Phase transformations in equiatomic CuZr shape memory thin films analyzed by differential nanocalorimetry

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Abstract
We have investigated the phase transformations in sputtered CuZr shape memory thin films using a differential nanocalorimetry technique that is capable of making calorimetric measurement on thin-film samples with a sensitivity as small as 12 pJ/K. We first present a general procedure to accurately measure the heat capacity and enthalpies of transformation of a sample, even if there is a significant difference in the heat capacities of sample and reference. We then demonstrate the technique by analyzing the phase evolution of equiatomic CuZr thin films and explore the conditions for the formation of the martensitic phase responsible for the shape memory properties of this alloy. We show that fast, low-temperature cycling through the martensitic transformation increases the hysteresis, which we attribute to the accumulation of defects during the martensitic transformation. If the austenitic phase is given sufficient time at elevated temperature to annihilate these defects, the transformation is stable under thermal cycling conditions.

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1. Introduction

Shape memory alloys (SMAs) undergo large recoverable shape changes as a result of a reversible martensitic transformation that may be induced by changes in temperature or stress. These alloys typically exhibit actuation energy densities an order of magnitude higher than any other solid-state actuator [1,2]. While many SMAs have been discovered to date, the subset of SMAs capable of actuation above 100 °C, known as high-temperature SMAs (HTSMAs), remains relatively unexplored [3]. Equiatomic CuZr is a potential HTSMA with a reported martensite-austenite onset temperature of 530 K [4,5], while even higher transformation temperatures can be achieved with the addition of alloying elements such as Ni and Co [5].

In this study, we investigate the behavior of CuZr thin films using a differential nanocalorimetry technique. Thin films of SMA are of interest because they can be used as actuators in micro-electro-mechanical systems [6]. They may also serve to develop new shape memory alloys using combinatorial synthesis techniques [7,8], provided the effects of the thin-film microstructure on the shape memory behavior are taken into account [9,10]. Because of the very small sample volumes involved, characterization of phase transformations in thin-film samples requires highly sensitive measurement techniques such as, for instance, nanocalorimetry. Nanocalorimetry is an emerging characterization technique that can be used to obtain thermodynamic and kinetics information for very small samples [11–13]. The technique relies on micromachined sensors to perform calorimetry measurements. Advantages include extraordinary sensitivity and a range of scanning rates, from isothermal to 10^5 K/s, that is not accessible with traditional calorimetry. Much like traditional calorimetry, a number of different experimental modes are possible, including scanning, differential, and power-compensated nanocalorimetry [12,14,15].

Differential nanocalorimetry is the equivalent of Differential Thermal Analysis (DTA) for bulk materials and has similar advantages and disadvantages. The differential technique was first developed by Allen and coworkers using a sample calorimetry sensor and a reference sensor, each with its own galvanically isolated power supply [14]. A slightly different version in which a single power supply is used, was later introduced by Rodríguez-.
Viejo [16]. This technique has the advantage that common noise from the power supply is rejected in the differential signal, significantly improving the signal-to-noise ratio. In this study, we have adopted the differential scheme proposed by Rodríguez-Viejo, but with different hardware components to further improve the signal-to-noise ratio, increase the scan rate, and allow alternating current (AC) measurements up to 20 kHz. We also use a more general approach to account for any heat loss differences between the sample and reference. We first provide a detailed description of the measurement setup, hardware, and data reduction methods used to perform differential nanocalorimetry measurements. The technique is then applied to sputtered films of equiatomic CuZr. We determine the heat treatments that are required to obtain the martensitic transformation in the CuZr samples and demonstrate that the martensitic transformation is stable under thermal cycling provided the austenitic phase is given sufficient time to recover from any defects generated during the transformations.

2. Experimental details

2.1. Nanocalorimetry device

All nanocalorimetry measurements were performed using a parallel nano-scanning calorimeter (PnSC) device. Details of the design and working principle of the PnSC device can be found in our previous work [7,8,17]. Briefly, as shown in Fig. 1, the device contains a 5 × 5 array of independently controlled nanocalorimeter sensors capable of thermal characterization of samples with very small thermal mass. Each sensor consists of a tungsten thermistor in a four-point measurement configuration that serves both as heating element and as resistance thermometer. The tungsten thermistor is fully encapsulated in a thin freestanding silicon nitride membrane, which, in turn, is supported by a silicon frame. During a typical calorimetry measurement, a current is applied to the thermistor. The current and the voltage drop across the thermistor are used to determine the power supplied to the sensor and the resistance of the thermistor, which is calibrated to temperature by measuring the resistance as a function of temperature in a vacuum furnace. All sensors were fabricated at the Harvard University Center for Nanoscale Systems using the process described in references [7,8,17].

2.2. Sample preparation and characterization

CuZr samples were deposited onto nanocalorimetry sensors by means of magnetron sputtering in a vacuum system (ATC, 1800, AJA Int., Scituate MA) with a base pressure better than 3 × 10⁻⁷ Torr. Samples were deposited by sputtering from 50.8 mm diameter elemental Zr (grade 702; ~170 W DC power) and Cu (99.999%; ~50 W DC power) targets obtained from Kurt J. Lesker Company. Before deposition of the CuZr samples, a HfO₂ layer with a thickness of 20 nm was grown on the nanocalorimetry sensors using atomic layer deposition (ALD, Cambridge NanoTech Inc.) to prevent reaction between the sample and the Si₃N₄ membrane. A shadow mask was used to ensure that CuZr deposition occurred only in the sample area between the voltage probes of the sensors. The thickness of the samples was measured to be 500 ± 50 nm using TEM cross-sections. The composition of the samples was measured to be Cu₅₀Zr₅₀ using X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha XPS System). To avoid any effects from surface oxidation, the surface of the sample was Ar sputtered in the XPS chamber to expose a pristine surface. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Discover System. All Cu₅₀Zr₅₀ samples were amorphous as-deposited. The microstructures of samples quenched from different temperatures were investigated using a FEI 2010 TEM operating at 200 keV. A Helios 660 Dual-beam Focused Ion Beam System was used to prepare sample cross-sections for transmission electron microscopy using a standard lift-out method. Low-temperature experiments were performed by immersing the nanocalorimetry sensors in isopropanol alcohol that was cooled to 230 K using liquid nitrogen.

2.3. Data acquisition system

The data acquisition (DAQ) system used to perform the calorimetry measurements was custom-designed to make differential measurements between two calorimetry sensors powered by the same current. As explained in the next section, such a measurement scheme has significant advantages in terms of reducing measurement noise and improving the sensitivity of the measurements. Fig. 2 shows a schematic representation of the system. The setup consists of several electronic sub-systems: (1) A current source for powering both sensors; (2) a differential electronic circuit for measuring and conditioning the voltage across the sample sensor Vₛ, the voltage across the reference sensor Vᵣ, and the differential voltage VΔ; and (3) a DAQ board for acquiring the various voltage signals and for controlling the current. The entire system is powered by low-noise and ground-isolated DC power supplies (Agilent E3630A and E3620A — not shown). Short BNC cables were used to convey the signals. All nanocalorimetry measurements were performed inside a stainless-steel vacuum furnace with a base pressure better than 3 × 10⁻⁶ Torr, which doubled as a Faraday cage to reduce external noise.

The current source is a modified Howland voltage-to-current...
3. Theory and data reduction

A very general analysis of differential nanocalorimetry was presented by Efremov et al. [20]. Here we specialize that treatment to the nanocalorimetry system used in this study and present a different treatment of heat losses to the ambient. As shown in Fig. 2, the output of a typical differential nanocalorimetry experiment consists of the differential voltage $\Delta V$, the voltage across the sample sensor $V_S$, the voltage across the reference sensor $V_R$, and the voltage across the precision resistor $V_r$. These quantities need to be related to the heat capacity of the sample and any enthalpy produced as a result of transformations or reactions in the sample, while minimizing the impact of measurement noise on the final result. The differential signal $\Delta V$ is relatively free of noise because common mode noise is rejected in the measurement and the large amplification of the signal minimizes bit noise. Similarly, the signals across the reference sensor, $V_R$, and the precision resistor, $V_r$, have relatively little noise because they can be averaged over many measurements. Therefore, the analysis of the nanocalorimetry experiment is performed as much as possible in terms of $\Delta V$, $V_S$, and $I$.

The temperature of a nanocalorimetry sensor is related to its resistance $R$ by

$$R(T) = R_0(1 + \lambda(T - T_0)).$$  

where $\lambda$ is the temperature coefficient of resistance of the heating element of the sensor, $T$ is the temperature of the heating element, $T_0$ is the ambient temperature, and $R_0$ is the resistance of the heating element at $T_0$. Using Ohm’s law, the temperature of the sample sensor, $T_S$, can then be written as

$$T_S = T_0 + \frac{1}{\lambda} \left( \frac{V_R + \Delta V}{IR_0} - 1 \right).$$  

Taking the time derivative of Eq. (2) and using Eq. (1) for the reference sensor yields after some manipulation the heating rate of the sample sensor, $\beta_S$,

$$\beta_S = \beta_R R_0^2 + \frac{1}{\lambda R_0^2} \frac{d\Delta V}{dt} - \frac{1}{\mu^2 R_0^2} \frac{df}{dt},$$  

where $\beta_R$ is the heating rate of the reference sensor. Fig. 3 illustrates the use of Eqs. (2) and (3) for the analysis of a nanocalorimetry experiment on a 500 nm CuZr sample. Fig. 3a shows the temperature history of the sample calculated using Eq. (1) for the non-differential mode and Eq. (2) for the differential mode — the results are comparable with no obvious noise for either measurement mode. By contrast, the difference in the heating rates shown in Fig. 3b is obvious: the heating rate calculated using Eq. (3) has significantly less noise than the heating rate in the non-differential mode.
At any given time, the energy balance of a calorimetric sensor dictates that
\[ P = V I = C_p \Delta T + P_{\text{loss}}. \]  
\[ (4) \]
where \( P \) represents the power supplied to the sensor, \( V \) is the voltage drop across the sensor, \( C_p \) is the total heat capacity of the sensor, and \( P_{\text{loss}} \) is the rate of heat loss to the environment. Applying Eq. (4) to both the reference and the sample sensor and taking the difference in the time domain yields
\[ \Delta C_p = C^s_p - C^R_p = \left( \frac{V S}{\Delta T} - \frac{V R}{\Delta T} \right) - \left( \frac{P_{\text{loss}}^S}{\Delta T} - \frac{P_{\text{loss}}^R}{\Delta T} \right). \]  
\[ (5) \]
We now evaluate each of the terms on the right-hand side of Eq. (5). The first term on the right-hand side of Eq. (5) can be rewritten as follows
\[ \Delta C_p^X = \frac{V S}{\Delta T} - \frac{V R}{\Delta T} \left( 1 + \frac{\Delta V}{V_R} \frac{p^R_{\text{cond}}}{\Delta T} \right). \]  
\[ (6) \]
Fig. 3c compares \( \Delta C_p^X \) evaluated using Eq. (6) with the value obtained from the non-differential measurement. The difference in noise level is evident. Accurate evaluation of the second term on the right-hand side of Eq. (5) is more difficult. Since both sensors in the experiment have very similar temperature histories, the heat losses from both sensors are similar and the second term amounts to a relatively small correction that grows with increasing temperature. The correction for heat loss to the ambient may be calculated using the following procedure. The heat loss consists of both conduction losses through the membrane of the sensors and radiative losses from the surface,
\[ \Delta C_{\text{loss}} = \frac{P_{\text{cond}}^S}{\Delta T} - \frac{P_{\text{cond}}^R}{\Delta T} + \left( \frac{P_{\text{cond}}^R}{\Delta T} - \frac{P_{\text{cond}}^S}{\Delta T} \right) + \left( \frac{P_{\text{rad}}^R}{\Delta T} - \frac{P_{\text{rad}}^S}{\Delta T} \right). \]  
\[ (7) \]
As described in Appendix B, the conduction losses \( P_{\text{cond}}^S \) and \( P_{\text{cond}}^R \) can be calculated by integrating an analytical model over the temperature histories of the respective sensors. For typical nanocalorimetry measurements, the correction associated with conductive heat losses is quite small, as illustrated in Fig. 3d. The radiative losses \( P_{\text{rad}}^S \) and \( P_{\text{rad}}^R \) are calculated by fitting the Stefan-Boltzmann law to the baselines of AC nanocalorimetry measurements performed on the sample and reference sensors using the procedure described by Xiao and coworkers \[18,19\], after subtracting the conduction loss. As shown in Fig. 3d, the correction due to radiative losses can be significant once the temperature exceeds 550 K. An alternate method to deal with heat losses consists of performing calorimetry scans at different heating rates. If the heat loss depends on sensor temperature only and is independent of temperature history, it can be determined from such measurements by various extrapolation methods as described in the literature \[16,21\]. This method requires several scans and does not work
well if irreversible transformations or reactions occur in the sample.

The value of $\Delta C_p$ calculated from Eq. (5) is the difference in heat capacities of the sample sensor and the reference sensor in the time domain. If the thermal mass of the sample is negligible compared to that of the sensor and both sensors have identical heat capacities, then $\Delta C_p$ is exactly equal to the heat capacity of the sample, $C_p^{\text{Sample}}$. In practice, the thermal mass of the sample is not necessarily negligible and both sensors have slightly different heat capacities, so that the sensors heat up at slightly different rates. Because the heat capacities of the sensors are temperature dependent, relating $\Delta C_p$ directly to the heat capacity of the sample is more difficult and small corrections need to be made. We make these corrections by measuring the difference in the heat capacities of both empty sensors using the differential setup and by measuring the heat capacity of the reference sensor as a function of temperature using AC nanocalorimetry following the procedure described by Xiao et al. [18,19]. These measurements are then transferred from the time domain to the temperature domain and the appropriate corrections are made to $\Delta C_p$ to yield $C_p^{\text{Sample}}$. The flowchart in Fig. 4 provides a schematic overview of the entire data reduction scheme.

3. Results

3.1. CuZr phase evolution

Fig. 5a–b shows the results of two consecutive nanocalorimetry scans on an amorphous, as-deposited CuZr sample using the differential scanning nanocalorimetry setup. Both scans go beyond the melting temperature of the sample. The heating rate is kept constant at approximately 2500 K/s by adjusting the current input, while the cooling rate is controlled by the heat loss to the environment. In the first scan, the sample goes through a crystallization reaction, a eutectoid reaction, and two melting reactions associated with the two eutectics that involve the CuZr phase, and a final melting transition. On cooling, a small solidification peak appears at approximately 1000 K. The temperatures $T_S$ and $T_C$ in Fig. 5a correspond to the glass transition temperature and the crystallization onset temperature, respectively. These temperatures are in good agreement with previous work by Lee et al. [22]. As demonstrated Lee et al. [22], the crystallization process results in two phases, CuZr$_2$ and Cu$_{10}$Zr$_7$, which are the equilibrium phases at the crystallization temperature according to the phase diagram in Fig. 5. The endothermic peak at $T_E = 1033$ K corresponds to the eutectoid reaction, $3 \text{CuZr}_2 + \text{Cu}_{10}\text{Zr}_7 \rightarrow 13 \text{CuZr}$. $T_E$ is approximately 45 K higher than the eutectoid temperature in the phase diagram because fast heating shifts the reaction to higher temperature for kinetics reasons and is in line with the activation energy of 1.8 eV measured previously [22]. The product phase, CuZr, has the B2 crystal structure (space group Pm3m). The peaks at $T_{m1}$ (1176 K), $T_{m2}$ (1187 K) and $T_{m3}$ (1208 K), correspond to the eutectic reaction of CuZr with Cu$_{10}$Zr$_7$, the eutectic reaction with CuZr$_2$, and the congruent melting transition of CuZr, respectively. The presence of the eutectic peaks indicates that the eutectoid reaction is incomplete and some CuZr$_2$ and Cu$_{10}$Zr$_7$ remain at temperatures higher than $T_E$. Because CuZr is a strong glass former [23], the sample is partially amorphous after quenching from the melt in the first scan (Fig. 5a). Consequently, the second scan in Fig. 5b again shows a crystallization reaction and a eutectoid reaction (Fig. 5b inset). In our previous work on this alloy using a non-differential calorimetry setup, the eutectoid reaction peak could not be distinguished in the second scan [22]. This clearly demonstrates the
superior signal-to-noise ratio obtained using the differential calori-
meter mode.

Previous work on bulk samples of CuZr alloys has shown that the high-temperature CuZr phase has shape memory properties \[24,25\]: If the B2 phase is cooled fast enough to avoid eutectoid decomposition, the phase goes through a martensitic transition forming a monoclinic CuZr phase (space groups Cm or P2\(_1\)/m) at low temperature. Here, we demonstrate that the same martensite-austenite (M-A) phase transformation is, under certain conditions, also observed in thin-film samples. A series of calorimetry measurements were carried out on an as-deposited sample, increasing the maximum temperature of the scan for each measurement. The results are shown in Fig. 6a. The first scan shows an as-deposited sample heated to a temperature right above the eutectoid temperature \(T_E\). This sample first crystallizes and then transforms to the B2 CuZr phase, which should form martensite on cooling. When the sample is heated a second time, however, no reverse martensitic transformation is observed, indicating that no martensite is formed on cooling after the first measurement. This finding is confirmed by XRD (Fig. 6b) and cross-sectional TEM (Fig. 7b). Firstov and co-workers \[25\] have shown that in bulk samples the martensitic phase transforms to austenitic CuZr at 590 K, a temperature that is significantly higher than the transformation temperature observed for thin films. This finding is consistent with previous work that has demonstrated that thin-film samples tend to transform at lower temperatures due to the smaller grain size typically observed in these samples \[9,10,26,27\]. Finally, as illustrated in Fig. 5a, if the maximum temperature of the scan is sufficiently high to fully melt the CuZr sample, no martensite is observed during the next scan because the sample remains mostly amorphous on cooling.

3.2. Stability of the martensite-austenite transformation under thermal cycling

In this section, we consider the stability of the martensitic transformation under thermal cycling conditions in CuZr samples that were previously heated to a temperature above \(T_{m2}\) and that were in the martensitic state at room temperature. Fig. 8a shows

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**Fig. 5.** (a) First calorimetry scan on an as-deposited CuZr sample. Heating and cooling curves are plotted with an offset. The crystallization peak at 850 K indicates that the as-deposited sample is amorphous. Upon melting, the heat capacity drops significantly because the emmissivity of the sample changes and the radiation heat loss is not correctly accounted for. (b) Second calorimetry scan on the same CuZr sample. Heating and cooling curves are plotted with an offset. The scan also shows a crystallization peak, indicating that the sample is partially amorphous after melt-quenching. (c) Cu-Zr phase diagram, from Filipov et al. \[28\] and Arias et al. \[36\]. Reprinted with permission from Springer Nature.
eight consecutive scans to a temperature of 1100 K, which is higher than the eutectoid temperature ($T_E = 1033$ K); Fig. 8b shows three consecutive scans to 750 K, lower than the eutectoid temperature. It is evident that the martensitic transformation is not stable and tends to fade away if the samples are thermally cycled to 750 K, but that the transformation is stable when cycled to 1100 K. Decomposition of the B2 phase into CuZr$_2$ and Cu$_{10}$Zr$_7$ below the eutectoid temperature would be the most obvious explanation for this behavior. However, heat treating a sample for 10 s at 822 K, below the eutectoid temperature, results in a full restoration of the martensitic transformation, ruling out decomposition as a mechanism (Fig. 9a). This finding is in agreement with a recent study of the rate of decomposition of bulk B2 CuZr by Filippov et al. [28]. The time-temperature transformation (TTT) diagram published by these authors indicates that decomposition takes 10 min to start at a temperature of 822 K. Further investigation demonstrated that the fading of the M-A peak is in fact caused by a decrease of the martensite start temperature ($M_s$). In Fig. 9b, we show results for a sample that was scanned multiple times to 750 K until the M-A peak had completely disappeared (black curve). This sample was then cooled to 230 K and scanned again. In the second scan, a strong M-A peak reappears at the same temperature as before (red curve), but no M-A peak is found in the third scan (green curve), which was obtained without cooling to 230 K. These observations confirm that the $M_s$ temperature decreased below ambient temperature as a result of low-temperature thermal cycling.

4. Discussion

4.1. Formation of the martensitic phase

Characterization of samples after different heat treatment procedures (heated to a temperature higher than $T_E$, $T_{m2}$, or $T_{m3}$) confirms that martensite only forms in these samples after being heated to a temperature between $T_{m2}$ and $T_{m3}$. At room temperature, samples heated to above the eutectoid temperature consist predominantly of the CuZr B2 phase, as shown by XRD (Fig. 6b) and cross-sectional TEM (Fig. 7a), with small amounts of CuZr$_2$ and Cu$_{10}$Zr$_7$. Possible causes for the absence of the austenite-martensite (A-M) transformation in these samples include: (i) The
transformation occurs below room temperature because the grain size is too small. (ii) The high-temperature B2 phase partly decomposes into CuZr\(_2\) and Cu\(_{10}\)Zr\(_7\) on cooling below the eutectoid point and the presence of these phases hinders the transformation. (iii) The phase formed by the eutectoid reaction contains a composition gradient or a high concentration of lattice defects that prevent the formation of martensite. It is unlikely that the small grain size is responsible for the absence of martensite. It is well known that a small grain size can depress the martensite transformation temperature or even completely suppress the transformation \[9,10\], but the grain size of the eutectoid sample is comparable to that of the partially melted samples, albeit slightly smaller (Fig. 7). In the partially melted sample, the martensite forms stacks of plate-shaped twins, each having a thickness of a few nanometers. These stacks form clusters that mark the shape of the austenite grains. The size of the smaller clusters is approximately 50 nm. In the eutectoid sample, however, there are grains larger than 50 nm that do not transform to martensite. To further rule out this mechanism, an eutectoid sample was cooled to 230 K, approximately 190 K below the \(M_t\) temperature reported for bulk materials by Blifi et al. [29]. A subsequent calorimetry scan did not show any evidence of martensite-to-austenite transformation (Fig. 10). Decomposition of the CuZr B2 is also unlikely, because both XRD and TEM confirm the existence of the B2 phase. Moreover, the partially melted sample, which has a similar cooling history as the eutectoid sample, does transform to martensite. Consequently, it is likely that the absence of martensite is the result of how the B2 phase is formed and that a high level of defects in the B2 phase prevents the formation of martensite. The first calorimetry scan in Fig. 5a shows several melting peaks, indicating that small amounts of CuZr\(_2\) and Cu\(_{10}\)Zr\(_7\) remain after the eutectoid reaction and participate in the eutectic reactions. These phases are also identified by XRD (Fig. 6b) and TEM (Fig. 7a). A previous study on bulk samples has shown that as-cast bulk equiatomic Cu-Zr contains CuZr, CuZr\(_2\) and Cu\(_{10}\)Zr\(_7\) [29]. The grain size of the CuZr\(_2\) and Cu\(_{10}\)Zr\(_7\) phases in these samples is on the order of a few microns. To eliminate these phases in the bulk, a heat treatment of more than 30 min above the eutectoid temperature is necessary. The short reaction time in the nanocalorimetry samples is evidently insufficient to form stoichiometric B2 phase and some CuZr\(_2\) and Cu\(_{10}\)Zr\(_7\) remain. The ensuing CuZr phase likely has a high level of defects with significant concentration gradients and possibly a large number of atoms in the wrong sub-lattice. By contrast, samples that are partially melted solidify into a high-quality B2 phase that

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**Fig. 8.** (a) The martensite-to-austenite transformation is stable in scans to 1100 K. (b) The transformation fades away in low-temperature scans to 750 K.

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**Fig. 9.** (a) After multiple low-temperature cycles, the martensite-to-austenite peak completely disappears (1st scan). If a heat treatment of 10 s at 822 K is performed (inset), the martensite-to-austenite peak reappears in the next scan (2nd scan). (b) After multiple low-temperature cycles, the martensite-to-austenite peak completely disappears (1st scan). Cooling the sample to 230 K brings the peak back in a subsequent scan (2nd scan). A 3rd scan performed without prior cooling confirms that the martensite start temperature has decreased below room temperature.
transforms to martensite on further cooling. The eutectic melting temperatures of CuZr-CuZr and CuZr-Cu$_{50}$Zr$_{50}$ are lower than the melting point of CuZr. Therefore, CuZr$_2$ and Cu$_{10}$Zr$_7$ react with CuZr and melt before the B2 phase melts. Upon solidification, the unmelted B2 grains act as nucleation sites for the growth of the CuZr B2 phase. The result is a high-quality CuZr phase, which then transforms into martensite at lower temperature. An analysis of the transformation enthalpies suggests that between the eutectoid and the eutectic reactions approximately 70% of the sample is converted to the B2 phase. A fully melted sample, on the other hand, has no easy nucleation sites and forms a metallic glass on cooling.

4.2. Defects formation during the martensitic transformation

The M-A transformation fades away upon low-temperature cycling as a result of a shift of the A-M transformation to lower temperatures. Our results also show that the shift in transformation temperature disappears if the sample spends sufficient time at elevated temperature, suggesting that this phenomenon is due to the formation of defects that stabilize the austenitic phase and that are annihilated by if the sample dwells at elevated temperature. These defects are not cleared away in fast, low-temperature cycles, but accumulate until the transformation is no longer observed. One nanocalorimetry cycle takes less than 1.5 s. A very brief anneal of 10 s at 822 K or a scan up to 1100 K is sufficient to remove the defects.

The formation of defects may be explained by the relatively large lattice mismatch between the austenite and martensite for CuZr. The lattice distortion matrix is calculated as

$$ U = \begin{bmatrix} 0.9703 & -0.0693 & -0.0693 \\ -0.0693 & 0.7468 & -0.1758 \\ -0.0693 & -0.1758 & 0.7468 \end{bmatrix} $$

where the lattice parameters of B2 phase were taken from reference [30] and those of the Cm phase from reference [31]. The lattice distortion matrix was calculated using the approach detailed by James and Hane [32]. As described by James et al. [33], the middle eigenvalue of the matrix is an indicator of the compatibility between austenite and martensite. If the middle eigenvalue $\lambda = 1$, then both phases are exactly compatible. Table 1 lists the middle eigenvalue of CuZr, along with that of other shape memory alloys. It is clear that the middle eigenvalue of CuZr is relatively far from unity compared to NiTi and NiTiCu. Thus, defects form during the martensitic transformation as a result of the very high localized stresses induced by the lattice incompatibility. Evidently, these defects, if they are not fully annealed, stabilize the austenite and hinder the formation of martensite in the subsequent scans. A similar phenomenon has been observed in some bulk Cu-Zn-Al and ZrCuNiCoTi shape memory alloys [34,35], where the formation of dislocations in the austenitic phase as a result of temperature cycling shifts the transformation to martensite to lower temperatures. The effect of the defects in these systems seems to be more persistent than in CuZr, where a relatively mild temperature excursion is sufficient to remove the defects.

### Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu$<em>{50}$Zr$</em>{50}$</th>
<th>Ni$<em>{50}$Ti$</em>{50}$</th>
<th>Ni$<em>{40}$Ti$</em>{40}$Cu$_{20}$</th>
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<td>$\lambda$</td>
<td>0.9226</td>
<td>0.9663</td>
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5. Conclusions

We have used a differential nanocalorimetry setup that enables calorimetric measurements on ultra-thin film with exceptional resolution to study the transformation behavior of CuZr thin films. When combined with a numerical method to directly evaluate the heat loss based on the thermal history of the sensors, the differential technique may be used even when sample and sensor have comparable thermal mass or when measurements are performed under non-adiabatic conditions. Differential nanocalorimetry measurements on equiatomic Cu$_{50}$Zr$_{50}$ thin-film samples prepared by magnetron sputtering show a fairly complex phase evolution. By changing the temperature to which a sample is heated, the resulting sample may, on cooling, contain a significant fraction of amorphous phase, the equilibrium phases CuZr$_2$ and Cu$_{50}$Zr$_{50}$, austenite, or martensite. High-temperature scans on the martensitic phase result in a stable martensitic transformation with good cyclability. Low-temperature, fast scanning cycles, however, lower the martensite start temperature. We attribute this observation to the accumulation of defects caused by the large lattice incompatibility between the austenite and martensite phases. These defects need to be annealed out if a stable transformation is desired. This requirement puts an upper limit to the frequency at which SMA actuators can operate.

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### Appendix A. Analysis of noise in the differential measurement system

The noise in the measurements consists mainly of three
components, as listed in Table A1, i.e., 1) the noise from the differential circuit, 2) the noise in the applied current, and 3) the digital bit noise from the DAQ board.

The noise from the differential circuit consists of the intrinsic Johnson noise introduced by the tungsten heating elements and the noise caused by the various amplifiers. The differential signal $\Delta V$ has intrinsic noise equal to $\sqrt{2}$ times the Johnson noise spectral density, $e_{\text{VT}} = \sqrt{4kT}$, where $k$ is the Boltzmann constant, $R$ is resistance of the heating elements at temperature $T$. The factor of $\sqrt{2}$ arises because $\Delta V$ is the difference of the voltage signals across the two sensors. In a typical measurement, the resistance of the heating element may vary from 9.6 $\Omega$ at room temperature to 24 $\Omega$ at 1500 K, with a corresponding voltage drop across an individual sensor of 0.4 V–2.8 V. Thus, for a measurement performed over this temperature range at a sampling rate of 100 kHz, the intrinsic noise density on the $\Delta V$ signal is approximately 0.57–2 nV/$\sqrt{\text{Hz}}$. The noise introduced by the amplifiers consists of three contributions: the amplifier input noise $e_{\text{in}}$, the amplifier output noise $e_{\text{o}}$, and the Johnson noise of the gain resistor $e_{\text{GC}}$. The values of the input and output noise of the AD8429 amplifiers are provided by the manufacturer [37] and are listed in Table A1. An amplifier gain factor of three requires a gain resistance of 3 k$\Omega$ with associated Johnson noise of 6.9 nV/$\sqrt{\text{Hz}}$. The total noise density introduced by one AD8429 amplifier is then $e_{\text{V,AD8429}} = \text{Gain}_{\text{AD8429}} \times \sqrt{(e_{\text{in}}/G)^2 + e_{\text{o}}^2 + e_{\text{GC}}^2} = 49\text{nV}/\sqrt{\text{Hz}}$. The SIM911 amplifier has a large gain factor and is therefore dominated by its input noise, $e_{\text{V,SIM911}} = e_{\text{in}} = 1.8\text{nV}/\sqrt{\text{Hz}}$ [38]. The total noise density in the signal from the differential circuit is then $e_{\text{V}} = \sqrt{2e_{\text{V,AD8429}}^2 + 2e_{\text{V,SIM911}}^2} = 70\text{nV}/\sqrt{\text{Hz}}$.

The main advantage of using a single current source to power both sensors is that the noise introduced by the current source is rejected in the differential signal, at least if the thermal mass of both sensors is exactly the same. If the thermal mass of the sensors is significantly different, however, the current source also contributes to the noise. The current noise is associated with noise in the control voltage supplied by the DAC on the DAQ board (DT9837C). The noise in the control voltage is 30 $\mu$V at 256 kHz, which results in a current noise $e_I$ of 6 nA/$\sqrt{\text{Hz}}$ for a current source with a 10 $\Omega$ current-monitoring resistor. The corresponding noise $e_{\text{V}}$ in the $\Delta V$ signal is then $e_{\text{V}} = e_I \times \text{Gain}$, where $\Delta R$ is the resistance difference between the sample and the reference sensors. If the thermal mass of sample and reference sensors is significantly different, the heating elements can have different temperatures and resistances at a given moment. For a typical measurement on a 500 nm CuZr sample, the maximum value of $\Delta R$ over a temperature range from room temperature to 1100 K is approximately 1.5 $\Omega$, which corresponds to a maximum of 9 nV/$\sqrt{\text{Hz}}$ in voltage noise. This noise can be reduced by using thinner samples to minimize the difference between the sample and reference sensors.

The noise on the $\Delta V$ signal in the previous paragraphs is calculated with respect to the un-amplified signal and is amplified along with the signal before it is acquired by the DT9837C DAQ board. The DAQ board has four 24-bit A/D converters. At 100 kHz, the A/D converters behave effectively as 16-bit converters, introducing around 1 $\mu$V/$\sqrt{\text{Hz}}$ of bit noise if the full voltage range ($\pm$10 V) is used. The $\Delta V$ signal is typically amplified by a factor greater than 100. Consequently, the bit noise introduced by the DAQ board is smaller than the noise in the amplified $\Delta V$ signal.

As an illustration of the noise analysis, we consider the heat capacity data of a 3 nm Sn film shown in Fig. A1. Allen and coworkers [20] derived a simple expression for the heat capacity of a sample in terms of the differential voltage $\Delta V$ if the thermal mass of the sample is negligible compared to that of the sensors:

$$\Delta C_p = -\frac{V_R}{2R_o^2e_R} \times \frac{d\Delta V}{dt}.$$  \hfill (A1)

The noise $\sigma$ in the heat capacity measurement can be expressed as

$$\sigma = \frac{2V_R}{2R_o^2e_R} \times \epsilon_{\Delta V}/\sqrt{N},$$  \hfill (A2)

where $\epsilon_{\Delta V}$ represents the noise in the differential signal, $f$ is the sampling frequency, and $N$ denotes the number of scans performed. The additional $\sqrt{2}$ coefficient is added to Eq. (A2) because two heat capacity measurements are performed to obtain $C_p^{\text{SIM}}$. The heat capacity in Fig. A1 was calculated using Eq. (A1) for 400 scans and then averaged. The measurements were performed using a sampling frequency of 50 kHz. The raw data were smoothed using a moving average of five data points, i.e., the effective data acquisition frequency was 10 kHz. The value of $e_{\Delta V}$ was taken to be around 7 $\mu$V from Table A1 at the signal frequency of 10 kHz. The value of $V_R$ at 400 K was 0.94 V; $R_o^2$ had a value of 9.6 $\Omega$ and $\lambda$ value of 0.0015. Substituting these values into Eq. (A2) yields a 6-sigma noise level of 1.7 nJ/K at 400 K, in good agreement with the results shown in Fig. A1. Heat capacity measurements with a resolution of approximately 20 pJ/K have been reported for a 5 nm indium film by Rodríguez-Viejo and coworkers [39]. The sensors used in this work had an addendum of 120 nJ/K, an $R_o^2$ value of 25 $\Omega$, and a $\lambda$ value of 0.0024. Measurements were performed at a heating rate of approximately 95 K/s and a data acquisition frequency of 50 kHz. The results of 500 scans were averaged and the results were smoothed using a moving average of ten data points. Under the same data acquisition conditions, the experimental setup in this work would achieve a resolution of 12 pJ/K with the same sensor.

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Appendix B. Calculation of conduction heat loss

The conduction loss, $P_{\text{cond}}$, for a given sensor is calculated by integrating an analytical model over the entire temperature history of the sensor as described in detail by Lee and coworkers [40]. The main approximations in the model are the assumptions that the thermal conductivity of the membrane does not vary with temperature and that radiation losses from the membrane can be linearized. For a discrete set of time-temperature data $(t_i, T_i)$, the heat loss at time $t_n$ can then be evaluated numerically as

$$P_{\text{cond}} = 2k_m A_m \left( \sum_{i=1}^{n-2} l_i + l_{i-1} \right). \tag{B1}$$

where $k_m$ and $A_m$ denote the thermal conductivity and the total cross-sectional area of the membrane. The terms $l_i$ and $l_{i-1}$ are defined as follows

$$l_i = \left( A_i + B_i t_{in} \right) \frac{1}{\sqrt{\alpha t}} \left( \frac{\text{e}^{\beta(t_n - t_i)}}{\sqrt{t_n - t_i}} - \frac{\text{e}^{\beta(t_i - t_n)}}{\sqrt{t_i - t_n}} \right) + \frac{\sqrt{\beta \pi}}{2 \sqrt{\alpha \beta}} \left( \text{erf} \left( \frac{\beta(t_n - t_i)}{\sqrt{\beta \pi}} \right) - \text{erf} \left( \frac{\beta(t_i - t_n)}{\sqrt{\beta \pi}} \right) \right),$$

$$I_{i-1} = -\left( A_{i-1} + B_{i-1} t_{in} \right) \frac{1}{\sqrt{\alpha t_{i-1}}} \left( \frac{\text{e}^{\beta(t_{i-1} - t_n)}}{\sqrt{t_{i-1} - t_n}} \right) - \frac{\sqrt{\beta \pi}}{2 \sqrt{\alpha \beta}} \left( \text{erf} \left( \frac{\beta(t_{i-1} - t_n)}{\sqrt{\beta \pi}} \right) \right). \tag{B3}$$

where

$$A_i = \frac{T_{i+1} - T_{i+1} - T_i}{t_{i+1} - t_i}, B_i = \frac{T_{i+1} - T_i}{t_{i+1} - t_i},$$

$$\alpha = \frac{k_m}{\rho_m C_{pm}}, \beta = \frac{8 \sigma_m \varepsilon_{SB}}{\rho_m C_{pm}}, \varepsilon_{SB} \text{ denotes the Stefan-Boltzmann constant. Values of the thermal properties of the SiN membrane were obtained from reference [41].}$$

References


