Hydrogen embrittlement of austenitic stainless steels revealed by deformation microstructures and strain-induced creation of vacancies

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Abstract

Hydrogen embrittlement of austenitic stainless steels has been examined with respect to deformation microstructures and lattice defects created during plastic deformation. Two types of austenitic stainless steels, SUS 304 and SUS 316L, uniformly hydrogen-precharged to 30 mass ppm in a high-pressure hydrogen environment, are subjected to tensile straining at room temperature. A substantial reduction of tensile ductility appears in hydrogen-charged SUS 304 and the onset of fracture is likely due to plastic instability. Fractographic features show involvement of plasticity throughout the crack path, implying the degradation of the austenitic phase. Electron backscatter diffraction analyses revealed prominent strain localization enhanced by hydrogen in SUS 304. Deformation microstructures of hydrogen-charged SUS 304 were characterized by the formation of high densities of fine stacking faults and ε-martensite, while tangled dislocations prevailed in SUS 316L. Positron lifetime measurements have revealed for the first time hydrogen-enhanced creation of strain-induced vacancies rather than dislocations in the austenitic phase and more clustering of vacancies in SUS 304 than in SUS 316L. Embrittlement and its mechanism are ascribed to the decrease in stacking fault energies resulting in strain localization and hydrogen-enhanced creation of strain-induced vacancies, leading to premature fracture in a similar way to that proposed for ferritic steels.
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Keywords: Austenitic stainless steel; Hydrogen embrittlement; Deformation structures; Vacancies; Stacking-fault energy

1. Introduction

Austenitic stainless steels (γ-SSs) are important structural materials for hydrogen energy systems, and hydrogen embrittlement (HE) is a key issue for establishing safe designs and further improving materials. HE of γ-SSs is sensitive to the types of γ-SSs, as demonstrated by the reduction of tensile ductility in a high-pressure hydrogen atmosphere [1,2] and crack growth rates in sustained or rising tensile loading [3] and fatigue tests [4] of hydrogen precharged specimens.

The mechanism of HE of γ-SSs has not yet been determined conclusively. Embrittlement has often been attributed to that of α'-martensite induced by plastic deformation of austenite [2,5,6]. However, contradictory results showing that α' introduced prior to testing reduces crack growth rates in fatigue [4] and tensile tests [7] in hydrogen environments have been reported for AISI 301, suggesting that α' is not always a preferred crack path in HE. Alternatively, involvement of ε-martensite, formed by dislocation dynamics in the γ-phase, in crack extension was observed by transmission electron microscopy (TEM) for SUS 304 (Japanese industrial standard type 304 stainless steel) and SUS 310 subjected to tensile straining under concurrent hydrogen charging [8,9].

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The primary role of strain-induced martensite in the embrittlement of unstable γ-SSs is feasible in situations such as heavy straining at low temperatures. However, even if the cracking of α'- or ε-martensite is involved in HE of γ-SSs, it does not directly signify per se the intrinsic function of hydrogen, and there are still issues to be examined further about possible hydrogen/plasticity interactions operating as the precursor of cracking in γ- and transformed phases.

HE occurs even in stable γ-SSs such as SUS 310 [8] and AISI 310S [10] under a high hydrogen fugacity. The effects of hydrogen on plastic behaviors of the γ-phase, such as shear localization [10,11], the decrease in the plastic zone size [8] and the increase in the densities of pile-up dislocations and stacking faults around the crack-tip [8], have been reported. Enhanced localization of slip bands by hydrogen in the vicinity of fatigue cracks in Type 316L has also been reported [12]. Tensile-fracture surfaces of hydrogenated AISI 310S [10] and AISI 316 [13] were characterized by fine facets with slip markings even on intergranular cracks [10]. A pronounced refinement of the γ grain size at the crack tip and along the crack in stable Types 310 and 304 under a hydrogen atmosphere [14] also implies that substantial localized plastic deformation takes place.

Shear localization and fractographic features concerned with plasticity are common to ferritic steels [15–21], for which the enhancement of dislocation mobility or of the strain-induced creation of vacancies due to the decrease in the formation energy of vacancy has been proposed in terms of the hydrogen-enhanced localized plasticity (HELP) [22] or hydrogen-enhanced strain-induced vacancy (HESIV) [23] mechanism as the cogent function of hydrogen. However, it is not evident that similar mechanisms operate in the γ-phase because of substantial differences in hydrogen solubility and diffusivity, as well as in crystal structures.

It should be noted that such hydrogen/plasticity interactions operate in the fracture process via the evolution of deformation microstructures and the creation of incipient cracks or voids. Accordingly, a further issue is the nature of hydrogen/plasticity interactions that directly cause HE. However, it is generally difficult to separate the roles of dislocation mobility and of defects in the effects of plasticity incident to dislocation activity. In this respect, positron annihilation spectroscopy (PAS) is a useful tool because of its selectivity of various lattice defects, specifically vacancies [24–26], thereby actually revealing the hydrogen-enhanced creation of strain-induced vacancies rather than dislocations in iron [27]. In γ-SSs, the evolution of carbon-decorated vacancies [28] and vacancy clusters that lead to the formation of microcracks [29] during fatigue was reported for Type 304 steels. A rapid increase in the average positron lifetime in the early stage of fatigue was also observed in SUS 316 [30] and AISI 316L [31].

In the present study, the mechanism of HE in γ-SSs has been investigated with respect to the stability of the γ-phase

incident to dislocation activity. Evolutions of deformation microstructures and associated lattice defects in SUS 304 and SUS 316L have been examined, utilizing positron lifetime measurements for detecting vacancy-type defects created during tensile straining. The operating mechanism of HE may differ depending on the concentration or fugacity of hydrogen. Hydrogen diffusivities in the γ-phase are substantially low, and previous studies were often conducted under very inhomogeneous distributions of hydrogen concentration [32] or with very thin specimens that might provide stress and strain states differing from practical situations. In the present study, specimens of 0.8 mm thickness with a uniform hydrogen distribution were employed by charging hydrogen under a hydrogen atmosphere of 10 MPa at 400 °C.

2. Experimental procedures

The materials employed in the present study were commercial SUS 304 and SUS 316L steel sheets of 0.8 mm thickness. The chemical compositions of the steels are shown in Table 1, where Md_{30}, i.e. the temperature at which tensile straining to 30% induces 50 vol.% of martensite, was calculated according to the formula in the table. The as-received steels were solution-treated to remove the residual strain introduced during fabrication processes by heating at 1000 °C for 60 s followed by air-cooling and pickling. Hydrogen was introduced under a hydrogen atmosphere of 10 MPa at 400 °C for 200 h in order to obtain a uniform distribution. Hydrogen concentrations along the depth from the surface of a specimen are shown in Table 2 in layers successively chipped off at various distances from the surface. The distributions were fairly uniform and the mean hydrogen concentrations were about 30–35 mass ppm. The reference materials without hydrogen charging were annealed in a vacuum at 400 °C for 200 h, resulting in a hydrogen concentration of about 1 mass ppm.

Flat specimens of 60 mm in length and 12.5 mm in width at the gauge section were prepared along the rolling direction and subjected to tensile straining at room temperature with a strain-rate of $8.3 \times 10^{-4} \, s^{-1}$. Elongation was recorded with an extensometer. After tensile testing, topographic features of the fracture surface as well as of the flat and side surfaces were examined by scanning electron microscopy. Deformation microstructures were analyzed by means of a scanning electron microscope equipped with a field-emission electron gun and an electron backscattering diffraction (EBSD) system (TSL ver. 5.1) with a beam diameter of 0.5 μm, transmission electron microscopy (TEM) using a Hitachi HF-2000 microscope operated at 200 kV, and X-ray diffraction (XRD) with Cu K_α radiation of 0.5 mm beam diameter for detecting strain-induced martensite. Specimens for TEM were prepared by a jet electropolishing technique using a 5% perchloric acid–acetic acid solution.

The positron annihilation lifetime was measured as the time lag between positron emission and annihilation. The