Elastocaloric cooling using shape memory alloy films

H Ossmer¹, C Chluba², B Krevet¹, E Quandt², M Rohde³ and M Kohl¹

¹ Karlsruhe Institute of Technology, IMT, P.O. Box 3640, 76021 Karlsruhe, Germany
² Christian Albrecht University Kiel, Institute for Material Science, 24143 Kiel, Germany
³ Karlsruhe Institute of Technology, IAM, P.O. Box 3640, 76021 Karlsruhe, Germany

E-mail: hinnerk.ossmer@kit.edu

Abstract. The elastocaloric effect in magnetron-sputtered Ni₅₀.₄Ti₄₉.₆ films of 20 µm thickness is studied by means of uniaxial tensile tests and infrared thermography. For the investigated films, the usable quantity of latent heat is about 7.2 J/g. When relieving the stress after tensile loading and subsequent temperature equalization at strain rates larger than \( \frac{\text{d}\varepsilon}{\text{d}t} = 0.2 \text{ s}^{-1} \), a maximum temperature change of \( \Delta T = -16 \text{ K} \) is observed as expected for adiabatic conditions. Compared to bulk specimens, the heat transfer times are reduced to about 850 ms due to the larger surface-to-volume ratio, which is attractive for rapid cooling.

1. Introduction

Shape memory alloys (SMA) absorb a large quantity of latent heat during reverse martensitic transformation [1]. Compared to magnetocaloric materials that have already been in the focus of research for several years, elastocaloric materials provide higher adiabatic temperature changes and do not require a large magnetic field [2,3]. Therefore, solid-state cooling by pseudoelastic SMAs is receiving large interest in recent years.

Pseudoelastic SMAs like the binary NiTi alloy undergo a diffusionless first-order phase transformation from austenite (A) to martensite (M) phase [4]. The stress-induced martensite (SIM) transformation is exothermic resulting in a temperature increase. When releasing a stressed sample after temperature equalization with the environment, the endothermic reverse transformation takes place resulting in a temperature decrease below ambient temperature. The theoretical maximum temperature change \( \Delta T_{\text{ad}} = \frac{L}{c_p} \) that can be obtained under adiabatic conditions, depends only on the latent heat \( L \) of the transformation and the material’s heat capacity \( c_p \). In the case of NiTi, values of latent heat reported in literature show a large scatter with maximum values as high as 35 J/g that strongly depend on stoichiometry, carbon and oxygen impurity concentrations [5]. From an engineering point of view, impurity concentrations have to be kept low to avoid brittleness. Chemical compositions have to be adjusted so that the transition temperatures meet the requirements of the application. Thermal treatments and functional fatigue need also to be considered as they significantly affect the latent heat [6]. Due to these reasons, values of latent heat being accessible for elastocaloric cooling applications may be considerably smaller.

Until now, research concerning the elastocaloric effect is mainly focused on bulk materials. Tensile test experiments on Cu-based alloys reveal a maximum temperature decrease during reverse martensitic transformation of 15 K [7]. A maximum temperature decrease by 17 K has been reported.
for a NiTi wire with a diameter of 3 mm [8]. The highest value of temperature decrease by about 28 K has been observed for NiTi belt-type specimens [9]. However, due to the rather large dimensions of the investigated specimens, heat transfer times are well above 10 s. Considerable improvements are expected for pseudoelastic SMA films as their large surface-to-volume ratio may enhance heat transfer and thus, enables the increase of cycling frequencies and cooling power. Therefore, it is advantageous to combine many SMA films to distributed film arrays instead of using a single bulk specimen for elastocaloric cooling.

This work presents a series of tensile tests and in-situ infrared (IR) thermography experiments on magnetron-sputtered NiTi films of 20 µm thickness to investigate the spatially and time-resolved course of phase transformation, the heat transfer dynamics, as well as the corresponding maximum temperature changes.

2. Experimental

NiTi films are produced by dc magnetron sputtering onto a cooled glass substrate with a thin Cu layer at a power of 300 W and Ar atmosphere of $10^{-7}$ mbar. The deposition rate is 3.8 nm s\(^{-1}\). Details on film deposition and structuring can be found in [10]. Investigated films have a thickness of 20 µm. For tensile testing, the films are structured to stripes of 1.75 mm width and 35 mm length by optical lithography and sacrificial layer etching. Since as-deposited films are amorphous, a heat treatment procedure is established that comprises two-step rapid thermal annealing at 650 °C for 10 min and at 450 °C for another 10 min.

The transition temperatures of the material are determined from electrical resistance measurements as shown in figure 1. The material exhibits a two-stage phase transformation from austenite to martensite via an intermediate R-phase. As the austenite finish temperature is below 20 °C, the material is pseudoelastic at room temperature. The specific heat capacity for austenite is determined to be 0.45 J g\(^{-1}\) K\(^{-1}\) by differential scanning calorimetry (DSC) using a synthetic sapphire standard (results not shown here).

A schematic setup of the experiment is depicted in figure 2. Uniaxial tensile tests (Zwick/Roell, Germany) are carried out with a 50 N force sensor. Samples are bonded to glass plates on both ends with a two-component adhesive. The plates are fixed by screws in the clamping of the tensile test machine. The reference clamping length is 20 mm for each sample. Tensile tests are performed at different strain rates between $10^{-4}$ s\(^{-1}\) and 20 s\(^{-1}\) in strain-control mode. A pre-load of 1 N is applied in order to avoid buckling of the NiTi film. The sample elongation (‘engineering strain’ \(\varepsilon\)) is periodically varied between 0% and 5%. At the end positions of each semi-cycle at \(\varepsilon = 0\) and 5%, the strain is held constant for 10 s in order to let the sample temperature equilibrate with the environment. All experiments are conducted at room temperature in air. Before recording experimental data, ten cycles are performed at low strain rate in order to obtain reproducible results.

During tensile tests, samples are monitored by an IR camera (FLIR, USA) with a spatial resolution of 25 µm to obtain time-resolved local temperature distributions. Since sputtered NiTi samples have a very flat and reflective surface, they are covered with a thin layer of graphite spray to increase emissivity.

3. Results and Discussion

A typical stress-strain curve for a pseudoelastic film sample is shown in figure 3. At small strain rate of $10^{-4}$ s\(^{-1}\) corresponding to quasi-stationary conditions, the stress-strain characteristics exhibit pronounced stress plateaus during forward and reverse transformation. In this case, heat exchange with the environment is faster than the release of latent heat. Stress-induced martensitic transformation starts at a critical strain of 1.3% and proceeds at a constant stress level of about 500 MPa. Upon unloading, the martensitic reverse transformation proceeds at a lower stress level of about 350 MPa resulting in a pronounced hysteresis.
Figure 1. Electrical resistance characteristics upon cooling and heating in the temperature range of phase transformation. The start (s) and finish (f) temperatures of phase transformations are indicated by arrows. Legend: M – martensite; A – austenite; R – rhombohedral phase.

With increasing strain rate, the stress-strain characteristics become steeper and the onset of the transformation is less sharp. Whilst part of the work applied during mechanical loading can be regained during unloading, the area enclosed by the stress-strain-curve of a full load-unload cycle corresponds to work which is dissipated. Irrespective of the direction of the martensitic transformation, dissipation always leads to a heating and therefore counteracts elastocaloric cooling. Based on the stress-strain characteristics recorded at different strain rates, we determine the work per unit volume for loading and unloading by numerical integration. The difference $\Delta W = W_{\text{load}} - W_{\text{unload}}$ that is plotted versus strain rate in figure 4, corresponds to the total dissipated work. A pronounced maximum is observed at a strain rate of $\frac{d\varepsilon}{dt} = 0.2 \, \text{s}^{-1}$.

The shape of the stress-strain characteristics is also affected by functional fatigue, which is discussed elsewhere [6].

During forward and reverse martensitic transformation, the release and absorption of latent heat leads to local heating and cooling of the sample, respectively. Figure 5 shows two series of time-dependent IR profiles recorded during loading and unloading at a strain rate of $0.1 \, \text{s}^{-1}$. Temperature fronts start from the clamping, where the film is interconnected to the sample holder that remains at room temperature. Heat conduction causes broadening of the heated regions. Lüders-like bands are observed similar to bulk specimens [9], but are clearly visible only in the absence of graphite coating, which causes blurring due to rapid heat conduction. Upon loading, the temperature rises to a maximum in a time interval that is proportional to the load rate and then decays due to heat transfer to the environment by air convection and heat conduction via the clamping. After stationary conditions are reached, unloading results in a strong undercooling below ambient temperature, followed by a more gradual increase of temperature due to heat transfer.

Figure 6 shows a typical time-resolved temperature characteristic in the center of the sample during reverse martensitic transformation at a large strain rate of $1.0 \, \text{s}^{-1}$. Temperature equilibration with the environment can be described by a single exponential decay. The corresponding time constant is determined by least-squares fit to be about 850 ms. The maximum temperature decrease is about $\Delta T = -16 \, \text{K}$. This result is in line with an estimate of the adiabatic temperature change according to $\Delta T_{\text{ad}} = L/c_p$ using a latent heat of about $7.2 \, \text{Jg}^{-1}$ and a specific heat capacity $c_p$ of $0.45 \, \text{Jg}^{-1}\text{K}^{-1}$. The value of $7.2 \, \text{Jg}^{-1}$ is lower than typical values for a complete martensitic transformation in NiTi alloys indicating that only a part of the two-stage transformation is accessible in the present case. Further adjustment of phase transformation temperatures by tailoring of stoichiometry and thermo-mechanical
treatment could be a means to increase the accessible latent heat and thus to further raise the temperature decrease.

**Figure 3.** Stress-strain characteristics upon loading and unloading of a NiTi sample for a strain rate of $10^{-4}$ s$^{-1}$.

**Figure 4.** Strain rate dependence of mechanical work during loading and unloading and corresponding mechanical work difference $W_{\text{load}} - W_{\text{unload}}$ of a complete loading cycle.

The cooling efficiency is described by the coefficient of performance (COP), given by the ratio of absorbed heat and mechanical work. Optimum results are obtained by assuming that the unloading work is recovered in a closed cooling cycle. Based on our results for the total dissipated mechanical work during loading and unloading at a strain rate of 1 s$^{-1}$, $\Delta W = 6$ MPa = 0.93 Jg$^{-1}$ (see figure 4) and the latent heat estimated from the nearly-adiabatic temperature change, $L = 7.2$ Jg$^{-1}$, we obtain a COP of 7.7 in this case. Theoretical estimates on the available COP of NiTi films indicate that this value could be further increased by a factor of two [11].

**Figure 5.** Time-dependent series of thermograms of a NiTi tensile test sample during loading (a) and unloading (b) at a strain rate of 0.1 s$^{-1}$. The time between two images is $\Delta t = 0.28$ s. The lower edge corresponds to the clamping.

**Figure 6.** Temperature evolution of a reference point in the center of a NiTi tensile test sample. The sample is released after pre-straining by 5% at a strain rate of 1 s$^{-1}$. After temperature decrease $\Delta T$ of -16 K, the temperature exponentially increases with a time constant $\tau$ of about 850 ms.
4. Conclusion

In this paper, we investigate the elastocaloric effect in magnetron-sputtered Ni\textsubscript{50.4}Ti\textsubscript{49.6} film samples of 20 µm thickness showing pseudoelastic stress-strain behavior at room temperature. Because of the small cross-section of the test samples with respect to their surface area, localized phenomena like the propagation of Lüders-like bands play a less pronounced role than in macroscopic wire and belt-like samples. The observed temperature fronts have a similar spatial extent as the sample itself.

While bulk samples show heating times in the order of 10 s [8], thermal equilibration within the film sample occurs within milliseconds. Hence, the cooling time is essentially determined by the strain rate. Adiabatic conditions are reached at strain rates larger than 0.2 s\textsuperscript{-1}. Rapid heat exchange with the environment occurs by air convection and heat conduction through the clamping within about 850 ms. These results are important for the engineering of elastocaloric cooling devices based on film samples. In this case, the film would be brought into physical contact with either a solid heat source or a liquid heat transfer medium. Both methods of heat exchange are expected to have shorter time constants than air convection, presumably enabling cycling rates of several Hertz.

We observe a maximum temperature decrease $\Delta T$ of -16 K during the reverse martensitic transformation at a strain release rate of 1 s\textsuperscript{-1}. This result is in line with reported values for NiTi wires. However, only a reduced quantity of latent heat of about 7.2 J/g has been accessible in the investigated test samples at room temperature. Therefore, we expect that the effect size can be further increased by tailoring the material properties. Regarding the maximum possible latent heat observed for NiTi-base alloys in the order of 20 J/g, an increase of effect size by a factor of two seems to be possible. The large effect size and rapid heat transfer being accessible in tailored NiTi-base alloys are highly attractive for solid state cooling and heat pumping applications.

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