High-performance elastocaloric materials for the engineering of bulk- and micro-cooling devices

Jan Frenzel, Gunther Eggeler, Eckhard Quandt, Stefan Seelecke, and Manfred Kohl

Pseudoelastic NiTi-based shape-memory alloys (SMAs) have recently received attention as candidate materials for solid-state refrigeration. The elastocaloric effect in SMAs exploits stress-induced martensitic transformation, which is associated with large latent heat. Most importantly, cyclic mechanical loading/unloading provides large adiabatic temperature drops exceeding 25 K at high process efficiencies. This article summarizes the underlying principles, important material parameters and process requirements, and reviews recent progress in the development of pseudoelastic SMAs with large coefficients of performance, as well as very good functional fatigue resistance. The application potential of SMA film and bulk materials is demonstrated for the case of cyclic tensile loading/unloading in prototypes ranging from miniature-scale devices to large-scale cooling units.

Introduction

Refrigeration and cooling account for a significant fraction of global energy usage. The need for reduction of energy consumption and greenhouse gas emissions has motivated research in new solid-state cooling concepts (ferroic cooling).¹ These include magneto-, electro-, or elastocaloric effects. Pseudoelastic NiTi-based shape-memory alloys (SMAs) are a very promising class of candidate materials for elastocaloric cooling.^{2,3} While NiTi SMAs are better known for being able to restore their initial geometry after large deformations,⁴⁻⁶ these materials have recently also been identified as a promising solid-state alternative to well-established vapor compression cooling systems.⁷

The elastocaloric effect (i.e., pseudoelasticity, a mechanical shape-memory behavior) relies on a reversible martensitic phase transformation,⁴⁻⁶ a specific type of solid-state transformation. It represents a shear process in the crystal lattice,⁸ and can be triggered by cooling or mechanical loading. **Figure 1** shows a schematic elastocaloric cooling cycle starting at the high-temperature austenite state, stage 0 in **Figure 1a**. During mechanical loading, a stress/strain plateau is reached where the parent phase, austenite, transforms into stress-induced martensite, stage 1 to stage 2. The reverse transformation,

stage 3 to stage 4, is characterized by an unloading plateau at lower stresses. Both transformation events are associated with large latent heat ΔH , and thus cause remarkable temperature changes in the SMA.

The area, W , in **Figure 1a** represents the mechanical work input (i.e., force and distance) required to drive an ideal cooling cycle. It is common to characterize the cooling efficiency by the coefficient of performance (COP), which represents the ratio between the cooling energy output ΔH and the required work input, W .⁹ **Figure 1b** shows different material stages of the cooling cycle. The forward phase transformation that occurs during loading between stages 1 and 2 results in the release of latent heat and thus in an increase in the SMA temperature. This heat amount needs to be absorbed by a heat sink, such that a lower temperature is again approached in the material. During unloading, the reverse transformation causes a significant temperature drop between stages 3 and 4. This drop, which corresponds to values between 15°C and 30°C for NiTi,⁹⁻¹¹ determines the lowest achievable temperature in a ferroic cooling process.

Present research on elastocaloric cooling follows two main directions. First, basic aspects related to the material behavior, such as heat effects, functional stability, and alloy design, are

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being investigated.^{9–14} Second, the use of solid-state materials in a cooling process requires new engineering approaches which are being explored.^{9,15–18} Thus, different process design concepts are being developed and evaluated. In the present article, we give a brief overview of recent progress and challenges in these interesting research fields. We consider the case of tensile loading, which allows for high-aspect ratios of the material and thus fast heat exchange as compared to compressive loading. On the other hand, tensile loading also facilitates the formation and growth of fatigue cracks. Nevertheless, this risk can be tackled by using suitable alloy compositions¹⁹ and material states with low defects densities.²⁰

Elastocaloric material behavior

Latent heat and hysteresis width

Four material parameters^{9,10} are important for elastocaloric cooling performance. The SMA must exhibit large latent heat ΔH ; low hysteresis width, which corresponds to a low work input, W ; and good functional and structural stability, sufficient for several years of service life ($>10^7$ loading/unloading cycles). It also must be able to deliver the elastocaloric effect in an envisaged temperature regime.

It is well known that the martensitic transformation and thus pseudoelastic behavior is governed by alloy composition^{10,14} and microstructure.^{21,22} Various research groups^{10,11,15} have made attempts to study the effects of alloy chemistry on cooling performance. Both latent heat and hysteresis width react sensitively to compositional changes.^{10,23–29} Latent heats between 8.5 and 35 J/g,²³ and thermal hysteresis widths ranging from ≈ 0 K to >70 K,^{23,26} are reported in the literature. We note that the thermal hysteresis width, which is often used as a preferred indicator in compositional screenings,^{25,26} is directly proportional to the mechanical hysteresis width²⁷ and thus to the required input work, W (Figure 1a). The results of a recent study²³ identify a dilemma that may limit the development of new elastocaloric SMAs. **Figure 2** shows that a correlation exists between the latent heat and the hysteresis width. It is difficult to obtain the desired combination

of small hysteresis width and large latent heat simultaneously. Nevertheless, Wieczorek et al.¹⁰ recently found a good compromise in a NiTiCuV SMA with an exceptionally high COP value of 20. This value is about $4\times$ higher than for binary NiTi.⁹ Schmidt et al.³⁰ made a first attempt to study the cooling performance of this material.

Functional stability

The lowest functional degradation of the material is very important for any application. For example, a pseudoelastic SMA would have to tolerate >15 million loading/unloading cycles in a cooling device operating at 0.2 Hz over five years with 50% average utilization. Research on quaternary NiTi-based SMAs revealed a pronounced effect of crystallographic compatibility on the hysteresis width and reversibility (i.e., functional stability in thermally induced phase transformations).²⁶ The crystallographic compatibility conditions can be derived from the transformation matrixes between austenite and martensite and are thus purely geometric. For crystallographic compatibility³¹ (where the two phases fit without the need for slip or for establishing stressed transition layers), the middle eigenvalue of the transformation matrix λ_2 must equal one. This can be achieved by fine-tuning the composition. This $\lambda_2 = 1$ condition affects the heights of the energy barriers between the transforming phases, which determine the width of the transformation hysteresis.

A higher degree of compatibility—so-called supercompatibility—can be obtained by additionally fulfilling other conditions that promote good fit and thus provide an even higher degree of flexibility, as was first demonstrated for $\text{Zn}_{45}\text{Au}_{30}\text{Cu}_{25}$.³² The influence of supercompatibility on functional and structural fatigue in stress-induced austenite-martensite

Figure 2. Key parameters for ferroic cooling—hysteresis width and latent heat.²³ Alloy design requires good compromise (small hysteresis width and large latent heat) between both factors.

transformations has been demonstrated for TiNiCuCo¹⁹ and ZnAuCu,³³ and it was recently reviewed in Reference 31. The composition Ti_{54.7}Ni_{30.7}Cu_{12.3}Co_{2.3} showed no measurable fatigue for 10 million pseudoelastic cycles¹⁹ (Figure 3). This indicates that supercompatibility between austenite and martensite has an important influence on the fatigue behavior. From investigations of different TiNiCu and TiNiCuCo alloys with a λ_2 -value close to one, the functional degradation behavior was found to also depend on micro-structural parameters such as grain size³⁴ and the nature of precipitates.¹⁹ It was found that Ti₂Cu precipitates, which form in Ti-rich alloys, lead to a near-to-perfect reversibility and repeatability up to >10 million pseudoelastic cycles (Figure 3). The coherency of Ti₂Cu precipitates in both phases, austenite and martensite, accounts for this excellent structural and functional property. These Ti₂Cu precipitates guide the phase transformation in a well-defined manner and thus act like sentinels, assuring that the austenite-martensite transformation repeatedly follows the same path during each cycle.¹⁹

Ferrocic cooling applications

Bulk material-based cooling demonstrators

The first successful large-scale elastocaloric cooling devices have been developed and demonstrated.³⁵ The concept forming the basis of these developments is mechanical loading and unloading of SMA tube elements in compression and use of the absorbed and released latent heats to cool a hydraulic fluid. In contrast, the work presented in this article focuses on NiTi-based ribbons or wires that are loaded in tension to develop scalable air-cooling devices. Inherently coupled to this design goal is the optimization of the process parameters in terms of cooling power and COP. This requires optimization of the amount of straining, the strain rate, and efficient synchronization between mechanical loading/unloading and heat transfer.

Extending the usual framework of calculating COP values, a graphical method similar to that used for conventional vapor compression cycles has been developed to illustrate relevant work and heat quantities in stress/strain and temperature/entropy diagrams.³⁶ This helps to predict optimized hybrid cycles by appropriately combining adiabatic and isothermal process branches. A comprehensive test rig was developed^{17,37–39} to experimentally validate process efficiency and to study the effects of material training/functional degradation on mechanical, caloric, and thermal properties (Figure 4).³⁰ In the device shown in Figure 4a, a pseudoelastic NiTi ribbon is subjected to mechanical cycling. During this process, it moves between two copper blocks, Figure 4b, which act as a heat sink (in contact with the SMA during straining) and a heat source (in contact during unloading)

Figure 3. Ultralow fatigue of Ti-rich TiNiCu and TiNiCuCo alloys, as demonstrated by next-to-identical first and 10⁷th pseudoelastic transformation cycles.¹⁹ These materials meet requirements for long-term stability in ferroic cooling applications.

of the ribbon), respectively. Figure 4c exemplarily shows a color-coded IR image, which documents temperature changes in the ribbon and the two Cu blocks. A challenge for the design of future elastocaloric cooling devices is the implementation of these concepts into continuously operating units that outperform current vapor compression systems. The first ideas are currently being implemented into a demonstrator with a patent-pending drive element to map experimentally optimized processes.³⁸ Simultaneously, due to the large number of parameters involved in the design, simulation tools have to be developed to narrow the design space.

Thin-film cooling devices

The implementation of elastocaloric cooling on a miniature scale involves opportunities and challenges. The use of free-standing elastocaloric films allows for efficient heat transfer between film and heat sink/-source, which is of critical

Figure 4. Elastocaloric test rig for NiTi ribbon characterization.¹⁷ During cyclic operation, a shape-memory alloy (SMA) ribbon moves between two copper blocks, which act as a heat sink (in contact with the SMA during straining) and a heat source (in contact during unloading of the ribbon). (a) Concept sketch with infrared camera, two linear axes for loading/unloading and heat transfer via copper blocks. (b) Ribbon and copper blocks at higher magnification. (c) Thermography image of the setup during operation. A significant temperature difference between both blocks is established after a few elastocaloric cycles.

Figure 5. (a) Schematic of a miniature-scale cooling device.¹⁸ Moving the shape-memory alloy film periodically between the lower (x_2) and upper (x_1) position loads/unloads the film, and, thus, heat is generated/absorbed. Due to alternate switching of surface contacts in both positions, the moving film causes a directed heat flux from heat source to heat sink. (b) Experimentally observed temperature changes of the device for various operation frequencies reaching a maximum temperature span of 14 K.

importance for high cooling performance. However, parasitic heat fluxes are difficult to control in small systems, and system integration is often challenging. In addition, localized phase-transformation events may affect heat transport.^{13,40,41} One important feature of film-based SMAs is that they allow for almost pure tensile loading even when subjected to out-of-plane deflection.

Figure 5a shows an example of a miniature cooling device where this loading principle is applied. Heating and cooling power is separated by bringing the SMA film alternately in contact with the heat source during unloading, upper position x_1 , and with the heatsink during loading, lower position x_2 . Switching heat fluxes and loading the film in one single mechanism makes the setup simple, which is crucial for miniaturization. A typical elastocaloric cycle includes moving the film up and down, which results in stepwise transfer of heat from the heat source to the heat sink. Thus, the temperature T_{source} decreases and T_{sink} increases, as can be seen in Figure 5b for various operation frequencies.

The device reaches a maximum temperature span ΔT of 14 K at room temperature, a maximum cooling power of 18 Wg^{-1} , and a maximum COP of 6 at zero thermal load neglecting actuation efficiency. Keeping in mind that the film sample has a mass of only 0.015 g, the results in Figure 5b highlight the potential of small-scale elastocaloric cooling devices. Furthermore, it has been shown that work recovery can minimize the required mechanical power input in film-based cooling devices.^{18,42} For practical applications, the heat-source element can be interconnected to a thermal load (e.g., an electronic chip or a heat-transfer fluid). Currently, the elastocaloric cooling device is limited by the adiabatic temperature span of the SMA material,⁴³ in this case, a NiTiCuCo alloy. This limit can be overcome by cascading several SMA films with tailored phase transition temperatures in a stack.

Summary, outlook, and challenges

Elastocaloric cooling principles have high potential for applications because (1) SMAs can provide high cooling efficiency, (2) they represent alternative engineering solutions for conventional cooling processes, and (3) both miniature and large-scale cooling units can be realized. Progress was recently achieved in alloy design where new NiTi-based SMAs with high cooling efficiencies and excellent fatigue lives were developed. These materials have to be studied to determine how they perform in actual cooling devices, and how process conditions can be optimized. For the development of new cooling devices, it may be necessary to extend the temperature range where the elastocaloric effect can be accessed. This will involve the development of cascaded cooling units where SMAs with different operating temperature ranges are combined.

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