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High ultimate tensile stress in nano-grained superelastic NiTi thin films

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Abstract

NiTi-films were fabricated by dc magnetron sputtering from melt-cast disc targets. The freestanding films revealed superelastic properties in tensile tests. At 37 °C superelastic properties were achieved showing a closed-loop hysteresis and a plateau of more than 5% strain. The ultimate tensile strength exceeded 1180 MPa for the sputtered films at a maximum strain of 11.5%. This remarkable improvement in mechanical properties over those reported in previous studies correlates with a textured, fine grained (50–200 nm), single phase microstructure, confirmed by transmission electron microstructure. Moreover, these grains revealed a texture which was not found in earlier studies concerning sputtered films. Finally, the prepared specimens did not reveal any evidence of disc or lens shaped Ti_3Ni_4 precipitates but a relatively homogeneous chemistry.

Keywords: Superelasticity; TiNi; Sputtering; Thin films; Nano-grained; TEM

1. Introduction

The intermetallic alloy 49 at.% Ti–51 at.% Ni is a prevalent material used for superelastic medical implants and devices. Prominent examples are catheter devices for minimal invasive surgery or stenting applications, e.g. endovascular stents [1–3]. Typically, theses devices are formed from tubes fabricated from bulk material by deep-hole drilling and subsequent wire drawing. It is envisioned that sputtering technology can be applied to fabricate tube geometries of NiTi with wall diameters from 5 to 50 μm with less than 1% variation [4–9]. This precision cannot be achieved by wire drawing and electro-polishing technology, which are typically limited to a wall thickness larger than 50 μm.

Sputtering of NiTi targets, however, reveals a characteristic loss of titanium, as the sputtering yield for Ni is higher than for Ti. Miyazaki et al. [10], Gyobu et al. [11], and Quandt et al. [12] compensated the titanium deficiency either by placing additional titanium on top of the alloyed target or by using Ti-rich (54 at.% Ti) targets. In our previous work [13], a variety of NiTi cast melted targets were examined for their sputtering properties which led to the deposition of 49 at.% Ti–51 at.% Ni films on silicon substrates. The use of a thin Au sacrificial layer permitted the realisation of freestanding films, which already exhibited superelastic properties in the range of 1.8% elastic strain [13]. This work describes a new fabrication process for the deposition of superelastic NiTi by magnetron sputtering, leading to superior mechanical properties. A microstructural explanation for this macroscopic behaviour is obtained by scanning electron microscopy (SEM) and in particular by transmission electron microscopy (TEM).

2. Experimental

NiTi targets for sputtering were fabricated at the Mechanical Engineering Department of the University of Bochum [13,14]. Thin films were deposited at 450 °C in the crystalline state on silicon substrates using a vonArdenne CS730 sputtering cluster machine. The base vacuum was about 1×10^{-7} mbar. Due to the different sputtering rates for nickel and titanium the film composition deviates from the composition of the target. Freestanding films were obtained by mechanical release of the NiTi films from the Si substrates.

The composition of the as-deposited films was determined by energy dispersive X-ray microanalysis (EDX: Oxford Instruments INCA 3.04). The film thickness was determined by a surface profiler (Tencor PL-10). Differential scanning calorimetry data were recorded between −60 and 150 °C at a typical rate of 10 K/min (Perkin-Elmer, DSC7). In order to start the DSC measurements at a well-defined state, samples were heated well above the formation temperature of austenite ($T > A_F$) and kept

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at a temperature of 150 °C for 3 min before starting the measurement.

Tensile testing of freestanding films was performed in a universal tensile test machine (Messphysik UTM Beta EDC 100N) with the sample being located within a temperature chamber (Shimadzu TCL-N382). The gauge length of the samples was 25 mm.

Microstructural analysis was carried out by means of a scanning electron microscope at 4 keV (LEO Supra 55) as well as a 200 keV transmission electron microscope (LEO 922A). For this purpose, preparation of the cross-sectioned freestanding NiTi film samples was performed by using a pair of scissors for cutting (SEM samples) and by ion milling at small angles (plan-view TEM samples).

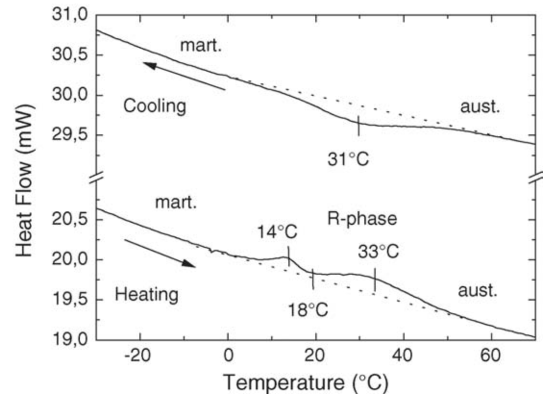

Fig. 2. Typical DSC analysis of a sputtered 49 at.% Ti–51 at.% Ni film deposited at 450 °C.

3. Results and discussion

In correspondence with EDX analysis published in our previous work, for the employed sputtering geometry a typical loss rate of 4–4.5 at.% Ti between melt-cast target and sputter deposited film was found [13]. Based on this knowledge, the target composition was chosen to be 53.5 at.% Ti–46.5 at.% Ni in order to obtain a slightly Ni-rich composition in the films. Care has been taken to minimise oxygen contamination during the melt-cast process for target preparation as well as for the sputtering system. According to the EDX analysis of the deposited crystalline films, a composition of 49 at.% Ti–51 at.% Ni was reached. Auger electron spectroscopy as well as EDX results showed that oxygen contamination was low and in the same range as commercially available NiTi bulk material (below 500 ppm) [14].

Secondary electron images of the NiTi film after removal of the substrate are depicted in Fig. 1 and give a film thickness of 21 μm. Due to the high deposition temperature of 450 °C, the sputtered films reveal a dense recrystallised microstructure due to the high volume diffusion of the atoms deposited (Fig. 1a and b). As summarised in the general classification by Thornton, this dense structure is classified as a zone 3 structure [15]. The triangular shaped structures in the material which emerge in the lower part of Fig. 1a were supposedly caused by a ductile deformation of the NiTi due to the preparation method.

Differential scanning calorimetric analysis was carried out to investigate the martensitic transformation and to determine transformation temperatures for different target compositions. A typical DSC curve is shown in Fig. 2, illustrating a martensitic transformation and the formation of the intermediate *R*-phase at $R^* = 14$ °C. The austenite peak temperature lies at $A^* = 33$ °C, whereas R_F (*R*-phase finish temperature) as well as A_S (austenite start temperature) are both about 18 °C. These values indicate the possibility of superelastic properties at blood heat (37 °C).

To demonstrate the superelastic effect within freestanding films, tensile testing was carried out at different temperatures. Freestanding NiTi films showed a typical martensitic behaviour at −10 °C (Fig. 3a). A strain of $\varepsilon = 5\%$ was achieved after application of 220 MPa stress which led to a permanent plastic deformation of 3.5% strain. Upon heating, the plastic deformation recovers and superelastic behaviour appears. Fig. 3b–d show typical superelastic curves repeatedly exceeding an elastic strain of 6.5% at body temperature as well as at 57 °C, whereas no stress induced martensitic transformation is achieved when the temperature exceeds A_D. The stress–strain diagram of the pure austenitic state at 120 °C is presented in Fig. 3d which shows as a

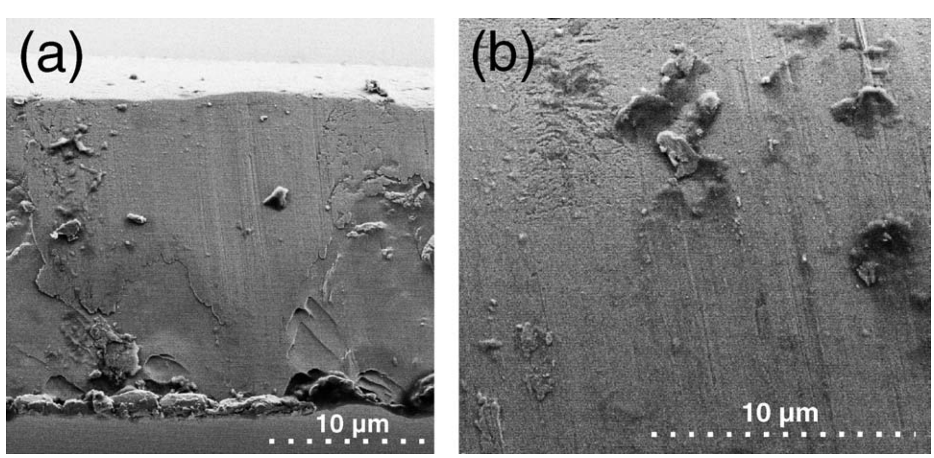

Fig. 1. SEM images of freestanding NiTi-films (21 μm in thickness) indicate a dense microstructure. The triangular shaped structures in the material which emerge in the lower part of (a) were supposedly caused by a ductile deformation of the NiTi due to the preparation method.