Characteristics of cracks formed at the surface of NiTi during a single cycle of pseudoelastic deformation

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Abstract. Pseudoelastic deformation of NiTi usually results in cracks at the surface. Cracking is promoted by surface oxide layers that form, e.g., during heat treatments required for shape-setting of minimally invasive implants. In connection with the advancing miniaturization of minimally invasive implants, the question arises whether their mechanical integrity may get impaired by such cracks. In the present work, the characteristics of the cracks was investigated in cross section with the help of targeted preparation using focused ion-beams. SEM and TEM on samples after a single cycle of pseudoelastic deformation revealed that cracks extend perpendicular to the loading direction in the surface oxide layer and change to angles between 90° and 45° in the Ni-rich layer below. Pores observed in the surface oxide close to the Ni-rich layer did not prevent the extension of cracks towards the NiTi bulk. When the cracks reach the NiTi, blunting of the crack tip was observed. The crack length essentially corresponds to the thickness of the surface oxide layer and the Ni-rich layer. The findings provide data for estimating crack propagation in according implants in the future.

1. Introduction

Pseudoelastic NiTi is a key material for developing novel implants for minimally invasive application [1, 2]. A current trend is the miniaturization of according implants to reduce the amount of material inserted into the human body and risks associated with surgery [3]. The miniaturization of implants, e.g., stents, brings challenges regarding their mechanical stability and integrity during extended application under alternating loads. In this context, potential damage to the surface of NiTi as a result of a single cycle of pseudoelastic deformation during the implantation procedure is of specific interest [4-6]. It was shown that a single cycle of pseudoelastic deformation can lead to damage at the natural surface of NiTi, especially in combination with previously formed surface oxide layers. With respect to the thickness of surface oxide layers, different outcomes were observed, including the formation of cracks or flaking of particles [7]. Such damage to the natural surface of NiTi may not only compromise the mechanical integrity of minimally invasive implants, but it may also expose Ni-rich sublayers with consequences regarding the compatibility of the material in a specific biological environment. Additionally, the cracks at the surface of the material may grow during the often small but alternating loads, eventually impairing the
mechanical integrity of the implant by fatigue fracture. Thus, the characteristics of such cracks are of interest. Considering the observation of pores close to the oxide / metal interface in a previous study, their arrangement and size with respect to the heat treatment time was also of interest [4]. A layer of pores parallel to the surface may affect the direction of cracks and help to guide them away from the bulk. Visualization of cracks has so far mainly been carried out using scanning electron microscopy in top view [8, 9]. However, important aspects including crack length, propagation or deflection and details regarding pores remain unclear.

In the present work, the characteristics of cracks at the natural surface of NiTi was observed in cross section using scanning electron microscopy and transmission electron microscopy. An important aspect is if cracks extend into the NiTi bulk already after a single cycle of pseudoelastic deformation.

2. Experimental and materials

2.1. Material condition and heat treatment
The study was carried out using pseudoelastic NiTi wire according to specification SE508 with a diameter of ~ 160 μm (Fort Wayne Metals). The surface of the wire was mechanically polished by the supplier. Wire segments were subject to annealing in a muffle furnace in air atmosphere as detailed in [10]. The annealing temperature was set to 540°C and the annealing to 2 min, 5 min, 10 min, 30 min and 60 min. After the heat treatment, the wire surface displayed a coloration as a result of the thin surface oxide layer. Of each condition, a wire segment was strained to the pseudoelastic limit of ~ 6 %.

2.2. Preparation of cross sections and analysis using scanning and transmission electron microscopy
For visualizing details of cracks and pores in the surface oxide layer by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), cross sections were prepared using a focused ion beam system (FIB, FEI Helios NanoLab 600i) [11]. After identifying a region of interest, the surface was covered locally by a Pt-layer with a thickness of ~ 50 nm applying electron-beam deposition inside the FIB. After tilting the sample by 52° perpendicular to the ion-beam, a second layer of protective Pt with a thickness of ~ 1 μm was deposited using the ion-beam. Slope cuts to a depth of 5 μm along a length of 10 μm were cut at 30 kV and 2.4 nA using the ion-beam perpendicular to the wire surface. After slope cutting, cleaning steps were applied by reducing the acceleration voltage step-wise to 5 kV in order to increase the quality of the cross sections by removing material affected by high ion energy.

Immediately after preparation, an overview of the samples along slope cuts was gained using the secondary electron/ in-lens detector of the FIB/SEM system. Although the imaging quality of the FIB/SEM system was limited, a layered structure in the surface region and features resembling pores and cracks became visible. For higher detail, lamellae for TEM were prepared and observed using a Jeol Jem-3010 operating at 300 kV.

For preparation of TEM lamellae, regions of interest were subject to a second slope cut parallel to the first one. Further preparation was carried out according to the common lift-out procedure for preparation of TEM lamellae. Final etching of the lamellae was done in several steps, reducing the acceleration voltage from 30 kV to 2 kV.
3. Results and discussion

3.1. Length and orientation of cracks after a single cycle of pseudoelastic deformation

In the following Figures, exemplary images of slope cuts are displayed for wires after heat treatment for 5 min (Figure 1), 10 min (Figure 2) and 30 min (Figure 3). In each Figure, the wire axis was set horizontally. The thickness of the surface oxide layer increases with annealing time from values of ~69 nm after 5 min to ~258 nm after 30 min (Table 1). Already during annealing for 5 min, a Ni-rich layer formed below the surface oxide layer as a consequence of the preferential oxidation of Ti, depleting the sublayer by Ti. The formation of a Ni-rich layer is well documented in the literature. The thickness of the Ni-rich layer was in the range of ~48 nm after 5 min to ~168 nm after 30 min of annealing (Table 1), close to the values determined for the surface oxide layer. For annealing times of 30 min and longer, it was shown, that the Ni-rich layer consists of intermetallic Ni₃Ti that does not exhibit pseudoelasticity as observed for NiTi [4]. For annealing times below 30 min, the phase of the Ni-rich layer has not been identified unambiguously.

Independent of the annealing time, cracks in the surface oxide layer and the Ni-rich layer are visible. The cracks expand from the wire surface into the material and end when reaching the NiTi bulk (Figures 1 to 3). It is interesting to note, that single cracks always damage both, the surface oxide layer and the Ni-rich layer. Cracks exclusively in one of the layers were not observed. Whereas the orientation of the cracks in the surface oxide layer is essentially perpendicular to the surface and thus perpendicular to the applied load, the orientation of cracks often changes when entering the Ni-rich layer towards an angle between 90° and 45° to the loading direction. This indicates towards a brittle behavior of the surface oxide layer and some ductility of the Ni-rich layer. The extension of cracks into the NiTi bulk is apparently hindered by plastic deformation in the vicinity of the crack tip, as visible from the blunting of the crack tip displayed in Figure 3.

![Figure 1](image_url) *Figure 1.* SEM image of a slope cut at the surface of a NiTi wire after heat treatment for 5 min. Between surface oxide layer and NiTi, a Ni-rich layer has formed. Cracks are visible in both, the surface oxide layer and the Ni-rich layer (indicated by white arrows). Pores are visible as dark spots at the bottom of the surface oxide layer (indicated by black arrows).
Table 1. Thickness of the surface oxide layer and the Ni-rich layer formed after annealing for 5 min, 10 min and 30 min, respectively.

| Annealing time (min) | Thickness of surface oxide layer (nm) | Thickness of Ni-rich layer (nm) |
|----------------------|---------------------------------------|-------------------------------|
| 5                    | 69 ± 8.2                              | 48 ± 8.8                      |
| 10                   | 115 ± 7.7                             | 89 ± 10.3                     |
| 30                   | 258 ± 28.8                            | 168 ± 20.7                    |

Figure 2. SEM image of a slope cut at the surface of a NiTi wire after heat treatment for 10 min. Cracks are visible in the surface oxide layer and the Ni-rich layer (white arrows). Pores are visible at the bottom of the surface oxide layer (black arrows).
Figure 3. SEM image of a slope cut at the surface of a NiTi wire after heat treatment for 30 min. A crack is visible in the surface oxide layer and the Ni-rich layer (white arrow). The crack stopped when reaching the NiTi bulk and a blunt crack tip is visible. Pores are contained at the bottom of the surface oxide layer (black arrows).

3.2. Effect of annealing time on the occurrence of pores in the surface oxide layer

Independent of the annealing time, pores were identified in the surface oxide layer close to the Ni-rich layer. The formation of the pores is likely a result of the Kirkendall effect. As mentioned earlier, such pores are of specific interest here, since they may help to deflect cracks and guide them away from the bulk. However, the limited resolution of the FIB/SEM system did not allow for identification of further details regarding arrangement and quantity (number/size) of the pores. According to the Kirkendall effect, the quantity of the pores is likely to increase with annealing time, if the thickness of the surface oxide layer increases.

For analyzing the effect of the annealing time on the formation of pores, TEM lamellae were prepared for samples annealed for 2 min to 60 min. Pores are visible in all cases inside the surface oxide layer close to the interface to the Ni-rich layer / NiTi (Figure 4). Although difficult to judge from quasi 2-dimensional samples, the quantity of pores appears to be similar for each condition, whereas the thickness of the surface oxide layer increases notably. This is in contrast to the expected behavior and indicates towards a change of the mechanism of oxide layer growth during annealing. Considering earlier work, the surface oxide layer was reported to grow inward for temperatures < 450°C and outward for higher temperatures [12, 13]. During heating the samples in the present work to 540°C, the surface oxide layer grew inward for ~ 1.5 min before the growth direction changed to outward [10]. The observed arrangement and quantity of the pores would be consistent with the conclusion that the pores essentially form during the initial inward growth of the surface oxide layer. A potential effect of the pores to deflect cracks would thus be independent of the annealing time. For further assessment, a potential impact of the annealing temperature should be considered.
Figure 4. TEM images of cross sections at the surface of NiTi wires after annealing for 2 min to 60 min (left to right). The arrangement and quantity of pores is similar independent of the annealing time, whereas the thickness of the surface oxide layer increases notably.

3.3. Impact of pores inside the surface oxide layer on flaking of oxide particles and propagation of cracks into the bulk

In a previous work it was demonstrated that oxide particles may flake off the NiTi wire during a single cycle of pseudoelastic deformation. In order to visualize details of a flaking site, a TEM lamella was prepared in cross section together with a lamella from a site without flaking (Figures 5 and 6). In the specific case, the previous deformation of the wire was increased to slightly exceed the limits of the pseudoelastic deformation. Whereas the pseudoelastic deformation reverts during unloading, a small amount of plastic deformation remained, facilitating the identification of cracks after unloading of the sample.

The characteristics of a crack is shown in Figure 5 for a site without flaking. The behavior is as observed previously using FIB/SEM. The crack extends essentially perpendicular to the loading direction into the material. Crack deflection at the pores at the bottom of the surface oxide layer is not visible. For the lamella attained from the flaking site, some oxide is visible at the top of the Ni-rich layer (Figure 6). In this case, the layer of pores has apparently acted as weak region, guiding a crack parallel to the surface. However, cracks are visible in the Ni-rich layer that remained attached to the wire in all observed cases.
Figure 5. TEM image of a NiTi wire after 30 min of annealing in cross section. The behavior is as observed previously using FIB/SEM.

Figure 6. TEM image of a NiTi wire after 30 min of annealing in cross section at a flaking site. The layer of pores has acted as weak region, helping to guide a crack parallel to the surface. Cracks in the Ni-rich layer are visible.

4. Conclusions
Details of cracks in the natural surface of NiTi after a single cycle of pseudoelastic deformation were visualized in cross section using SEM and TEM. The following aspects are compiled regarding the characteristics of according cracks:

- cracks in the surface oxide layer extend perpendicular to the loading direction, consistent with the brittle behavior of the surface oxide layer
- cracks in the Ni-rich layer below the surface oxide layer exhibit an angle between 90° and 45° to the loading direction, indicating some ductility of the layer
- cracks stop when reaching the NiTi bulk and blunting of the crack tip is observed
- pores form independent of the annealing time at the bottom of the surface oxide layer and contribute to flaking of oxide particles, but do not prevent the formation of cracks in the Ni-rich layer

An estimation of the crack length becomes possible considering the thickness of the surface oxide layer and the thickness of the Ni-rich layer. Both layers crack during the first cycle of pseudoelastic deformation. Accordingly, the crack length corresponds to the combined thickness of both layers and is expected to remain < 200nm for conditions representative for application. Thus, the cracks do not immediately limit the mechanical integrity, even of delicate NiTi minimally invasive implants with feature sizes below 100 μm. The potential growth of such cracks during small but alternating loads remains to be assessed in the future. Regarding the compatibility of the material in a specific biological environment, it is interesting to note that flaking of oxide particles does not necessarily expose the Ni-rich layer below the oxide, since the separation occurs along the pores at the bottom but inside the oxide. Accordingly, some oxide remains on the material. However, since oxide particles with dimensions of a few μm and exhibiting sharp edges may cause adverse reactions in a biological host, their formation should be avoided as discussed in [7].
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