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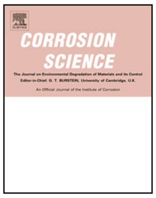

Effects of crevice geometry on corrosion behavior of 304 stainless steel during crevice corrosion in high temperature pure water

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ABSTRACT

The new device of crevice corrosion in high temperature water was designed. Effects of crevice geometry on corrosion behavior of 304 stainless steel during crevice corrosion in high temperature water have been investigated. Both width and length of the crevice affect the oxidation behavior of 304 SS. Different crevice widths result in different distributions of dissolved oxygen concentration and eventually affect the development of oxides within the crevice. The crevice length mainly influences the pH value within the crevice solution. The influencing mechanisms of the crevice geometry on oxidation behavior in high temperature water during crevice corrosion are also discussed.

1. Introduction

Type 304 stainless steel (SS) has been widely used as one of the structural materials in nuclear power industry due to its excellent corrosion resistance. However, it is still prone to localized attack after long-term service [1,2], typically such as crevice corrosion. Crevice corrosion often occurs in occluded regions, so it is more difficult to detect than general corrosion and there is often a long incubation period before attack begins. But once it is initiated it could accelerate the damage of materials within crevice rapidly. Therefore crevice corrosion is one of the most destructive and dangerous forms of aqueous corrosion [3–7].

Crevice corrosion is an undesirable degradation of the structural materials in nuclear power plants (NPPs). Many key parts of NPPs like the tube in steam generator (SG), the structure parts in reactors and the forging parts in control systems may be attacked by crevice corrosion easily [8–10]. All these materials in NPPs may be seriously degraded by the attack of crevice corrosion during their services. The main reasons of crevice corrosion of the structural materials in NPPs are the presence of the geometric crevices. It may result in a restriction of mass transport between the crevice and bulk solutions. Therefore, the ionic concentrations within the crevice become much higher than those in the bulk solution. This makes the solution within the crevice become more aggressive and then damages the passive film. In conclusion, crevice corrosion in NPPs may be one of the most serious material degradations and have received much attention in recent years.

Many researchers [4,5,11–13] have studied the behavior and mechanisms of crevice corrosion and two mechanisms [14] have been proposed to explain the crevice corrosion, namely, critical crevice solution (CCS) and potential drop mechanism. For the CCS mechanism, the depletion of oxygen within the crevice may finally result in the acidification of crevice solution. This can cause breakdown of the passive film and result in a rapid corrosion of metal. For the potential drop mechanism, the depletion of oxygen may finally result in a potential drop within the crevice and in turn cause the crevice corrosion. Both theories have the same viewpoint that oxygen is depleted within the crevice. Therefore, the dissolved oxygen (DO) concentration within the crevice solution is one of the most important factor that affects the crevice corrosion behavior. It is generally believed that many factors [15], such as the crevice geometry (crevice gap, crevice depth, exterior surface to interior crevice area ratio, number of crevice sites), the bulk solution environment (DO, temperature, pH value), and the alloy composition (major constituents, minor additions, impurities) can influence the process of crevice corrosion.

Many researchers have investigated the effects of different factors on crevice corrosion behavior of alloys [16–21]. Some work was focused on the effects of temperature on the crevice corrosion resistance of alloys [16,20]. The resistance against crevice corrosion is often expressed as a critical temperature, above which the crevice corrosion possibly occurs. Actually, the temperature changes primarily affect the critical breakdown potential of passive films. It was found that both the repassivation potential and

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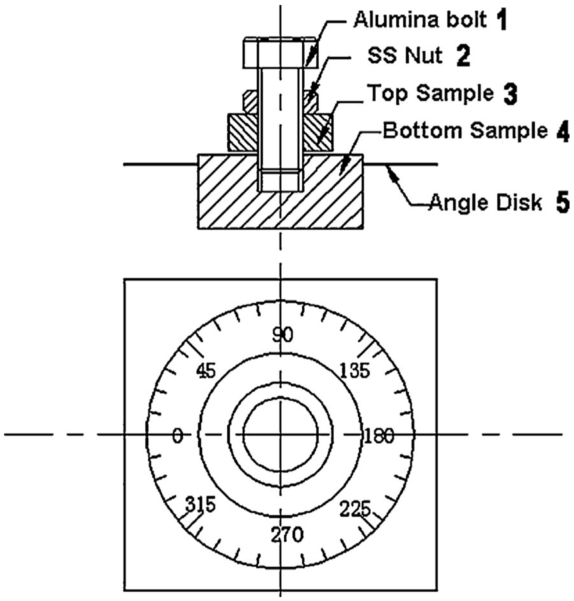

Fig 1. Schematic diagram of crevice corrosion device in high temperature water.

the breakthrough potential showed a linear decrease with increasing temperature. Some work was focused on the effects of alloy elements and ions in solution on the crevice corrosion resistance of alloys [18,21]. It was found that the nitrogen element in SS dissolved through crevice corrosion as $NO^{-}{}_{3}$, markedly suppressing the corrosion. It was also found that the presence of sulphate ions suppressed the anodic dissolution reactions and increased the endurance of chloride attack on Alloy 600. However, little work has been done to study the effects of crevice geometry on crevice corrosion of metal, especially in high temperature pressurized water due to the difficulties of simulating tests. It is difficult to construct an accurate crevice device which is suitable for the test in high temperature pressurized water environments. So it is quite difficult to clarify the influence of crevice geometry on crevice corrosion in high temperature pressurized water environments. Song [19] studied the geometry scaling for crevice corrosion. It was reported that the main geometry factors affecting crevice corrosion are crevice length (L) and crevice gap (δ_0). The geometry scaling factor should be L^2/δ_0. However, the above results are theoretical without the support of experimental evidence.

The present work is to develop an exposure testing device of crevice corrosion in high temperature pressurized water which can control the crevice geometry accurately and to investigate the structures, morphologies and compositions of the oxide films within the crevice after exposure tests under different crevice geometry conditions, using X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The influencing mechanism of crevice geometry on crevice corrosion behavior of 304 SS in high temperature pressurized water is also discussed.

2. Experimental

2.1. Crevice specimen and apparatus of testing loop

The new simulating test device of crevice corrosion in high temperature water used in the present work was designed and made (Fig. 1) which could adjust the crevice geometry including crevice gap, crevice depth, exterior surface to interior crevice area ratio accurately. The specimens for the crevice tests consisted of two parts, specimen (4) and crevice former (3), both of which were made from 304 SS and were cylindrical. The sizes of specimen and crevice former were different. The specimen and crevice former were fixed with an alumina bolt (1). The alumina bolt used in the present work for two purposes. Firstly, alumina has both excellent mechanical performance and corrosion resistance at high temperature, which are suitable for the experimental studies in high temperature aqueous solution. More importantly, the alumina bolt has excellent insulation performance in high temperature water. As described in the quoted paper, during the crevice corrosion, anodic regions in the crevice couple with cathodic regions on the bold surface through the transportation of charge via electrons through the metal and ions through the solution [14]. Therefore, if a 304 SS bolt was used to fix the two parts of the specimen, the electrons may transport through the bolt. This may affect the crevice corrosion behavior during the tests. In fact, a zirconia bolt, which has a better corrosion resistance than an alumina bolt, can also be used in the present work. Both kinds of bolts used have little influence on the experiment results.

Table 1
Compositions of 304 SS used in the present work (wt.%).

C	Si	Mn	S	P	Cu	Co	B	Ni	Cr	Fe
0.035	0.66	1.88	0.005	0.023	1.00	0.06	0.0018	9.27	18.65	Bal.

The specimen was immovable and the crevice former was rotatable. Firstly, make the crevice former attached with the specimen closely. The crevice width under this condition was 0. Then make the crevice former rotated slowly. The rotating of the crevice former can make it move along with the bolt, therefore, the crevice width changed. In brief, the width of crevice was adjusted accurately through the rotating angle of the crevice former. In order to keep a constant crevice width, a type of 304 SS nut was used to fix the crevice former (2). The alumina bolts used in this study were M6 bolts (whose pitch is 1 mm), so the width of the crevice could be calculated through the rotating angle of the crevice former easily. For instance, when the rotating angle of the crevice former was 45 °, the crevice width can be calculated as $45°/360° \times 1\,\text{mm} = 0.125\,\text{mm}$.

Exposure tests of the above crevice specimens in high temperature pressurized water were carried out in a refreshed autoclave made of 316 SS with a volume of 2 L. The autoclave was also pre-oxidized before the exposure tests. Detailed information on the testing loop and control system has been described in the previous work [22].

2.2. Materials and testing conditions

The composition of 304 SS used in the present work is listed in Table 1. Crevice test specimens were cut from a mill-annealed plate with a thickness of 50 mm. The plate has been solution annealed at a temperature ranging from 1050 to 1150 °C and may be slightly cold worked during fabrication. Fig. 2 shows the detailed sizes of the top and bottom parts of the specimens that have been used in the present work for different crevice widths (Fig. 2a) and crevice lengths (Fig. 2b). The crevice length can be varied by changing the diameter of the crevice former (3). As shown in Fig. 2b, the diameter of specimen (4) was fixed to be 30 mm, when the diameter of crevice former was 14, 18 and 22 mm, the corresponding crevice length was 4, 6 and 8 mm, respectively. The specimens were mechanically abraded with emery paper up to #2000 successively and washed ultrasonically in ethanol before exposure tests. The crevice specimens were exposed to 290 °C and 8 MPa pure water containing 3 ppm O_2. The specimens were immersed in the autoclave for 150 h and the testing conditions are summarized in Table 2.