

# Studies on Weldment Corrosion in Different Corrosive Environments

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**Abstract.** This paper reports on the performance of Electron Beam Welded (EBW) low alloy steel AISI 4140 and stainless steel AISI 304 in air as well as molten salt environments of Na<sub>2</sub>SO<sub>4</sub>-60%V<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>SO<sub>4</sub>-60% NaCl at 650°C. The corrosion kinetics has been established by thermo-gravimetric technique during the initial stages. In this work, X-ray diffraction, scanning electron microscopy/energy-dispersive analysis and electron probe micro analysis techniques were used to analyze the corrosion products. It is well observed from the experimental results that the weldments suffered accelerated corrosion in K<sub>2</sub>SO<sub>4</sub>-NaCl environment and showed spalling/sputtering of the oxide scale. Furthermore, corrosion resistance of weld interface was found to be lower than that of parent metals in molten salt environment. It is also inferred from the results that NaCl is the one of the main

corrosive species in hot corrosion, involving mixtures of  $K_2SO_4$ –NaCl and which is responsible for internal corrosion attack.

## 1. Introduction

This Dissimilar metals are widely used in critical high service temperature applications. Hence the studies on their weldments have gained importance in recent past. Generally, the combination of low alloy steel and austenitic stainless steel weldments are extensively used for boiler tubing application at elevated temperatures because of its relatively low cost, good weldability and creep resistance [1, 2]. Since these steels exhibit vastly different physical, thermal, mechanical and metallurgical characteristics, they are prone to defects during welding as well as in service environment [3, 4]. Particularly, the failure of dissimilar weldments involving low-alloy steel with austenitic stainless steel has been studied by a number of investigators and factors that contribute to failure have been seldom taken up for research. Advanced welding process like electron beam welding can offer a solution to the problem of sensitization, dilution and cracking of elements in conventional welding. Even though electron beam welding is a comparable alternative, the problem of carbide formation is not yet completely eliminated for the joints when they are exposed to cyclic high temperature service conditions. Usually, low-grade fuels with high concentrations of sulfur, vanadium and sodium are used in oil- and coal fired power generation. During combustion, alkali metal sulfates and  $V_2O_5$  vapors combine with other ash constituents that deposit onto the component surfaces. The boilers exposed in off-shore industrial rigs undergo hot

corrosion when the sodium chloride from the ocean breeze mixes with  $\text{Na}_2\text{SO}_4$  from the fuel and deposits on the hot-section of the components. This results in severe corrosion attack by oxidation, sulfidation, chloridation and even hot corrosion [5]. It is to be noted that hot corrosion is the serious problem for the weldments exposed to environment containing mixture of the salt  $\text{K}_2\text{SO}_4$ – $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$ – $\text{V}_2\text{O}_5$ . The existence of such corrosive condensation layer on the surface leads to hot corrosion which can considerably reduce the service life of high temperature components [6–8]. The steel's performance in oxidizing environments is well established, but weldment behavior in corrosive environments, particularly those containing sulfidizing and chlorides have not been studied extensively.

In the present investigation, an attempt has been made to evaluate the hot corrosion behavior of electron beam welded AISI 304 and AISI 4140 metals exposed in air as well as molten salt environment consisting of eutectic mixture of  $\text{Na}_2\text{SO}_4$ –60%  $\text{V}_2\text{O}_5$  and  $\text{K}_2\text{SO}_4$ –60%  $\text{NaCl}$  at 650 °C under cyclic conditions. Thermogravimetric technique was used to establish the kinetics of corrosion. The products of hot corrosion studies have been analyzed using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray studies (EDAX) and Electron Probe Micro Analyzer (EPMA) techniques.

## 2. Experimentation

In this study, experiments were carried out on a Low KV electron beam welding machine. and the welded specimen and its cross sectional macro structure are depicted in Fig 1. Studies by the authors involving detailed metallurgical and

mechanical properties of electron beam welded samples are published elsewhere [18]. Specimens for hot corrosion tests are fabricated using electron beam welding machine. These specimens are initially having the dimensions of 100×50×6 mm. To facilitate the hot corrosion tests, the samples are cut into rectangular pieces (20 × 15 × 6 mm) with weld zone in the middle of the specimens. Mirror polishing down to 1 μm by alumina on a cloth polishing wheel is carried out before the corrosion run. Immediately, a coating of uniform thickness with 3–5 mg/cm<sup>2</sup> of salt mixture was applied with a camel hair brush on the preheated sample (250 °C). Cyclic hot corrosion studies were performed on these specimens by subjecting in the air as well as molten salt (Na<sub>2</sub>SO<sub>4</sub>–60% V<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>SO<sub>4</sub>–60% NaCl) environments for exactly 50 cycles and the duration of each cycle is for 1 h 20 mins in which heating is for one hour at 650 °C in a silicon carbide tube furnace followed by 20 mins of cooling at room temperature. During the corrosion tests, the weight change measurements were taken at the end of each cycle. The samples after corrosion tests are subjected to characterization studies using SEM/EDAX and XRD analysis.

### 3. Results

The corrosion kinetics of specimens with and without molten salt deposits is depicted in Fig 2 as a plot of weight gain per unit area vs. function of time (number of cycles). These figures indicate that the weight gain kinetics under air oxidation shows a steady-state parabolic rate law, whereas the molten salt environment is a multi stage weight-gain growth rate. XRD analysis has been performed on the weldments before as well as after corrosion run and is shown in Fig 3. Investigations

showed that the phases such as FeNi and Ni<sub>3</sub>C, Cr–NiMo, CrNiFe, Ni<sub>3</sub>C, and Cr–Si–C are observed in the as-welded samples. Fe<sub>2</sub>O<sub>3</sub> has been predominated with lower intensities of NiCr<sub>2</sub>O<sub>4</sub>, NiO and FeNi in the air oxidation samples at 650°C. Whereas Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> dominate with greater peak intensities with a lesser intensities of (Cr, Fe)<sub>2</sub>O<sub>3</sub>, FeNi and FeS on the hot corroded samples under molten salt environment at 650°C. SEM Surface morphology of dissimilar weldment after hot corrosion treatment by keeping 650°C is shown in Fig 4–6. EDAX analysis for the weldment after air oxidation as well as molten salt environment [Na<sub>2</sub>SO<sub>4</sub>–60% V<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>SO<sub>4</sub>–60% NaCl] shows Fe<sub>2</sub>O<sub>3</sub> to be the predominant phase in the entire region. However Cr<sub>2</sub>O<sub>3</sub> content is higher in the scale of heat affected zone of AISI 304. Moreover some minor constituents of MoO<sub>3</sub>, MnO and NiO were observed on the weldment as seen in Fig 4–6.

#### 4. Discussions

The results obtained in air oxidation at 650°C show a better corrosion resistance as compared to molten salt environment. The authors reported the detailed study of the mechanical properties of AISI 4140 and AISI 304 dissimilar metals made by electron beam welding process in their earlier publication [10].

Thermo-gravimetric curve of molten salt environment studies shows the tendency of multi stage weight-gain growth rate (Fig. 2). It could be due to changes in reaction rate which are associated with the formation of a laminated inner-oxide layer made up of fine and coarse grain spinel oxide as suggested by Hurdus et al [11]. The kinetics of hot corrosion with K<sub>2</sub>SO<sub>4</sub>–NaCl mixtures shows rapid weight

gain compared to  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$  as well as air oxidation. In a molten salt environment, sulfur was incorporated into scale and leads to a sulfide formation in the alloy substrate. Therefore, as the formation of protective oxide scale was inhibited by the presence of NaCl, chlorides and sulfides tend to form in the alloy substrate as indicated leading to the propagation of hot corrosion as suggested by Charng et al., [12]. The parabolic rate constants  $K_p$  for weldment after exposed in air oxidation,  $\text{Na}_2\text{SO}_4\text{-60% V}_2\text{O}_5$  and  $\text{K}_2\text{SO}_4\text{-60% NaCl}$  were 0.652, 5.917 and  $35.511 \times 10^{-6} \text{ (g}^2 \text{ cm}^{-4} \text{ s}^{-1})$  respectively.

SEM/EDAX analysis of the corroded sample shows,  $\text{Fe}_2\text{O}_3$  in the scales of weldment after the corrosion cycles signifies non-protective conditions in  $\text{Na}_2\text{SO}_4\text{-60% V}_2\text{O}_5$  and  $\text{K}_2\text{SO}_4\text{-60% NaCl}$  at 650 °C (Fig 4-6). The formation of  $\text{Fe}_2\text{O}_3$  in the spalled scale has also been reported to be non-protective during their hot corrosion study on  $\text{Fe}_3\text{Al}$ -based iron aluminides in  $\text{Na}_2\text{SO}_4$  atmosphere [13, 14]. The corrosion rate of the weldment in  $\text{Na}_2\text{SO}_4\text{-60% V}_2\text{O}_5$  is higher as compared to air oxidation at 650 C° due to the formation  $\text{NaVO}_3$  as proposed by Kolta et al., [15]. As  $\text{NaVO}_3$  acts like a catalyst and also serves as an oxygen carrier to the base alloy, it tends to oxidize the basic elements rapidly. Furthermore, the increase in magnitude of weight gain is due to the accelerated corrosion in  $\text{K}_2\text{SO}_4\text{-60% NaCl}$  environment which also opined by Kofstad [16]. It is widely agreed that the corrosion rate will be more severe when the temperature is higher than the melting point of salt deposits. It is observed that the corrosion rate in  $\text{K}_2\text{SO}_4\text{-60% NaCl}$  environment is higher in magnitude as compared to  $\text{Na}_2\text{SO}_4\text{-60% V}_2\text{O}_5$  and air oxidation environments. It is observed that the thickness of scale is more on 4140 side than 304 side after exposed in  $\text{Na}_2\text{SO}_4\text{-60% V}_2\text{O}_5$  environment. After the hot corrosion treatment, it is

observed that the effect of hot corrosion is more on 4140 side as evident from the degree of scaling and spalling of scale. It is observed that the scales get detached by means of the formation of new scale within already growing scale. This is usually attributed to the two-way flow of the reactants [17].

At the end of corrosion tests, it is noticed that the weld interface of the dissimilar weldment is more degraded as compared to base metals (Fig 4–6). Corrosion morphology of the weldment exposed in  $K_2SO_4$ –60% NaCl shows that the weld interface is more prone to formation of fragile scale than base metals. This implies that NaCl plays a vital role in hot corrosion [18]. Moreover the melting of  $K_2SO_4$ –60% NaCl mixture at 650 °C makes the weldments susceptible to accelerated oxidation due to acidic and basic-fluxing mechanism. Many researchers have pointed out that the formation of sodium chromate ( $Na_2CrO_4$ ) could result from oxy-chloridation even the temperature is lower than the melting point of salt deposits [19]. As  $Na_2CrO_4$  is formed, the salt will wet the specimen surface which eventually leads to a mechanism of hot corrosion dominated by molten salt and is further validated by XRD analysis (Fig 3). The analysis of the scale shows predominant  $Fe_2O_3$  with low intensities of  $Cr_2O_3$ ,  $Na_2CrO_4$ ,  $SO_3$  and  $MoO_3$ . This is in confirmation with past studies on the hot corrosion studies in molten salt environment on boiler tube steel [19].

## 5. Conclusion

From the experimental studies, some of the important conclusions obtained are as follows.



- [1] The weight gain of salt coated welded specimen follows a parabolic rate law during hot corrosion. Rate of oxidation was observed to be higher in the earlier cycles of the study in all the aforementioned environments, which may be attributed to the fact that during transient period of oxidation, the scales formed may be providing protection to the underneath metals.
- [2] In case of salt coated specimens, the surface scale is more porous and spalled out, thereby providing an easy diffusion path for the corrodents. The scale formed due to hot corrosion mainly contains  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ ,  $\text{NiCr}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ .
- [3] The corrosion rates for the investigated electron beam welded dissimilar metals based on the overall weight gains after 50 cycles in all the environments could be arranged in the following order:  $\text{K}_2\text{SO}_4\text{--}60\% \text{ NaCl} > \text{Na}_2\text{SO}_4\text{--}60\% \text{ V}_2\text{O}_5 > \text{Air}$

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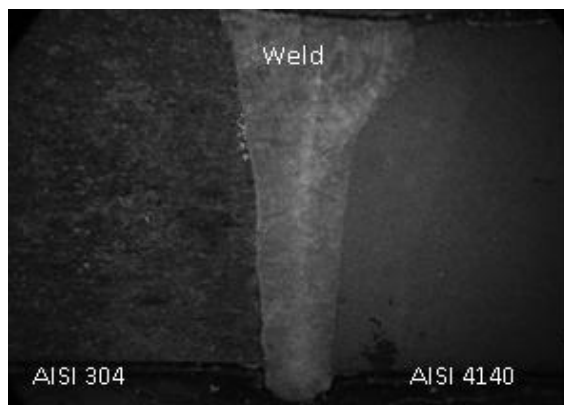


Figure.1

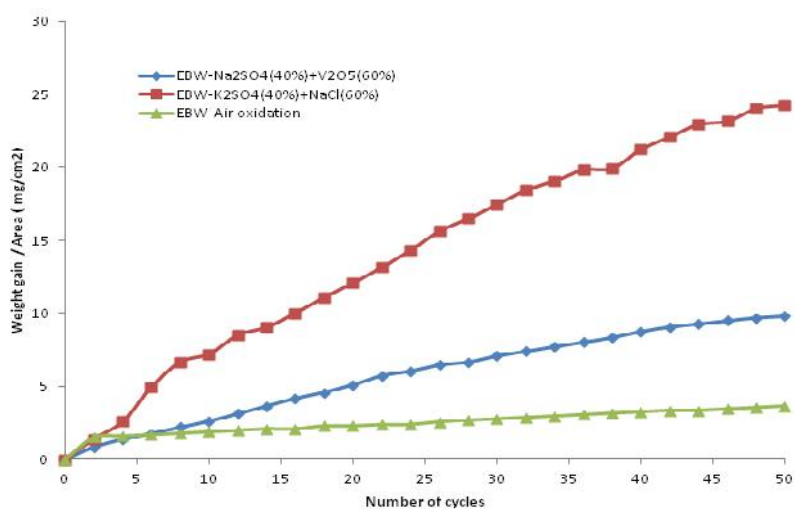


Figure.2

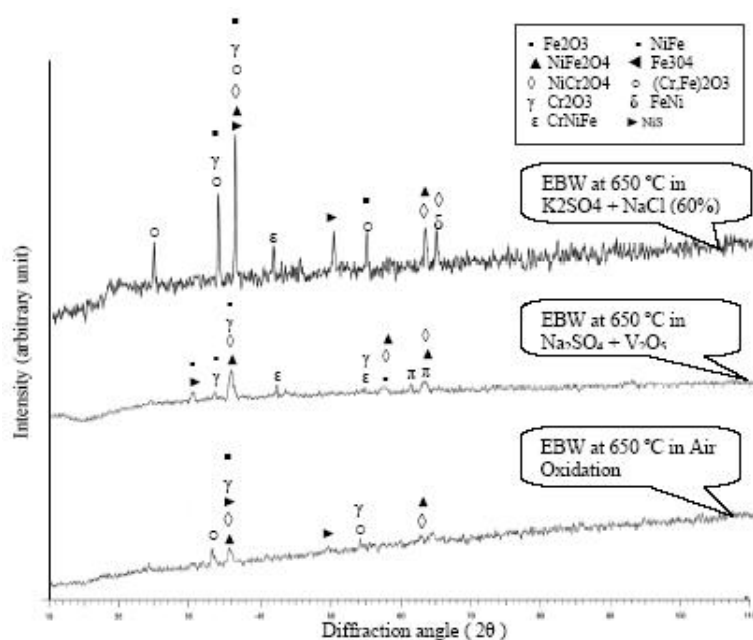


Figure.3

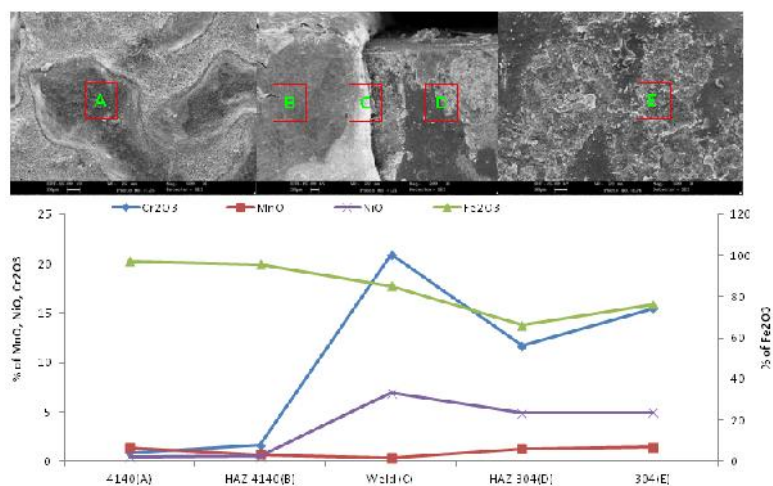


Figure.4

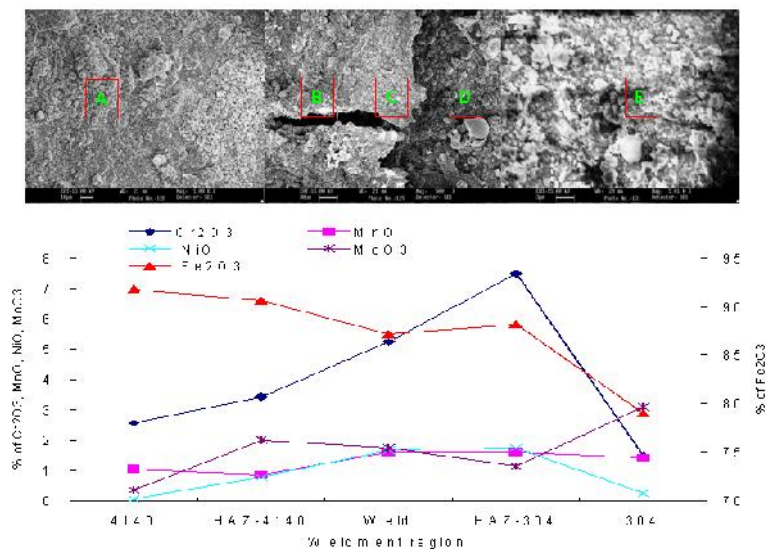


Figure 5

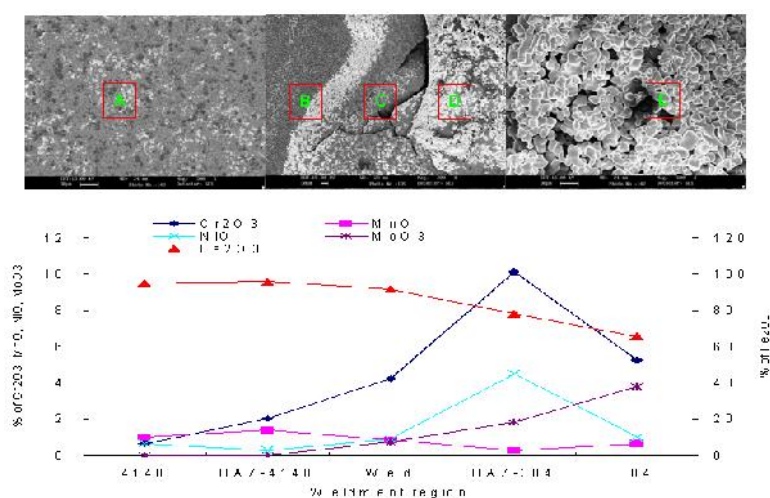


Figure 6

## Legends of figures

Figure.1 Macrograph welded specimen

Figure.2 Plots of cumulative weight gain (mg/cm<sup>2</sup>) as a function of time

Figure.3 XRD patterns for hot corroded samples at 650 °C.

Figure.4 SEM/EDAX graph shows the EBW weldment of AISI 4140 and AISI 304 exposed at 650 °C in air oxidation after 50 cycles.

Figure.5 SEM/EDAX graph shows the EBW weldment of AISI 4140 and AISI 304 exposed at 650 °C under K<sub>2</sub>SO<sub>4</sub> + NaCl (60%) after 50 cycles.

Figure.6 SEM/EDAX graph shows the EBW weldment of AISI 4140 and AISI 304 exposed at 650 °C under Na<sub>2</sub>SO<sub>4</sub> + V<sub>2</sub>O<sub>5</sub> (60%) after 50 cycles.