

Effects of reduced sulfur on the corrosion behavior of Alloy 600 in high-temperature water

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Abstract

The effects of reduced sulfur on the corrosion behavior of Alloy 600 MA were investigated in deaerated 0.01 M of sodium sulfate (Na_2SO_4), sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$), and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solutions using potentiodynamic polarization and stress corrosion cracking (SCC) tests at 300 °C and 340 °C. The polarization curves of Alloy 600 MA showed a stable passivity in the Na_2SO_4 solution; however, the solutions of $\text{Na}_2\text{S}_4\text{O}_6$ and $\text{Na}_2\text{S}_2\text{O}_3$ showed accelerated anodic dissolution. The SCC susceptibility of Alloy 600 MA increased in the following order: in the $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_4 , and $\text{Na}_2\text{S}_4\text{O}_6$ solutions. Results of deposits and spectra taken from an energy dispersive X-ray system confirmed the existence of reduced sulfur.

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1. Introduction

Sulfur has been identified as one of the major impurities introduced into the secondary water of pressurized water-reactors [1]. Sulfur can originate from various sources, such as feed water, cooling water in-leakage, resin sources, and condenser leaks. Under steam generator operating conditions, sulfates (SO_4^{2-} , +6), the most common sulfur species, are reduced by hydrazine to a lower-valence sulfur species, such as tetrathionate ($\text{S}_4\text{O}_6^{2-}$, +2.5), thiosulfate ($\text{S}_2\text{O}_3^{2-}$, +2), or sulfide (S^{2-} , -2). Many researchers have investigated the effects of reduced sulfur in a wide pH range with or without additives [2–5]. The presence of reduced sulfur species on the surfaces of pulled tubes having stress corrosion cracking (SCC) was also identified [6]. In the present work, measurements of electrochemical polarization and SCC tests were employed in order to investigate the effects of reduced sulfur species on the corrosion behavior of Alloy 600 MA.

2. Experimental procedure

The material used was a commercial Alloy 600 MA with a 22.23 mm outer diameter and a wall thickness of 1.27 mm. The tubing was mill-annealed (MA) at 960 °C for 10 min. The chemical compositions of Alloy 600 MA are shown in Table 1. We prepared test solutions using distilled water (>17 M Ω cm) with additions of reagent-grade 0.01 M of sodium sulfate (Na_2SO_4), sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$), and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). For the electrochemical polarization tests, the dimensions of the test samples were 10 mm \times 5 mm. We used an external Ag/AgCl/0.01 M KCl (SSCE) electrode and a platinum wire as a reference electrode and a counter electrode, respectively. We conducted the tests using a static-autoclave system at 300 °C with an EG&G 273A potentiostat. For the SCC tests, the shape and geometry of the test sample are shown in Fig. 1 [7]. Reverse u-bend (RUB) test samples were made with tubular tensile test samples 20% pre-strained by a tensile testing machine (Instron 8872). The test samples were then altered to produce parallel branches by bending each tube into a u-shape using a three-point bending tool. We conducted the SCC tests using a static-autoclave system at 340 °C at corrosion potentials. We inspected the test samples to identify cracks every 240 h, and every 480 h with a stereomicroscope,

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Table 1
Chemical compositions of Alloy 600 in wt.%

C	0.01
Ni	75.1
Cr	15.4
Fe	8.0
Si	0.1
Mn	0.3
S	<0.001
Cu	0.2
Ti	0.17
Al	0.22

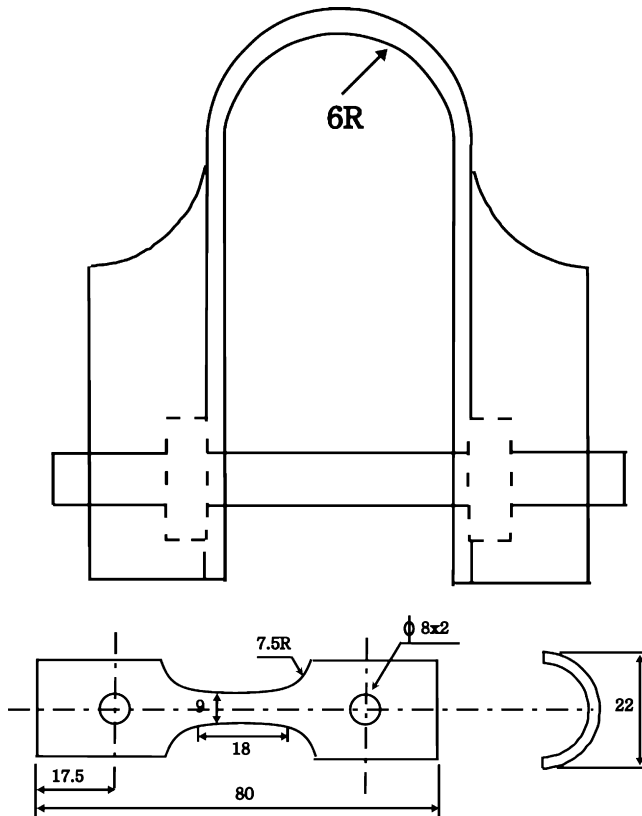


Fig. 1. Test sample of 20% pre-strained reverse u-bend [7].

and subsequently examined cracked test samples by scanning electron microscopy (SEM) combined with energy dispersive X-ray spectrometry (EDS). The deposits were analyzed by low angle X-ray diffractometry (XRD).

3. Results and discussion

Fig. 2 shows anodic polarization curves for Alloy 600 MA in 0.01 M solutions of SO_4^{2-} , $\text{S}_4\text{O}_6^{2-}$, and $\text{S}_2\text{O}_3^{2-}$ at 300 °C with a scanning rate of 0.5 mV/s. In the SO_4^{2-} solution, Alloy 600 MA shows three anodic peaks at $-630 \text{ mV}/_{\text{SSCE}}$, $-450 \text{ mV}/_{\text{SSCE}}$, and $-360 \text{ mV}/_{\text{SSCE}}$. The transpassive breakdown potentials are $-40 \text{ mV}/_{\text{SSCE}}$ and $480 \text{ mV}/_{\text{SSCE}}$. Two passive ranges are shown at a low potential passivity of Ni+Cr and at a high potential passivity of Ni. This indicates that Alloy 600 MA is preferentially passivated during heating. In the pres-

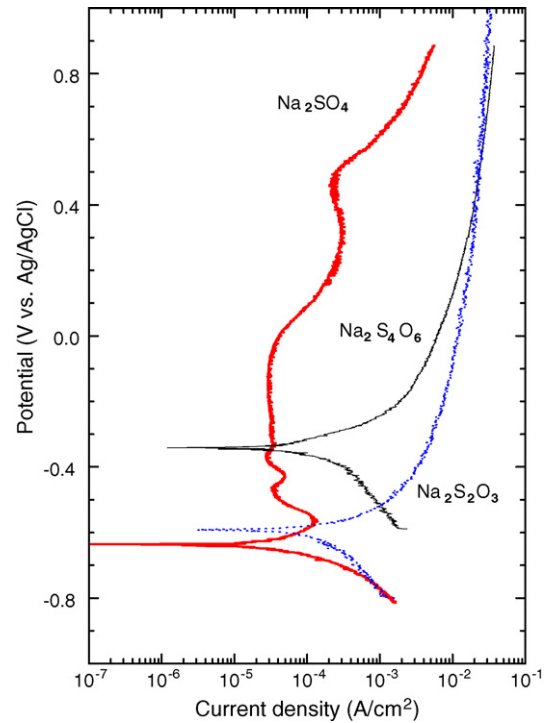


Fig. 2. Polarization curves for Alloy 600 MA in deaerated 0.01 M Na_2SO_4 , $\text{Na}_2\text{S}_4\text{O}_6$, and $\text{Na}_2\text{S}_2\text{O}_3$ solutions at 300 °C.

ence of $\text{S}_4\text{O}_6^{2-}$ and $\text{S}_2\text{O}_3^{2-}$, the polarization curves showed similar behaviors, although the corrosion potential of $\text{S}_4\text{O}_6^{2-}$ was 250 mV higher than that of $\text{S}_2\text{O}_3^{2-}$. Both anodic current densities increased to a point dramatically above the corrosion potentials.

The SCC susceptibility of Alloy 600 MA increased in the following order: in the $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , and $\text{S}_4\text{O}_6^{2-}$ solutions. The surface morphologies of the cracked test samples showed intergranular SCC. In the $\text{S}_4\text{O}_6^{2-}$ solution, the test sample cracks were deep and penetrating. This trend was not observed in the SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ solutions. In the SO_4^{2-} solution, Alloy 600 MA showed SCC after 2160 h and had no H_2S scent. An XRD analysis was not possible, because no deposits were found on the surfaces of the test samples. In the $\text{S}_4\text{O}_6^{2-}$ solution, two Alloy 600 MA test samples showed SCC after 240 h. In the $\text{S}_2\text{O}_3^{2-}$ solution, one test sample showed SCC after 3600 h and the other after 4560 h. Additionally, in both the $\text{S}_4\text{O}_6^{2-}$ and $\text{S}_2\text{O}_3^{2-}$ solutions, a scent of H_2S was identified after testing. The surfaces of the test samples were covered with thick, black deposits composed of mainly of Ni_7S_6 in the $\text{S}_4\text{O}_6^{2-}$ solution, and Ni_3S_2 in the $\text{S}_2\text{O}_3^{2-}$ solution. Results of a XRD analysis and the presence of the scent of H_2S confirmed that $\text{S}_4\text{O}_6^{2-}$ and $\text{S}_2\text{O}_3^{2-}$ reduced to a lower-valence sulfur species. These reduced sulfur species accelerated anodic dissolution significantly and led to a general corrosion. We analyzed the surface films after the SCC testing using an EDS. In the SO_4^{2-} solution, as shown in Fig. 3, the spectra taken from the EDS is comprised of a double layer consisting of an inner Cr-rich oxide layer and an outer thick porous-nickel-sulfide layer. The Cr oxide layer is uneven and probably composed mainly of amorphous oxides

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