Effect of hydrogen embrittlement towards thermal and mechanical behavior of NiTi shape memory alloy

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Abstract. NiTi arch wires are susceptible to hydrogen embrittlement upon contact with dental brackets in oral cavity during orthodontic treatment. This study investigated the effect of hydrogen absorption and diffusion over time towards the thermal and mechanical properties of NiTi shape memory wire. The hydrogen absorption process was carried out via electrolytic charging at constant current density for 16 hours in 1.0 weight percent (wt.%) sodium sulphate solution. The hydrogen charged wires were aged at room temperature in air for different durations to allow further inward diffusion of the hydrogen into the specimens. The results show that after hydrogen charging, the latent heat of forward and reverse martensitic phase transformation of the NiTi wire changed from 19.96 to 11.98 J/g, and 19.21 to 13.42 J/g, respectively. Further suppression and disappearance of thermal transformation peaks were observed as the charged specimen aged for 7 days. The transformation stress level on tensile deformation increased by almost 90 MPa after hydrogen charging, and exhibited non-flat stress plateau after further aging.

1. Introduction

Nickel titanium (NiTi) is a popular biomaterial in orthodontic application for its ability to deliver constant recovery force after deformation owing to its shape memory behavior, in addition to its favorable biocompatibility. NiTi orthodontic arch wire and stainless steel dental bracket are one of the most commonly used wire-bracket combinations in the orthodontic treatment. The treatment of teeth malocclusion has been benefited from the almost constant recovery force generated by the deformed NiTi orthodontic wire to initiate and promote the tooth movement. However, the contact between the two different alloys in the oral cavity with the presence of electrolyte, for instance the saliva and mouthwashes will give rise to the galvanic corrosion [1, 2]. The galvanic corrosion has caused the degradation of NiTi arch wire in oral cavity over a long treatment duration, such as loss of ductility and even fracture [3].

The loss of functionality and fracture of NiTi orthodontic arch wire during treatment has been claimed to be caused by hydrogen absorption and subsequent embrittlement effect [3–5]. The hydrogen embrittlement has caused the fracture of the charged NiTi wire in tensile deformation test to occur before and during the stress-induced martensite phase transformation [3, 6, 7]. On top of that, the cross-
sectional views of the failure surfaces have shown that the fracture of the wire happened in a brittle manner, without necking and reduction of area as observed in the as-received wire specimen [3, 7]. In addition to the hydrogen charging, the aging of the charged wire specimens in air under room temperature has also shown the similar effect towards the NiTi alloy [7].

This paper studied the effect of hydrogen charging and aging toward thermal martensite transformation and tensile deformation behavior of NiTi shape memory alloy. The set-up for hydrogen charging in this study used stainless steel and NiTi alloy as electrodes in order to resemble the actual condition in clinical orthodontic treatment. The galvanic current measured between the NiTi wire and stainless steel bracket combination is only in the range of nano-amperes (nA) [8, 9]. However, in order to accelerate the charging process and to achieve a significant amount of hydrogen concentration in a short time, the higher current density was used in this study. Both the hydrogen charging and aging have shown to affect the thermal phase transformation behavior of the NiTi alloy, while the aging has more significant effect towards the tensile deformation behavior as compared to hydrogen charging.

2. Experimental procedure

NiTi wire with composition of 50.6 atomic percent (at.%) Ni and diameter of 0.5 mm was used in this study. The as-received wire specimens were cut into length of 50 mm, followed by heat treatment at temperature of 600 °C for 30 minutes. The heat-treated wires were polished using SiC abrasive paper, followed by cleaning using acetone and distilled water. The hydrogen charging of the NiTi wires was achieved through electrolytic charging using a direct current (DC) power generator. The NiTi wire specimens were immersed into the 1.0 wt.% sodium sulphate (Na₂SO₄) solution and cathodically charged, together with 304 austenitic stainless steel anode. The schematic representation of the experimental setup is shown in figure 1 below. The current density used in the electrolytic charging process was set at 1000 A/m². A multimeter was connected in series to the electrical circuit to measure and monitor the electrical current. The hydrogen charging was carried out for 16 hours. The aging of the charged wire specimens was carried out under room temperature in air for 1, 4 and 7 days, respectively.

The changes in the thermal phase transformation behavior of the hydrogen charged and aged wire specimens were characterized using TA Q20 differential scanning calorimeter (DSC). The wire specimens were initially heated to a temperature of 150 °C, followed by cooling to a temperature of -100 °C and subsequently heated to a temperature of 150 °C, at a constant cooling and heating rate of 10 °C/min, respectively. The effect of hydrogen charging and aging towards the tensile deformation behavior of NiTi wire was evaluated via tensile deformation test. The tensile test was conducted at room temperature using Instron 3367 universal tensile machine equipped with a 30 kN load cell. The gauge length of the wire specimens was set at 20 mm. The wire specimens were deformed up to 10% strain followed by unloading. The loading and unloading rates were set at 1 mm/min, respectively.

![Figure 1. Schematic diagram of the experimental setup for hydrogen charging of NiTi wire.](image-url)
3. Results and discussion

Figure 2 shows the DSC curves of NiTi specimens after hydrogen charging for 16 hours and subsequently aged at different durations. It is seen that the as-annealed wire specimen possesses a sharp and high thermal transformation peak during cooling and heating. The martensite start (M_s) and austenite finish (A_f) temperatures of the annealed specimen occur at -6.06°C and 20.97°C, respectively. The hydrogen charging and aging for 1 day have not affect the reverse transformation temperatures of the wire specimens during heating, while the aging for 4 and 7 days have shift the A_f temperatures from 20.97°C to 27.14°C and 27.29°C, respectively. It is observed that the enthalpies of forward and reverse thermal martensite phase transformation have change from 19.96 to 11.98 J/g, and 19.21 to 13.42 J/g, respectively after hydrogen charging. The aging of the charged specimens in room temperature further suppresses the phase transformation until the near complete disappearance of both forward and reverse transformation peaks, as seen from the wire specimen aged for 7 days. The charging and aging process has more effect on the forward transformation (A → M) as compared to the reverse transformation (M → A), which is in agreement with the previous studies [10, 11]. In addition to the reduction of the enthalpy of phase transformation, several new transformation peaks are observed from the specimens aged for 4 and 7 days. The suppression of thermal martensite phase transformation is caused by the hydrogen absorption and diffusion over time from the sub-surface into the core of the wire specimens. The diffusion of hydrogen reduces the volume of the hydrogen-free NiTi matrix, while the presence of hydrogen in the NiTi matrix creates additional resistance for the reverse transformation, thus causing it to occur at several stages.

Figure 2. DSC curves of NiTi wire specimens charged at 1000 A/m² for 16 hours and aged at room temperature.

Figure 3 shows the tensile deformation behavior of the hydrogen charged and aged wire specimens. The stress-strain curves of the as-annealed and hydrogen charged wire specimens manifest the shape memory effect and martensite reorientation of the NiTi alloy, as the testing temperature is just above its A_f temperature. The as-annealed wire specimen has the transformation stress level of around 245 MPa,
which is the lowest among all the tested specimens. The hydrogen charging causes the transformation stress levels to increase from 245 MPa to 332 MPa, with the increment of ~90 MPa as compared to the as-annealed specimen. The aging at room temperature for 1 to 7 days has increases the transformation stress as much as ~150 MPa from 245 MPa to 398 MPa, while causing the transformation stress plateaus to propagate in a non-flat manner. The increase of the critical stress levels at the onset of the stress plateaus as seen from the aged specimens suggests that the diffusion and presence of hydrogen hinder the martensite reorientation, causing more energy needed to initiate the transformation process [12]. Additionally, the residual strain of each charged and aged wire specimen after complete unloading during the tensile deformation is lower than the as-annealed specimen.

Figure 3. Tensile deformation behavior of NiTi wire specimens charged at 1000 A/m² for 16 hours and aged at room temperature for 1 to 7 days.

4. Conclusions
The hydrogen absorption and diffusion were found to suppress the thermal phase transformation of NiTi alloy. The enthalpies of forward and reverse phase transformation were decreased from 19.96 to 11.98 J/g, and 19.21 to 13.42 J/g, respectively, in addition to the disappearance of transformation peaks. On the other hand, the hydrogen charging caused the martensite reorientation to occur at a higher transformation stress level, with increment of the transformation stress level as much as 90 MPa. The diffusion of hydrogen into the NiTi alloy matrix caused the stress-induced martensite phase transformation to exhibit non-flat stress plateau behavior.

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**Acknowledgements**

The authors are grateful for the financial support provided by Universiti Sains Malaysia under the research grant FRGS 203/PMEKANIK/6071405.