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High temperature corrosion and electrochemical behavior of INCONEL 625 weld overlay in $PbSO_4$–Pb_3O_4–$PbCl_2$–CdO–ZnO molten salt medium

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ABSTRACT

Molten salt-induced corrosion, electrochemical behavior, and degradation mechanisms of the alloy Inconel 625 weld overlay, deposited on the surface of the carbon steel through an automatic gas metal arc welding (GMAW) process, were investigated. OCP, EIS, potentiodynamic polarization, weight-loss measurement, SEM/EDX, XRD, DTA, and ICP/AAS techniques were utilized to study the electrochemical and corrosion behavior of the weld overlay alloy 625 exposed to a molten salt medium containing 47 $PbSO_4$-23 ZnO-13 Pb_3O_4-10 CdO-7 $PbCl_2$ (wt.%) at 600, 700, and 800 °C for 24 h. EIS data fit well into an equivalent circuit representing a two porous/non-protective scales model.

1. Introduction

Strength and structural integrity of carbon steel tubes, resistance of the tubes to high temperature and high pressure water and steam used in heat transfer, and economical considerations are the key reasons of utilizing carbon steel to manufacture waterwall tubes in industrial boilers such as waste-to-energy boilers (WTE), industrial waste incinerators, coal-fired boilers, oil-fired boilers, KIVCET flash smelter boilers used in pyrometallurgical process of lead and zinc, and black liquor recovery boilers, to name just a few [1,2]. However, the waterwall tubes, constructed of carbon steel, have to be protected against the harsh corrosive conditions of the boilers because of a relatively weak resistance of carbon steel to corrosion at elevated temperatures, particularly when salt deposits on the tubes [1]. Formation of the salt deposits and molten phases on the carbon steel tubes and the consequent corrosion attacks are the major concerns in the boilers. Typically, 5–10% of the total annual cost in waste heat recovery boilers is attributed to corrosion and related maintenances [3–5].

The application of alloy 625 weld overlay or cladding applied by the automatic gas metal arc welding (GMAW) process on the carbon steel tubes is known as the current prevailing method of providing protection for the waterwalls of the industrial boilers. Weld overlaying is a technique with the capability of performing a dense coating layer which is chemically bonded with the base metal [1,6]. An important proven strength of the alloy 625 weld overlay is its resistance to stress corrosion cracking and thermal fatigue under normal working conditions of the boilers [1,7,8]. Furthermore, the alloy 625 weld overlays possess satisfactory corrosion resistance and welding workability [3,9]. It is not always possible to carefully predict the lifetime of the alloy 625 weld overlay because its lifetime is highly dependent on the corrosive nature of the boiler environment and the deposited corrosive salts/molten phases that form on the overlaid tubes [3]. Microstructure and integrity of the weld directly affect the durability and performance of the alloy 625 weld overlay. Susceptibility of the alloy 625 weld overlay to solidification cracking, microstructural evolution, Laves phase formation, and microsegregation of alloying elements, particularly Mo and Nb, during the welding process as well as dilution of the carbon steel substrate are the major concerns affecting the corrosion resistance of the weld overlay [1]. Providing protection for boiler tubes by means of the weld overlay in the presence of molten salt deposits in the system has always been challenging because corrosion and failure of the applied weld overlay are widely encountered at high temperatures [1]. Because of the existing interest and demand for applying the alloy 625 weld overlay on the carbon steel waterwall tubes in the industrial boilers, KIVCET [1,10] and WTE boilers [3,6] as two common examples, to provide protection for the tubes and considering the prevalent occurrence of corrosion attack and consequent failure of the weld overlay in the presence of molten salt phases [4,11], many research works have been focused on studying the corrosion of the alloy 625 weld overlay in boiler applications.

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Corrosion-fatigue was identified by Luer et al. as the failure mechanism of alloy 625 weld clad boiler tubes in a supercritical, pulverized, coal-fired boiler after less than 24 months of service [12]. Cracks and internal corrosion initiated at the preferentially-corroded Mo- and Nb-depleted dendrite cores, and propagated along the axis of the columnar dendrites [12]. The mechanism of the internal corrosion penetration through the dendrites of the weld overlay is very similar to internal oxidation attack within the alloy matrix or intergranular oxidation attack followed by general oxidation in the wrought alloy [13,14]. The effects of temperature fluctuation and gas temperature on the corrosion behavior of an alloy 625 weld overlay deposited on the surface of SA 213 steel for WTE boiler applications were investigated by Kawahara [15]. Ishitsuka and Nose reported the fast dissolution of the protective Cr_2O_3 oxide as hexavalent chromium ions, CrO_4^{2-} ions, in molten chloride and chloride/sulfate mixtures which mainly form in the WTE boilers [16]. When condensed molten phases contained chlorine and sulfur, the formation of corrosion products with a lamellar structure was observed on the boiler tubes constructed of alloy 625, as a consequence of oxidation, sulfidation, and chlorination at the alloy/scale interface [17].

Despite a wide range of conducted studies on the corrosion of alloy 625 weld overlay in different molten salt environments, there is still a knowledge gap related to corrosion resistance and electrochemical behavior of the alloy 625 weld overlay in molten salt mixtures containing high concentrations of heavy metals such as lead, zinc, and cadmium, together with chlorine, oxygen, and sulfur. These molten salt mixtures form on the waterwall tubes of designated industrial boilers in lead production plants, particularly in the radiant boiler of the KIVCET smelters [1,10]. Molten salt-induced corrosion of the alloy 625 weld overlay in the industrial boilers significantly reduces the lifetime of the boiler tubes which ultimately leads to the failure of the waterwalls manufactured by carbon steel. The present research was devoted to studying molten salt-induced corrosion behavior of an alloy 625 weld overlay cladding in a molten salt medium containing a high concentration of lead, zinc, and cadmium, together with chlorine, oxygen, and sulfur.

2. Experimental procedure

2.1. High temperature electrochemical study and weight-loss measurement

An alloy 625 weld overlay was applied on the surface of a carbon steel substrate by an automatic gas metal arc welding (GMAW) process. Multiple welding passes, 10 welding passes in total, were performed to fully cover the surface of the substrate with a single layer of the weld deposit. A single-layer GMAW weld overlay was followed by a gas tungsten arc welding (GTAW) wash pass. The GTAW wash pass remelted the GMAW deposit without any filler addition. The technical parameters of these two welding processes are presented in Table 1. In both welding techniques, amperage, voltage, and travel speed were carefully controlled in the mentioned ranges to assure that the maximum heat input did not exceed the allowed maximum heat input rates, as mentioned in Table 1, at any time during welding. This procedure is a methodology to deposit the alloy 625 weld overlay on waterwalls constructed of carbon steel in large-scale industrial waste heat boilers for protection purposes, for example, in the radiant boiler of the KIVCET smelter which is a modern direct smelting process in the pyrometallurgical process of lead and zinc. The average thickness of the deposited alloy 625 weld overlay was about 3.40 ± 0.500 mm, determined by a cross-sectional SEM analysis of the weld overlaid substrate. The chemical composition of the carbon steel base metal, alloy 625 consumable filler metal which was utilized in the GMAW process, and deposited alloy 625 weld overlay on the surface of the carbon steel substrate is presented in Table 2. The chemical compositions were determined by inductively coupled plasma/atomic absorption spectroscopy (ICP/AAS: Inspectorate-International Plasma Laboratory, IPL, BC, Canada). Optical photomicrograph of the deposited alloy 625 weld overlay is presented in Fig. 1. In order to observe the microstructure, the polished samples were etched for 5 min in a solution containing 5 mL H_2SO_4, 3 mL HNO_3, and 92 mL HCl [18].

Open circuit potential measurement (OCP), potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and weight-loss measurement techniques were utilized to study molten salt-induced corrosion and electrochemical behavior of the alloy 625 weld overlay. A three-electrode electrochemical cell arrangement was prepared for conducting the electrochemical tests. The electrochemical cell was constituted by the working electrode (weld overlay alloy 625), and two 1.2 mm diameter/500 mm long platinum wires (American Elements, CA, USA) as auxiliary and pseudo-reference electrodes, which immersed directly in the molten salt medium. Platinum wires were woven together to produce a mesh-like counter electrode. The mesh-like counter electrode (CE) to the working electrode (WE) surface ratio was equal to 5 (CE: WE = 5:1).

The justifications for selecting pure platinum wires as the pseudo-reference and counter electrode were discussed elsewhere in detail [14]. It was confirmed that pure platinum is a suitable choice to be utilized as a pseudo-reference and counter electrode because platinum wires do not react with the molten salt during the electrochemical tests and no degradation of the platinum electrode in the molten salt medium occurs (see Ref. [14] for further details). All the potentials cited in the text are given versus pure platinum as the pseudo-reference electrode. When the application of platinum as a pseudo-reference electrode is concerned, it is not always possible to identify the redox electrochemical couple of the electrode, particularly in multi-component molten salt mixtures [19].

The alloy 625 weld overlay working electrodes had a rectangular shape with dimensions of 20 × 10 × 2 mm. For preparation of the working electrodes, rectangular pieces of the alloy 625 weld overlay were cut from the deposited weld overlay. The samples were then ground to 600-grit silicon carbide paper, rinsed with distilled water, ultrasonically degreased with acetone, and dried under a warm air stream. A wire made of 80Cr–20Ni (wt.%) was spot welded to each sample to provide an electrical connection between the working electrode and potentiostat. The sample-wire joint point was masked by refractory cement (Ceramabond: Aremco Products Inc., NY, USA). The potentiostat used in the electrochemical experiments was a Princeton Applied Research (PAR) model 273A with M352 analysis software. A frequency analyzer (PAR 1025) was

Table 1
Technical details of GMAW and GTAW process.

	Type of polarity	Amperage range (A)	Voltage range (V)	Minimum travel speed ($m\ s^{-1}$)	Maximum heat input rate ($J\ m^{-1}$)
GMAW	DC reverse (DCEP)	190–225	21–27.5	0.01	593,622
GTAW	DC straight (DCEN, non-pulsed)	350–435	12–16.5	0.01	687,559