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Positron microscopic analysis of crack failure in stainless steels

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Employing a focused positron beam with a lateral resolution of approximately 30 μm, we performed two dimensional scanning studies of stainless steels with stress corrosion cracking (SCC). A stainless steel with fatigued crack was also measured for comparison. Results suggest a quite unique failure mechanism for the specimen with SCC. In contrast to normal crack propagation effect associated with vacancies and dislocations, smaller Doppler broadening line shape (*S*) parameters were observed around the SCC crack tip than those corresponding to the undamaged area. It could be ascribed to some chemical influences, like oxidation, took place at grain boundaries.

1 Introduction Many studies on stress corrosion cracking (SCC) of stainless steels [1–3] in high-temperature and high-pressure water environments have been carried out aiming to understand and to predict the degradation of structural materials used in nuclear reactors. In principle, SCC is the cracking induced from the combined influence of tensile stress and a corrosion environment. The required tensile stresses may be in the form of directly applied stresses or in the form of residual stresses. As the detection of such fine cracks can be very difficult due to its small size, the damage is not easily predicted and therefore SCC is clarified as a catastrophic form of corrosion.

The Doppler broadening of positron annihilation radiation has been shown to be sensitive to vacancy-type defects in stainless steels caused by plastic deformation, fatigue damage, etc. [4, 5]. It is normally believed that dislocation networks are involved in crack nucleation and propagation processes, as proved by transmission electron microscopy (TEM). Formation of vacancies may also be involved in this process though they are invisible to the electron microscope. Hence, positron annihilation spectroscopy principally enables a sensitive and nondestructive detection of the crack as well as fracture formation in its early stage (actually, this is very important because the crack initiation time occupies almost 70% of the total time to fracture). Nevertheless, it must be noted that conventional positron annihilation experiments are usually performed utilizing mm-size positron source, thereby information about lateral distribution of defects in very-localized places (micrometer-order sized) around a crack tip is difficult.

The development of highly focused and brightness-enhanced positron beams for defect studies is turning popular [6, 7]. Recent advances in a positron microbeam being developed in our group enable positron annihilation Doppler broadening measurement of small testing specimens (e.g. patterned metal

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grids) under a spatial resolution of about 30 μm. The goal of this study is to preliminarily assess the possibility of applying positron microscopy to study a relatively complicated system, i.e. SCC specimen [8], which suffers combined chemical and physical treatments. For comparison, a stainless steel specimen with fatigued crack was also examined.

2 Experimental A 0.5-inch thick compact tension (0.5T-CT) specimen was fabricated from heat-treated (650 °C×15 h + water-cooling) SUS304 stainless steel. Important compositional elements include Ni (8.93%), Cr (0.04%), Mn (1.20%), C (0.05%), and Si (0.65%) in weight percent. Prior to SCC test, the sensitized SUS304 specimen was precracked in air at room temperature by fatigue and subsequently side-grooved. After that, the specimen was put into a simulated boiling water reactors (BWR) water with 8 ppm dissolved oxygen (DO) concentration at a temperature of 288 °C. External load was applied to the specimen for crack growth. The stress intensity at branched crack tips was estimated to be 13 MPa√m at the end of the SCC test.

A solutionized (1050 °C×0.5 h + water-cooling) SUS316L specimen (important constituent elements include Ni (12.55%), Cr (17.54%), Mo (2.11%), Mn (0.83%), C (0.008%) and Si (0.43%) in weight percent) was also pre-cracked in air, and then constant load testing was carried out at 288^0C in water until ductile crack was finally generated. The crack tip stress intensity was about 19 MPa√m.

A focused positron beam (Fig. 1(a)) was obtained by using the optics for conventional scanning electron microscopy (SEM) consisting a projector lens, a middle lens and an objective lens. Before the projector lens, positrons were focused to a diameter of about 2 mm using the electrodes and electromagnetic lenses. By scanning the beam across a sharp metal knife edge in front of a silicon wafer, the beam size can be adjusted until it reaches the smallest diameter of about 80 μm (Fig. 1(b)). Lateral resolution under the above beam size is approximately 30 μm, which was deduced by performing two-dimensional scan of a stainless-steel plate having evenly distributed holes (Fig. 1(c)) and subsequent comparison between the size of holes indicated from the Doppler broadening *S* parameter image (Fig. 1(d)) and that in the optical microscope image.

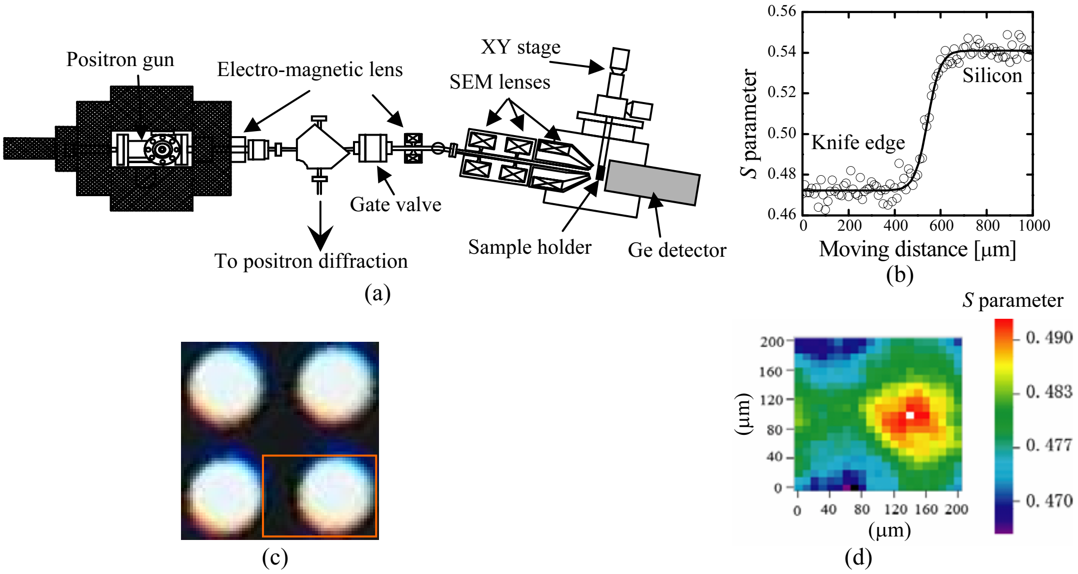
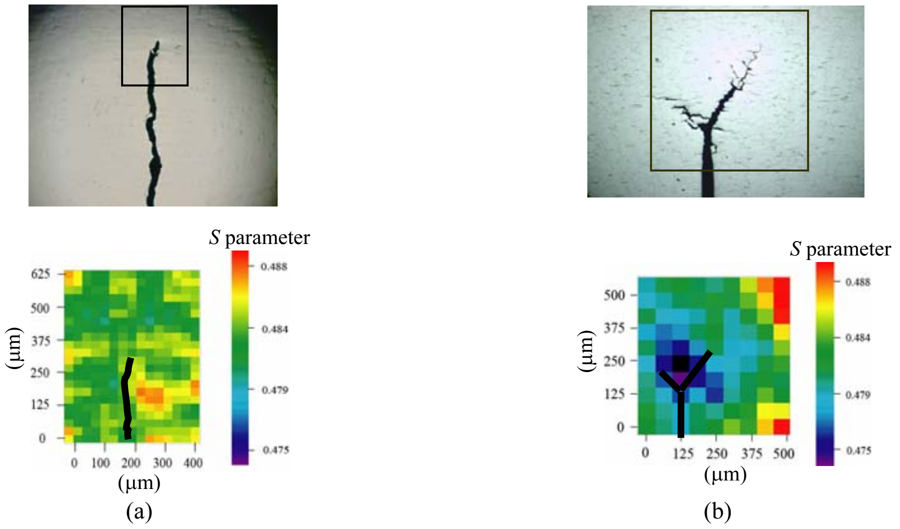


Fig. 1 (a) Set-up of the focused positron beam used in this study, (b) Beam size determined by scanning across a knife edge in front of a silicon wafer, the *S* parameter curve was further differentiated to get a beam size, (c) Optical microscope image and (d) Doppler broadening *S* parameter image of a stainless steel plate having holes with 130 μm in diameter and 65 μm separation between adjacent holes. *S* parameter distribution along a line slice through the centre of the *S* parameter hole image indicates a diameter of approximately 100 μm and thereby a beam resolution of about 30 μm. The frame shown in (c) corresponds to the scanned area shown as (d).

3 Results and discussion Figure 2(a) shows the obtained positron annihilation *S* parameter image of the stainless steel having fatigued crack. Optical microscope image for this specimen are also shown for comparison. It is generally accepted that fatigued cracks in metals and alloys are originated from the self-organized accumulation of microscopic defects, e.g. dislocations. The number of dislocations increases dramatically during plastic deformation, and dislocation reaction induces vacancy clusters. It is also expected that vacancy clusters as well as voids originated from vacancy clusters coalescence decrease in size with increasing distance away from the damaged zone close to a crack tip. At the same time, for positrons annihilate in an open-volume defect, a narrowing of the annihilation induced 511 keV gamma-ray line, i.e. increasing of *S* parameter, is usually observed. This is originated from the increased contribution of annihilations with valence electrons having smaller momentum compared with core electrons. Therefore, two-dimensional scan around the fatigued crack tip should principally lead to a larger *S* parameter near the crack and a smaller one far away from it. However, experimental results for the present specimen do not follow the above expectation very well, since clear pattern forming a shape as the fatigued crack shown in the optical image in Fig. 2(a) is not observed in the corresponding *S* parameter image. Although a fraction of this image has relatively large *S* values, their distribution is rather scattered. It may indicate that certain amount of vacancies and dislocations around the fatigued crack tip were annealed out as the specimen was kept at 288 °C for several hundred hours; it is also possible that vacancies at this temperature become mobile and migrate to sinks where dislocations are sessile [9]. In either case, to obtain an *S* parameter image with good contrast around the crack tip becomes difficult.



(a) (b)

Fig. 2 Upper part of this figure shows the optical images of stainless steels having fatigued crack (a) and SCC (b); lower part of this figure shows the two-dimensional *S* parameter mapping of the framed area in each corresponding optical image. The solid lines shown in the *S* parameter images are to guide the eyes.

Figure 2(b) shows the optical as well as positron annihilation *S* parameter images for the stainless steel having SCC. Surprisingly, quite different results from that of the fatigue cracked specimen appeared: *S* values around the SCC crack tips are considerably smaller than that of the surrounding area without damage. Unobserved *S* increment assures us to conclude that concentration of dislocations and vacancies around the SCC crack tips is not high. Actually, plastic deformation around such type of crack tip was already found weaker than that around the fatigued crack tip [8]. Nevertheless, existence of open-volume defects definitely would not contribute to reduced *S* parameters no matter how high their concentration is. We must turn to consider new possibilities, which predominantly determine the Doppler broadening of annihilation radiation.

It is noted that the present SCC crack is in intergranular type, because the crack follows grain boundaries and the bulk of the stainless steel grains remain largely unaffected. Intergranular corrosion is usually associated with chemical segregation effects (impurities have a tendency to be enriched at grain boundaries) or specific phases precipitated on the grain boundaries. Such precipitation can produce zones of reduced corrosion resistance in the immediate vicinity [10]. For sensitized stainless steels, Cr has a tendency to be enriched at grain boundaries thus lead to a local depletion of Cr immediately adjacent to these Cr precipitates, which provides a selective path for intergranular corrosion by specific media, such as oxidizing (nitric, chromic). The thickness of the oxide layer may be in nm order [2], so a large fraction of incident positrons will be injected into the metal grains neighbouring to the crack. After thermalization these positrons may diffuse to the metal/oxides interface and annihilate there. In the presence of oxygen in condensed medium or liquids, e.g. silicon oxide/silicon interface, oxygen-containing polymers and polar liquid molecules, positrons tend to annihilate with high-momentum valence electrons of oxygen and contributes to a considerably small Doppler broadening *S* parameter. This might be a factor to be taken into account for explaining the observed small *S* values around the SCC crack tip. However, a definite confirmation of the oxygen effect could only be obtained by performing positron annihilation coincidence Doppler broadening (CDB) measurements, which is not yet possible with the present instrument. Furthermore, exact composition of the possible oxides could be a mixture of several constituent elements (listed in Experimental section) in the SUS304 specimen. Nonetheless, positrons tend to annihilate on oxygen maintaining large magnitude of positron affinity, suppose oxidation may take place.

It should be mentioned that carbides ($M_{23}C_6$) were found at grain boundaries apart from the SCC crack tips, but their effect on positron annihilation process is possible only when misfit between carbides and host lattice is created [11]. Such situation is not evident here because in the *S* parameter map, one cannot find enlarged *S* values surrounding the crack tips compared with that for the undamaged bulk area.

4 Conclusion Positron microbeam turns out to be a promising tool to elucidate crack propagation and tip oxidation mechanism in stainless steels with stress corrosion cracking, since positrons are not only sensitive to open volume type defects as normally believed, but also preferentially annihilate on certain chemical element like oxygen compared with the constituent metal elements in stainless steels. The present study implies that oxidation might play a key role in the SCC crack formation in sensitized stainless steel in high temperature oxygenated water. The reduced *S* parameters around the SCC crack tips suggest that vacancies concentration is not high there. It is essential to further improve the peak-to-background ratio of the obtained Doppler broadening spectra, and then a quantitative discussion about the element effect on SCC propagation could be possible.

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