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Improved fracture properties of Ni-Ti superelastic alloy under sustained tensile load in physiological saline solution containing hydrogen peroxide by hydrogen charging

Takehiro Shimada [a], Ken'ichi Yokoyama [a, *], Jun'ichi Sakai [b]

[a] Department of Materials Science and Engineering, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu 804-8550, Japan
[b] Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, 2-8-26, Nishiwaseda Shinjuku-ku, Tokyo 169-0051, Japan

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ABSTRACT

We have attempted to improve the fracture properties of Ni-Ti superelastic alloy under a sustained tensile load in physiological saline solution containing hydrogen peroxide by charging with a small amount of hydrogen, which causes negligible hydrogen embrittlement. For hydrogen charged in the parent phase, no pitting potential is observed in anodic polarization curves for the present test solution; the time to fracture increases under an applied stress even in the elastic deformation region of the martensite phase. Upon aging after hydrogen charging, the pitting potential varies widely and the increase in the time to fracture slightly decreases. Hydrogen charging increases the time until a rapid shift of the corrosion potential in the less noble direction, corresponding to the breakdown of surface oxide films. The final fracture is mainly caused by overloading due to localized corrosion irrespective of hydrogen charging. For hydrogen charged in the martensite phase, i.e., the specimen not subjected to interactions between hydrogen and the stress-induced phase transformations, the time to fracture increases by more than that of the specimen subjected to the interactions. The present study indicates that a small amount of hydrogen charging is effective for inhibiting the localized corrosion of Ni-Ti superelastic alloy under applied stress in physiological saline solution containing hydrogen peroxide, thereby improving the fracture properties. In addition, changes in the hydrogen states and/or defects induced by the interactions between hydrogen and phase transformations probably play an important role in improving the fracture properties.

1. Introduction

Ni-Ti superelastic alloy is extensively used in biomedical applications on account of its superior mechanical properties, good corrosion resistance and biocompatibility [1–4]. However, devices made of this alloy, such as stents, sometimes fracture after implantation [5–10]. One of the reasons for the fracture is localized corrosion under an applied stress related to the stress-induced martensite transformation in physiological saline solution containing hydrogen peroxide generated by an inflammatory response [11,12]. The synergistic effects of hydrogen peroxide with a high oxidation capability and sodium chloride with a high potential to induce corrosion probably lead to the localized corrosion. The localized corrosion in such environments must be inhibited to improve the fracture properties of the alloy.

To inhibit the localized corrosion, improving the corrosion resistance by surface modification may be feasible and various methods have been attempted [13–19]. However, coating the surface of Ni-Ti superelastic alloy is not a suitable method of surface modification because coating layers are broken during superelastic deformation [20,21]. As a method other than coating, we have demonstrated that by removing the initiation sites of corrosion pits including inclusions on the surface of the alloy by immersion in nitric acid solution, the corrosion resistance is improved and the time to fracture markedly increases under an applied stress in physiological saline solution containing hydrogen peroxide [22]. However, the improvements are confined only to the surface layer of the alloy and not the matrix itself. Ideally, intrinsic improvements in the corrosion resistance of the matrix of the alloy are necessary.

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* Corresponding author. Department of Materials Science and Engineering, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu 804-8550, Japan.
E-mail address: yokken@post.matsc.kyutech.ac.jp (K. Yokoyama).

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To improve the corrosion resistance of the matrix of Ni-Ti superelastic alloy, we have recently shown that the localized corrosion under an applied anodic potential in physiological saline solution without hydrogen peroxide is completely inhibited by charging with a small amount of hydrogen, which causes negligible hydrogen embrittlement [23]. Moreover, the inhibition of localized corrosion by hydrogen charging is maintained under not only static applied stress but also dynamic cyclic tensile deformation [24]. The additional advantages of this method are its simplicity and low cost. However, the detailed mechanisms of the inhibition of localized corrosion by hydrogen charging are not yet understood. Hence, it is unclear whether the inhibition of localized corrosion by hydrogen charging is effective in other environments such as physiological saline solution containing hydrogen peroxide. If the localized corrosion in other environments is inhibited by hydrogen charging, it can be considered as a versatile method for improving the corrosion resistance of the alloy. Furthermore, to elucidate the inhibition mechanisms, various findings, such as the effects of the hydrogen content and states in the alloy, should be accumulated for future study.

The purpose of the present study is to improve the fracture properties of Ni-Ti superelastic alloy under an applied stress in physiological saline solution containing hydrogen peroxide by a small amount of hydrogen charging. In addition, the effects of hydrogen states on the fracture properties are investigated by the comparison of specimens not subjected to and subjected to the interactions between hydrogen and phase transformations [25–27].

2. Experimental procedure

For comparison, the present study was performed under similar experimental conditions to those reported in our previous articles [11,12,23,24], although the manufacturer's serial number of the specimens was different. A commercially available Ni-Ti superelastic alloy (Ni: 55.9 mass%, Ti: balance) wire with a diameter of 0.5 mm was cut into specimens. Immediately before the experiments, the surface of the specimens was carefully finished with 600-grit SiC paper and ultrasonically cleaned in acetone for 5 min. The critical stress for the martensite transformation and the tensile strength at room temperature (25 ± 2 °C) were 501 ± 5 and 1509 ± 9 MPa, respectively. The percentage decrease in the cross-sectional area of the fractured specimen, i.e., the reduction in area, was 57%.

Hydrogen charging was performed cathodically at a current density of 10 A/m^2 for 10 min without applied stress (parent phase; B2) in 0.9% NaCl aqueous solution at room temperature. The amount of charged hydrogen was measured by thermal desorption analysis (TDA), which was conducted with a gas chromatograph at a heating rate of 100 °C/h using Ar at a flow rate of 50 mL/min as the carrier gas. Measurements were conducted at 5 min intervals, starting from 15 min after the removal of the specimen from the charging solution. To reduce experimental errors, TDA was conducted at least twice. Typical hydrogen thermal desorption curves of the charged specimen and the specimen after TDA (background) are shown in Fig. 1(a). The amount of charged hydrogen was calculated by subtracting the amount of desorbed hydrogen obtained from the background curve from the amount of desorbed hydrogen obtained from the charged specimen curve. The mean amount of charged hydrogen was 33 mass ppm. For the present charging conditions, no hydride was detected on the surface of the specimen by X-ray diffraction, as reported previously [23]. To investigate the effects of the hydrogen content on the surface of the specimen, the specimen was aged in air at room temperature for 240 h after hydrogen charging. In this case, hydrogen diffuses toward the center of the specimen without diffusing out from the specimen, thereby uniformizing the hydrogen content in the entire specimen [28,29].

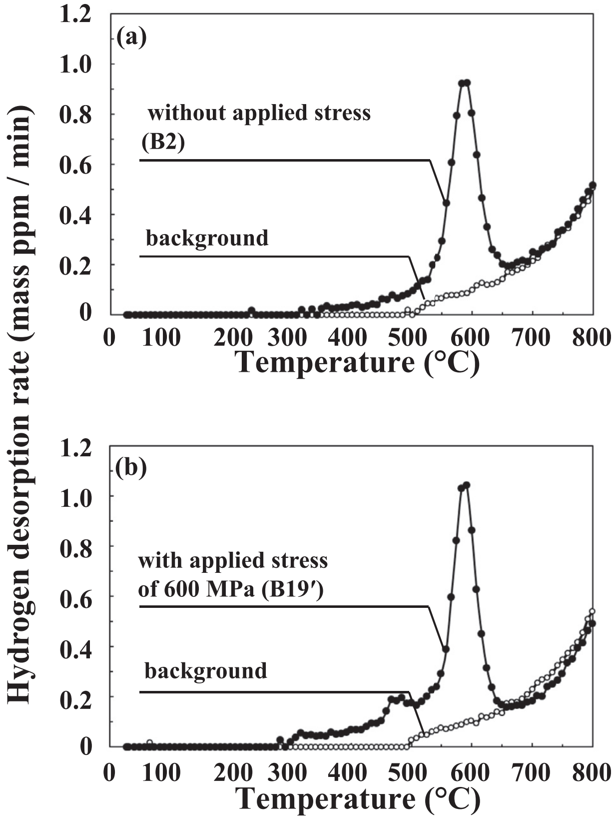

Fig. 1. Hydrogen thermal desorption curves for hydrogen-charged specimens (a) without and (b) with applied stress of 600 MPa and background obtained by remeasurement after TDA.

The immersion test solution used in the present study was physiological saline solution containing hydrogen peroxide (0.15 M NaCl + 0.3 M H_2O_2), as described in detail previously [11]. The potentiodynamic anodic polarization curves of the specimens were measured at least three times in the test solution under an aerated condition at room temperature without and with an applied stress of 600 MPa, i.e., the elastic deformation region of the martensite phase B19′. The polarization measurement was started 10 min after immersion in the solution, starting from the corrosion potential in the anodic direction with a sweep rate of 20 mV/min. The counter and reference electrodes used were a platinum electrode and a saturated calomel electrode (SCE), respectively.

A sustained tensile-loading test, as described previously [11], was performed at room temperature, using 200 mL of the test solution, fourfold the amount used in our previous studies [11,12], to decompose hydrogen peroxide during the test. The effects of the decomposing hydrogen peroxide during the test on the time to fracture were described in our previous article [11]. The sustained tensile stress was applied immediately after the hydrogen charging or aging. After applying stress, the test solution was injected to immerse the specimen. The applied stress was calculated as the ratio of the applied load to the initial cross-sectional area of the specimen and was varied to determine the fracture life characteristics, that is, time to fracture versus initial applied stress. Immediately after fracture, the specimens were removed from the test solution, cleaned with acetone and dried in ambient air. The test was terminated when no fracture occurred after 1000 h. The fracture surfaces were examined by scanning electron microscopy