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Determination of Transformation Properties of Thin Medical Grade Ni-Ti Wire by High-Resolution Bend and Free Recovery Testing

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Thin medical grade Ni-Ti wires, pseudo-elastic at ambient temperature, were annealed to set the final shape and the properties of the material. In order to investigate the influence of the annealing, high-resolution bend and free recovery tests were carried out. With the newly constructed device, the reverse deformation (free recovery) of the bent wires was recorded in detail. Wire segments with a weight of <1 mg are sufficient to attain reliable results. The high resolution of the testing device is based on a precise temperature control and a video monitoring system equipped with a microscope lens. In addition to the determination of the transformation temperatures, which is possible with common bend and free recovery tests, the high resolution allows for the identification and quantification of the reverse deformation stages attributed to the martensite-to-austenite transformation and the occurrence of the R-phase. The variations of the transformation properties attained by evaluating the different types of reverse-deformation curves are presented and discussed.

Keywords advanced characterization, biomaterials, heat treating

1. Introduction

The application of thin Ni-Ti wire for medical devices and implants requires specific and reliable information about material properties as, e.g., the transformation temperatures (Ref 1, 2). Short-time annealing that is necessary to set the shape of medical implants and devices has significant influence on the transformation temperatures (Ref 3). In order to warrant the functionality of an implant device, the transformation properties including the temperature range of the transformation and the corresponding reverse deformation degree are also of critical importance. Since the loading and straining conditions affect the transformation behavior and the transformation temperatures (Ref 4), the testing method should reproduce the loading and straining conditions of the material during its application (Ref 5). In surgical applications, the major deformation of pseudo-elastic Ni-Ti implants occurs when they are collapsed to small sizes and positioned through small catheters inside the patient. There, they further unfold and, thereby, fulfill their vessel-supporting or -occluding purpose. Similar straining conditions, such as during transcathetral surgeries, which result in bending of the wires, are generated during the bend and free recovery test. Since the type of deformation of the wires during this test is similar to that occurring in specific medical applications of interest, the determination of transformation temperatures and transformation characteristics is assumed to be of higher significance than when applying other methods without deformation or mechanical loading.

Results of bend and free recovery tests available in the literature occasionally exhibit low accuracy due to imprecise temperature control during the testing (Ref 6), or due to correlation of temperature and reverse deformation by only a small set of data points (Ref 7).

The experimental setup for bend and free recovery tests according to the standard test procedure ASTM F2082-03 (Ref 8) is based on contact methods to measure the reverse deformation of the material, but a non-contact method is suggested. Sometimes, in the production of medical implants, a thin wire with a diameter of <150 µm is required. Use of thin wire results in comparably small forces generated during the free recovery. In this case, the measurement of the reverse deformation with contact to the specimen is prone to deviations of the measured transformation temperatures and the transformation characteristics. In order to attain a reliable characterization of the transformation properties of thin wires, a new device has been constructed (Ref 3). The device combines a non-contact measurement technique of the reverse deformation, a precise temperature control by combining heating and cooling system, a temperature sensor right next to the specimen, and a detailed recording of the reverse deformation of the wire using a camera system equipped with a microscope lens. Using this device, not only the influence of annealing on the transformation temperatures (Ref 3), but also the effects on the transformation properties and the occurrence of the R-phase can be determined.

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2. Experimental

Medical grade pseudo-elastic Ni-Ti wire with a diameter of ~150 μm and a Ni content of 50.8 at.% complying with the requirements of the standard SE508 was used. The manufacturing process is proprietary to the producer, and no details of annealing temperature and period of the straight annealing process were provided. However, it is clear from previous investigations that a certain defect density resulting from the drawing process remains stored inside the material. This was confirmed by annealing experiments that resulted in recrystallization under certain conditions (Ref 9). Similar to the application for medical implants, the thin Ni-Ti wires were neither solution-treated nor recrystallized before the heat treatments applied in the present study.

In order to investigate the influence of short-time annealing, long wires were treated in a muffle furnace at temperatures ranging from 450-610 °C for a period from 2 min to 30 min to simulate a shape-setting treatment, and to modify the materials surface with respect to biocompatibility aspects (Ref 10). After the annealing, pieces of 8 mm length (<1 mg) were cut off the straight wires to be subjected to bend and free recovery tests.

Since the transformation properties of Ni-Ti are sensitive to mechanical loading, a non-contact optical method was chosen for the experimental setup (Fig. 1). The horizontal resolution of the video camera was 1024 pixels, and paired with the microscope lens, the identification of slightest differences in the wire position during their reverse deformation could be detected. A cooling/heating system that allows for controlling the temperature with an accuracy of ±0.1 °C in temperature ranging from −55 °C to +45 °C has been built and attached to the specimen chamber that was filled with ethanol (Fig. 1). According to the specifications of the material, the "as received" wire is assumed to be fully martensitic at −55 °C. The dimension of the specimen holder inside the measurement chamber was adapted according to the wire diameter to attain a defined strain from 2-2.5% of the external wire segment after bending as required in (Ref 8). After cooling the measurement chamber, the wire was placed on the specimen holder inside the ethanol. Due to the small amount of material, the temperature of the wire assimilates almost instantaneously to the temperature of the ethanol inside the measurement chamber. Afterward, the wire was bent until the desired curvature was obtained. The heating rate was set to 0.6 °C/min. The temperature of the ethanol bath was measured close to the specimen by a Ni/CrNi thermocouple, and pictures of the wire were taken by the video monitoring system, continuously. The constant slow heating rate ensured a uniform temperature inside the measurement chamber during the testing, and it allowed for the assimilation of the temperature of the wire to that of the ethanol.

3. Results and Discussion

Figure 2 shows a sequence illustrating the reverse deformation of a thin Ni-Ti wire during the free recovery. The pictures were recorded by the internal camera during heating of the ethanol bath. Figure 2(a) represents the bent wire at −55 °C and Fig. 2(d) was taken at 45 °C. Due to the microscope lens, the outline of the 150 μm thin wire is clearly visible after adjusting the focus. In the upper left corner, the thermocouple for measuring and recording the temperature is visible in a distance of ~2 mm from the wire.

Evaluating the reverse deformation of the differently annealed wires leads in general to 3 different types of reverse-deformation curves (Fig. 3). Due to the slow heating rate, each curve is defined by a set of more than 1000 data points. Type-1 curve (Fig. 3a) shows a single S-shape with definite beginning and end of the reverse deformation and a slope between these characteristic points. The curve is clearly attributed to a martensite-to-austenite transformation without R-phase. The transformation temperatures A_s (austenite-start) and A_f (austenite-finish) can be determined by tangent method (Ref 8).

Type-2 reverse-deformation curve (Fig. 3b) shows a double S-shape. The major portion of the reverse deformation occurs during the first S-shaped stage. The second stage has only a minor contribution to the total reverse deformation. This is attributed to a transformation path martensite-to-R-phase-to-austenite. The transformation from R-phase-to-austenite can only cause a deformation of ~10% of the deformation the transformation from martensite-to-austenite can. This is based on the differences in the crystal structures of the phases (Ref 11). The alteration of the dimensions of the unit cells of the different crystal structures from martensite-to-austenite or martensite-to-R-phase, respectively, are significantly larger than that from R-phase-to-austenite. Therefore, the detailed identification of the occurrence of R-phase and the accompanying small reverse deformation in the curves is difficult by bend and free recovery testing with lower resolution. If the resolution is not sufficient, the second S-shape of the reverse-deformation curve cannot be identified. However, using the presented

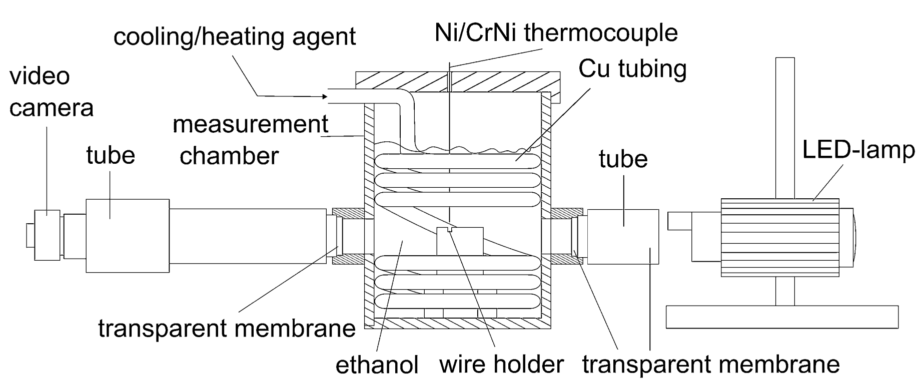

Fig. 1 Sketch of the high-resolution bend and free recovery test device

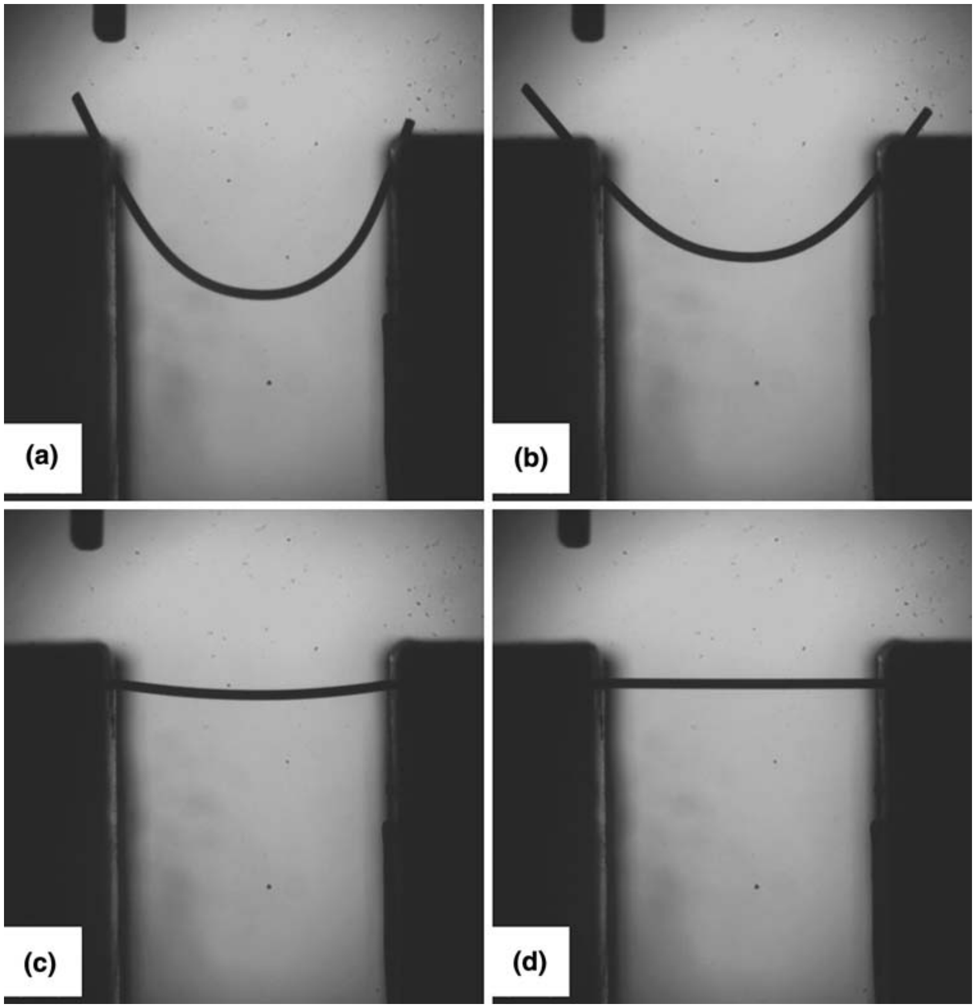

Fig. 2 Sequence illustrating the reverse deformation of a wire inside the measurement chamber from −55 °C (a) to +45 °C (d); in the upper left corner, the thermocouple is visible in a distance of ~2 mm from the wire

device, the R-phase-to-austenite transformation is clearly measurable, and in accordance to the evaluation of the transformation temperatures for Type-1 curves, in addition to the A_s and A_f temperatures, the R'_s and the R'_f temperatures can be attained from the curves of Type 2.

Type-3 (Fig. 3c) reverse-deformation curves are more complex. The curve does not show a double S-shape, but two different almost linear regimes. This indicates that the R-phase occurs in between the martensite-to-austenite transformation. However, the contribution of the second nearly linear stage to the total reverse deformation is ~30% and, therefore, too large to be caused solely by the R-phase-to-austenite transformation. Type-3 curves can be explained by the simultaneous occurrence and the overlap of both, the martensite-to-austenite and the martensite-to-R-phase-to-austenite transformations, possibly at different locations. Such a behavior has been demonstrated and described as multi-stage transformation in the literature (Ref 12). Unfortunately, the identification of all the characteristic transformation temperatures cannot be carried out using the tangent method. Only the R'_s and the A_f temperatures can be determined evaluating Type-3 curves.

The different types of reverse-deformation curves show a smooth transition depending on the prior annealing parameters. Type-3 curves were measured for the "as received" Ni-Ti wires. Though the exact conditions of the production process of the wires are not provided by the manufacturer, the occurrence of the R-phase can be attributed to the stored dislocations and the high defect density inside the material (Ref 12).

The smooth transition of the initial Type-3 curves to Type-1 or Type-2 curves seems to depend on the annealing temperature, mainly. An important temperature range for annealing has been identified to be ~520 °C. Annealing above 520 °C leads to Type-1, while annealing below leads to Type-2 reverse-deformation curves. The variation of annealing time does not cause a significant change of the type of the reverse-deformation curves, but with increasing annealing time, the characteristics of the curves become more articulated and clearer.

The origin of this behavior is complex and probably based on recovery, recrystallization, and precipitation processes that can occur separately or in combination during the annealing of the pre-deformed alloy. The results suggest that at temperatures above 520 °C, the defect density, which probably causes the occurrence of the R-phase, is reduced effectively. Therefore, a transformation path of martensite-to-austenite emerges. At temperatures below 520 °C, the reduction of the defect density during annealing is uncertain, but it was shown that annealing

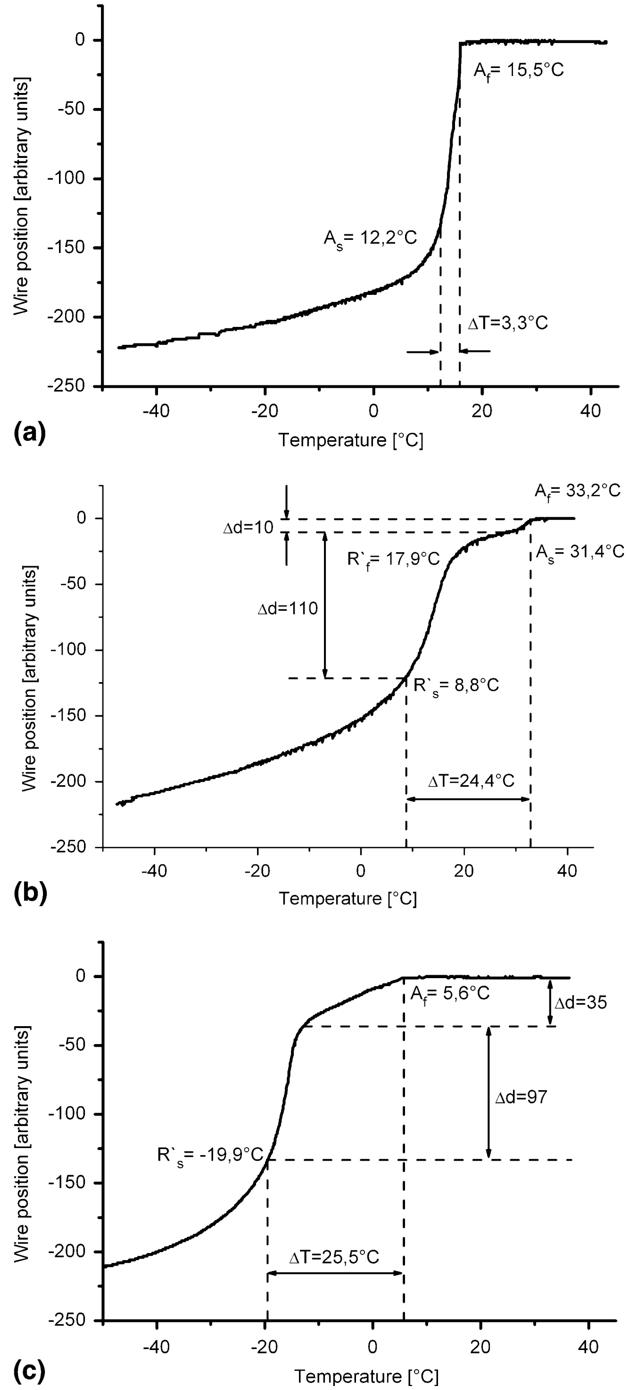

Fig. 3 Three types of reverse-deformation curves attained by bend and free recovery corresponding to the (a) reverse phase transformation from martensite-to-austenite, (b) martensite-to-R-phase-to-austenite transformation, (c) simultaneous martensite-to-austenite and martensite-to-R-phase-to-austenite transformations

in this temperature range leads to the formation and growth of Ni_4Ti_3 precipitates that promote the formation of the R-phase (Ref 12).

4. Summary

The influence of short-time annealing on the transformation properties of thin Ni-Ti wire was investigated by high-resolution bend and free recovery tests. Three different types of reverse-deformation curves related to a martensite-to-austenite, a martensite-to-R-phase-to-austenite and an overlapped martensite-to-R-phase-to-austenite and martensite-to-austenite transformation were identified. The major aspect for the change of the transformation characteristics appears to be the annealing temperature. Short-time annealing below and above ~520 °C causes two different types of reverse-deformation curves.

The contribution of each stage of the different transformation paths to the total reverse-deformation of the investigated wires can be quantified using the newly proposed device. Based on the results, the optimization of the materials behavior, e.g., the transformation path and the reverse-deformation degree can be attained and set with respect to medical application.

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