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Letter

High temperature electrochemical sensor for in situ monitoring of hot corrosion

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ABSTRACT

Real time hot corrosion monitoring is still a challenging issue in coal-based power generation systems. It is not easy to achieve reliable and repeatable data such as quantitative relations between corrosion progress and data readings. This research work demonstrates an application of a new high temperature electrochemical sensor system with a reliable reference electrode to provide a clearer picture of the corrosion degradation. The hot corrosion behavior of a Ni-based superalloy was studied in the presence of a synthetic coal ash and a synthetic flue gas containing sulfur dioxide using our proposed high temperature electrochemical sensor.

Hot corrosion is a form of accelerated oxidation which affects alloys exposed to high temperature combustion gases containing small amounts of certain impurities [1]. Because of its high thermodynamic stability in the mutual presence of sodium and sulfur impurities in an oxidizing gas, Na_2SO_4 is often found to be the dominant salt in a hot corrosion system [1]. A thin film deposit of fused sulfate salt on the alloy surface in the hot oxidizing gas accelerates the corrosion kinetics and thus, the effective and reliable in situ hot corrosion monitoring system is necessary for the avoidance of unscheduled shutdowns.

A three identical electrode array sensor (two working electrodes and a pseudo-reference electrode of the same materials as the working electrode) for real time hot corrosion monitoring has been demonstrated [2–6]. However, there is insufficient correlation between the data from electrochemical corrosion measurements and the corrosion rates of materials in service [3,5,7,8]. Through analysis of the currently available data, it is believed that the major shortcoming of the identical electrode array sensor is the lack of a reliable high temperature reference electrode which provides the reference point for all the electrochemical readings and analysis. With regard to Na_2SO_4-induced hot corrosion, the specific Na^+ ion probes such as Ag/Ag^+/mullite or $Ag/Ag^+/\beta\text{-}Al_2O_3$ or Ag/Ag^+/fused-silica [9] could be used as high temperature reference electrodes.

Our proposed sensor was based on a four-electrode system (two identical working electrodes (WE1 and WE2), one reference electrode (RE) and one counter electrode (CE)). The schematic design of the sensor is shown in Fig. 1a. The working electrode was constructed of the alloy to be tested. In this study, Ag/Ag^+/fused-quartz reference electrode was chosen. The sealed fused-quartz (GE 214) structure, which was to function as the ion conducting membrane of the Ag/Ag^+ electrode, was prepared by first sealing one end of a fused-quartz tube that consisted of a silver electrode wire (2.0 mm in diameter) immersed in the sulfate mixture electrolyte (10 mol% Ag_2SO_4 + 90 mol% Na_2SO_4). A tungsten wire (0.2 mm in diameter) was connected to the silver wire as a lead wire. The conventional glass blowing technique with the assistance of the hydrogen–oxygen flame was used to achieve the encapsulation of the reference materials. The platinum wire was used as a counter electrode. A photograph showing the dimensions of the sensor components is presented in Fig. 1b.

The sensor was specially designed to utilize the response of several electrochemical measurements from a single electrochemical probe. In this research, electrochemical noise (EN), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) measurements were used to study the corrosion behavior of a new Ni-based superalloy, inconel alloy 740 in a thin coal ash film environment. The EIS measurement was performed after measuring the open circuit potential for one hour between 1 Hz and 1×10^6 Hz with FRA system. The amplitude of the input sine signal was 10 mV and the interval of one EIS measurement was about 15 min. Simultaneous measurements of potential noise and current noise were conducted for 24 h. The EIS and EN measurements were carried out alternately during an exposure time of 123 h. PDP was measured with a scan rate of 0.5 mV s^{-1} after 123 h.

The Ni-based superalloy was obtained from U.S. Department of Energy, National Energy Technology Laboratory (NETL) and it has the following chemical composition (in wt.%): Ni-49.45, Cr-24.67, Fe-0.62, Co-19.98, Mo-0.50, Nb-1.47, Al-1.23, Mn-0.3, Ti-1.23, Si-0.29. Before exposure to a hot corrosion the alloy was given the following sequence of heat treatment: 1150 °C for 4 h followed by air

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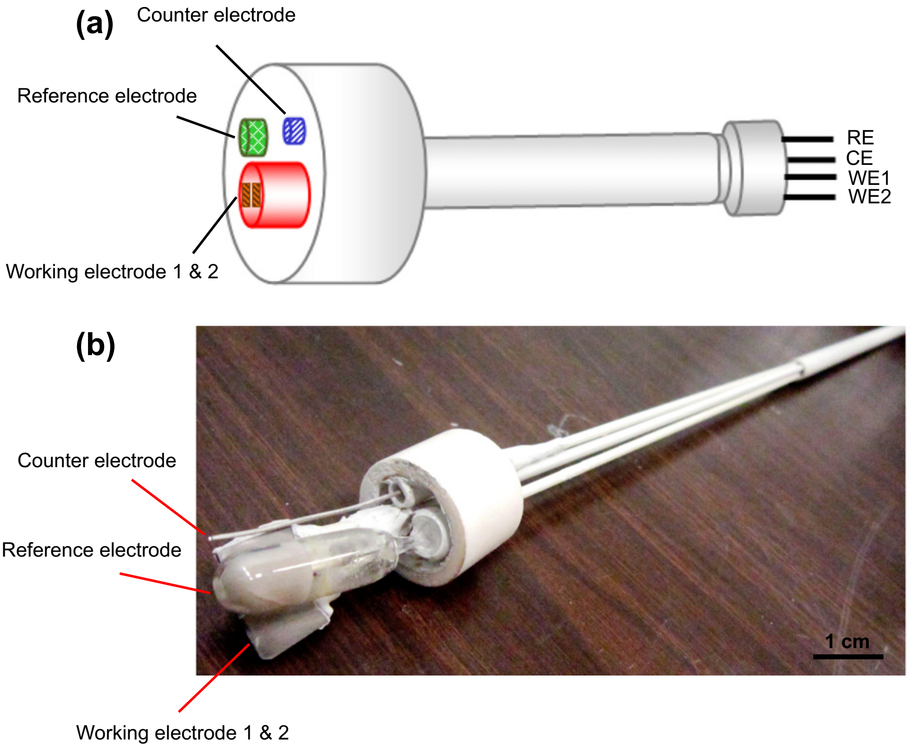

Fig. 1. (a) Schematic design of our proposed high temperature corrosion sensor, and (b) photograph showing the dimensions of the sensor components.

cooling; 1120 °C for 1 h followed by air cooling; 850 °C for 16 h followed by air cooling. The working electrode specimens with the size of 10 mm × 10 mm × 3 mm were cut from the alloy plate, followed by grinding up to 600# SiC paper. A tungsten wire was spot welded to one end of each specimen for an electric connection. A thin film of a synthetic coal ash mixture was established on the alloy surface to obtain a layer thickness of about 1 mm. The coal ash mixture consisted of reagent-grade 29.25 wt.% SiO_2, 29.25 wt.% Al_2O_3, 29.25 wt.% Fe_2O_3, 5.625 wt.% Na_2SO_4, 5.625 wt.% K_2SO_4 and 1 wt.% NaCl. The synthetic flue gas was composed of (in vol.%): 15 CO_2, 4 O_2 and 1 SO_2 and 80 N_2. The flow rate of the pre-mixed flue gas was 150 ml min^{-1} and the operation temperature was 800 °C. The electrochemical test data were analyzed using the Metrohm Autolab/PGSTAT302N with the Nova data acquisition system.

The EN is the most suitable technique for monitoring corrosion processes in situ and its special advantage includes the possibility to detect and analyze the early stages of the localized corrosion process as well as corrosion rates. Typical time series plots of electrochemical noise test data are shown in Fig. 2. The corrosion initiation stage was characterized by gradual potential shifting towards a more positive direction. The potential of the alloy shifted nearly 300 mV (from 100 to 400 mV vs. Ag/Ag^+) (Fig. 2a). The corresponding graph of current noise showed sudden spikes and the positive current density values decreased significantly (Fig. 2b). The positive current density values indicate the preferential dissolution of one electrode only [8]. The results suggest that recrystallization occurs of the protective oxide layer on the alloy surface. The recrystallization process near the surface can facilitate the inward movement of oxygen through a large number of grain boundaries, and then the inward-diffusing oxygen reacts with Al in the alloy to form Al_2O_3. Areas are protected in which the recrystallization process is more rapid than the initiation of corrosion [10]. The potential values were stable after a longer exposure time (Fig. 2a) and the corrosion propagated with negative (galvanic) current density values (Fig. 2b). Noise resistance has been shown to act as a useful indicator of the corrosion rate and data treatment in the time domain (R_n) and the frequency domain (R_{sn}) enabling the corrosion rate calculation. The noise resistance data processing included trend removal of the signal by minimum square linear fitting using the fast Fourier transform (FFT). The comparison of R_n and R_{sn} values is shown in Fig. 2c. The values of R_{sn} and R_{sn} differ significantly even though they are based on the same original data. This result confirmed with other researcher's result [5]. In the case of corrosion systems which are poorly stationary, misleading results can be produced with either fast fourier transform (FFT) or Maximum Entropy (MEM) method [11]. It could be one of the reasons that R_{sn} is more sensitive to change in an unstable hot corrosion conditions than R_n. The localization index proved to be an indicator for the type of corrosion observed. It can be calculated as the ratio between the standard deviation of the measured current, σ_i and the root mean squared value of the current, I_{rms}. The values of this indicator can be between 0 and 1. A value close to 0 is observed for systems in which the measured current values show only small deviation with respect to the average current value. On the other hand, the localization index will be close to 1 when the individual current values are significantly deviating from the average current value. The results showed that the alloy is liable to suffer localized corrosion during 123 h (Fig. 2d).

The EIS measurement can identify controlling mechanisms such as charge transfer or diffusion, and the solution resistances. The impedance spectra for the thin coal ash film corrosion of the alloy were similar during the initiation and propagation stages of corrosion, and are composed of a very small depressed semicircle at high frequency and a line at low frequency (Fig. 3a). These typical features of an impedance spectrum suggested that the overall corrosion could be controlled by the diffusion of oxidants in the melts. The impedance was highly resistive after 123 h exposure. The impedance spectra upon repassivation indicate a double time-constant behavior, suggesting the presence of both passive and active areas in the pit [12]. The impedance is essentially resistive