Vacancies in NiTi shape memory alloys

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Abstract. NiTi shape memory alloys were examined with a mono-energetic positron beam. The thermal vacancy formation enthalpy was found to be 0.77 ±0.08 eV. Upon heating NiTi the martensitic S value is retained to temperatures significantly above the phase transition temperature and then decreases towards the austenitic value only gradually. In contrast upon cooling, a narrow transition region at 81.5 ±1.5 °C is observed. The magnitude of the transition strongly depends on the annealing temperature.

1. Introduction
The implementation of smart materials called shape memory alloys offer the promise of extensive savings in weight and fuel consumption as well as lower failure rates in commercial and military aircraft. Shape Memory Alloys (SMA) can oscillate between pre-trained shapes in response to temperature variations. SMA actuators operate without power lines, mechanical linkages or hydraulic systems. They can be implemented into relatively small devices such as rotor blades of vertical take-off and landing craft or into jet engine air intakes as well as exhausts. Tremendous flexibility in shapes can be achieved to reduce environmental noise or improve aerodynamic performance. Nickel titanium (NiTi)-based alloys commonly known as Nitinol™ offer great promise in these areas. The transition temperature for the shape change can be adjusted in a wide range from 0 °C to about 100 °C by minute changes of about 1.3 wt% in the ratio of nickel to titanium. At low temperatures NiTi maintains a martensitic structure, which is soft and easy to deform. Upon heating beyond the transition temperature it transforms into the harder austenitic structure. A sizable temperature hysteresis between the heating and cooling cycles occurs. Upon transition into the austenitic phase a specimen will return to its trained and “memorized” shape. Shape training can be accomplished by clamping the specimen into the desired shape during a brief anneal at about 550 °C.[1,2] More elaborate procedures lead to much better memory retention – the details of which are confidential vendor property.

Commercial implementation of NiTi SMAs is currently not quite possible because of a lack of understanding of the detailed and microscopic materials processes that underlie the shape memory effect. When SMA raw materials are processed and trained to perform as actuators, not every specimen performs within the desired specifications. Often training has to be repeated many times at great cost in time and manpower. A broad range of standard diagnostic tests failed to predict what treatments produce the desired results. The root cause for these variations may stem from atomic sized defects involving vacancies. Positron annihilation spectroscopies are applied to explore these

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properties. Only a small number of lifetime measurements have been published since early work by Würschum et al. and Araki et al.[3,4]

2. Samples and techniques
A number of sample materials in sheet form have been acquired from several vendors. The work discussed here focuses on sheets purchased from Johnson Matthey with a high transition temperature $A_f$ of 110 °C where $A_f$ is the temperature where the transition to the austenitic phase is complete. The sheets are received in a cold rolled and “flat annealed” state. All were coated with a layer of native black TiO$_x$ oxide. The samples were etched in a mixture of HF-nitric and H$_2$O in the approximate ratio of 1:1:2 respectively to remove the oxide. Samples of 2 by 2 cm$^2$ or 1 by 3 cm$^2$ are cut from 0.1 mm thick sheet. As a test a sample was “trained” into a simple U-shape strip. Following the manufacturer’s instructions the sample was clamped into the desired shape and annealed at 500 °C for about 10 minutes. More reliable shape memory behaviour requires much more elaborate procedures which are proprietary information of commercial vendors. After random deformation at room temperature it returns to the “trained” U-shape at $\sim$100 °C as expected. Repeating the deformation and heating cycle in air reveals a rather rapid “memory loss” after a few cycles. Clearly, the more elaborate training regimen performed by commercial users are required. Positrons from the beam at Washington State University were implanted about 5 um into the sample to obtain bulk properties. Annealing was carried out in-situ in the positron beam.

3. Measurements and discussion
To investigate the formation rate and accumulation of vacancy like defects a sample was bent multiple times 180° and again 180° in the opposite direction with a radius of about 5 mm. Figure 1 shows the change in S parameter as a function of the number of bending pairs. With increasing number of bending pairs the S parameter rapidly increases and saturates after about 100 pairs with a value of 3% above the as received “flat annealed” starting state. This is consistent with the formation of vacancies.

![Figure 1: Change in S parameter as a function of bending pairs (solid symbols, bottom scale) and subsequent annealing to a temperature listed on the top scale (open symbols). Data are normalized to the as-received flat annealed state.](image)

Subsequently the sample was annealed to increasing temperatures followed by a measurement upon cooling to room temperature. These data are also shown in figure 1. The sample returned to
approximately the as received state only after annealing as high as 700 °C. It should be noted that every annealing step occurred above the A_f transition temperature. In fact, typical training conditions do not involve temperatures above 150 °C. Clearly the actuators accumulate a large concentration of vacancies over the course of the training period as well as during regular operation.

To evaluate the enthalpy to form thermal vacancies $H_v$, an as received (and etched) sample was heated in situ to 700 °C and cooled slowly at $\sim 2 \, ^\circ\text{C/min}$ while measuring the S parameter rapidly with relatively poor statistical uncertainty. They are shown in figure 2 while the sample was in the austenitic phase only. The insert shows a frequency count plot for data between 85 and 150 °C. The Gaussian distribution is consistent with an error bar of about 0.005 in S. The enthalpy for thermal vacancy formation was obtained by fitting the data with the function.[5]

$$S_f(T) + S_b \xi \exp(-\frac{H_v}{k_b T})$$

$$S(T) = \frac{1 + \xi \exp(-\frac{H_v}{k_b T})}{k_b T}, \quad S_f(T) = S_b(300K) + \Delta S(T - 300K)$$

Here $S_b(300K)$ and $\Delta S$ are the S values for bulk austenitic NiTi and the change in S due to thermal expansion respectively. The equation $\xi = C^0 \mu \lambda^0$ contains the frequency factor and the vacancy concentration and trapping rate while $k_b$ is the Boltzmann constant. A vacancy formation enthalpy of $H_v = 0.77\pm0.08 \, \text{eV}$ results in the best fit. The defect type (Ni or Ti vacancies) was not identified and remains subject of future studies.

![Figure 2: Change in S parameter while the sample is cooling from 700 °C. Each data point was accumulated for 1 min. The spread of the S values for T<150 °C is shown in the insert with a Gaussian fit. The statistical error is about 0.005 in S. The solid line is a fit of the thermal vacancy formation enthalpy $H_v$.](image)

Figure 3 shows the data collected during temperature increases and decreases as well as across the phase transition from martensitic to austenitic and back. A “flat annealed” etched sample was used. While the sample is heated above the transition temperature and beyond, S drops gradually up to a temperature around 350 °C and then follows the cooling trend as shown in figure 2. While cooling past
the phase transition a rapid change in S back the martensitic value at room temperature is observed. The transition occurs within less than 2 ºC at 81.5±1.5 ºC. During increasing temperatures the initial S values is retained to temperatures significantly above the A$_f$ phase transition temperature. If the temperature rise is halted at an intermediate temperature below 300 ºC (not shown here) the S value of that temperature is observed until the sample is cooled below ~81 ºC. At that point S rises back to the starting value at room temperature. A detailed understanding of the data awaits further work. The relation between S and W follows a single straight line for the full temperature range. This indicates the presence of only a single type of defect.

![Figure 3: Change in S parameter during increasing and decreasing temperature from room temperature to 700 ºC. The solid line represents a running average of 10 short measurements as in fig. 2. The arrows indicate the sequence. The dashed line is the fit of the thermal vacancy formation enthalpy.](image)

4. Conclusions
NiTi shape memory alloy with a high A$_f$ = 110 ºC was examined by with positron Doppler Broadening studies. A vacancy formation enthalpy of 0.77±0.08 eV was measured. S and W parameters show hysteresis with a much wider temperature spread than expected from martensitic to austenitic structure transitions. SW-data follow a single line, indicating a single defect type.

Acknowledgements
The authors acknowledge valuable discussions with Dan Clingman. This work was supported by the Joint Center for Aerospace Technology and Innovation of Washington State, USA.

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