Vorgezogener Versuch A:

Formgedächtnislegierungen (Shape Memory Alloys – SMA)

Nicole Schai
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1 Abstract

With the experiments presented in this report, the typical characteristics stated in literature like memory shape, different crystalline forms and workload performed during martensite-austenite transformation of a NiTi alloys should be approved. The sound of dropping pieces of NiTi martensite and austenite as well as bending qualities were qualitatively measured. The further, the work performance was measured with a springforce meter. The temperature boundaries (As and Af) of martensite-austenite transformation were evaluated by heating an NiTi spring slowly and measuring contractions. Finally temperatures above 500°C were approved to be high enough in order to give a new shape to an NiTi alloy. The outcomes of the experiment correlate with literature and approve the theory of inner structure of NiTi.
2 | INTRODUCTION

On a macroscopic scale, Shape Memory Alloys are – as their name already reveals – alloys which remember a certain shape. They can be deformed but when heated up to an alloy-specific temperature, they will return to the shape they had before. In order to teach a new shape to an alloy, temperatures above 500°C are essential. The following experiments were made with a NiTi alloy.

The crystalline form explains the above listed characteristics. When heated up, NiTi has a body centered CsCl structure. It is therefore tense and not easy to bend. The high-temperated state of a SMA is called austenite. The cooling down of the material leads to a deformation of the inner structure. Layer number one moves a short distance to one side, whereas the layer just underneath moves exactly to the opposite side. The atoms move along the shere sides in opposite directions. The low-temperature state is called martensite. As a direct consequence of the inner structure, martensite is more easily to bend. Twinned martensite can be deformed to whatever shape desired. Only if the deformed martensite is heated up again to a temperature between 80-300°C, the atoms will return to the body centered CsCl structure and the NiTi alloy will regain its original shape. The temperature at which deformed martensite starts to become austenite is called As, the temperature at which the deformation is completed is called Af. The exact values of As and Af depend on the Ni-content of a NiTi alloy.

![Different states of NiTi alloy](www.2)

Fig. 2 | Different states of NiTi alloy. Austenite (high-temperature state) has a body centered CsCl structure and is therefore not very elastic. Cooling down leads to martensite (twinned martensite) in low-temperature state. When deformed (loaded), the martensite has a monoclinic structure. The structure will return to CsCl structure of austenite when the material is heated up again. (www.2)

Responsible for the memory-characteristics of the alloy are defects in the crystalline structure. Squeezed in between the atoms, they will push them back to the CsCl structure as soon as the alloy is warm enough so the atoms can move. Is the alloy heated up to over 500°C however, the defects will move too. They will take a position in the crystalline structure where there is most free space. In other words all atoms position themselves in a way where the energylevel is the lowest.

The following experiments were made in order to specify and approve the above listed characteristics such as crystalline structure, the possibility to teach a new form to an alloy at temperatures above 500°C, exact As and Af temperature as well as the strength of the deformation from deformed martensit back to austenit. The alloy used was NiTi, also known as nitinol [1].
3 MATERIAL AND METHODS

There were five different experiments made. The goal was to approve the theory of the different inner structures of austenite and martensit.

3.1 Inner structure

Two different experiments were made in order to approve literature. First, two pieces of NiTi alloy (the phase of them was unknown) were dropped down on a glass surface. One was slightly blue, whereas the other was only metal-gray. Afterwards they were heated up with an industrial fan ($T = 160^\circ C$) to about $100^\circ C$. They were dropped down on the glass again. The sound the pieces made was qualitatively measured.

As a second experiment, the tow pieces of NiTi alloy were bended at room temperature by hand. Again, the tenseness was qualitatively reported.

3.2 As/ Af temperature

As the As/ Af temperature is different for every NiTi alloy, the experiment should show the specific temperatures for the in hand alloy. It depends on the Ni content in the alloy.

A 500ml beaker was filled with tap water. It was put on a heating plate. A magnetic stirrer made sure the temperature was equal throughout the whole beaker. A thermometer was immersed in the beaker (so it would not touch the magnetic stirrer) and fixed with a holder. Main part of the experiment was a NiTi spring. It was pulled to a length of 10 centimeters and fixed with another wire (not NiTi alloy) to an arm of the holder. The spring was also immersed completely into the tap water in the beaker. The length of the spring was measured with a metal ruler on a regular basis as listed below. For the measuring, the spring was pulled out of the beaker completely.

The water in the beaker was now heated up quickly to $50^\circ C$ (it was known that the As temperature lies above this level). Now the heating procedure was slowed down. As long as there was no contraction of the spring noticed, values of length and temperature were reported only every $2^\circ C$. As soon as there was contraction, the values were listed on a $1^\circ C$ basis. When the length values started to stagnete, we returned to $2^\circ C$ steps. The experiment was stopped at a watertemperature of $82^\circ C$.

The length and temperature values were listed in a graph and the As / Af temperature read from the graph (see Results).

3.3 Creating a new shape

In part three of the experiments, a NiTi wire should get a new memory-shape. A piece of 20cm of NiTi wire was fixed with bolt and nut assemblies on a perforated metal plate. The complete assembly was put in the preheated oven at $500^\circ C \pm 50^\circ C$. After 7 minutes the fixed wire was taken out of the oven. After 10 more minutes, the plate as well as the wire were cooled down to room temperature and the wire could be taken away from the plate. The wire was then deformed and heated up with an industrial fan to check whether the wire would return to its new memory-shape.
3.4 Work performance of phase transformation (martensite to austenite)

As a setup for this experiment, a springforce meter was fixed on a holder. A NiTi spring was pulled to about 8 centimeters and fixed between the springforce meter and a weight situated exactly underneath the springforce meter. The spring was pulled to a length so the springforce meter displayed a pretension of \( F_0 \) of about 1.4 Newton. The length of the springforce meter spring \( l_0 \) was reported. The NiTi spring was now heated with an industrial fan (\( T = 160°C \)) until there was no more contraction noticed. The deformed martensite has now fully returned to austenite. The new length of the spring of the springforce meter \( l_1 \) as well as the force displayed by the springforce meter \( F_1 \) was reported. The lengthening of the springforce meter spring is equal to the contraction of the NiTi spring. The experiment was repeated 4 times.

The work performed by the NiTi force was calculated with the following formula:

\[
\int_{l_0}^{l_1} Dl \cdot dl = \left[ \frac{1}{2} D l^2 \right]_{l_0}^{l_1} = \frac{1}{2} \times 50Nm^{-1} \times l_1^2 - \frac{1}{2} \times 50Nm^{-1} \times l_0^2
\]

(length \( l \) in meters)

3.5 Hypothesis

We expect the NiTi alloy to behave according to the characteristics listed in literature [1]. The sound of martensite should be dump, the one of austenite clear. As martensite is heated up, however, the sound of it should change towards the one of austenite. This is supposingly the consequence of the change in inner structure of martensite to austenite.

The \( As \) and \( Af \) temperature must lie somewhere between room-temperature and 500°C. Up to room temperature, we know that there is a clear difference between martensite and austenite. Above 500°C the defects start to move as well and as a result we would give a new memory-shape to the alloy. Literature talks of values from room temperature up to 100°C [1]. Expected values for the NiTi alloy used in this experiment range therefore between 40°C and 100°C.

Temperature above 500°C should lead to defects moving within the cristall structure. The oven treatment should therefore give a new memory-structure to the NiTi-wire. Once cooled down and deformed, heating temperature between 80°C and ca. 200°C return the wire to the new memory-structure.
4 RESULTS

4.1 Inner structure

The dropped down pieces of NiTi alloy sounded different at room temperature. The slightly blue piece had a crystall clear sound. The metal-coloured one sounded dump. After the heating procedure, there was no noticeable difference of the sound of the blue piece. On the other hand, the sound of the metal-coloured piece was now similar to the blue one (Tab. 1). Due to the heat, the two pieces had turned to the same inner structure.

Tab. 1: Sound of two different pieces of NiTi alloy (one blue, one gray). Qualitatively reported first at room temperature and secondly at 80°C.

<table>
<thead>
<tr>
<th>Room Temperature</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>blue</td>
<td>cristall, clear</td>
</tr>
<tr>
<td>metal</td>
<td>dump</td>
</tr>
</tbody>
</table>

The two pieces showed different bending qualities. The metal-coloured piece was easily deformed by hand whereas it was nearly impossible to bend the blue piece without breaking it into pieces.

4.2 As / Af temperatures

The temperature and length of a NiTi spring were reported regularly. Table 2 shows the exactly measured values of Temperature and length of the spring. The contraction started around 58°C and was perfectly completed at a temperature of 75°C. In Figure 3, the length of the spring is plotted against the rising temperature.

Tab. 2 Reported temperature and length values. Temperature in degree Celsius, ±0.5°C length in centimeters ± 0.05 centimeters.

<table>
<thead>
<tr>
<th>Temperature [ °C ]</th>
<th>Length [ cm ]</th>
<th>Temperature [ °C ]</th>
<th>Length [ cm ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>10.0</td>
<td>66</td>
<td>6.0</td>
</tr>
<tr>
<td>43</td>
<td>10.0</td>
<td>67</td>
<td>5.4</td>
</tr>
<tr>
<td>48</td>
<td>10.0</td>
<td>68</td>
<td>5.1</td>
</tr>
<tr>
<td>50</td>
<td>10.0</td>
<td>69</td>
<td>4.9</td>
</tr>
<tr>
<td>52</td>
<td>10.0</td>
<td>70</td>
<td>4.7</td>
</tr>
<tr>
<td>54</td>
<td>10.0</td>
<td>71</td>
<td>4.4</td>
</tr>
<tr>
<td>56</td>
<td>10.0</td>
<td>72</td>
<td>4.2</td>
</tr>
<tr>
<td>58</td>
<td>10.0</td>
<td>73</td>
<td>4.1</td>
</tr>
<tr>
<td>60</td>
<td>9.6</td>
<td>74</td>
<td>4.1</td>
</tr>
<tr>
<td>61</td>
<td>9.1</td>
<td>75</td>
<td>4.0</td>
</tr>
<tr>
<td>62</td>
<td>8.6</td>
<td>76</td>
<td>4.0</td>
</tr>
<tr>
<td>63</td>
<td>8.6</td>
<td>78</td>
<td>4.0</td>
</tr>
<tr>
<td>64</td>
<td>8.0</td>
<td>80</td>
<td>4.0</td>
</tr>
<tr>
<td>65</td>
<td>6.6</td>
<td>82</td>
<td>4.0</td>
</tr>
</tbody>
</table>

As shown in Fig. 3, the contraction takes place in the temperature region between 58°C and 74°C. The evaluated values of As and Af are read from the graph. For As this is 59°C ± 2°C, for Af 71°C ± 2°C. These are not calculated values and might vary slightly depending on how the graph is read.
4. RESULTS

Fig. 3 Length of NiTi Spring graphed against temperature. As the temperature goes up, the spring starts to contract at about 59°C (As). The contraction is completed at 71°C (Af).

4.3 Creating a new shape

The NiTi wire was baked in the oven at 500°C ± 20°C for 7 minutes. After cooling down and deformation, the wire was heated up again and turned back into its memory-shape. The experiment was therefore completed well with the expected results.

4.4 Work performance of phase transformation

The work performed by a contracting NiTi spring was calculated from the spring constant \( D = 50 \text{Nm}^{-1} \) and the difference of the initial length \( (l_0) \) and the final length \( (l_1) \) of the springforce meter. (Tab. 3).

<table>
<thead>
<tr>
<th>Cycle</th>
<th>( f_0 ) [N]</th>
<th>( f_1 ) [N]</th>
<th>( l_0 ) [cm]</th>
<th>( l_1 ) [cm]</th>
<th>( \Delta f = (f_0-f_1) ) [N]</th>
<th>( t ) [s]</th>
<th>( W ) [J] * 10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.40</td>
<td>3.35</td>
<td>2.8</td>
<td>6.7</td>
<td>1.95</td>
<td>7</td>
<td>97.38</td>
</tr>
<tr>
<td>2</td>
<td>1.35</td>
<td>3.35</td>
<td>2.7</td>
<td>6.7</td>
<td>1.95</td>
<td>7</td>
<td>94.00</td>
</tr>
<tr>
<td>3</td>
<td>1.40</td>
<td>3.35</td>
<td>2.8</td>
<td>6.7</td>
<td>1.95</td>
<td>10</td>
<td>92.63</td>
</tr>
<tr>
<td>4</td>
<td>1.40</td>
<td>3.35</td>
<td>2.8</td>
<td>6.7</td>
<td>1.95</td>
<td>13</td>
<td>92.63</td>
</tr>
<tr>
<td>5</td>
<td>1.40</td>
<td>3.35</td>
<td>2.8</td>
<td>6.7</td>
<td>1.95</td>
<td>8</td>
<td>92.63</td>
</tr>
</tbody>
</table>

The average work performed by the NiTi spring is therefore 93.85 * 10^{-3} Joules. The standard deviation is 2.06 Joules.
5 Diskussion

Firstly, the inner structure needs to be looked at closely. The slightly blue piece of NiTi sounded crystal clear when dropped onto a glass plate. As there could be no change noticed when heated up, it has to be assumed that there was no significant change in the inner structure. The crystal clear sound must come from a straight and linear structure with only a small possibility for the atoms to move. As already listed in literature [1], austenite has a cubic centered CsCl structure. This correlates with the inner structure of the blue piece of NiTi. On the other hand, the metal-coloured piece sounded dump at room temperature. As it was martensite, sound waves could not pass easily through the shered structure of martensite. Due to the more flexible structure, the atoms have the possibility to move slightly and dumpen soundwaves. When heated up, the metal-coloured piece regained its austenite structure and consequently sounded like austenite.

The As /Af temperature could be evaluated at As = 59°C ± 2°C and Af = 71°C ± 2°C. These are values taken from the graph. Mathematical calculation might give more exact values. The nonlinear points in the graph could have several reasons. Firstly the metal ruler could have been more exact and it was difficult to read the exact length. Secondly, the spring could have been pulled out of the water before it had adapted the temperature of the tap water completely. Important to see, however, is, that the temperature at which deformed martensite turns back to austenite is far above room temperature as well as far lower than the temperature needed in order to give the alloy a new memory-shape. Due to this difference, the different states (martensite, austenite) can be easily separated. The corresponding temperature values for austenite – martensite transformation (Ms, Mf) correlate with the As/Af temperatures. They are only a couple of degrees lower. Ms = Af-x °C, Mf = As-x °C. As this fact is known [1] it would be enough to calculate one of the two temperatures. However, it is difficult to calculate Ms or Mf values. One cannot see at what temperature the inner structure of martensite is complete. There is no outer deformation during the process from austenite to martensite.

The different cycles of the experiment which showed the work performance of a NiTi alloy spring did not give significantly different results. The average work performed was 93.85 * 10^-3 Joules with a standard deviation of 2.06 Joules. During the experiment, the time of heating was measured, too. As shown in ‘Results, Table 3’, this time span was very different in every cycle. The performed work, however, did not change accordingly. This leads to approval of the assumption, that once martensite has become austenite, the heating can go on for longer, but it does not change anything about the inner structure. A certain amount of temperature is needed for the transformation to take place, but further energy input has no more affection.

Shape memory alloys are used in many different areas of industry. A main branch is the medical industry. SMA’s allow only small cuts for operations. Due to their own shape transformation there is no more need for bigger instruments. Further more, NiTi alloy is a material which can perform work for many times in a row. As they can return to a memory shape, they are the perfect material for the electrical industry. Switches, for example, which should turn off after a certain period of time can depend on parts of SMA’s which return to a certain position as they get warm. The characteristic of being able to change shape just by heat opens up new technological possibilities. On top of all, the temperatures at which changes in the inner structure of NiTi starts to change can be well regulated. They depend mainly on the content of Nickle in the alloy. It is probably this specific characteristic which makes NiTi being spread all over the industry. In medicine, for example, stants need to return to their memory shape at average body temperature. On the other hand, switches should turn off only after they had been turned on for a longer time and the heat inside due to electricity. The As temperature should therefore be higher.
6 SOURCES

6.1 Literature

[1] STUDIENGANG Materialwissenschaft ETH Zürich
    Skript Vorgezogener Versuch A: Formgedächtnislegerungen (Shape Memory Alloys – SMA)

6.2 Websites

www.1
    SMA/MEMS Research Group (2001), Shape Memory Alloys
    www.phiengineering.com/nitinol.htm (17.08.2001)

www.2
    PHI Engineering

7 FIGURES

FIG. 1 PHI Engineering, www.1 .................................................................................................................. 1

FIG. 2 Different states of NiTi alloy. Austenite (high-temperature state) has a body centered CsCl
    structure and is therefore not very elastic. Cooling down leads to martensite (twinned martensite)
    in low-temperature state. When deformed (loaded), the martensite has a monoclinic structure. The
    structure will return to CsCl structure of austenite when the material is heated up again. (www.2) 4

FIG. 3 Length of NiTi spring graphed against temperature. As the temperature goes up, the spring starts
    to contract at about 59°C (As). The contraction is complete at 71.5°C (Af). ................................. 8

8 TABLES

TAB. 1 Sound of two different pieces of NiTi alloy (one blue, one gray). Qualitatively reported first at
    room temperature and secondly at 80°C. .................................................................................................. 7

TAB. 2 Reported temperature and length values. Temperature in degree Celsius, ±0.5°C length in
    centimeters ±0.05 centimeters ............................................................................................................. 7

TAB. 3 Work performed by a NiTi spring during phase transformation from deformed martensite to
    austenite. The experiment was done five times (Cycle). f₀ = pretensioning of the springforce meter ±
    0.05N, f₁ = final by the springforce meter displayed force ± 0.05N, l₀ = initial length of the
    springforce meter spring ± 0.1cm, l₁ = final length of the springforce meter spring ± 0.1cm, τ = time
    of heating with industrial fan (max. temperature 300°C) in seconds, W = Work performed in Joules
    (kg*m²*s⁻²) ± 4.75 * 10⁻³. The work is calculated from the difference in springlength and spring
    constant of the springforce meter D=50Nm⁻¹. .............................................................. 8

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