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Effect of sensitization on corrosion fatigue behavior of type 304 stainless steel annealed in nitrogen gas

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ABSTRACT

Effect of sensitization on fatigue behavior of type 304 stainless steel in laboratory air and in 3% NaCl solution was studied using specimens annealed in high temperature nitrogen gas. Annealing in high temperature nitrogen gas was performed at 1100 °C and at 1200 °C for 30 h, resulting in the solid solution of nitrogen and the precipitation of chromium nitride (CrN). The mechanical and fatigue properties were significantly improved by annealing. The improvement was due to the solid solution of nitrogen and the precipitation of CrN. Fatigue strengths of the untreated specimen in laboratory air and in 3% NaCl solution are nearly the same. However, fatigue properties of the annealed specimen in 3% NaCl solution change for the worse, because chromium (Cr) -depleted zones were formed along grain boundaries during the heat treatment, resulting in the remarkable sensitization.

In order to prevent the sensitization, the re-solution treatment (RST) which enhanced the dissolution of CrN and the water quenching treatment (QT) which avoided the precipitation of CrN was performed. As a result, the fatigue properties of the RST and QT specimens in 3% NaCl solution were slightly improved, but were still lower than that of the untreated one. Since the oxalic etch tests proved the formation of Cr-depleted zone also in the RST and QT specimens, the influence of sensitization could not be fully eliminated by the both treatments.

1. Introduction

The excellent corrosion resistance of austenitic stainless steel type 304 (18Cr–8Ni) brings on the wide use in chemical, biomedical and mechanical engineering fields [1,2]. However, low strength and poor wear resistance of type 304 steel are the weak points when used as structural and mechanical components [3,4]. Some surface treatment techniques are known to improve the mechanical properties of type 304 steel. Recently, the annealing treatments in high temperature nitrogen gas are applied to stainless steels and Ti alloys to improve the mechanical properties and hardness by the solid solution of nitrogen into matrix [5–9]. This method is a kind of chemical heat treatment and is different from so-called nitriding [6]. Nitrogen is one of the austenite (gamma $<\gamma>$) stabilizing elements for austenitic stainless steels and can improve mechanical properties, fatigue strength [10,11], and corrosion resistance [11–14].

In the previous study [15], authors had reported that the fatigue and the mechanical properties of type 304 steel were highly improved by the annealing in high temperature nitrogen gas. It is well known that the γ-phase in type 304 steel is metastable as expected from its chemical composition, 18Cr–8Ni, taking place in the strain-induced martensitic transformation during fatigue loading [10,11]. However, the strain induced martensitic transformation during fatigue test was successfully suppressed by the annealing in high temperature nitrogen gas, that is, γ-phase was stabilized by an addition of nitrogen [15].

In general, the martensitic phase (α′-phase) has higher environmental sensitivity than γ-phase, thus the strain-induced martensitic transformation decreases the corrosion resistance of type 304 steel [16,17]. Since the γ-phase in type 304 steel was stabilized by the annealing in high temperature nitrogen gas [15],

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it is expected that the corrosion fatigue properties could be also improved by this treatment.

In the present study, the annealing in high temperature nitrogen gas was applied to type 304 stainless steel. Since stainless steels are generally required to be used in aggressive environments, the fatigue test should be performed in corrosive environment. But corrosion fatigue properties of type 304 steel annealed in high temperature nitrogen gas have not been fully studied yet. Therefore, in the present study, the fatigue tests in 3% NaCl solution were performed using type 304 stainless steel annealed in high temperature nitrogen gas, and the corrosion fatigue properties were discussed from the viewpoint of sensitization.

2. Experimental procedures

2.1. Materials and annealing treatment in nitrogen gas

The material used is type 304 stainless steel (18Cr–8Ni), whose chemical compositions (wt%) are as follows; C: 0.05, Si: 0.29, Mn: 1.69, P: 0.038, S: 0.029, Ni: 8.19, Cr: 18.65, Fe: bal. [15]. Material was solution-treated at 1080 °C for 1 h followed by water quenching. After the solution treatment, material was machined to smooth round-bar fatigue specimens with a diameter of 5 mm and a gauge length of 5.04 mm as shown in Fig. 1. Prior to fatigue tests, the gauge section was mechanically polished using progressively finer grades of emery paper followed by buff-finishing. A vacuum furnace was filled with nitrogen gas at 0.1 MPa. The specimens were stored in high temperature nitrogen gas at 1100 °C or 1200 °C for 30 h [15]. Hereafter, the specimens heat treated at 1100 °C and 1200 °C are designated as the “1100 °C annealed specimen” and the “1200 °C annealed specimen”, respectively. In addition, the specimen without annealing treatment in nitrogen gas is referred to as “untreated specimen”.

Fig. 2 shows specimen preparation and heat treatment procedures. The details of each treatment, RST (re-solution treatment) and QT (water quench treatment) in Fig. 2 will be mentioned later (see in Section 3.2.1).

2.2. Experimental procedures

Fatigue tests were performed using an Ono-type four-point rotary bending fatigue testing machine with a capacity of 98 Nm operating at a stress ratio of -1 and at a frequency of 60 Hz. Testing conditions were in laboratory air and in 3% NaCl solution. The solution was trickled continuously on the specimen surface through the metering pump from a reserved tank. The microstructures and fracture surfaces of the specimens were examined in detail using a scanning electron microscope (SEM). The precipitates were analyzed by an energy dispersive X-ray spectroscopy (EDX). The distribution of nitrogen concentration was measured using an electron probe microanalyser (EPMA). A measurement of hardness was carried out using a Vickers microhardness tester (test load 4.9 N, loading time 30 s). The residual stress was measured by an X-ray diffraction (XRD). A Cr-Kα X-ray radiation was used at 50 kV and 40 mA. The $\sin^2\psi$ method was applied for the residual stress measurement [15].

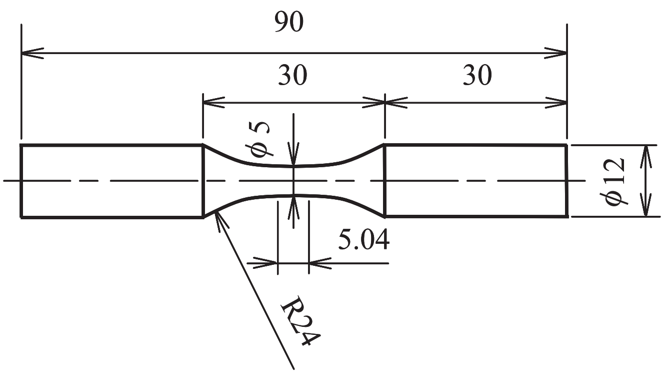

Fig. 1. Configuration of specimen for fatigue tests.

3. Results

3.1. Deterioration of corrosion fatigue properties in annealed specimens

3.1.1. . S–N diagrams in 3% NaCl solution

Fig. 3 represents an *S–N* diagram in laboratory air and in 3% NaCl solution. The annealing treatments in nitrogen gas improved the fatigue properties in laboratory air (open symbols) in comparison with the untreated specimen, especially the annealing at 1100 °C highly improved the fatigue properties. The fatigue limit was 250 MPa, 380 MPa and 290 MPa for the untreated, 1100 °C and 1200 °C annealed specimens, respectively under a stress ratio of -1. In the previous study, it was indicated that the improved fatigue properties in the annealed specimens were due to the solid solution of nitrogen and the precipitation of chromium nitride (CrN) [15].

In 3% NaCl solution (solid symbols), the fatigue strength at 10^7 cycles was 240 MPa, 200 MPa and 160 MPa for the untreated, 1100 °C and 1200 °C annealed specimens, respectively. Based on this figure, the fatigue property of the untreated specimen in corrosive environment is nearly the same as that in laboratory air. On the other hand, the corrosion fatigue properties of the annealed specimens were significantly lower than those in laboratory air.

3.1.2. Anodic polarization curves and surface morphologies

The corrosion fatigue properties of the 1100 °C and 1200 °C annealed specimens significantly deteriorated as compared with the untreated specimen (Fig. 3). In order to evaluate the corrosion resistance of each specimen, anodic polarization behavior was measured by the potentiostatic approach. Conditions of anodic polarization measurement are listed in Table 1. Fig. 4 shows the anodic polarization curves in each material, where the potential was plotted as a function of current density. Anodic polarization curves were obtained using three samples for each specimen. As can be seen in this figure, the total differences among three curves are very small. The pitting potentials, E_p, are nearly the same, but current density is slightly higher in the untreated specimen, indicating that the annealed specimens should have slightly higher corrosion resistance. However, the corrosion fatigue properties of the annealed specimens were much lower than that of the untreated specimen (Fig. 3), and these lower fatigue properties of the annealed specimens in 3% NaCl solution could not be estimated from the anodic polarization behavior shown in Fig. 4.

In order to investigate the deterioration of corrosion fatigue properties in the annealed specimens, the specimen surfaces were observed in detail after the anodic polarization tests. Fig. 5 reveals optical micrographs showing the surface morphologies after the polarization tests. Many corrosion pits (diameter <100 μm) within grains are uniformly seen in the untreated specimen (Fig. 5a). No selective attack against grain boundary was recognized. Corrosion pits are denser and larger than in the 1100 °C and 1200 °C annealed specimens (Fig. 5b and c). On the other hand, in the 1100 °C annealed specimen (Fig. 5b), the formation of network-like corrosion pits is seen along the grain boundaries (width 10–15 μm). In the 1200 °C annealed specimen (Fig. 5c),