Application of Straining Electrode to The Study on High Temperature Corrosion

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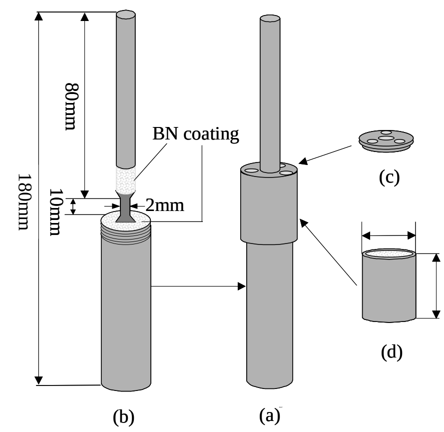
A tensile stress test combined with an electrochemical polarization technique employing a molten sulfate electrolyte, namely a high temperature straining electrode (HTSE) system, has been developed for the study on high temperature corrosion. The HTSE was applied to examine spalling and cracking characteristics of oxide films on Type 304 stainless steel at 773 K. The stainless steel was polarized in a passive potential in the molten sulfates and the anodic current was monitored during deformation to detect cracking and spalling of oxide films. This system has been also applied to examine the characteristics of anodic dissolution and subsequent passivation occurring in the molten sulfates immediately after the mechanical breakdown of oxide films.

An electrochemical cell designed for the HTSE system is shown in **Fig.1**. It was composed of three parts; a specimen (b), cover disk (c) and crucible (d), all of which were made of Type 304 SS. The specimens were machined from stainless steel rods to a shape shown in Fig.1 (b). A 304 SS tube of 15 mm in inner diameter and 40 mm in height was served as a crucible for holding the molten salt. The tube was thread-cut on the inner wall up to 10 mm from the bottom and attached to the specimen with the screw as shown in Fig.1. The inner wall of the crucible was insulated with the BN cement. To avoid the leakage of the molten salt through the screw part between the specimen and crucible, the crevice was sealed with BN cement. The crucible was covered with a 304 SS disk (Fig.1(c)) to keep the atmosphere under pure nitrogen gas during experiment. A ternary composition of 25mol% K_2SO_4 - 25mol% Na_2SO_4 - 50mol%$ZnSO_2$ was used as an electrolyte at 773 K. A reversible electrode of Zn (liquid) /Zn^{2+} was used as reference electrode without any special solid membrane. A platinum wire was used as counter electrode. The 304 stainless steel specimens were employed in the HTSE test after passivation or preoxidation. The passivation was performed at 773 K in the same molten sulfate just before the HTSE test. Meanwhile, for the preoxidation, the specimens were oxidized under pure oxygen atmosphere for 50 h at 973 K, to form thick oxide films. All measurements were carried out at 773 K. The schematic drawing of whole system of the HTSE is shown in **Fig.2**. The strain rate of 8.3×10^{-2} s^{-1} (5 min^{-1}) was employed for the linear strain test. For the stepwise strain, each stain step height was 2% and was maintained for 10 s or more. The rising speed of the strain step was varied from 8.3×10^{-2} – 8.3×10^{-3} s^{-1}. During deformation, anodic current induced by the deformation was measured with the potentiostat every 10 ms and stored thorough an A/D converter in a personal computer.

The current response Δi for Type 304 SS passivated by anodic polarization at +0.300 V to deformation at strain rate of 8.3×10^{-2} s^{-1} is shown in **Fig.3**, together with the stress vs strain curve. The Δi is given by subtracting the steady state anodic current from the total current measured during deformation. Thus, the Δi is attributed to anodic dissolution of stainless steel mainly through the cracks and spallation of the oxide films induced by the deformation of stainless steel substrate. It can be seen that the Δi was not observed in the elastic deformation region shadowed in Fig.3, whereas the Δi rapidly increased in the plastic deformation region. This trend is similar to passive films of alloys in aqueous solutions. On the other hand, preoxidized specimen showed current response even to elastic deformation.



Ｆｉｇ.1 Schematics of high temperature straining electrode cell (a) straining electrode cell, (b) specimen, (c) cover disk, (d) tube (crucible wall)

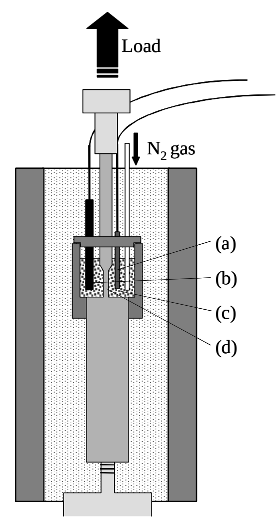


Fig.2 Schematics of high temperature straining electrode system (a) Pt counter electrode, (b) Zn/Zn^{2+} reference electrode, (c) molten salt and (d) specimen

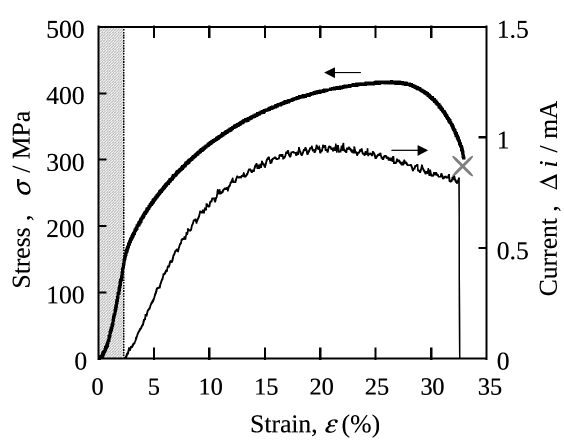


Fig3. Stress-strain curve and anodic current induced by the rapid straining for Type 304 polarized at 0.300 V in the sulfate melt at 773K (strain rate : 8.3×10^{-2} s^{-1})