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Hot Corrosion of Weldments

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Abstract

Hot corrosion of the weldment is the result of the reaction between oxidation and sulfidation, which affects welded joints exposed to combustion gases containing sulfate coal ash at high temperature. It is also demonstrated that welding processes, weld consumables, temperature of exposure, and mixture of salt environment are important factors in hot corrosion of the weldment.

Hot corrosion is the main failure mode of welded components in the hot sections of gas turbines, boilers, metallurgical furnaces, and petrochemical installations. In this regard, the cyclic heating and cooling can mainly influence the corrosion behavior due to possible thermal stress on the weldment and their corrosion products. Hence, the maximum service temperatures of welded joints are decreased when exposed to hot corrosion environments.

Keywords: molten salt, air oxidation, weldment corrosion, dissimilar weldments, cyclic corrosion

1. Introduction

Joints of similar or dissimilar metals are used widely in various industrial applications owing to both technical and economic benefits. The production of high-quality welds with a high degree of consistency is achievable for the application in ambient conditions. However, the complexity arose while joining dissimilar metals, including the solidification cracking, microfissuring, and liquation cracking at the weld zone and heat-affected zone (HAZ) due to the differences in the coefficient of thermal expansion and chemical composition. Although there are numerous applications in which similar/dissimilar welds are employed, the current

discussion on this chapter is limited to high-temperature corrosion in power generation/high-temperature turbine environments.

Most of the failure analyses have shown that failure was experienced in the weld zone since it is generally inferior to its counterpart. The composition, morphology, and the secondary precipitates in the weldment undergo undesirable transformations in the aggressive high-temperature environments. Most of the research on high-temperature corrosion has been directed toward the correlation of the in-service failures of the weld joints to the microstructural degradation caused during welding. However, in recent years, systematic investigations in the laboratory setup report influence of welding processes, welding consumables, and different environments on hot corrosion behavior of weldments at the elevated temperatures.

Hot corrosion of the weldment is the result of reaction between oxidation and sulfidation which affects welded joints exposed to combustion gases containing sulfate coal ash at high temperature [1, 2]. It is also demonstrated that welding processes, weld consumables, temperature of exposure, and mixture of salt environment are important factors in hot corrosion of the weldment.

Failure of welded components in the hot sections of gas turbines, boilers, metallurgical furnaces, and petrochemical installations primarily occur due to hot corrosion [3, 4]. In this regard, the cyclic heating and cooling can have a huge influence on the corrosion behavior due to possible thermal stress on the weldment and their corrosion products. Hence, when exposed to aggressive corrosion environments, it is preferred that the maximum service temperatures of welded joints are decreased.

The deposition of K_2SO_4, Na_2SO_4, V_2O_5, $NaCl$, and KCl in many components in power plants is potentially harmful with regard to hot corrosion since these salts are the primary constituents of hot corrosion. Further, the deposition of chloride-rich salts on these components is considered detrimental, causing accelerated corrosion in the weld joints [5–9]. Internal oxidation/localized selective leaching in the weldment can particularly deteriorate the creep and fatigue lives of alloys due to phenomenon such as crack initiation at the grain boundaries.

In general, the service temperatures range between 400 and 650°C in typical superheater tubes, and the salt deposition converts to its molten phases. Nielsen et al. [8] have reported that the highest service temperature of weld joints was below 600°C. It is cost-effective, and hence it is necessary to improve the corrosion resistance of the weld by means of different welding techniques and filler wires for the future power plants.

The effect of hot corrosion becomes more aggressive at 600°C, due to the formation of low-melting alkali sulfates, which are eutectic mixtures, resulting in high sulfidation tendencies [10–15]. This tendency decreases when the operating temperatures are higher than 800°C, due to the reduced stability of the sulfate compounds at these temperatures [16–19].

In general, hot corrosion of the welded joints is more severe, due to the various metallurgical changes during the welding process and also due to the existence of a potential gradient along the weldment. These changes, although, will not have any deteriorating effect on the structural applications. However, there will be a huge impact on the corrosion resistance behavior of

welded joints, which mandates the evaluation of such components for their corrosion properties. In addition to the metallurgical effects, temperature of service and salt environment plays an important role in the corrosion resistance of the welded joints.

2. Effect of welding process

The amount of heat generated and their heat-transfer efficiency to the material to be welded were found to be different for various welding processes. The heat input supplied to the materials plays an important role in altering the metallurgical structures. More the heat input, wider the heat-affected zone (HAZ) and phase changes in the weld zone. The higher the welding speed, higher will be the temperature gradient, and hence less time for metallurgical changes. Similarly, current pulsing reduces the heat input during welding. In pulsed current welding processes, heat is supplied to the material only during the peak ON time, and during the peak OFF time, a meager amount of power is supplied just to maintain the arc, but not to extinguish. This results in sufficient time for the weldment to cool intermittently, thereby facilitating nucleation resulting in refined grains.

The effects of welding processes, the exposed environments, and temperature on weld corrosion behavior were investigated by Arivazhagan et al. [20, 21]. The authors studied the cyclic hot corrosion behavior of dissimilar weldments of AISI 4140 and AISI 304 made by friction welding (FRW), gas tungsten arc welding (GTAW), and electron beam welding (EBW). Studies were carried out with and without the salt mixtures of $Na_2SO_4 + V_2O_5$ (60%), Na_2SO_4 + NaCl (50%), K_2SO_4 + NaCl (60%), and Na_2SO_4 (40%) + K_2SO_4 (40%) + NaCl (10%) + KCl (10%) in the temperature range from 500 to 900°C under cyclic conditions. The typical macrograph of hot corroded dissimilar weldment in the molten salt environment is represented in **Figure 1**. The weight loss during each cycle is measured to evaluate the corrosion rate and kinetics.
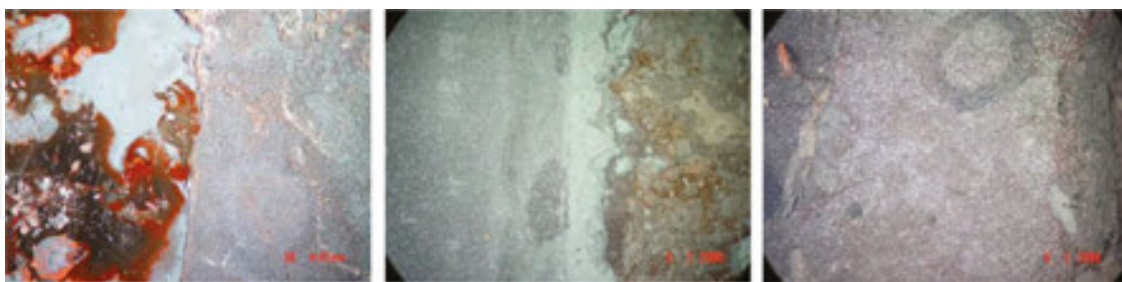

Figure 1. Macrographs of FSW (a), EBW (b), and GTA (c) welded AISI 4140 and AISI 304 subjected to molten salt environment at 600°C.

The kinetics of hot corrosion with molten salt mixtures shows higher growth rate of scale formation, which is much more severe under hot corrosion than with simple air oxidation. Although hot corrosion of the weldments is found to be in an accelerated manner in the molten salts, the salt composition plays an important role. In all the environments, the scales formed on the weldment were found to be oxides of Fe, Cr, and Ni and observed to be fragile and had

a tendency for spalling. The reason for the same could be attributed to the below-mentioned factors:

(a) Coefficient of thermal expansion differs for each base metal, weld, and the scale, which generates the stress.

(b) Stresses are generated during cooling, which may affect the adhesion property of the scale.

(c) Severe strain is developed due to the precipitation of oxides from the liquid phase and interdiffusion of intermediate layers of these oxides.

(d) Formation of scale within the growing scale as a result of two-way flow of the corrosive elements. Example: reactants, such as oxygen, diffuse to the inner region, while the diffusion of chromium from base metal is outward.

The study accounts for the influence of different welding processes, environments, and temperatures on the corrosion behavior of the dissimilar weldments (**Figure 2**).
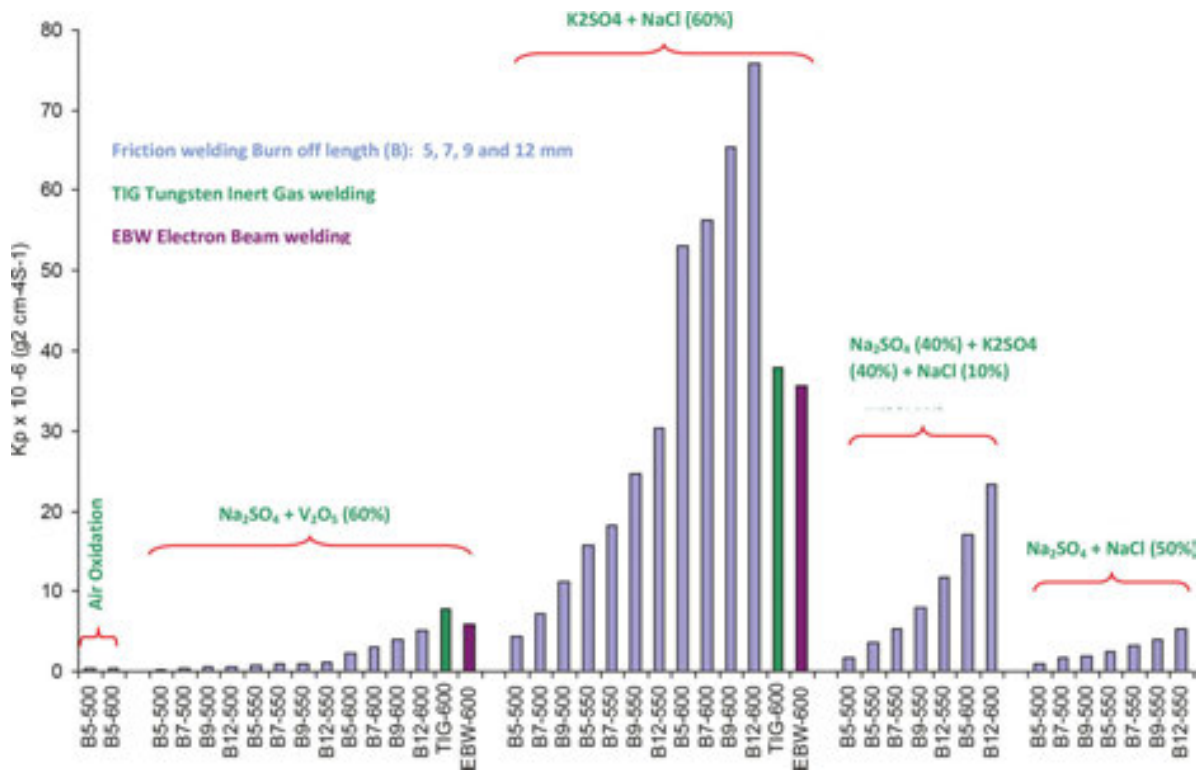

Figure 2. Bar charts showing parabolic rate constant K_p [$10^{-6}(g^2/cm^4/s^1)$] for dissimilar weldment subjected to cyclic oxidation in air and at molten salt environment for 50 cycles.

Irrespective of the temperature of testing or the salt composition, the oxidation rates and the overall weight gains for the investigated dissimilar weldments could be arranged in the following order, namely GTAW > EBW > FRW.

Further, the weld zone of dissimilar joints made by GTAW and EBW is more prone to corrosion due to the heterogeneous microstructure as compared to FRW. This phenomenon is the result

of the continuous spalling of the scale from the weld zone due to the damage occurring in the protective oxide layer, which provides path for the corrosive gases to reach the base material and thus allows significant grain boundary corrosion [22, 23].

From the bar charts, it can be inferred that the friction-welded dissimilar metals have shown low corrosion resistance against the given molten salt environments as compared to that against the air under cyclic conditions. The maximum weight gain in $Na_2SO_4 + V_2O_5$ (60%) environment at 600°C is 50 times higher than that of the one exposed to air under cyclic conditions, whereas, it is of 190 times in the environment of $K_2SO_4 + NaCl$ (60%). In the case of Na_2SO_4 (40%) + K_2SO_4 (40%) + $NaCl$ (10%) + KCl (10%), the weight gain is around 100 times as compared to the weldment exposed to air, whereas it is around 50 times in the environment of $Na_2SO_4 + NaCl$ (50%). XRD diffractograms and EDS analysis have indicated the phases formed identical to those formed during oxidation in molten salt in almost all the corroded samples. At 700 and 900°C, higher corrosion rates were observed due to the rapid reaction of molten salt when the friction-welded dissimilar weldments are exposed to the $Na_2SO_4 + V_2O_5$ (60%) environment.

The weight gain after 50 cycles of hot corrosion studies in all the environments could be arranged in the following order:

$K_2SO_4 + NaCl$ (60%) > Na_2SO_4 (40%) + K_2SO_4 (40%) + $NaCl$ (10%) + KCl (10%) > $Na_2SO_4 + V_2O_5$ (60%) > $Na2SO4 + NaCl$ (50%) > Air

The weight gain of weldment made by EBW and GTAW exposed to $Na_2SO_4 + V_2O_5$ (60%) is around 1.5 times higher than that of the weight gain of weldment made by FRW. The weight gain of weldment made by FRW exposed to $K_2SO_4 + NaCl$ (60%) is around 1.2 times higher than that of the weight gain of the weldment made by EBW and GTAW. It shows that the environment of $K_2SO_4 + NaCl$ (60%) is more aggressive for the weldment made by FRW as compared to the one made by EBW and TIG. Also, from the investigation, it was observed that the weight gain for the weldment made by EBW and TIG, exposed to $K_2SO_4 + NaCl$ (60%), is around two times higher than that of the weldment exposed to $Na_2SO_4 + V_2O_5$ (60%).

From the overall analysis of exposed samples in the three environments of study, the of scales formed on the weldments are identified as oxides of iron and chromium by X-ray diffract grams and is confirmed by the EDS analysis. From the EDS data, the scale on the weld zone of EBW and GTAW weldments contains higher amount of Cr_2O_3 and NiO, which is also higher as compared to that of friction weldment when exposed under $K_2SO_4 + NaCl$ (60%) at 600°C. It can be inferred from this that EBW and GTAW weldments have provided maximum resistance to corrosion as compared to the friction weldment in the above-said environment. This may be attributed to the fast formation of a continuous chromia scale on the weld zone due to the easy diffusion of Cr and Ni toward the weld zone from the sides of alloy 304. The EDS elemental analysis for most of the cases indicated the higher content of Fe_2O_3 and Cr_2O_3 on the scale over weldment, which may be due to the enrichment of this zone with Fe and Cr (**Figure 3**).
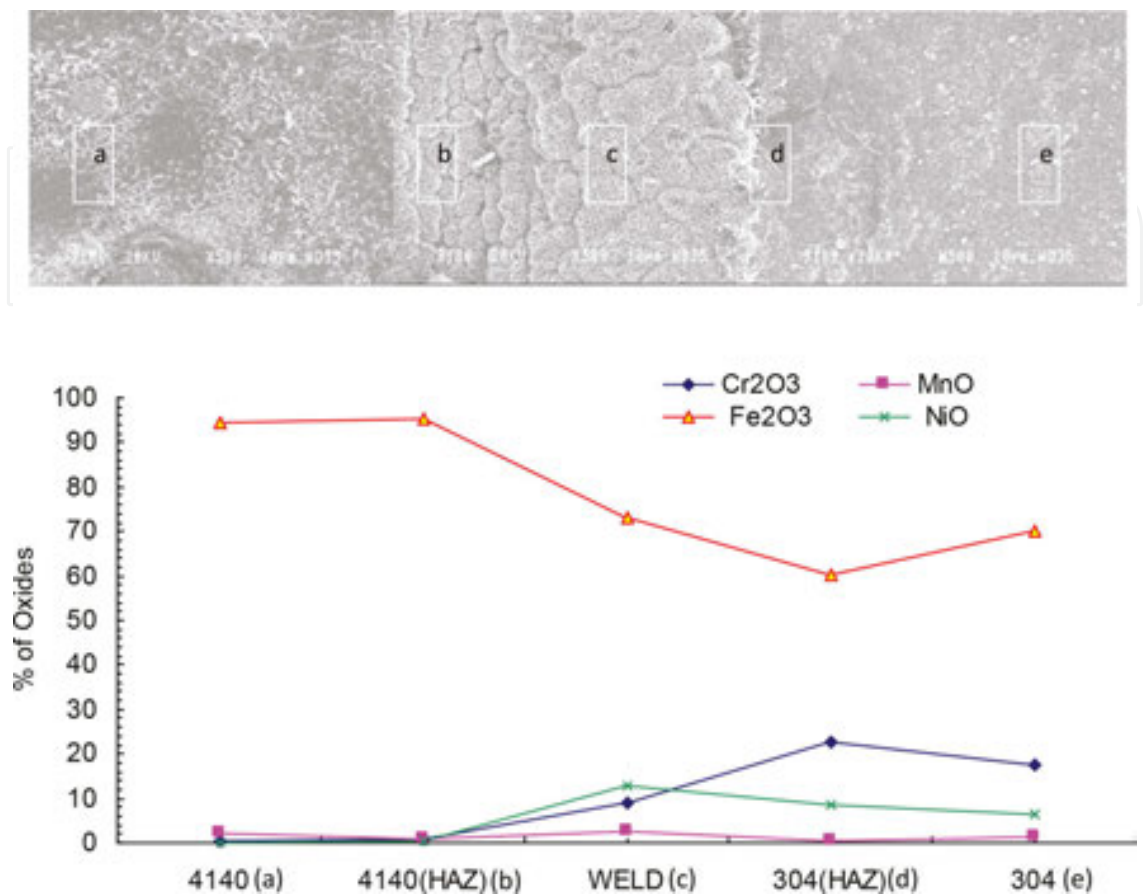
Figure 3. SEM/EDAX graph shows the friction weldment exposed at 600°C under molten salt environment after 50 cycles.

Arivarasu et al. [24] investigated the hot corrosion behavior of low-alloy steel AISI 4340 and austenitic stainless steel AISI 304L. Dissimilar weldment joined by continuous current gas tungsten arc welding (CCGTAW) and pulsed current (PCGTAW) gas tungsten arc welding (GTAW) techniques, using filler metals ER309L, ERNiCr-3, and also in autogenous process, was investigated.

In this study, the oxychlorination of these joints at 600°C in eutectic mixture of K_2SO_4 + 60% NaCl molten salt environment was investigated. In the weld and in the interfaces employing samples welded with pulsed current, the reaction of molten salt was higher than that of the CCGTAW process. Two reasons could be attributed to this behavior: first, the microstructure showed fragmented delta ferrites (**Figure 4**) at numerous locations of the weld zone in the pulsed mode, resulting in the formation of micro-electrochemical cells, which act as sites for corrosion initiation, leading to higher corrosion rate. Second, the ferrite content in the pulsed current is higher than that in the continuous current mode, as represented in **Table 1**. At

temperatures around 600°C, ferrite will decompose into σ-phase precipitates + austenite. This σ-phase results in the removal of Cr from the solid solution, resulting in the deterioration of the corrosion resistance of the austenitic stainless steel, which is in accordance with the literature [25–27].
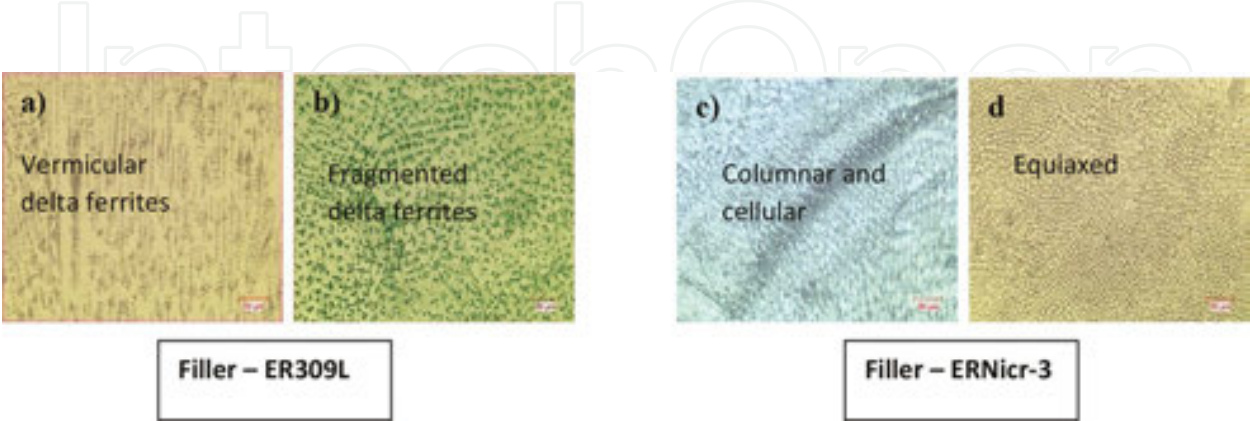

Figure 4. Microstructural variations in (a) CCGTA–ER309L, (b) PCGTA–ER309L, (c) CCGTA–ERNiCr-3, and (d) PCGTA–ERNiCr-3.

	Process	CCGTAW	PCGTAW
1	CAP	2.8	4.2
2	Root	0.65	2.6

Table 1. Average ferrite analysis in the weld zone of ER309L.

Thermogravimetric plots (**Figure 5a**) show that higher weight gain of 6.65 mg/cm^2 (217%) is observed in dissimilar joint fabricated by PCGTA welding processes as compared to the CCGTAW processes, in which is 1.71 mg/cm^2. Also, the corrosion rate K_p for the continuous current technique (0.133 × 10^{-7} g^2/cm^4/s) is less than that of the pulsed current technique (1.74 × 10^{-7} g^2/cm^4/s), which signifies that the corrosion resistance of CCGTAW is better than that of the PCGTA technique. The cumulative weight gain (**Figure 5b**) of CCGTAW process when employing ERNiCr-3 filler is 6.07 mg/cm^2 (91%) higher than that of the PCGTA process (1.71 mg/cm^2), suggesting that pulsed current mode is better corrosion-resistant than the continuous mode. The corrosion rate for CCGAW is 2.68 times higher than that of the PCGTA–ERNiCr-3 weldments (**Figure 5c**). The presence of fine equiaxed grains (**Figure 4c, d**) obtained by employing the pulsed current mode, when compared to the columnar dendrites in the continuous current mode, is attributed to the higher corrosion resistance of the pulsed mode [28, 29]. It was also reported that the fine-grained equiaxed microstructural solidification would improve the corrosion resistance than a coarse-grained microstructure.
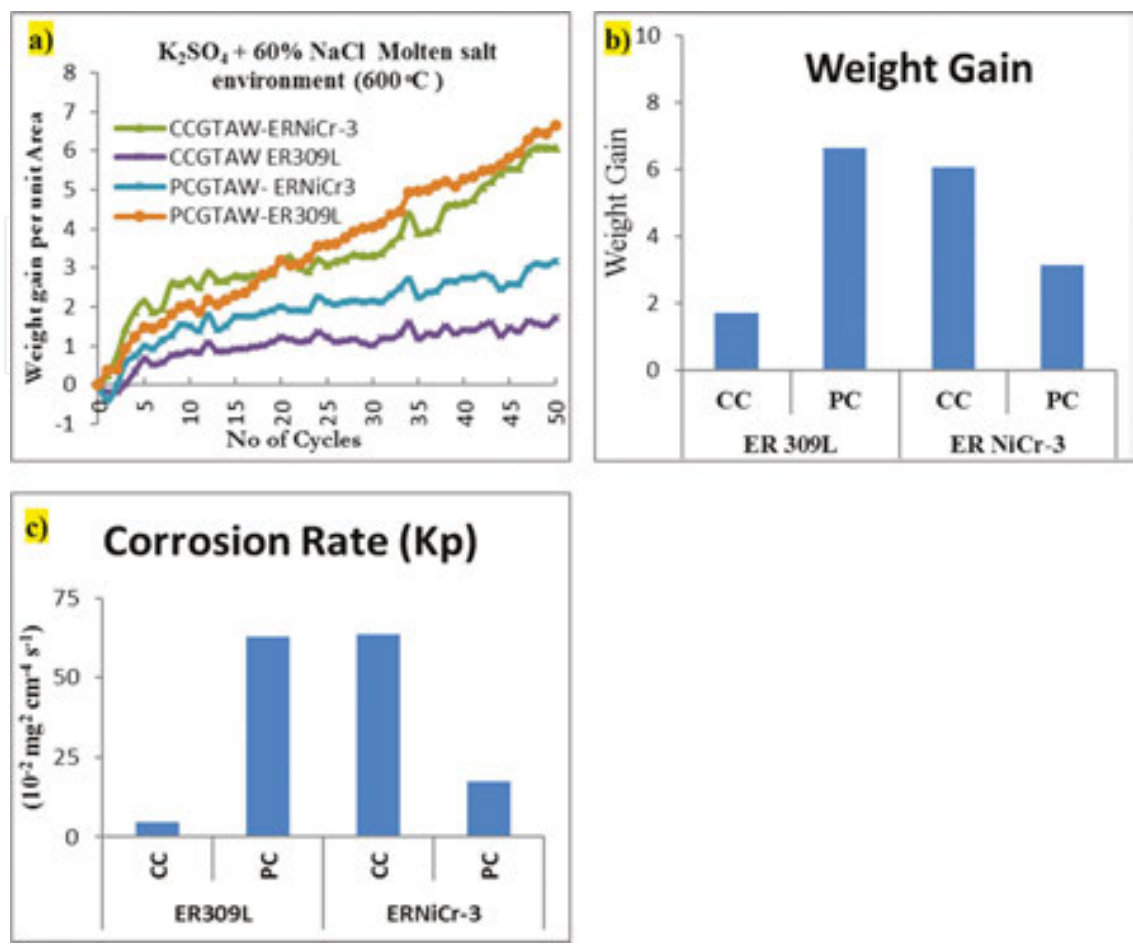
Figure 5. Analysis of hot corroded dissimilar AISI 4340 and AISI 304, showing (a) thermogravimentric, (b) chart weight gain, and (c) corrosion rate.

3. Effect of filler wire

One of the most important issues in the case of weld joints is the selection of proper filler materials. If the selection of filler wire is not appropriate, some weld defects such as fusion zone segregation, secondary phase formation, and dilutions deteriorate the corrosion behavior of the weld drastically. Furthermore, if the filler metal has lesser corrosion resistance than the parent metals, it would result in preferential corrosion attack on the weld metal. In general, overalloyed filler metals are used in the weldments to compensate for the loss of alloying elements by the welding fume and to protect the local area where there is less composition due to the segregation in the welds. A few parameters for the criteria of selection of filler metals include chemical composition, nearer corrosion potential in the galvanic series with respect to base metals, and additional alloying elements which improve corrosion resistance (e.g., addition of Ti/Ni in ER309L to eliminate chromium carbide precipitation, which subsequentially eliminates grain boundary corrosion/sensitization in elevated temperatures).

A matching filler wire gives a homogeneous nucleation/microstructure at the weld fusion zone, whereas an overmatching filler gives a heterogeneous nucleation/microstructure at various zones, leading to localized galvanized corrosion due to differences in the electrochemical potentials. The composition difference between the filler and base metal also influences the elemental migration during welding process. It is one of the major concerns, which affects the corrosion behavior of a weldment. Selection of filler metal and its dilution with the base metal also play a major role in the weldment's corrosion behavior, when exposed to the aggressive environments.
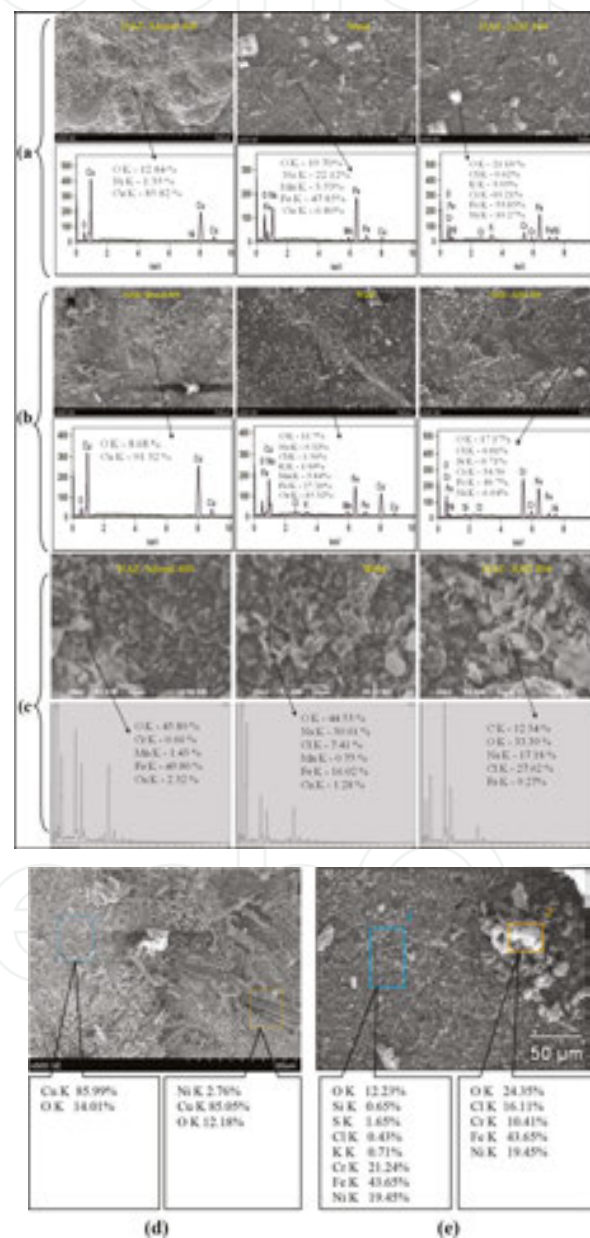

Figure 6. SEM/EDAX analysis of hot corroded GTA-welded dissimilar Monel 400 and AISI 304 (composite region) employing (a) E309L, (b) ENiCu-7, and (c) ENiCrFe-3 filler wires; (d) parent metal—Monel 400 and (e) parent metal—AISI 304 subjected to the molten salt environment of K_2SO_4 + 60% NaCl at 600°C.
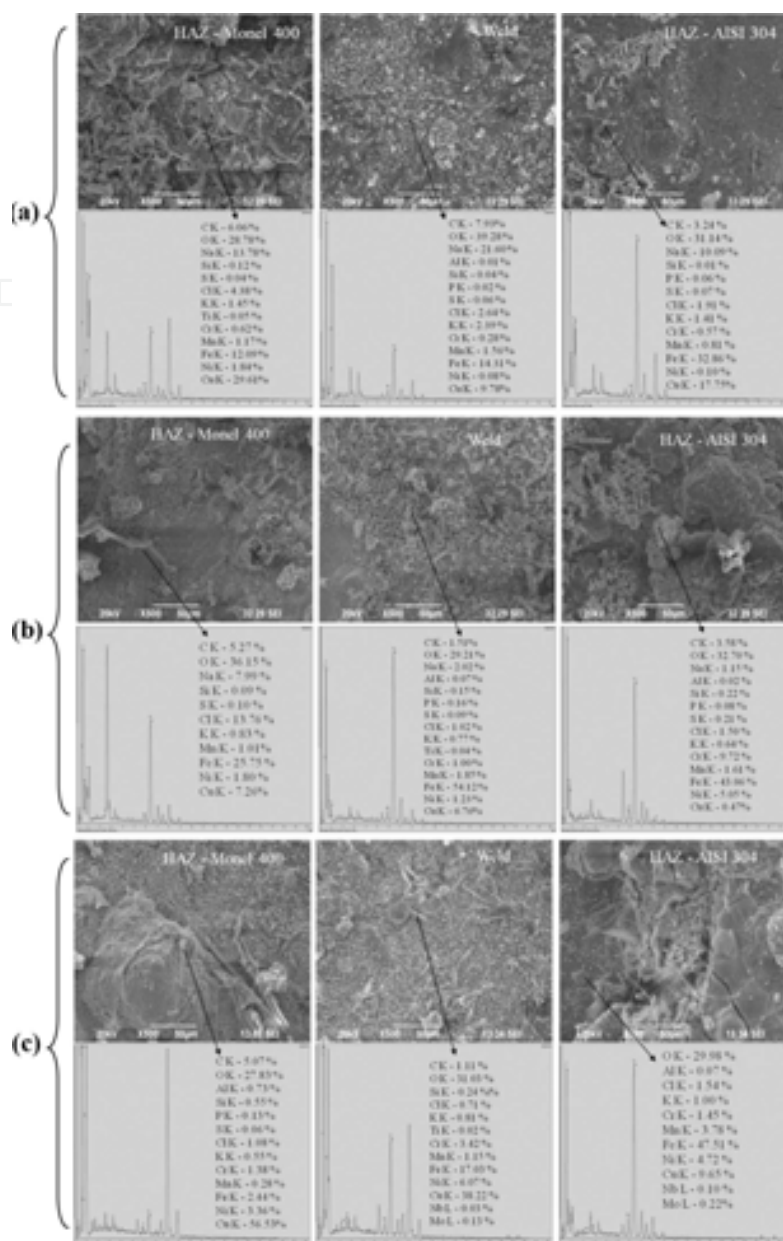
Figure 7. SEM/EDAX analysis of hot corroded PCGTA-welded dissimilar Monel 400 and AISI 304 (composite region) employing (a) E309L, (b) ENiCu-7, and (c) ENiCrFe-3 filler wires subjected to the molten sat environment of K_2SO_4 + 60% NaCl.

Devendranath et al. [30, 31] studied the effects of various filler wires (E309L, ENiCu-7, and ERNiCrFe-3) on the hot corrosion behavior of Monel 400 and AISI 304 dissimilar weldment subjected to cyclic air oxidation and a K_2SO_4 + NaCl (60%) molten salt environment at 600°C. The author investigated the dilution of different filler metals with base metals and the influence on weldment corrosion in the different environments. The authors reported that Fe and Cr are not completely soluble in the Ni–Cu alloy. The authors witnessed the formation of Fe-rich phases in the weld of Cu–Ni alloy and steel, which causes localized galvanic corrosion in the weld fusion zone [30]. Further, the author concluded that ENiCu-7 weld is found to be less

reactive, as the enrichment of Ni in the weld zone improved the corrosion properties primarily resulting from the nickel oxide which makes the molten salt less active (**Figures 6** and **7**). The formation of chlorides of Fe and Cr was witnessed in both CCGTA and PCGTA ENiCrFe-3 weldments. These metallic chlorides are highly volatile, leaving behind pits and voids in the subsurface of the metal. In molten salt environments, especially in the chromium-depleted regions, the corrosion morphologies show large amounts of subscale attack. Chromium chloride ($CrCl_3$) converts into oxide at very low oxygen pressure, iron chloride at significantly higher oxygen pressure, and a much higher oxygen partial pressure is needed to convert nickel chloride into NiO, especially at low temperatures. This means that evaporating chromium chlorides are oxidized closer to the metal surface than iron and nickel chlorides. Active oxidation, involving transport of metal chlorides in the liquid salt phase, destroys the normally protective Cr_2O_3 scale. In an environment with NaCl deposits, adding aluminum to the alloy to generate a protective Al_2O_3 scale should be able to increase the high-temperature corrosion resistance in a chloride environment.

Gokulkumar et al. [32] investigated the corrosion products of continuous current gas tungsten arc (CCGTA) and pulsed current gas tungsten arc (PCGTA) welded dissimilar Inconel 625 and AISI 316 L using ERNiCrMo-3, ER2209, and ERNiCr-3 filler metals subjected to cyclic hot corrosion in air and K_2SO_4 + NaCl (60%) molten salt environment at 650°C.

The author has well established that the salt mixture of K_2SO_4 and NaCl concentrate on the protective layer and partially diffuse through the porous scale. It was observed that the corrosive elements, such as Na, K, and Cl, liquefied the protective oxide scale at 650°C, and hence protection of the weldment is deteriorated. It is due to the formation of corrosive species, such as chlorides and sulfides, and these products are not fully protective in nature.

It is also concluded that the weldments exposed to the mixture of K_2SO_4 and NaCl were prone to a more aggressive attack in terms of corrosion than that of air oxidation.

The weld fusion zone produced by super-alloy fillers such as ERNiCrMo-3 and ERNiCr-3 contains higher Cr and Ni content; therefore, on the basis of standard free energy of Ni and Cr, it is possible to form Cr-rich oxide scale on its surface at 650°C, which provides an adequate protectiveness.

ERNiCrMo-3 weldment was found to have higher corrosion resistance as compared to other filler wires. This could be due to the formation of a protective oxide layer containing Ni, Cr, and Mo, which is more intact and more adhesive in nature. But, in the case of ER2209 weldment, the scale had more pores, poor adhesion, and a spalling nature. The corrosive environment had penetrated deeply into the weld and the weld interface.

It is also inferred that the corrosion rate of the weldments was influenced not only directly by the synthetic fused salt chemistry but also by the relative amount of corrosion-resistant elements such as Cr, Ni, and Mo. It is also clearly recorded that the weldment produced by employing Ni-rich austenitic fillers containing substantial amounts of Ni, Cr, and Mo demonstrated higher corrosion resistance than the stainless steel filler wire (**Figure 8**).

From the investigation, among the welding processes, the welds produced by PCGTA welding technique by using ERNiCrMo-3 filler wire have shown better corrosion resistance than other
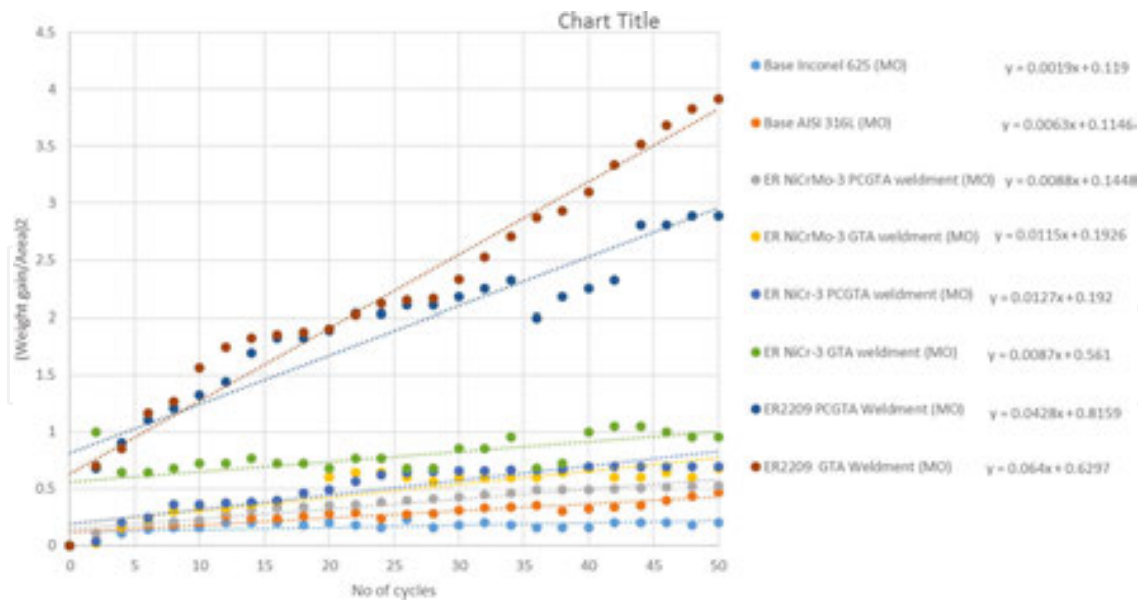
Figure 8. Thermogravimetric graph (weight gain/area)^2 of GTA and PCGTA weldment employing ERNiCrMo-3, ER2209, and ERNiCr-3 filler metals as well as base metals subjected to hot corrosion in the mixture of K_2SO_4 + NaC1 (60%) environment at 650°C.
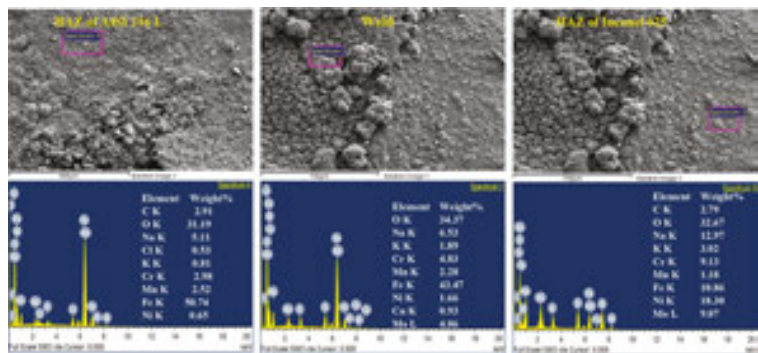

Figure 9. SEM/EDAX analysis of molten salt hot corroded dissimilar Inconel 625 and AISI 316 L weldment employing ER2209 filler metal.

filler wires. This can be inferred from the corrosion products determined by combining the SEM/EDS and the XRD that the scale contains Cr_2O_3 and Ni–Cr, Ni–Cr–Mo spinel oxides due to diffusion-controlled reaction. It is also observed from the investigation, among the filler wires, that the weldments produced by ERNiCr-3 and ERNiCrMo-3 fillers have shown higher resistance than ER2209 weldment (**Figure 9**).

Arivarasu et al. [24] investigated the effect of filler wires such as ER309L and ERNiCr-3 on hot corrosion behavior of low-alloy steel AISI 4340 and dissimilar weldment of austenitic stainless steel AISI 304L by employing CCGTAW and PCGTAW processes.

In the case of employing ER309L filler, the continuous current has better corrosion resistance than the pulsed current. The filler forms a considerable amount of ferrites for improved

metallurgical aspects in terms of avoiding microfissuring during welding and has resulted in fragmented ferrites in the case of pulsed current than the vermicular ferrite in the continuous current technique.

Also, filler wire ERNiCr-3, which is an overmatching (nickel based) filler, employed to attain a better mechanical property has resulted in higher weight gain and corrosion rate than the ER309L filler employed in the continuous current mode. This is because it introduces additional zones of varying chemical composition, leading to increased electrochemical activity in the higher temperature than the one with ER309L filler, which has compatible composition with one of the base material E309L.

As per the literature, pulsed current is supposed to produce fine-grained structures, irrespective of the fillers employed and shall lead to better mechanical properties. But, from the experimental results stated above, it is evident that in terms of corrosion behavior, there shall not be a set thumb rule, and it is based on the compositional and microstructural variations that form during different processes. This shows that the filler metal and the process individually have the ability to alter the corrosion resistance of a weldment at higher temperature.

4. Recommendations

One of the key successes to improve weld corrosion resistance is the selection of suitable welding processes with reduced heat input and appropriate/matching composition of filler metal, resulting in fewer variations in the microstructures. The hot corrosion behavior of the weld could be improved by choosing welding techniques with lower heat input by employing high-alloy filler wire. Selecting appropriate welding consumables could reduce the dendritic and interdendritic segregations, which reduce the localized galvanic effects in turn to improve the corrosion behavior of the weld. A heat treatment can be an effective way to improve the corrosion resistance of the weld by avoiding residual stress, segregation, localized galvanic cell, and unwanted negative phases. Adopting an interpass heat treatment during welding could avoid the hydrogen cracking of the welded components in the service environment.

Finally, it is highly impossible to eliminate the high-temperature corrosion. However, this could be minimized by selecting suitable welding techniques, processes, parameters, and weld consumables.

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