Research Article

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Sulphur and vanadium-induced high-temperature corrosion behaviour of different regions of SMAW weldment in ASTM SA 210 GrA1 boiler tube steel<https://doi.org/10.1515/htmp-2020-0035>

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Abstract: Corrosion at elevated temperature is a serious problem in running thermal power plants because of the use of low-grade fuels that contain substantial amounts of sulphur, vanadium, sodium etc. This article reports the high-temperature corrosion of weld metal and heat-affected zone (HAZ) of shielded metal arc-welding (SMAW) weldment in GrA1 steel in a molten salt (Na_2SO_4 –60% V_2O_5) environment at 900°C under cyclic conditions. The thermogravimetric technique was used to observe the kinetics of corrosion. The corrosion products formed on weld metal and HAZ of SMAW welded steel were characterized by scanning electron microscopy with energy dispersive X-ray analysis (EDX) and X-ray diffraction pattern. Weld metal was found to oxidize at a higher rate than those of HAZ due to the presence of sodium and sulphur in the inner oxide scale as confirmed by EDX, and this leads to high corrosion rate (in terms of weight gain).

Keywords: corrosion, welding, GrA1 steel, molten salt

1 Introduction

Thermal power plants are one of the significant industries suffering from severe corrosion problems resulting in substantial losses [1]. Ferritic steels are broadly used in these power plants in several forms especially as boiler tubes; these steels have a good combination of mechanical properties particularly high thermal and creep resistance, weldability and protection from corrosion at elevated temperature [2,3]. A large

number of welds were found in a typical steam generating system, and it has been discovered that heat-affected zone (HAZ) from welding may severally degrade from prolonged services [4]. High-temperature corrosion became known with the failure of boiler tubes, and later with the serious assault of gas turbine airfoil materials [5]. High-temperature corrosion happens whenever salt or ash deposits accumulate on the surfaces of alloys and alter the environment–alloy reactions that would have happened if the deposit had not been present [6]. The remains of ashes have high concentrations of vanadium, sodium and sulphur, mainly as Na_2SO_4 – V_2O_5 complex and sodium–vanadate mixtures. Vanadium, sulphur and sodium are frequently present as impurities in residual oils used as fuel [7,8]. Molten sulphate–vanadate deposits, resulting from the condensation of combustion products of residual fuels, are extremely corrosive to high-temperature materials in combustion systems [9]. The use of sulphur- and vanadium-containing fuels exceeds the design limit of temperature and pressure during operation, which have a detrimental effect on the performance of boiler tubes [10]. The present study has been carried out to evaluate the high-temperature corrosion behaviour of different regions of SMAW welded steel in a molten salt environment at 900°C. The X-ray diffraction (XRD) and scanning electron microscopy with energy-dispersive X-ray analysis (SEM/EDX) have been used to characterize the corrosion product after high-temperature corrosion at 900°C.

2 Experimental procedure

2.1 Preparation of weldment and specimen

ASTM SA 210-GrA1 (GrA1) steel was acquired from the thermal power plant at Bhatinda (India). The chemical compositions are shown in Table 1. Steel tubes (5 mm thickness $\times$ 33 mm diameter) after machining with a bevel angle of 37.5° of V-groove, root face of 1 mm and

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Table 1: Chemical composition (wt%) for GrA1 boiler tube steel

Type of steel	ASTM code	Composition	C	Mn	Si	S	P	Fe
GrA1	SA210 Grade A1	Nominal	0.27	0.93	0.1	0.058	0.048	Bal.
		Actual	0.2952	0.5977	0.2873	0.0056	0.0089	Bal.

Figure 1: Macrographs of different regions of SMAW weldment in GrA1 steel subjected to high-temperature corrosion in Na₂SO₄–60% V₂O₅ at 900°C for 50 cycles: (a) weld metal and (b) HAZ.

root gap of 1 mm were welded together by a shielded metal arc-welding (SMAW) process using basic-coated electrode AWS A5.1 E7018 at a constant arc current of 95 A and a voltage of 12 V. The welding parameters were published in the earlier paper by Kumar et al. [11]. A cross-sectional portion of the weldment was cut and polished along the long transverse area and etched in 2%

nital for 20 s before they were analysed by optical microscopy. A diamond wafering saw was used to cut the specimens 15 × 5 × 2 mm³ of HAZ and weld metal from the weldment along the longitudinal direction. The specimens were polished with silicon carbide paper and then with emery paper after which the cloth-wheel polished before being corroded.

Figure 2: Weight gain plot for different regions of SMAW weldment in GrA1 steel exposed to Na₂SO₄–60% V₂O₅ at 900°C for 50 cycles.

Figure 3: Weight gain square (mg^2/cm^4) plot for different regions of SMAW weldment in GrA1 steel exposed to cyclic hot corrosion in Na_2SO_4 –60% V_2O_5 at 900°C for 50 cycles.

2.2 High-temperature corrosion test

High-temperature corrosion studies were performed in a molten salt (Na_2SO_4 –60% V_2O_5) environment for 50 cycles. Each cycle consisted of 1 h heating at 900°C in a silicon carbide tube furnace taken after 20 min of cooling at room temperature. Moreover, the cyclic conditions also resemble the actual industrial conditions. A coating of uniform thickness with 3 – $5 \text{ mg}/\text{cm}^2$ of Na_2SO_4 –60% V_2O_5 was applied with a camel hairbrush on the preheated specimens (250°C). The weight change measurements were taken towards the end of each cycle with the facility of an electronic balance of model 06120 (Contech), Mumbai, India, with a sensitivity of 1 mg. The spalled scale, assuming any, was also included at the time of measurements to determine the overall rate of corrosion. The exposed specimens were analysed using SEM/EDX and XRD for surface analysis of their scales.

3 Results and discussion

3.1 Visual examination and thermogravimetric data

The macromorphology of the oxide scale for different regions of SMAW weldment after high-temperature corrosion in Na_2SO_4 –60% V_2O_5 at 900°C for 50 cycles is presented in Figure 1. For weld metal, dark colour scale showed up in the general surface from the first cycle itself,

spalling was seen during the 22nd cycle, and cracks were observed. Likewise, the appearance of blackish colour in the oxide scale of HAZ was noticed from the first cycle, small spalling of the oxide scale in HAZ has showed up around the 15th cycle and significant cracks were found in the oxide scale of HAZ from the 42nd cycle onwards. Weight change expressed in mg/cm^2 is plotted in Figure 2 as a function of time expressed in the number of cycles for the weld metal and HAZ regions of SMAW weldment in GrA1 steel. Total weight gain after 50 cycles of high

Figure 4: XRD profiles for different regions of SMAW weldment in GrA1 steel exposed to Na_2SO_4 –60% V_2O_5 at 900°C for 50 cycles.

Figure 5: Surface morphology and EDX analysis for different regions of SMAW weldment in GrA1 steel exposed to Na_2SO_4 –60% V_2O_5 at 900°C for 50 cycles: (a) weld metal, 1,000 $\times$ and (b) HAZ, 1,000 $\times$.

temperature corrosion of weld metal is almost 1.2 times more than the total weight gain value of HAZ. The (weight gain/unit area)² plot against the number of cycles shown in Figure 3 further confirmed that the parabolic law is followed by weld metal and HAZ. The values of parabolic rate constant K_p ($10^{-8} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$) are 6.055 and 4.148 for weld metal and HAZ, respectively.

3.2 XRD Analysis of the exposed specimens

XRD analysis for corroded weld metal and HAZ is shown in Figure 4, and these diffractograms have relatively comparable phases for every one of the regions. As evident from the composition, all the regions have revealed the formation of iron oxide (Fe_2O_3), though intense peaks of Fe_2O_3 are shown in the oxide scale of the weld metal.

3.3 SEM/EDX analysis of the exposed specimens

SEM morphology and EDX analyses for different regions of SMAW weldment in GrA1 steel after cyclic corrosion are shown in Figure 5. The oxide scale of weld metal contains nodules both large and small in size as shown in Figure 5(a). The top oxide scale is mainly composed of Fe (96.41%) and Mn (3.28%), whereas the inner oxide scale is composed of Fe (91.34%) with Na (2.60%), Mn (2.82%), Si (1.30%) and S (1.12%). The SEM micrograph shown in Figure 5(b) for HAZ in GrA1 steel also demonstrates the development of comparable kinds of oxides comprising Fe (97.11%) with a small amount of Mn and Na at point 2. The grain boundaries are rich in the oxide of Fe (96.98%) and Mn (2.31%) at point 1.

The weld metal indicated a higher rate of corrosion in contrast with its counterpart HAZ (Figure 2). The primary

reason was discovered that the cracking and spalling of oxide scale were because of the difference in thermal coefficients of oxides in the scale from the metal as observed by Niranatumporn et al. [12], Khanna [2] and Young [3]. Cracks in oxide were started by uneven expansion and contraction; through these cracks, the corrosive gases can enter to the metal and permit significant grain boundary corrosion attack as such penetration of sodium and sulphur was discovered in the internal oxide scale of weld metal, which was confirmed by EDX; this leads to a higher corrosion rate as reported by Kumar et al. [13]. HAZ oxidized at a lower rate due to the formation of lower extents of cracking, resulting in lesser corrosion rate difference with weld metal. Fe_2O_3 was seen to be the main phase (Figure 5) in the oxide scale and detected to be nonprotective in nature as suggested by Kolta et al. [14], Raman and Muddle [15] and Lai [16]. Most of these phase formations have also been reported by Sidhu and Prakash [17], while a study was being conducted in the same molten salt environment at the same temperature for base steel.

4 Conclusions

In view of thermogravimetric studies, the following points have been concluded:

- (i) Weld metal showed the formation of high intensity of Fe_2O_3 as revealed by XRD investigation. Weight gain of weld metal was more, which was due to the formation of cracks in the oxide scale. The HAZ indicates less weight gain.
- (ii) The weight gain of weld metal and HAZ specimens follows the parabolic law in molten salt which specifies that the corrosion rate is diffusion controlled. The susceptibility to high-temperature corrosion of different regions of SMAW weldment in GrA1 steel has been observed to be in the following order: HAZ < weld metal.

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