Ni}_{1.22}\text{Cr}$ , respectively, would yield different responses still. Fig 6 and 7 illustrate the measured drop in electrical resistivity (at room temperature) observed in Filler Metals 72 and 72M, respectively, after exposure under various conditions. Figure 8 illustrates the correlation between electrical resistivity and thermal conductivity (room temperature data are shown) for a variety of materials. These dramatic increases in hardness and in overall thermal conductivity offer huge benefits in overall thermal efficiency and operating efficiency in reduced maintenance costs. Two super critical boilers are currently being fitted with 304-H reheater tubing with 72M overlays critically positioned to replace conventional erosion shields that often fall off and require maintenance for reattachment. Another utility is using 72M overlays over 347H tubing to protect their soot blower lane superheaters against erosion damage without loss of good thermal conductivity. Thermal fatigue testing was performed to insure the CTE difference between 72M and 347H would not cause any problems during service. The results of the testing showed no tendency for cracking in either material even in the presence of intentionally placed mechanical notches in the test specimens.



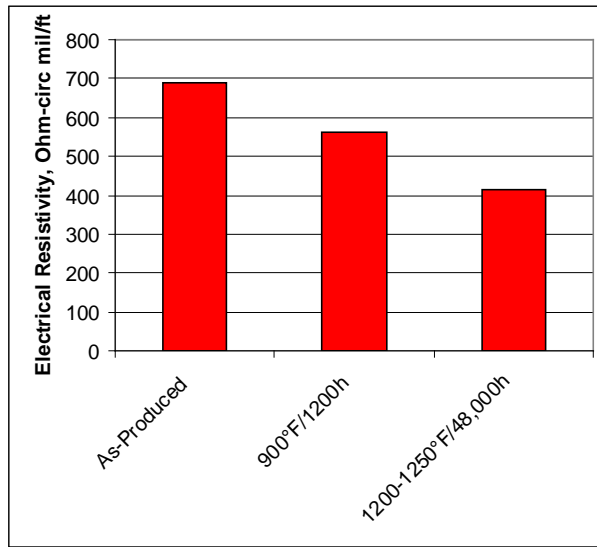


Fig. 6. Electrical resistivity measurements for wrought Filler Metal 72 samples before and after exposure under the indicated conditions.

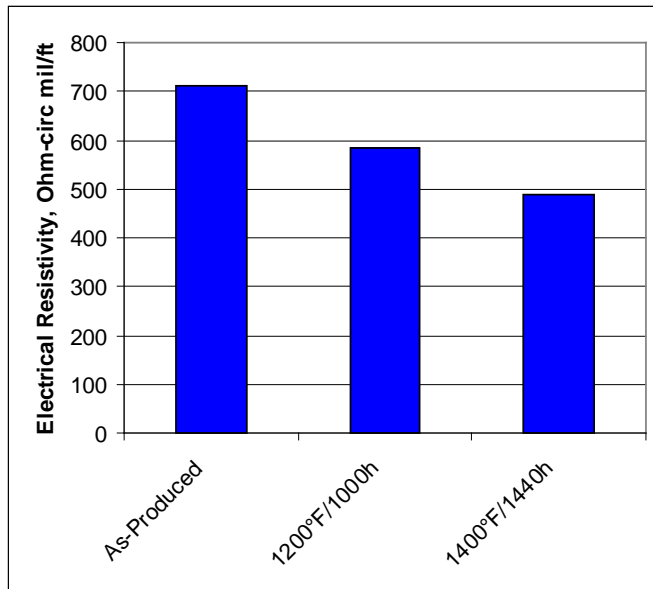


Fig. 7. Electrical resistivity measurements for wrought Filler Metal 72M samples before and after exposure under the indicated conditions.

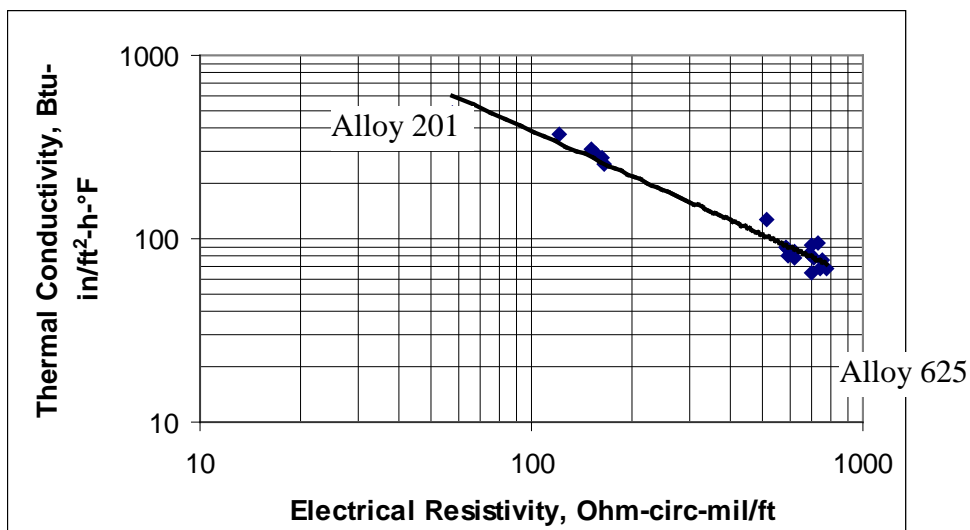


Fig. 8. Thermal conductivity versus electrical resistivity for a variety of materials ranging from Nickel alloy 201 at the low end of resistivity to alloy 625 at the high end.

### Application Methods for Weld Overlay

As shown in the previous figures, weld overlays have been produced using various welding processes. By far the most commonly used processes are the GMAW and pulsed-GMAW processes. These processes have been used for both shop and field fabricated overlays. More recently, the automatic GTAW process and the submerged arc welding (SAW) process have been used for shop fabrication quite successfully as shown in the sample in Figure 3. The most recent welding process to be used in shop fabrication is the HWLBW process shown in Figure 9. This process is currently being applied for fabricating re-heater tubing for the Southern Company to deposit Filler Metal 72M over 304H stainless steel. Figure 10, shows a cross section of one of those overlays and Table 4 shows successive scans of SEM analyses starting at the top surface and moving toward the fusion line. Note that the composition is homogenous and shows an overall dilution rate of about 5%. Due to the extremely low corrosion rate of less than .001"/year, exhibited by alloy 72M overlays, the alloy can be applied as a thinner layer than other materials to great advantage. The HWLBW process is capable of depositing very thin layers at very low dilution levels. In this case, alloy 72M is being deposited at .035" to .040" thick. This thin layer provides outstanding corrosion resistance and lower thermal resistivity due to its thinness. This weld overlay provides an initially lower "delta T" or temperature drop from the outside surface to the inside surface where steam is being reheated. This lower "delta T" helps to reduce the thermally induced fatigue stresses generated when thermal cycles are experienced and provides greater thermal conductivity to reheat steam more efficiently. Another obvious advantage is that with a thinner overlay, there is less weld metal required which provides an economic incentive of lower cost overlays. Finally, the metallurgical changes that occur with increased service life also contribute to higher thermal conductivity which provides for improved overall boiler thermal efficiency.



Fig 9. Hot Wire Laser Beam Weld Overlay using INCONEL Filler Metal 72M.



Fig 10. Longitudinal Cross-Section of 72M Overlay.

Table 4. SEM Analyses of Cross-Section of 72M Overlay of Figure 10

Spectrum	Al	Si	Ti	Cr	Mn	Fe	Ni
Line Spectrum(1)	0.99		0.38	35.77		4.9	54.29
Line Spectrum(2)	0.97	0.34	0.69	36.04		4.32	53.61
Line Spectrum(3)	1.06	0.37	0.73	35.54		4.11	52.71
Line Spectrum(4)	1.08		0.4	36.17		5.91	52.68
Line Spectrum(5)	0.93		0.38	35.86		4.82	54.75
Line Spectrum(6)		0.43		20.43	1.08	61.14	13.51
Line Spectrum(7)		0.49		18.81	1.3	66.74	8.1
Line Spectrum(8)		0.54		18.52	1.36	66.68	8
Line Spectrum(9)		0.47		18.66	1.3	67.34	8.26
Line Spectrum(10)		0.52		18.51	1.38	67.11	8.04

### Laboratory Test Program Results

In an effort to measure and report alloy weld overlay performance under controlled conditions, Special Metals/PCC performed hot corrosion testing. Results obtained in Special Metals laboratories compared the corrosion performance of several nickel-based alloys and overlays in a simulated low-NO<sub>x</sub> corrosion environment. The test environment consisted of the following gas mixtures at 1000°F (538°C):

Reducing Cycle: N<sub>2</sub>-16%CO<sub>2</sub>-10%H<sub>2</sub>O-5%CO-2%H<sub>2</sub>S (flow rate 500 sccm).

Oxidizing Cycle: N<sub>2</sub>-17.2%CO<sub>2</sub>-10.75%H<sub>2</sub>O (CO and H<sub>2</sub>S turned off).

Table 5 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 [8-12].

Table 5. Inlet and Calculated Equilibrium Compositions of Simulated Low-NO<sub>x</sub> Boiler Environment

	Oxidizing-Sulfidizing		Oxidizing	
	Inlet	Outlet	Inlet	Outlet
N <sub>2</sub>	67	67.2	72	72
CO <sub>2</sub>	16	19.4	17.2	17.2
H <sub>2</sub> O	10	6.8	10.75	10.75
CO	5	1.45		
H <sub>2</sub> S	2	1.97		
SO <sub>2</sub>		4.9E-10		
H <sub>2</sub>		3		
pS <sub>2</sub>		2.07E-08		
pO <sub>2</sub>		1.64E-28		3.10E-10

Fig. 11 shows the depth of attack values of different alloys after exposure in simulated low-NO<sub>x</sub> 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-based 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.

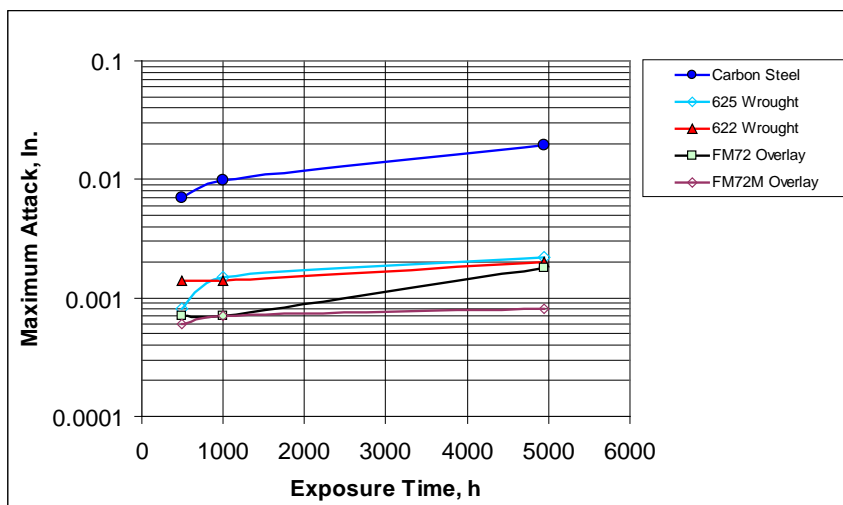


Fig. 11. Depth of attack results after exposure in simulated low-NO<sub>x</sub> corrosion test at 1000°F (538°C) for 4940 hours.

Fig. 12 and 13 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.

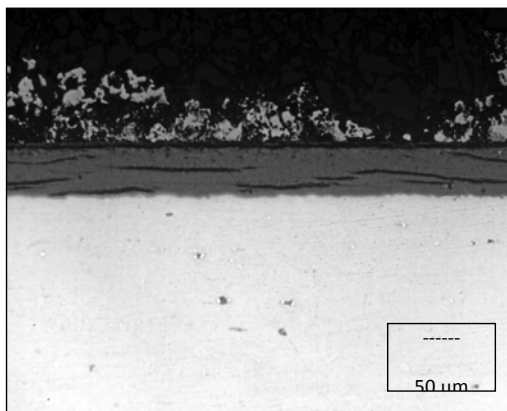
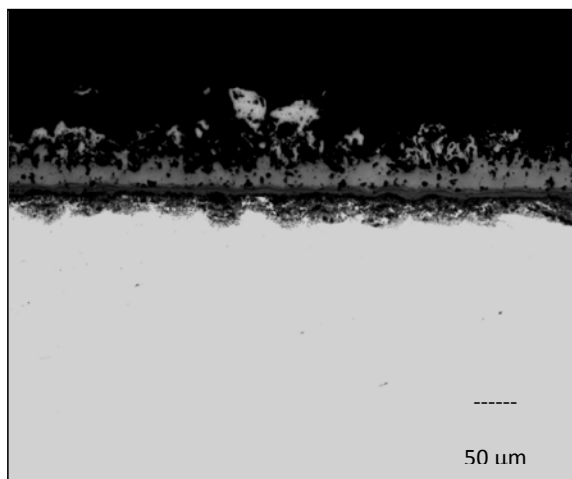
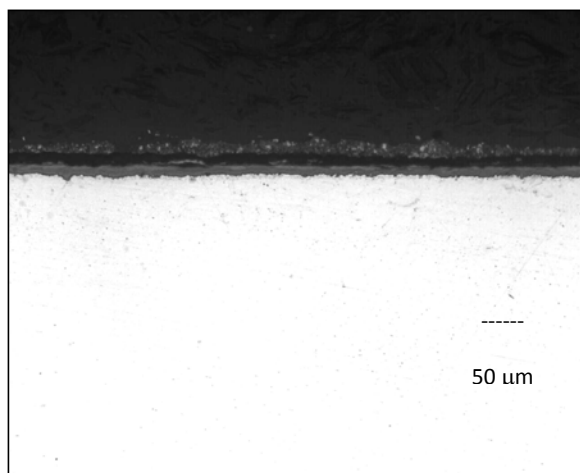


Fig. 12. Photomicrograph showing alloy 625 wrought sample after exposure for 4940 hours in simulated low-NO<sub>x</sub> boiler environment at 1000°F (538°C).

Depth of attack results shown in Figure 11 for the filler metal 72 overlay sample are 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. 13 and 14 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 in Fig.15, which shows the estimated performance of each alloy in one year with a half-cycle extrapolation.



*Fig. 13. Photomicrograph showing filler metal 72 sample after exposure for 4940 hours in simulated low-NO<sub>x</sub> boiler environment at 1000°F (538°C).*



*Fig. 14. Photomicrograph showing filler metal 72M sample after exposure for 4940 hours in simulated low-NO<sub>x</sub> boiler environment at 1000°F (538°C).*

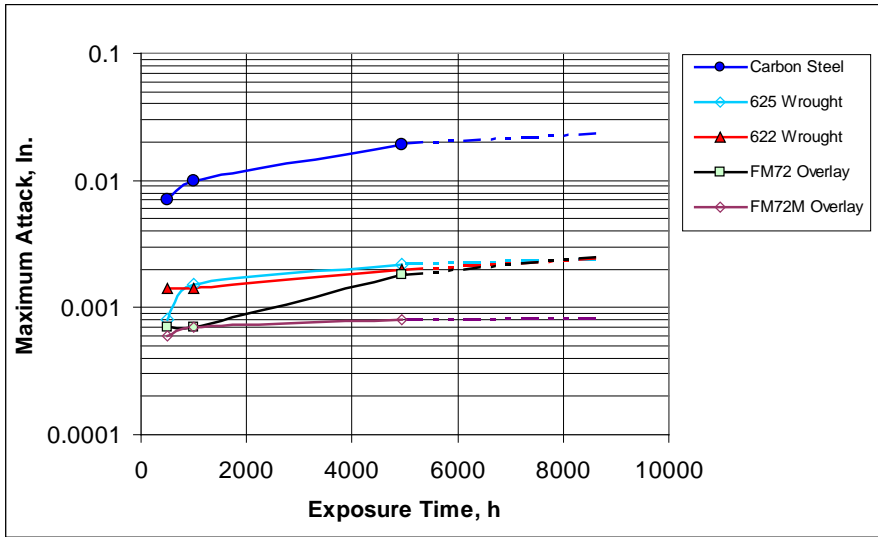


Fig. 15. Depth of attack results after exposure in simulated low-NO<sub>x</sub> corrosion test at 1000°F (538°C) for 4940 hours, showing extrapolation to one year (8760 hours).

## Conclusions

Weld overlay technology for protection of boiler tubing and super-heaters and re-heaters 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 super-heater and re-heater service for many years now. The new modification of 72, Filler Metal 72M, shows promise as an improvement over Filler Metal 72. These materials are now being evaluated as water-wall overlay materials as well. Initial results for Filler Metal 72 after seven years of service are extremely encouraging, while trials with Filler Metal 72M have a little more than 2 years exposure to date. 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  $\Delta T$  through the overlay and tube wall to the steam or water on the inside. The decreased  $\Delta T$  results in lower thermally induced strain, particularly in high heat-flux areas, which offers 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.

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