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B.L. Pelton, Slater, A. Pelton

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EFFECTS OF HYDROGEN IN TiNi

B. L. Pelton*, T. Slater**, and A. R. Pelton**

*Charles Evans & Associates, 240 Santa Ana Court, Sunnyvale, CA 94086

**Nitinol Devices & Components, 48501 Warm Springs Blvd. #117, Fremont, CA 94539

ABSTRACT

Titanium-Nickel (TiNi) alloys, similar to other Ti-based materials, are sensitive to hydrogen (H) content. Superelastic TiNi wires were exposed to a heated solution of H_3PO_4 for various times in order to introduce H. Mechanical and transformation properties of these TiNi-H wires were measured as a function of bulk H composition. This study determined that concentrations of $H > 400$ wppm reduce ductility, embrittle the affected microstructure and increase the plateau stress. With 1809 ppm, the transformation temperatures were suppressed, and the sample fractured at $< 1.5\%$ strain. The novel use of dark field light optical microscopy and scanning electron microscopy were used to determine the extent of the affected microstructure. The more conventional analytical technique, SIMS, was used to confirm the presence of H in the regions displaying brittle fracture.

INTRODUCTION

TiNi alloys are experiencing increased use in medical and commercial products because of their unique shape memory and superelastic properties. Current applications include guidewires and stents for cardiovascular procedures, orthodontic devices, eyeglass frames, cellular telephone antennae, and fasteners. These finished components often require processing in H-containing environments, such as electropolishing, electroplating and soldering procedures.

Thermodynamic studies of the TiNi-H system indicate that H is absorbed into TiNi to form an extended solid solution with a maximum concentration of $TiNiH_{1.4}$; this absorption is accompanied by a lattice expansion of up to 10% by volume [1-3]. Under other conditions, a titanium hydride ($3TiNi + 2H_2 \rightarrow 2TiH_2 + TiNi_3$) forms, which also involves a volume expansion of at least 10%

[4]. There remains, however, a paucity of published data on the effects of H on the properties of TiNi. Asaoka [5-7] focused on relatively mild concentrations of H (estimated to be 10-50ppm) and their effect on the cyclic properties of Ti-Ni-H and Ti-Ni-Cu-H alloys. It was concluded that both ductility and strength decreased with increasing H. However, there were no correlations made between H concentration, properties and microstructure, nor were higher levels of H investigated. Therefore, this study will characterize these effects by evaluating the response of TiNi-H to mechanical and transformation properties and correlate the results to microstructure.

EXPERIMENTAL PROCEDURE

Four-point bend and tensile tests, and differential scanning calorimetry (DSC) were performed on superelastic \varnothing 1.5mm Ti-50.8 at% Ni wires which were exposed to heated H_3PO_4 for various times. The mechanical tests were done according to the procedures outlined by Wick, et al. [8]. Portions of each tested wire were analyzed for bulk H content. The fracture surfaces from these tests were imaged with dark field light optical microscopy (DF-LOM) and with scanning electron microscope (SEM). JEOL T300 and 5300 SEMs were used at 25kV and 30kV.

A H^+ map was acquired from the edge of the wires using secondary ion mass spectroscopy (SIMS) of the control ($H=3\text{ppm}$) and 1809ppm samples. The SIMS analysis was performed on a CAMECA IMS 4f with a primary beam of Cs^+ , a primary accelerated voltage of 10keV, and a primary beam current of 80 nA. The raster sized covered a $250 \times 250 \text{ mm}^2$ area, producing an image with a diameter of 150mm.

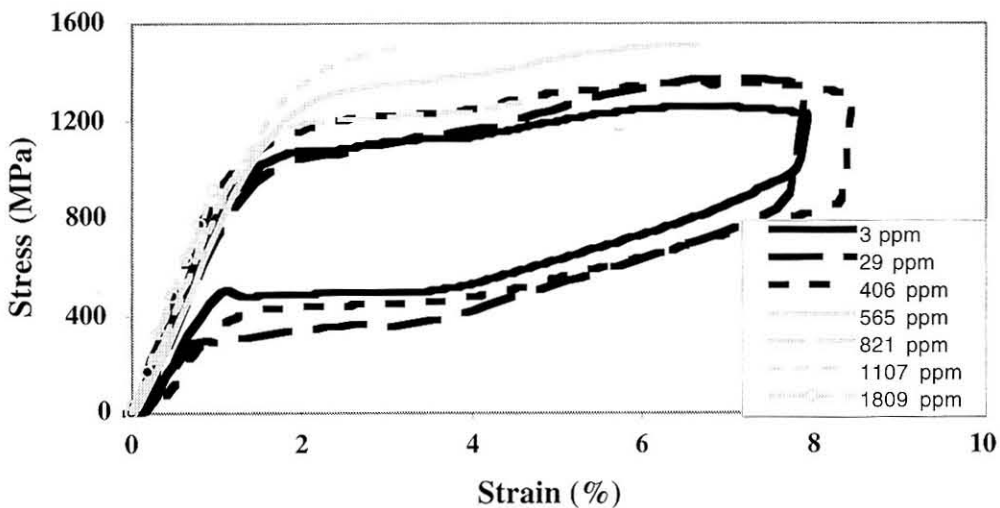


Figure 1. Four point bend stress-strain curves of Ti-Ni-H

RESULTS AND DISCUSSION

The effects of H on the bend ductility of Nitinol wire are shown in Figure 1. The control sample was deflected to 8% strain and unloaded, showing perfect superelastic behavior [8]. Samples with 29 ppm and 406 ppm H also survived this strain cycle, whereas samples with 565-1809 ppm bulk H failed at strains <8%. Note that the fracture strain dramatically decreases as the bulk concentration of H increases. Furthermore, it is interesting that there is a general trend of increasing plateau stress with increasing H. This trend is contrary to the results of Asaoka [5-7] for lower H.

The effects of H on the transformation temperature of the wires with 3, 406 and 1809 ppm H were monitored with DSC and are shown in Figure 2. The DSC trace of the control sample is typical of superelastic wires. As the H content increased, there was a pronounced shift in the transformation temperatures and decrease in the relative enthalpy of the reactions. With 1809ppm H, both the transformations were completely suppressed, similar to the work of Li and Wu [9].

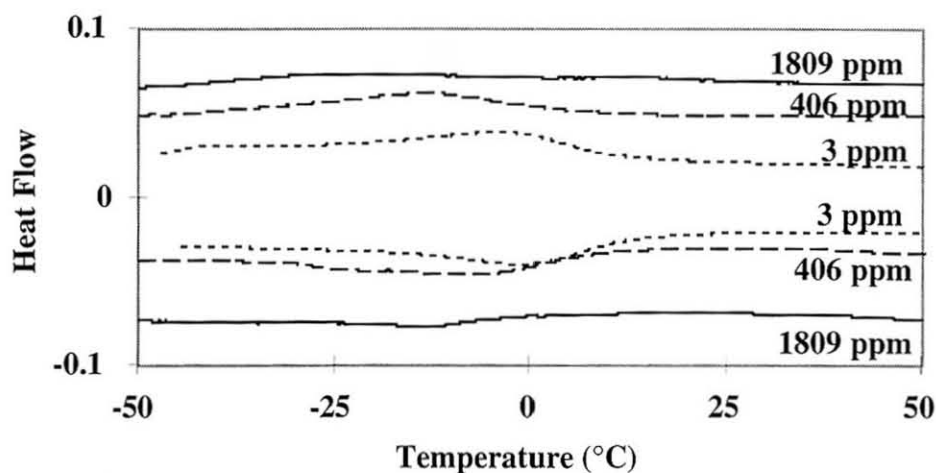


Figure 2. DSC analysis of control (3ppm), 406ppm H, and 1809ppm H

The DF-LOM images of the bend-fracture surfaces are illustrated in Figure 3. Note that a distinct change in the mode of fracture occurs near the outer edge of the wire, and that this outer “band” increases in width with increasing H. This band represents the transition from brittle to ductile fracture, and likely marks the extent of H diffusion into the wires. The widest band and the largest cracks were observed with 1809 ppm H. The SEM micrographs of the tension-fracture samples are shown in Figure 4. The control sample (Fig. 4a) displays ductile cup-cone fracture with substantial necking prior to failure (>15% strain). This fracture mode is in contrast to the brittle fracture in the 1809 ppm H sample (Fig. 4b). The brittle circumferential band in tension is ~130mm, which is similar to that observed in bending. Also, there is such a low ductility (<1.5%) that there was no necking observed.

The elemental map of H shown in Figure 5 was obtained with SIMS and reveals the distribution of H in the control and the 1809ppm H specimen. The analysis was performed near the edge of the wire in both samples. The very dark regions in both images represent an artifact of the acquisition produced by a defect in the channel plate used to detect the H⁺ ions. The brighter regions observed in the edge of the 1809 ppm H sample confirms that the highest concentration of H is in the region associated with the most brittle fracture. As with other Ti-based alloys, it is likely that the H enters the microstructure along grain boundaries, dislocations and voids. As the exposure times increase, H accumulates in sufficient quantities to expand the lattice, which leads to the cracking; an example of this cracking is illustrated in Fig. 3d.

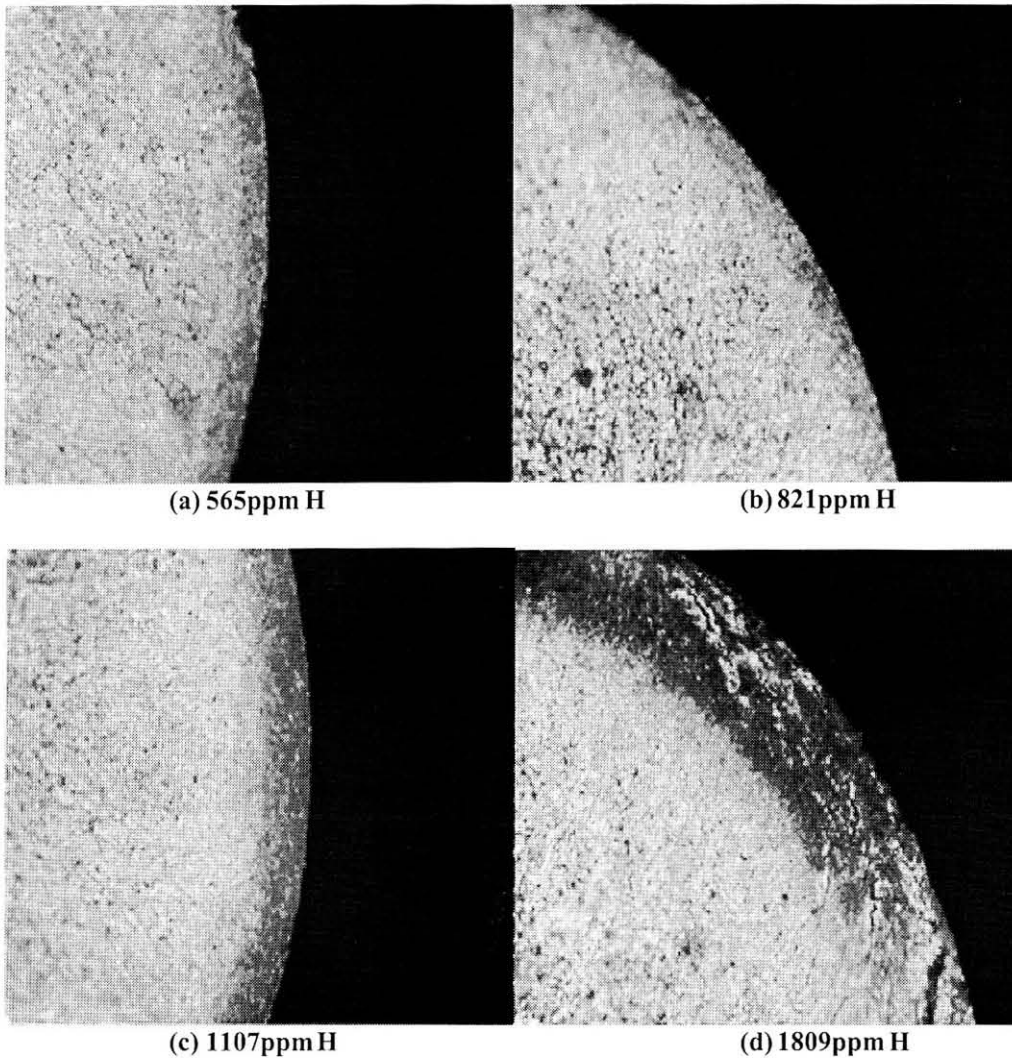


Figure 3. DF-LOM images of fracture surface from bend tests

It is well known that the diffusivity of H is quite high in B2 alloys; between 500-900°C, the diffusivity of H in TiNi is $D(\text{cm}^2/\text{s}) = 4.7 \times 10^{-3} \exp(-480 \times 10^{-3} \text{ eV}/k_B T)$. Furthermore, it is known that H is extremely mobile in the TiNi lattice even at relatively low temperatures. As such, the non-trapped H at these lower concentrations can freely migrate out of the sample as long as the surface oxide layer is permeable. This may explain the difficulty of retaining 50-300ppm H in the tested samples. However, at higher concentrations, sufficient H becomes trapped at lattice defects and forms the extended TiNi-H solid solution. EDS on the fracture surface of the most embrittled wire did not detect regions of Ni enrichment consistent with the formation of TiNi_3 [4]. Therefore, if hydrides are present, they are probably small and confined to the grain boundaries.

In an earlier study, DF-LOM and SEM were used to image H at grain boundaries of Ti-Ni-Fe alloys that were exposed to $>300^\circ\text{C}$ and high H_2 partial pressures [11]. With these higher, trapped H concentrations, it is reasonable that the upper plateau tends to increase with increasing H. The H-saturated dislocations, grain boundaries and other defects act as potent barriers to martensite formation. This is also seen in the DSC curves which show that increasing H decreases the M_s .

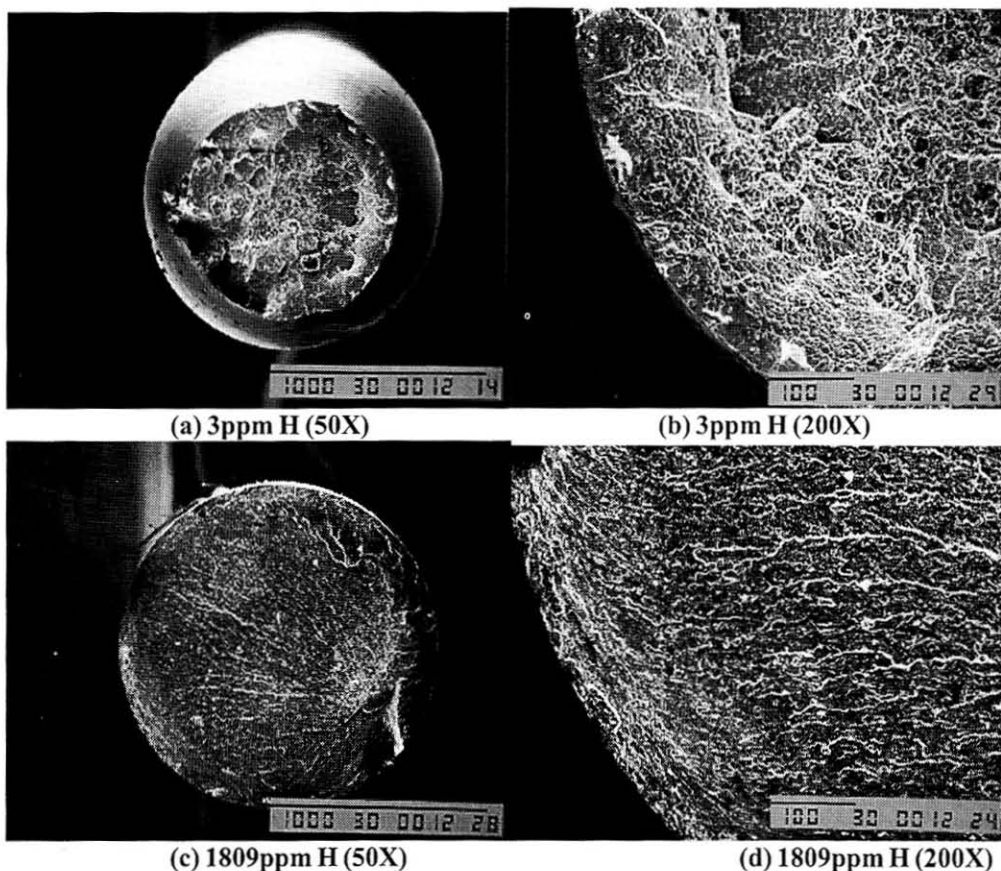


Figure 4. SEM images of fracture surface from tensile tests

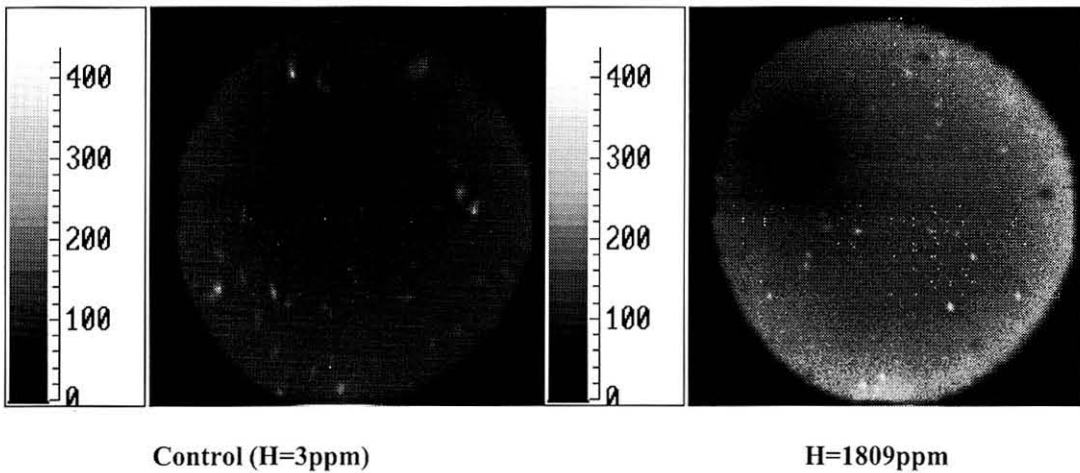


Figure 5. SIMS H image of control and H=1809ppm (image=150mm in diameter)

CONCLUSIONS

The reduction in ductility with a corresponding increase in bulk H suggests a direct correlation between the mechanical properties of TiNi and bulk H content. Tensile and bending tests both indicate that absorption of hydrogen by TiNi wires reduces ductility for H concentrations greater than 400ppm. The data suggests that H concentrations in the 50-300ppm range are extremely mobile at room temperature and escape the samples prior to analysis. At higher levels, H is trapped at interfaces and dislocations and cause the increase in plateau stress and decrease in transformation temperatures. Reduced ductility is due to the formation of an extended TiNi-H solid solution which causes a 10% lattice expansion. It was further observed that DF-LOM and SEM are novel and simple tools which may be used to determine the microstructure most affected by elevated concentrations of H.

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