Thermal Stabilization of NiTiCuV Shape Memory Alloys: Observations During Elastocaloric Training

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Abstract The paper presents novel findings observed during the training process of superelastic, elastocalorically optimized Ni–Ti-based shape memory alloys (SMA). NiTiCuV alloys exhibit large latent heats and a small mechanical hysteresis, which may potentially lead to the development of efficient solid-state-based cooling processes. The paper starts with a brief introduction to the underlying principles of elastocaloric cooling, illustrating the effect by means of a typical thermodynamic cycle. It proceeds with the description of a custom-built testing platform that allows observation of temperature profiles

and heat transfer between SMA and heat source/sink during high-loading-rate tensile tests. Similar to other SMA applications, a training process is necessary in order to guarantee stable performance. This well-known mechanical stabilization affects the stress–strain hysteresis and the cycle-dependent evolution of differential scanning calorimetry results. In addition, it can be shown here that the training is also accompanied by a cycle-dependent evolution of temperature profiles on the surface of an SMA ribbon. The applied training leads to local temperature peaks with intensity, number, and distribution of the temperature fronts showing a cycle dependency. The homogeneity of the elastocaloric effect has a significant influence on the efficiency of elastocaloric cooling process and is a key aspect of the specific material characterization.

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Introduction

Superelastic shape memory alloys have been known for biocompatibility [1–3] and good damping properties [4, 5]. Ni–Ti-based stents have been established in the market for years [6], and the damping properties have been studied in a large number of scientific works [7, 8]. In addition to these established fields, elastocaloric cooling has recently started to attract interest as a further possible application for superelasticity and is currently being investigated as part of the German Science Foundation (DFG) Priority program SPP 1599 Ferroic Cooling [9]. The interest is based on the large latent heats of the stress-induced phase transformation between austenite and martensite, which

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can potentially be used for the development of novel cooling processes. The elastocaloric effect in SMAs was already described by Refs. [10–12] and, in addition to the magnetocaloric, electrocaloric, and barocaloric effect, it represents a further possible physical mechanism for cooling processes based on ferroic materials [13]. The high potential [14] of these solid-state cooling processes and the potential to establish environmentally friendly alternatives to conventional vapor-compression-based processes increase the interest in these technologies.

Magnetocaloric cooling is the most established ferroic cooling technology [15–17]. However, an increased interest in the elastocaloric effect is noticeable as well [18–22]. The comparison of different materials shows that Ni–Ti-based shape memory alloys provide the most promising elastocaloric properties. The latent heats of binary Ni–Ti alloys (22 J/g) are significantly higher than the latent heats of other SMAs, e.g., CuZnAl (6.2 J/g) and CuAlNi (6.8 J/g) [14]. These heats are in direct correlation with the absorbable heat during an elastocaloric cooling process [21, 23]. The efficiency of an elastocaloric cooling process depends on the latent heat, the mechanical work, and the homogeneity of the elastocaloric effect. Even though commercially available superelastic Ni–Ti alloys suitable for elastocaloric cooling already exhibit large latent heats of 15 J/g [24], the mechanical hysteresis is comparatively high and can be reduced significantly by means of optimized alloy compositions. In order to improve elastocaloric material properties, new Ni–Ti-based alloys have been developed [25], featuring small mechanical hysteresis and high cyclic stability. Furthermore, the elastocaloric cooling cycle requires heat transfer at high and low temperature level. To this end, superelastic material behavior at low temperatures is required, which can be achieved with low martensite to austenite transformation temperatures. A strong correlation between the transformation temperature and the latent heats can be observed in many Ni–Ti-based alloy systems leading to small latent heats for low transformation temperatures [26].

Based on an extensive study of more than 70 alloy compositions [26], a quaternary NiTiCuV alloy was developed with optimized elastocaloric properties and will be investigated within this work. The investigation of the elastocaloric cooling process and the elastocaloric material properties requires a scientific test setup capable of performing cooling cycles and simultaneous measurement of mechanical parameters (strain and strain rate) as well as thermal parameters (temperature change and homogeneity of elastocaloric effects). Such a test platform was developed [27] and has been used to investigate cooling properties of NiTiCuV.

In this paper, we put a special emphasis on the well-known mechanical stabilization of the material during

training and, to the best knowledge of the authors, for the first time, also document thermal stabilization behavior by visualizing the cycle-dependent evolution of temperature profiles. In addition to these investigations, we round off the picture with data for the stabilization of the caloric properties of NiTiCuV investigated by means of differential scanning calorimetry (DSC).

Basics of an Elastocaloric Cooling Process

Elastocaloric cooling processes have specific material requirements, and new test methods are required in order to investigate properties of materials that could be used for elastocaloric cooling. The following chapter gives a brief introduction to the underlying principles for elastocaloric cooling. Furthermore, a custom-built testing platform is presented, enabling the investigation of elastocaloric materials and cooling processes.

Process Description

Elastocaloric cooling processes are based on thermodynamic cycle processes; however, different process controls are applicable compared to traditional cooling processes. For example, similar to the conventional vapor-compression-based cooling process, the elastocaloric cooling process also transfers heat at different temperature levels where heat is absorbed from a heat source at low temperature and is transferred to a heat sink at high temperature. The heat transfer of the vapor-compression process occurs isothermally during the phase transformation of the refrigerant, and this principle is based on the Carnot cycle. In contrast to the conventional process, a typical elastocaloric process shows an adiabatic phase transformation and is similar to the Brayton cycle. Similar to the conventional process, the elastocaloric process can be divided into four phases as shown in Fig. 1. The IR images in Fig. 1 show exemplary experimental data of a 40 cycle continuing cooling experiment using NiTiCuV ribbon as cooling medium.

1st phase The heat absorption from the heat source takes place at low temperature levels and constant strain. A thermal equilibration process starts and leads to increasing SMA temperature and decreasing heat sink temperature.

2nd Phase Fast loading, i.e., increased strain, of the SMA leads to an adiabatic temperature increase of the material. During this stress-induced phase transformation from austenite to martensite, the material is in a contact-free state (see Fig. 1). The achieved temperature change of the elastocaloric material strongly depends on latent heats, loading rate, strain, and environmental conditions [12]. The rate dependency of the applied mechanical field and the

Fig. 1 Adiabatic elastocaloric cooling process following a Brayton cycle. The four process phases are shown by means of IR images. The images show the temperature change of the heat source/sink after 40 cooling cycles of an experiment while studying a NiTiCuV ribbon sample

resulting temperature change are a well-known material characteristic and depend on the environmental conditions [24, 28], the specimen dimensions [29] as well as the caloric material properties.

3rd Phase The heat transfer to the heat sink takes place at high temperature levels and constant strain. A thermal equilibration process starts leading to decreasing SMA temperature and increasing heat sink temperature, respectively.

4th Phase Adiabatic unloading, i.e., reduced strain, starting at the temperature level of the heat sink, leads to a temperature decrease of the elastocaloric material below ambient temperature. The achieved temperature drop is, in analogy with loading, dependent on loading rate, strain, and latent heat; furthermore, the minimum SMA temperature also depends on the martensite to austenite transformation temperature. If this temperature is reached, the transformation stops until the temperature rises again [21, 24].

The stress–strain diagram (Fig. 2a) and the temperature–strain diagram (Fig. 2b) show the strain and strain rate-dependent stress as well as temperature changes of the NiTiCuV ribbon during the previously described adiabatic cooling cycle. The stress–strain diagram in Fig. 2a shows a stress increase in the SMA ribbon during contact to the heat

source (1st phase) which is caused by the contact force between ribbon and heat source. This force is required to achieve good heat transfer between SMA and heat source/sink. The adiabatic loading in the 2nd phase leads to a significant stress and temperature increase, whereas the transformation plateau from austenite to martensite shows a steep slope due to the temperature increase of approx. 22 K (see Fig. 2b) during the phase transformation [30, 31]. The heat transfer to the heat sink at constant strain (3rd phase) induces a temperature and stress decrease. Although one would like to achieve a complete phase transformation after loading, the transformation from austenite to martensite remains incomplete and causes a temperature dependent stress decrease during the heat exchange at constant strain. This behavior is typical for experimental procedures with fast loading and subsequent heat exchange at constant strain [21, 29] and is caused by the advancing phase transformation of the polycrystalline material. The endothermic phase transformation from martensite to austenite (4th phase) leads to a significant temperature and stress decrease during unloading. The NiTiCuV ribbon reaches a minimum temperature of 280 K which is 21 K lower than the initial temperature after separation from the heat sink (see Fig. 2b). The material shows a complete stress recovery after unloading due to the optimized

Fig. 2 Stress–strain diagram (a) and temperature–strain diagram (b) of a NiTiCuV ribbon at the 40th cycle of an elastocaloric cooling process. The arrows indicate the cycle direction, the numbers and the color of the curves assign the mechanical and thermal material behavior to the four phases of the adiabatic cooling process

elastocaloric material properties, which will be discussed in the following section.

In order to establish a new cooling technology, the efficiency has to be comparable to established technologies. The efficiency of the elastocaloric cooling process can be determined by measuring the required cycle work and absorbed heat. The mechanical work of an elastocaloric cooling process is represented as the area inside the stress–strain curve (see Fig. 2a) or the area inside a force–deformation curve, respectively. The absorbed heat can be determined based on temperature changes of the heat source with consideration of the heat capacity. In addition, the temperature change of the SMA shows the process control-related cooling performance

of the alloy (see Fig. 2b). Based on the temperature change of the SMA during contact to the heat source (1st phase, Fig. 2b) and the required cycle work, a coefficient of performance (COP) of 5.97 can be calculated for the 40th cycle of the presented cooling process. In addition to the dependency of the COP on the material properties and the process control parameters, the COP also depends on the thermal boundary conditions (temperature of the heat sink/source) which changes during the cooling process and has to be taken into account by interpreting the COP. As an analogy to the conventional vapor-compression-based process, the absorbed heat can also be represented as an area in an idealized temperature entropy diagram as shown in Ref. [23]. This allows for a direct visual illustration of efficiency numbers by studying the respective areas for different processes and, furthermore, enables a direct comparison to the well-known diagrams used in vapor-compression thermodynamics.

Scientific Test Platform for Material Characterization and Process Investigation

For determination of the efficiency and to investigate the underlying physics of an elastocaloric cooling process, a novel experimental testing system was designed. This test setup allows for studies of SMA materials elastocaloric properties and cooling cycles. Figure 3a shows the schematic of the setup, which is capable of independent control of strain-induced phase transformations and heat transfer. This concept allows for a full investigation of elastocaloric cycle processes, which are not limited to the described Brayton-like process. Typical SMA sample dimensions are 90-mm length, 1–2-mm width and 0.5–0.8-mm thickness. The realized system (Fig. 3b) enables comprehensive and simultaneous monitoring of the mechanical (strain, strain rate, stress) and thermal (SMA temperature, homogeneity of elastocaloric effects and heat sink/source temperature) parameters. A high-performance IR camera (ImageIR 9300, Infratec) is used to investigate the homogeneity of the elastocaloric effects. Furthermore, the heat sink and the heat source are positioned side by side below the SMA ribbon and are thus in the field of view of the IR camera at any time (see Fig. 3b). This allows for continuous monitoring of the heat transfer and the temperature distribution during a running cooling process. In addition, platinum temperature sensors (PT 100) are used to measure the absolute temperatures inside the heat sink/source. A linear direct drive motor allows loading and unloading the SMA at strain rates up to 1 s^{-1} . A second linear direct drive motor, in combination with a pneumatic cylinder, is used to switch contact of the SMA between the heat sink and heat source, thus, controlling the heat transfer to and from the SMA. Two load cells are used to independently measure the tensile force and the contact force of the SMA. A more

Fig. 3 Schematic of the scientific test setup (a) and realized setup (b). The design enables simultaneous measurement of mechanical and thermal process parameters during cooling processes and material characterization. The SMA ribbon and heat source and sink are in the field of view of the IR camera during the entire process

detailed description of the setup and an investigation of the influence of the control variables on the cooling process are given in Ref. [27]. The modular design of the setup allows characterization of different SMAs and also the study of training effects during mechanical cycling.

Material Stabilization During Elastocaloric Mechanical Training Procedures

The investigation of an elastocaloric cooling process always includes a characterization of the SMA material with regard to its elastocaloric properties. This characterization procedure includes tensile tests at different strain rates in order to determine the maximum temperature change of the SMA under adiabatic conditions [27, 29]. Furthermore, the characterization includes the investigation

of local temperature peaks which appear during the stress-induced phase transformation [21, 24, 32, 33], whereas a homogenous temperature distribution is required for an efficient heat transfer during the cooling process. The homogeneity of the temperature distribution shows a strong rate dependency [24, 28, 34]; in order to optimize the heat transfer, the mean temperature change of the elastocaloric sample has to show a maximum [27]. Before the material can be characterized, however, it has to be trained in order to stabilize the material behavior, which is the focus of the presented work.

Mechanical Stabilization

The stress–strain diagram in Fig. 4 shows the mechanical stabilization of a NiTiCuV sample over 100 training cycles at a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ while the maximum load stress was limited to 500 MPa. The investigated sample has a cross section of 1.06 mm^2 and a length of 90 mm. The quaternary alloy with a composition of $\text{Ni}_{45}\text{Ti}_{47.25}\text{Cu}_5\text{V}_{2.75}$ was produced by applying an optimized arc melting procedure, which is documented in Refs. [35] and [36]. 5 at.% Cu was added and substituted Ni-content to decrease the misfit between the austenitic and the martensitic lattice. The mechanical hysteresis decreases with increasing number of training cycles, which in turn leads to a decrease of mechanical work. The required work input for a loading and unloading cycle of the stabilized material is approx. 26 % smaller as the required work for the first training cycle. Furthermore, 2.75 at.% V was added to reduce the martensite to austenite transformation temperature. The low transformation temperature leads to stable superelastic material behavior at temperatures down to 273 K, which is required for a cooling process operating at low temperatures. A detailed investigation of the influence of V on the transformation temperature of Ni–Ti-based alloys is given in Ref. [26]. Furthermore, the described alloy composition

Fig. 4 Stress–strain diagram of 100 training cycles for a NiTiCuV SMA. The red curve shows the last ten cycles of the stabilized mechanical material behavior (Color figure online)

leads to very stable mechanical behavior. The residual strain of 0.25 % (see Fig. 4) is small compared with the Ni–Ti alloys investigated by Refs. [30, 37, 38]. The improved fatigue properties achieved by adding Cu to NiTiCu alloys were also investigated by Refs. [25] and [39].

Caloric Stabilization

Differential scanning calorimetry measurements of the sample before and after the training shown in Fig. 5 demonstrate that in addition to the mechanical stabilization, a change of the caloric material properties is also noticeable. A comparison of the caloric and thermal material stabilization shows that a small change in the mechanical material behavior can be correlated to a small change of the caloric material properties. Similar stabilization effects of the caloric material properties during thermal transformation cycles were shown for quaternary NiTiCuPd alloys [40]. The training leads to a reduction of the latent heats (ΔH) of 3.2 J/g during the austenite to martensite transformation and a reduction of 1.8 J/g for the reverse transformation. In addition, the transformation temperatures decrease stabilizing the superelastic material behavior at low temperature. Different mechanisms are potentially responsible for the reduction of the latent heats. Dislocation slip in superelastic Ni–Ti wires was investigated by Ref. [41] and led to residual strain and a decreasing transformation stress, similar to the results in Fig. 4. Furthermore, [42] and [43] observed the accumulation of dislocation which results into plastic deformation and the formation of stabilization martensite. Which of the effects is dominantly dependent on the material composition and the texture, whereas small grain sizes show significant smaller residual strain [41]. The effects which are

responsible for the change of the mechanical properties may also be responsible for the decreasing latent heats.

Thermal Stabilization

Differential scanning calorimetry measurements enable precise investigations of the caloric material properties; however, they provide only limited information of the elastocaloric material properties of the trained sample. A typical DSC measurement is performed by cutting of a small part of the sample, whereby the information of the caloric properties of the remaining sample get lost, unless the DSC measurement is performed for each part of the sample, which would be very time consuming. Thus, additional measurements of the thermal material properties in a global manner are further required in order to characterize the full elastocaloric material properties. The investigation of the temperature distribution in the NiTi–CuV ribbon during the training shows that a thermal material stabilization takes place (see Figs. 6, 7). The comparatively high strain rate during training causes a significant temperature increase of approx. 13 K leading to the formation of local temperature fronts. This training influences the material stabilization similar to isothermal training cycles at higher temperatures [38, 39] which cause significantly higher functional and structural fatigue in comparison to training at lower temperatures. However, this training is necessary to stabilize the material behavior under cooling process-related conditions.

The IR images in Fig. 6 show homogenization effects of the elastocaloric effect during 90 cooling cycles. The training procedure was divided into 12 sessions with 2, 3, and 5 cycles for the first 3 sessions and 10 cycles for the remaining 9. This allows for a direct comparison of the first cycle of each individual session, thus avoiding the influence of preliminary cycles. The corresponding stress and strain values of the IR images are marked in the stress–strain diagram (see Fig. 6a) and temperatures profiles at four different conditions are compared. Temperature fields are acquired at 4 % loading (see Fig. 6b) relative to the residual strain and at –4 % unloading (see Fig. 6c) with respect to the maximum strain, to ensure identical mechanical and transformation conditions. Measurements at maximum and minimum strain allow comparison of the temperature profiles at the beginning of the heat transfer during a Brayton-like cooling process. Figure 6b, c, d, e shows the material stabilization after approx. 30 training cycles. Figure 6b, d shows that after 90 training cycles, the temperature distribution is more homogeneous, and the intensity of the temperature peaks in Fig. 6d is reduced by 4 K. The homogenization of the temperature profile during unloading is significantly smaller. Fig. 6c shows that the width of the temperature peaks is slightly increased, and

Fig. 5 DSC measurements of the NiTiCuV sample before and after 100 training cycles. The latent heats as well as the transformation temperatures decrease during thermomechanical training

Fig. 6 Mechanical stabilization of the material during 100 training cycles **a** (see also Fig. 4) and the corresponding temperature profile in 12 different cycles at four conditions each **b** temperature profile at 4 % strain during loading with residual strain taken into account.

c Temperature profile after 4 % unloading starting at maximum strain. **d, e** temperature profiles at the end of loading and unloading, respectively

Fig. 6e shows a change of the temperature minimum of 0.5 K. This asymmetry between the stabilization effect during loading and unloading can also be observed in the mechanical material response in Fig. 6a. The stress at 4 % loading decreases by 47 MPa, whereas the stress at −4 % unloading with respect to maximum strain decreases by 26 MPa. Furthermore, by regarding the DSC measurements shown in Fig. 5, differences between the stabilization of the caloric material properties during the austenite

to martensite and the martensite to austenite transformation can also be observed. The high transformation stress and the high temperature during the austenite to martensite transformation lead to a significant larger stabilization and homogenization effect as the low temperatures and the low transformation stress during the reverse transformation. A further advantage of the applied thermographic approach is shown in Fig. 7. Here, the time-resolved representation of the temperature distribution allows for a more detailed

Fig. 7 Stress–strain diagram of three trainings cycles (a), the residual strain was taken into account and the stress level at maximum strain was kept constant. The time-resolved temperature profiles of the three cycles b, c, d show one line of the IR image over time for every

200 ms with the *black line* indicating the start of the reverse transformation. After the training, the temperature profiles show a stabilized and nearly homogeneous elastocaloric effect

investigation of the localized phase transformations. The time-position diagrams shown in Fig. 7b, c, d depict one line of the IR images along the SMA ribbon over time for every 200 ms. The evolution of the phase fronts and the starting points of the reverse transformations during unloading indicate that an almost complete phase transformation is achieved after 90 training cycles, whereas the reverse transformation of the first cycle shows an incomplete phase transformation. Figure 7a shows a slightly increased strain after the first two cycles, which is due to the limit of 500 MPa set for the stress. The strain increase after the second cycle leads to a larger elastocaloric effect and an increase of transformed material. Furthermore, the number of phase fronts increases by increasing number of training cycles and leads to a more distributed elastocaloric effect. Also in Fig. 7 a, stronger stabilization effect during loading in comparison to unloading can be observed. A homogeneous transformation is important for an efficient heat transfer. Therefore, the rate-dependent size and homogeneity of the elastocaloric effect will be investigated during the material characterization, which is typically performed after the training procedure. The characterization procedure

[27], which is similar to the experiments of [24] shows that higher strain rates lead to a larger and more homogeneous elastocaloric effect. To this end and to achieve an adiabatic phase transformation, high strain rates are applied during the cooling processes [27].

Conclusions

The presented work reported on the elastocaloric effect in NiTiCuV ribbons. A basic elastocaloric cooling cycle has been introduced on the basis of an adiabatic cycle process to give a motivation for the elastocaloric process-related training procedure. Furthermore, a scientific testing platform capable of performing various elastocaloric cooling processes as well as thermomechanical material characterizations and training procedures was used to study the training effects in NiTiCuV alloys under realistic process conditions. The investigated NiTiCuV alloys provide promising elastocaloric properties and show small functional fatigue effects during thermomechanical training. Exact control and comprehensive monitoring of the

mechanical, caloric, and thermal parameters during the training enable a careful study of the interaction between the different parameters. The mechanical stabilization and the residual strain influence the latent heat, the transformation temperature, and the homogeneity of the elastocaloric effect. In addition, a material characterization procedure, which includes tensile tests at different rates, has to be applied in order to investigate the rate dependency of the size and the homogeneity of the elastocaloric effect. The decrease of the mechanical hysteresis and the residual strain results in a decrease of latent heats and transformation temperatures, whereas the mechanical as well as caloric parameters show a significantly larger change during the austenite to martensite transformation. The transformation from martensite to austenite is very stable, which has a positive impact on the performance of the cooling process. Further material investigations and the use of the material in a real cooling process will show the efficiency of the novel material.

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