Local and depth resolved photothermal characterization of NiTi shape memory alloys

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Photothermal methods based on IR radiometry, photopyroelectric detection and thermoreflectance have been applied to NiTi shape memory alloys to characterize the thermal properties of the as-prepared samples and to determine the changes of the thermal properties induced by thermal and mechanical treatment and cycling. Using photopyroelectric detection, the integral diffusivity of the treated and non treated samples has been determined. Depth profiles of the thermal properties of the mechanically and thermally cycled ribbon samples were measured using photothermal radiometry. A photothermal microscope based on thermoreflectance was applied to monitor the thermal properties across the ribbon edge and to image the thermal and optical variations inside a groove which had been milled into a NiTi shape memory specimen.

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Introduction

Shape memory alloys (SMA) such as NiTi are used in various technological applications (e.g. as sensors or actuators) due to their specific property to restore their original shape after having passed a temperature cycle [1]. Microscopically the shape memory effect relies on the structural transformation from austenite to martensite, which can be induced by temperature changes or tensile stress. Thus, heat input and heat transport are key processes for shape memory devices. In an transient heating process the input across the surface depends on the thermal effusivity $\varepsilon$, whereas the propagation of heat inside the sample is governed by the thermal diffusivity $\alpha$. As these thermal properties play a crucial role for the functional efficiency of shape memory devices the measurement and control of these thermal parameters are of great importance for any application of the SMA. For industrial applications it is also important to know how the properties of shape memory alloys are affected by machining or by thermal and mechanical cycling. Concerning these problems it is obvious that especially local and depth resolved examinations are necessary, e.g. with respect to inhomogeneous stress distribution during mechanical cycles. In this work, we have applied several photothermal techniques for the examination of differently treated NiTi samples. We have done measurements on as-prepared solution treated NiTi, mechanically cycled NiTi, thermally cycled NiTi, and micro milled NiTiNb. Additionally, we have analyzed the effects of rolling on the surface properties of NiTi ribbons.

Experimental

For the excitation and detection of thermal waves we used a photopyroelectric (PPE) experiment [2], photothermal radiometry (PTR) [3] and photomodulated optical reflectance (PMOR) [4] of which the experimental set-ups have been described in the referred publications. In the PTR experiment the thermal wave was excited at the front side of the sample by a laser beam of 2-3 mm diameter. IR irradiation was detected at the same side of the sample (reflection configuration of thermal wave). The PMOR measurements were performed with an Ar-ion laser as pump beam (diameter 5-10 µm) and with a HeNe laser as probe beam in collinear arrangement.

Results

a) PPE Measurements: For the measurement of the integral thermal properties with the photopyroelectric (PPE) technique, samples had been cut from polycrystalline ribbons of Ni$_{50.7}$Ti$_{40.3}$. Then the samples pieces were exposed to different treatments before the measurement: (i) as-prepared solution-treated material, (ii) mechanically cycled by bending, and (iii) thermally cycled in heating and cooling cycles of up to 400 K. The PPE signals in the transmission configuration of thermal waves were measured in the frequency range between 0.5 and 4 Hz, in order to penetrate the sample thicknesses between 1 and 3 mm. Assuming 1-dimensional heat transport, the phase lag at the rear surface of the sample is given by:

$$\Delta \phi = \frac{l_s}{\sqrt{\alpha / \pi f}}$$

(1)

Plotting the measured phase lag versus $f^{1/2}$, the thermal diffusivity is derived from the slope $m$ of the measured data (Fig.1).

$$m = \frac{2}{\pi} \frac{l_s}{\sqrt{\alpha}}$$

(2)
The deviations of the slope at the very low frequencies are due to 3-dimensional heat propagation. The thermal diffusivity of the as-prepared sample has been determined to be 2.68 mm^2/s. This value compares very well with the literature data of equiatomic NiTi. Although the differences produced in $\alpha$ by thermal and mechanical cycling are not very large, they are already detectable by the PPE method. The thermal diffusivities deduced from the respective slopes are 2.38 mm^2/s for the thermally cycled sample and 2.94 mm^2/s for the mechanically cycled sample. Thus, the thermal diffusivity is obviously affected with treatment, which is attributed to the generation of defects and the release of stresses in the material. In the case of the thermally cycled sample, and more pronounced for the mechanically cycled sample there is also a slight deviation from the square root behaviour at higher frequencies, which seems to be related to changes of the thermal properties close to the surface, as confirmed by the depth-sensitive PTR studies described below.

b) Depth profiling by photothermal radiometry (PTR):
For a reliable determination of the depth profile of the thermal properties underneath the surface, frequency-dependent PTR has been applied over a large frequency interval. A relatively wide pump beam has been used, to allow quantitative interpretation based on 1-dimensional heat transport. As the measured amplitudes and phases are affected by device characteristics, these values have been normalized by using special reference samples. Figures 2 and 3 show the normalized data measured for the thermally cycled and the mechanically cycled NiTi in comparison with a theoretical approximation based on a 3-layer model. As reference signals $S_{ref}$ for normalization we used an as-prepared NiTi strip. The inverse normalized signal amplitudes

$$S^{-1}_{n}(f^{-1/2}) = \frac{S_{n}(f)}{S_{ref}(f)} = \frac{\varepsilon_{s}}{\eta_{s}} \frac{\lambda \rho c}{\sqrt{\pi k p_{c}}}$$ (3)

plotted versus the inverse square root of the modulation frequency yield information on the changes of the relative effusivity depth profile induced by thermal and mechanical cycling, respectively: As can be seen from the signal of the thermally cycled sample ($\square$ in Fig. 2), the changes of the optical absorption $\eta_{s}$ and effusivity $\varepsilon_{s}$ at the very surface, in the limit $f^{-1/2} \rightarrow 0$, are relative small, and the changes of the effusivity as function of penetration depth, with growing $f^{-1/2}$, are also small. Between $f = 4$ Hz and 10 kHz, the corresponding normalized phases (Fig. 3) show also a small deviation from the constant phase angle $\phi = 0$, which is typical for the homogenous body. As there were no significant temperature gradients during the thermal cycles, this relatively homogeneous behaviour of the thermally cycled sample may be expected.

The mechanically cycled sample ($\times$), however, shows strong variations of the relative effusivity depth profile (Fig. 2), which has been approximated by a three-layer model consisting of a first layer of reduced effusivity beneath the surface, an intermediate layer of higher effusivity, and the bulk.
material with lower effusivity again. The increase of the effusivity in the intermediate layer may be due to the release of stresses related to defects and the reduced effusivity at the very surface may be related to the formation of micro-cracks. In Fig. 3 the normalized photothermal phases of the mechanically cycled sample are plotted in comparison with the three-layer solution using the same parameters as for the amplitudes. In the intermediate frequency range the experimental data are well described by the same set of parameters. The deviations at low frequencies may be due to 3-dimensional heat propagation, which is not described by the theory, whereas the deviations at high frequencies may be due to the noise level. In principle, it can be seen that the inhomogeneous stress distribution during the bending cycles induced a layered structure of thermal properties, which can quantitatively be described by multilayer solutions.

c) Photothermal thermoreflectance microscopy

The first measurement series with the PMOR microscope was concerned with the mechanically cycled ribbon sample the thermal depth profile of which is described in the previous section. In this experiment the photothermally modulated reflectance signal has been registered along the vertical cross section of the NiTi-ribbon. Fig. 4 shows a line scan at constant modulation frequency (f=30 kHz). Starting at the centre of the lateral side, it shows a non modulated reflection signal (0) of small variations and a modulated reflection signal (1) with regular larger variations. While the non-modulated reflection signals only give information on the optical properties, the modulated reflection signals give information on both the optical and thermal properties. Approaching the sample edge, the tendencies of decreasing and increasing signals between the two probes show strong differences. While the non-modulated signals between the scan positions 400 µm and 550 µm remain nearly constant which means that the reflectance does not change, the modulated reflection signals decays considerably, which means that according to equ. (3) the effusivity \( e_s \) of the surface layer within the range of the thermal wave \( x \gg \mu_{th} = \sqrt{\varepsilon_s/\rho_{p}} \) increases considerably, by more than 25% if we compare with the signal (0) in Fig. 2. Closer to the edge, between the scan positions 530 µm and 630 µm, the modulated signals increase again, which means that a decrease of the effusivity just beneath the surface cannot be excluded, in good agreement with Fig. 2.

Apart from the variations of the optical properties, the main information which can be obtained from the line scan of Fig. 4 is that the effusivity of the sample shows a depth profile which can be described by a three-layer structure and that the thickness of the first layer of reduced effusivity is about 50 to 60 µm and that the thickness of the second layer with higher effusivity is about 140 to 160 µm. These results are in quite good agreement with the results obtained by PTR (Fig. 2).

The photothermal microscope also provides a tool to monitor modification on a microscopic scale of the thermal properties induced by milling and drilling of the specimens. In the frame of this work an area of 128 µm x 75 µm inside 2mm wide groove produced in a disc of NiTiNb by a micro-miller has been imaged. Comparing the optical and the photothermal phase and amplitude images one can conclude that the thermal properties beneath the surface have been changed due to the stresses produced by the surface machining process. In addition we can verify that the variations of the thermal properties and those of the reflexion properties counter-correlate.

Summary and Outlook

Photothermal methods based on IR detection, photopyroelectric detection and thermoreflectance have been applied to samples of NiTi shape memory alloys which had been exposed to thermal and mechanical cycling, mechanical stresses and surface treatment. All applied techniques yield clear evidence of the change of the thermal properties by mechanical cycling or mechanical treatment such as milling. Thermally cycled specimens, on the other hand, show minor modifications of the thermal properties, which may be due to a relatively homogenous treatment.

On the other hand depth sensitive studies by photothermal radiometry point towards an effective layer structure of the thermal effusivity for mechanically cycled NiTi. Photothermal microscopy based on the thermal reflectance has been successfully applied to explore the thermal properties of micron scaled devices such as a groove in the material produced by a micro-miller.

Although, photothermal investigation delivered new and interesting information about NiTi and the influences on sample treatment, the knowledge about physical processes affecting thermal properties is still comparatively low.

References: