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High Temperature Studies on Welded Joint in Molten Salt Power Plant Environments

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Abstract: Understanding the performance of welded joint at high temperature corrosive environment has become an objective of scientific investigation recently. This work encompasses the investigations carried out on the Gas tungsten arc welded AISI 4140 and AISI 304 in air-oxidation, molten salt environment of Na_2SO_4-60%V_2O_5 and $_2SO_4$-60% NaCl at 650 °C under cyclic condition are discussed. The resulting oxide scales in the weldment have been characterized systematically using surface analytical techniques. From the results of the experiments, it is observed that the scale thickness on low alloy steel side was found to be higher as compared to stainless steel side. Furthermore, weld interface has been found to be more susceptible to degradation than base metals due to inter diffusion of element across the interface and the formation of intermetallic compound. The influences of air oxidation and molten salt environments on the hot corrosion behavior of the weldment have been discussed in this paper.

Keywords: Metal Joining; High temperature Corrosion; Molten salt Environment.

1. Introduction

Dissimilar metals are widely used in critical high service temperature applications. Hence studies on their weldments have gained importance in recent past. Generally, 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]. In power plant engineering applications it is necessary to join low alloyed ferritic steels to austenitic chromium-nickel-molybdenum stainless steels. Primary boilers and heat exchangers operate at high temperatures with corrosive environmental conditions that make low-alloy steels and austenitic stainless steels the best choice [3].Primary boilers and heat exchangers operate at high temperatures with corrosive environmental conditions that make low-alloy steels and austenitic stainless steels the best choice [4]. The role played by chlorides [5], which enter through ingressed air in marine atmospheres, is also important in deciding the degree of corrosion. The role of NaCl in hot corrosion by Na_2SO_4 has been discussed in detail [6, 7]. In this article, the effect of air as well as mixture of Na_2SO_4-60%V_2O_5 and K_2SO_4-60% NaCl on hot corrosion behaviour of GTA welded AISI 304 and AISI 4140 specimens are studied. Studies by the authors involving detailed metallurgical and mechanical properties of GTA welded samples are published elsewhere [4].

2. Experimentation

Materials conforming to the AISI standards are procured and their chemical composition is shown in Table.1**.** A Standard "V" Groove butt joint of dissimilar AISI 4340 and AISI 304 plates is prepared, Autogeneous full penetration welding is carried out on the dissimilar joints with Gas tungsten Arc welding process . The process parameters for the GTAW welded samples is shown in the Table.2. A Macrostructure of the dissimilar butt joint is examined and the joint is found to have a sound weld without any weld defects Fig.1.

To facilitate the hot corrosion tests, three samples are cut into rectangular pieces (20 × 15 × 5 mm) with weld zone in the middle of the specimens and mirror polished. To remove the moisture from the sample and also for the salt to adhere to the surface uniformly the sample is preheated to 250 °C. Immediately, a coating of uniform thickness with 3–5 mg/cm2 of salt mixture was applied on the preheated sample. On these specimens, cyclic studies were performed in the air as well as molten salt (Na_2SO_4-60%V_2O_5 and K_2SO_4-60% NaCl) 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 spalled scale was also retained during the measurement of the weight change to determine the total rate of corrosion. The samples after corrosion tests are subjected to characterization studies using SEM/EDAX, XRD and EPMA for surface and cross-sectional analysis of the scale.

Table.1 Chemical composition of AISI 304 and AISI 4140

Parent Metal	C	Cr	Mn	Ni	Si	Mo	Fe
AISI 304	0.06	18.4	1.38	8.17	0.32	----	Balance
AISI 4140	0.40	1.1	0.75	----	0.31	0.28	Balance

Table.2 GTA welding parameters

Type of Weld	Welding parameter	Value
GTA Welding	Current (DCSP) (Amp)	300
	Voltage (volt)	**23**
	Argon Flow rate (lpm)	14
	Torch traveling Speed (cm/ sec)	0.2

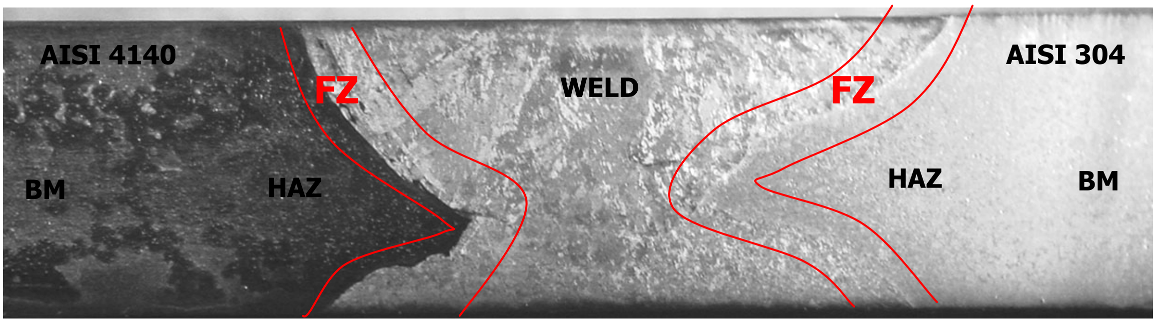

Figure.1 Macro structure of GTA welded AISI 4140 and AISI 304 dissimilar metals.

3. Results and Discussions

Metals and alloys undergo oxidation when exposed at elevated temperatures in air which may be may be protective or non-protective.Whereas the metals exposed in molten salt environment could accelerate the corrosion rate due to combined form of oxidation, chloridation and sulphidation. The macrographs for hot corroded samples dictate that the weld interface is more prone to hot corrosion (Fig 2.). Fig 3 shows the 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.The parabolic rate constants Kp for wledment after exposed in air oxidation, Na_2SO_4-60% V_2O_5 and K_2SO_4-60% NaCl were 2.96, 7.72 and 37.85 ×10 -6 (g^2cm^{-4} s^{-1}) respectively. It is noted that, the hot corrosion in molten salt environment was observed to be more extensive. Moreover, higher corrosion rate is observed during initial hours of study and is mainly attributed to the rapid oxygen pick up by diffusion of oxygen through the molten salt layer and is found to be identical to the results reported by Sidhu and Prakash [8], Tiwari and Prakash [9] during their hot corrosion studies. As revealed by XRD, different phases of various reaction products were formed on the weldments after corrosion cycles. Air oxidation at 650 °C, Fe_2O_3 has been predominated with small amount of $NiCr_2O_4$, NiO and FeNi. Hot corrosion under molten salt environment at 650 °C shows that Fe_2O_3 and Cr_2O_3 as the predominant phases and $NiCr_2O_4$, $(Cr, Fe)_2O_3$, FeNi and FeS are observed with low intensity. 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 [10-12]. 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 4). 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 [13].

SEM/EDAX analysis of the corroded sample shows, Fe_2O_3 in the scales of weldment after the corrosion cycles signifies non-protective conditions in air-oxidation, Na_2SO_4-60%V_2O_5 and K_2SO_4-60% NaCl at 650 °C (Fig 5-7). Corrosion morphology of the weldment exposed in K2SO4-60% 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 [14-16]. It is observed that, the corrosion rate in K_2SO_4-60% NaCl environment is higher in magnitude as compared to Na_2SO_4-60%V_2O_5 and air oxidation environments.

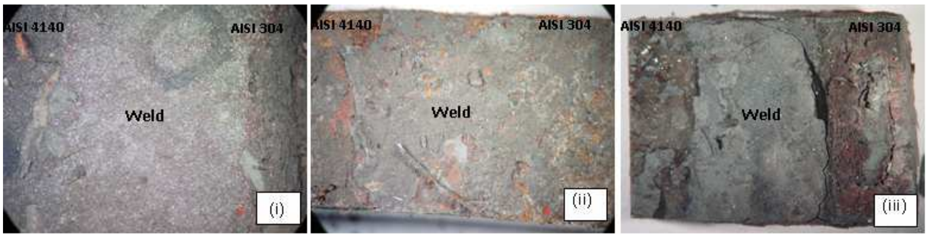

Figure. 2 Macrographs dissimilar TIG Welded AISI 4140 and AISI 304 subjected to cyclic hot corrosion at 650 °C. (i) Air oxidation, (ii) $Na_2SO_4 + V_2O_5$ (60%) and (iii) K_2SO_4-60% NaCl after 50 cycles.

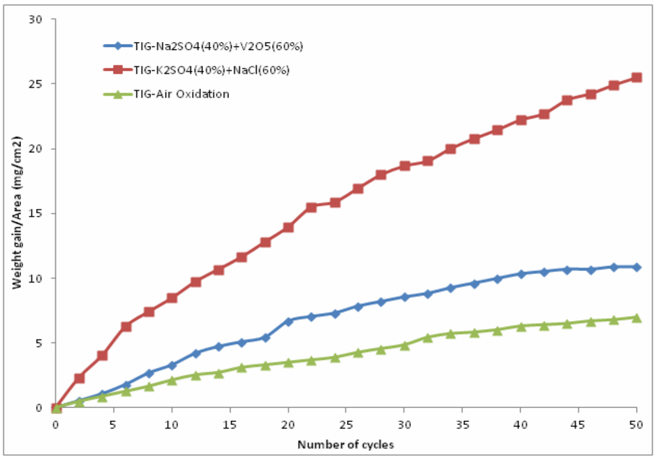

Figure. 3 Plots of cumulative weight gain (mg/cm2) as a function of time (number of cycles).

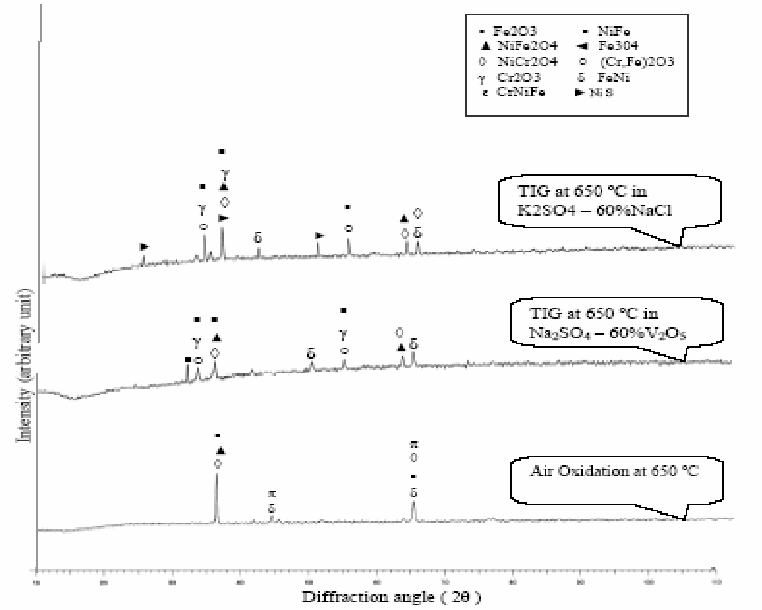

Figure. 4 X-Ray diffraction patterns for hot corroded dissimilar TIG weldment of AISI 4140 and AISI 304 exposed in air, Na_2SO_4 + V_2O_5 (60%) and K2SO4 + NaCl (60%) at 650° C for 50 cycles.

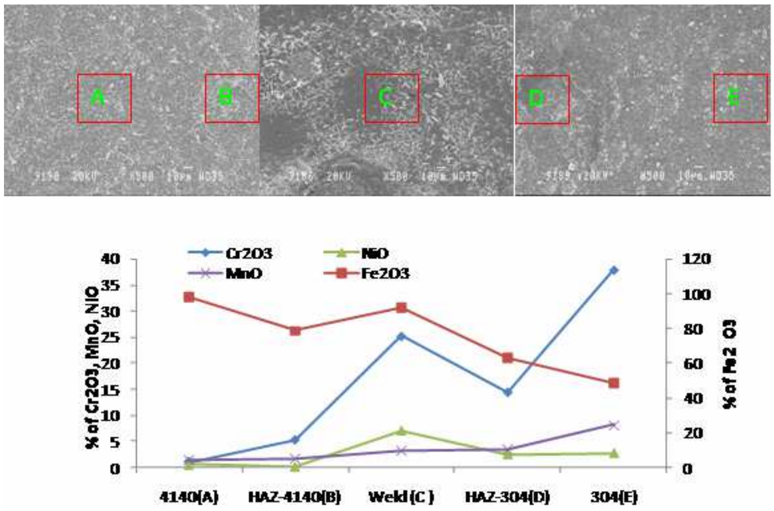

Figure 5. SEM/EDAX shows the GTAW weldment of AISI 4140 and AISI 304 exposed in air at 650° C after 50 cycles.

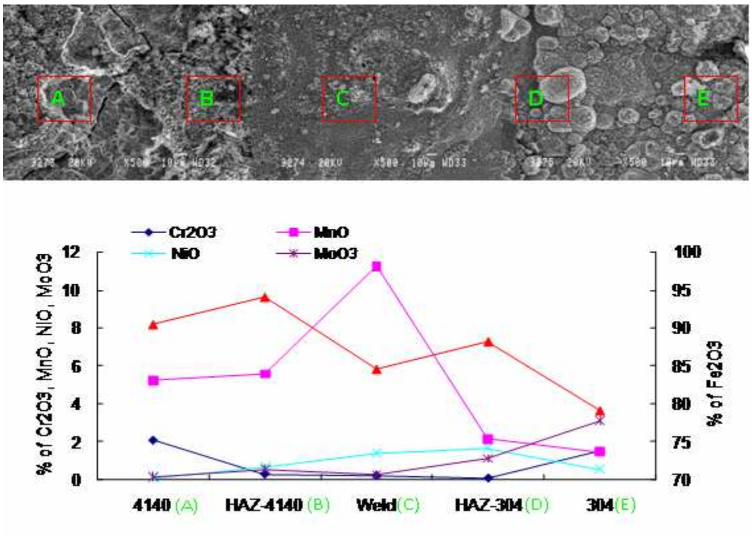

Figure 6. SEM/EDAX shows the GTAW weldment of AISI 4140 and AISI 304 exposed in K_2SO_4 + NaCl (60%) at 650° C after 50 cycles.

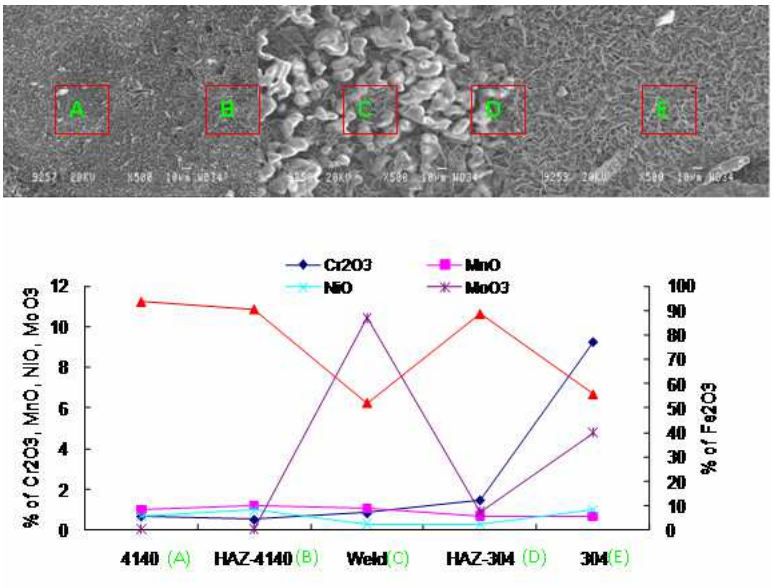

Figure 7 . SEM/EDAX shows the GTAW weldment of AISI 4140 and AISI 304 exposed in Na_2SO_4 + V_2O_5 (60%) at 650 ^{o}C after 50 cycles.

4.Conclusions

The conclusions from the present study containing weldment of AISI 304 and AISI 4140 dissimilar metals obtained by Gas Tungsten ARC welding. All the weldments was critically examined for cyclic hot corrosion studies in molten salt environment of Na2SO4 + V2O5 (60%) and K2SO4 + NaCl (60%) and air oxidation. The salient conclusions from the present study are enumerated below:

(a) From SEM/EDAX analysis on the dissimilar weldment it is observed that chromium and nickel diffuse towards AISI 4140 from the AISI 304 and diffusion of iron from AISI 4140 side towards AISI 304.

(b) A distinct weld region with enrichment of chromium, nickel, iron and carbon is prominent the weld zone.

(c) The corrosion rates for the investigated GTA welded dissimilar metals based on the overall weight gains after 50 cycles hot corrosion studies in all the environments could be arranged in the following order: K_2SO_4 + NaCl (60%) > Na_2SO_4 + V_2O_5 (60%)

(d) There is noticeable weight gain in the in dissimilar weldment. This may be attributed to the galvanic type of attack arising out of heterogeneity in composition – weld interface material, HAZ and the base materials.

(e) Rate of oxidation was observed to be high in the early cycles of the study in all the investigated 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.

(f) Dissimilar weldment suffered accelerated hot corrosion in the chloride + sulfate mixed molten salt environment in the form of intense spalling and sputtering of its scale.

(g) The cracking of oxide scale on the weldment as observed in the present study might be attributed to different composition of base metals, weld metals and oxide formed.

(h) The scale on HAZ of 4140 is thicker and prone to spalling which may be attributed to the iron oxidized in preference of Cr in the alloy 4140 where Cr content is less and the part of this Cr is present as carbide. This amount of Cr is not sufficient for forming a protective layer of Cr_2O_3 on the surface.

(i) The higher content of Fe_2 O_3 and Cr_2 O_3 on scale over weld zone may be due to enrichment of this zone with Fe and Cr as indicated by EPMA.

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