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Observation by atomic force microscope of corrosion product during pitting corrosion on SUS304 stainless steel

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Abstract

Using in situ observation by atomic force microscope, it was found that the corrosion product plays an important role on the growth of corrosion pits on SUS304 steel in NaCl solution and the current density for pit growth was much higher than that applied on the entire surface.

Keywords: Image analysis; Atomic force microscopy (AFM); Corrosion; Austenitic steels; Surface; Corrosion product

1. Introduction

Austenitic stainless steels are widely used in many corrosive environments for their high resistance to general corrosion which is due to the formation of a protective passive film on the surface. However, pitting corrosion is often triggered at the chromium-depleted zones around sulfides or carbides [1–3]. In addition, the corrosion product is formed over pits and accelerates the pit growth [2,3]. Although many hypotheses and theories on pitting formation have been proposed [1–7], the models used are constructed without direct observation of corrosion product. Accordingly, in situ observation of the formation of corrosion products is necessary to clarify the mechanism of pitting corrosion.

Recently, the development of scanning tunnel microscope (STM) has provided for in situ observation of the formation and dissolution behaviors of passive films on metal surface [8–11]. However, different properties of passive films and the drift of the corrosion potential of the probe usually influence the tunnel current and the accuracy of images [11,12]. On the other hand, atomic force microscope (AFM) is suitable for in situ observation without current flow between the probe and the specimen surface [11]. Although the pitting corrosion process on stainless steels has been observed by AFM [12–17], the role of the corrosion product in the pitting corrosion process has not been discussed. Here in this work, in situ observation of pitting corrosion process of solution- and sensitization-treated austenitic stainless steel SUS304 was carried out in 3.5 mass% sodium chloride solution by AFM.

2. Experimental procedures

The material used for specimen was commercially supplied solution-treated SUS304 stainless steel sheet (C: 0.05 mass%, Si: 0.63%, Mn: 0.90%, P: 0.032%, S: 0.002%, Cr: 18.05%, Ni: 8.10%, Fe: Bal.). Some of them

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were sensitization-treated at 923 K for 9 ks. All the specimens were polished down to 0.06 μm alumina and ultrasonically cleaned in acetone before test.

The in situ observation was carried out in 3.5 mass% sodium chloride solution at room temperature (298 K) using a three electrode cell mounted on the piezo scanner of AFM (Shimadzu, Inc. SPM-9500). The specimen was used as anodic electrode, and two platinum wires were used as cathodic and reference electrodes. The current densities to trigger pitting corrosion were 1, 5 or 10 A/m^2, which are over the passive current density (measured by anodic polarization curve). Two observation methods were adopted in the present research. One was in situ continuous observation, where the corrosion current was applied continuously to the specimen surface during continuous observation. Another was in situ interrupted observation, where the observation was carried out with an interval to reduce the influence of probe scanning on the corrosion reaction, i.e., the probe was brought down in the solution to observe the specimen surface without current, and then the probe was lifted up about 100 μm over the surface to apply constant corrosion current for a period. After stopping the applied current, the probe was brought down again to observe the same surface area.

3. Results and discussion

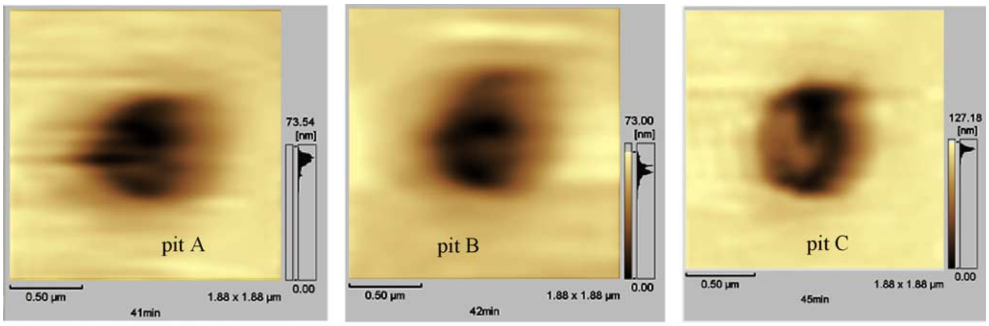
3.1. Solution-treated specimen

Fig. 1 shows an example of in situ observation of a corrosion-pit on the solution-treated specimen under the current density of $i = 10$ A/m^2. The pit became larger with increasing corrosion time from $t = 2.46$ to 2.70 ks. No corrosion product was found over the pit, perhaps because the corrosion product of low density has been removed to other places by the continuous scanning of the probe or resolved in the solution with the fast dissolution of the substrate. In this case, the high scanning rate of AFM is necessary to observe the detail of corrosion process, but the image resolution would be decreased.

Fig. 2 shows a series of in situ interrupted observations of pits on the solution-treated specimen under $i = 5$ A/m^2. Two large pits (D and E) appeared after $t = 1.5$ ks (a), but the size of them did not change with increasing time. In addition, no corrosion product was found over the two large pits. As described before (Fig. 1), it might have been removed or dissolved in the solution. A corrosion product crust appeared on a small pit as shown in (b). Since the pit-hole is shallow, it seems that the pit growth was still at its early stage. It is known that the corrosion product crust perfectly covered the pit just before $t = 1.5$ ks at the first scanning of the area (the picture was not saved), but by the time of the next scanning a part of the crust was destroyed and the inner part was exposed. Noise lines were found across the corrosion product, and they disappeared after $t = 7.2$ ks corrosion. This indicates that the part of the corrosion product might have been removed by the probe scanning. Pitting corrosion did not progress even after 7.2 ks. This phenomenon is explained by the decrease in the concentration of chloride and hydrogen ions in the pit due to the destruction of the crust and the stirring of the solution in the pit by probe scanning. As a result, re-passivation on the inner surface of the pit easily occurred and the corrosion almost stopped. It has been reported that the dissolution of manganese sulfide inclusions and their vicinities of the Cr-depleted zones in a solution-treated stainless steel always trigger the pitting corrosion [1–3]. The corrosion product crust observed in Fig. 2 corresponds well with the reported pitting corrosion process [3]. The covering of corrosion product crust over the pit can create an acidic environment to accelerate the pitting corrosion.

3.2. Sensitization-treated specimen

Fig. 3(a)–(c) show in situ interrupted observation results of a pit on the sensitization-treated specimen at $i = 1$ A/m^2 between corrosion time $t = 0.6$ and 1.2 ks. An irregular-shaped pit (marked as pit F) was found after $t = 0.6$ ks, but it hardly progressed even after $t = 3.0$ ks. This indicates the occurrence of re-passivation



(a) t=2.46ks **(b)** t=2.52ks **(c)** t=2.7ks

Fig. 1. AFM images of solution-treated SUS304 stainless steel during corrosion in 3.5 mass% sodium chloride solution at 298 K ($i = 10$ A/m^2).