Wide-temperature-range perfect superelasticity and giant elastocaloric effect in a high entropy alloy

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ABSTRACT
The high entropy alloy concept offers unique opportunities for the design of advanced materials with unprecedented properties. However, hitherto most of the research efforts are focused on structural materials. Here, by employing the core effect of severe lattice distortion in high entropy alloys, a novel functional NiCuTiHf0.6Zr0.4 high entropy alloy exhibiting intriguing wide-temperature-range perfect superelasticity in a broad temperature range from 263 to 463 K and giant elastocaloric effect with the maximum adiabatic temperature change of 9.3 K is developed. This work opens the door for designing high-performance superelastic and elastocaloric functional materials with the high entropy alloy concept.

IMPACT STATEMENT
A novel functional high entropy alloy with intriguing wide-temperature-range perfect superelasticity and giant elastocaloric effect is successfully developed by employing the severe lattice distortion which leads to high yield strength.

1. Introduction
The concept of high entropy alloys (HEAs) [1,2], also called multi-principal element alloys or complex concentrated alloys, has recently evoked considerable interest in the materials science community [1–5]. HEAs are usually defined as the alloys containing at least five principal elements with the concentration of each element being between 5 and 35 at.% [1]. This HEA concept draws the attention of researchers to the unexplored vast realm of the central region of the hyper-dimensional complex composition space [3], away from the vertices, edges and faces that have already been explored. Owing to the core effects of high configurational entropy, sluggish diffusion and large lattice distortion [3], HEAs may exhibit unexpected properties such as high strength, great ductility, excellent thermal stability [4], and superior wear and corrosion resistance [5]. Therefore, increasing efforts have been devoted to the design of novel HEAs from both the experimental and theoretical perspectives. So far, most of the investigations on HEAs are concentrated on structural properties. Here it is demonstrated that the HEA concept can be successfully applied to achieve wide-temperature-range superelasticity and elastocaloric effect.

Superelasticity represents the large reversible deformation of solid materials in response to the application and removal of a uniaxial stress, which has wide applications in actuators and sensors. Elastocaloric
effect refers to the temperature change of the materials under adiabatic conditions or the entropy change under isothermal conditions upon the application of a uniaxial stress, and it is the most promising caloric effect to be used for environment-friendly and high-efficiency solid-state refrigeration which can replace the present vapor-compression refrigeration that produces environmentally harmful gases [6,7]. Large superelasticity and elastocaloric effect have been obtained in shape memory alloys (SMAs), in which both the superelasticity and elastocaloric effect originate from the stress-induced reversible martensitic transformation (SIMT) [8], with the superelasticity employing the transformation strain and the elastocaloric effect taking advantage of the latent heat of the transformation. However, the prevailing Ni–Ti SMAs only exhibit superelasticity and elastocaloric effect typically within a narrow temperature range (tens of Kelvin) and at temperatures below 363 K [9], except for a nanocrystalline alloy with a different mechanism of continuous second-order stress-induced transition which leads to small superelastic strain and elastocaloric effect [10]. Since materials are often subjected to change in temperature during their service, wide-temperature-range superelasticity is very important for many critical applications in severe environments with a large temperature variation, such as deep space exploration and seismic protection [9]. Furthermore, the temperature region within which elastocaloric effect occurs is of vital importance for the refrigeration capacity in solid-state cooling applications [7,11]. Therefore, it is imperative yet challenging to explore novel materials with wide-temperature-range superelasticity and elastocaloric effect for advanced sensing, actuation and solid-state refrigeration applications.

The temperature range for SIMT ($\Delta T_{SIMT}$) in SMAs is governed by the yield strength ($\sigma_y$) and the sensitivity of critical stress for stress-induced transformation to temperature ($d\sigma/dT$): a higher $\sigma_y$ or a lower $d\sigma/dT$ leads to a wider $\Delta T_{SIMT}$ [12,13]. Strikingly, the core effect of severe lattice distortion in HEAs can lead to remarkable solid solution hardening and thus high yield strength [3], while the sluggish diffusion effect does not prevent the occurrence of diffusionless martensitic transformation [14–16]. Therefore, it is a novel strategy to employ the HEA concept to design alloys with wide-temperature-range SIMT (and thus wide-temperature-range superelasticity and elastocaloric effect). With this strategy, a Ni–Cu–Ti–Hf–Zr HEA with perfect superelasticity in a broad temperature range from 263 to 463 K and giant elastocaloric effect (with the maximum adiabatic temperature change of 9.3 K) in a wide temperature range at least from 303 to 423 K has been developed. This work opens the door for designing novel high-performance superelastic and elastocaloric materials with the HEA concept.

2. Materials and methods

Polycrystalline NiCuTiHf$_{0.6}$Zr$_{0.4}$ HEA button ingots were fabricated by arc melting. Different specimens were cut from the as-cast ingots. The phase transformation temperatures were determined by differential scanning calorimetry (DSC) measurements. The crystal structure evolution was studied by in situ synchrotron high-energy X-ray diffraction (HEXRD) experiments with a wavelength of 0.1173 Å. The superelastic and elastocaloric effects were investigated by compressive tests. The specimens of $\Phi 2 \times 4 \text{ mm}^3$, cut from the middle of the ingots (see Figure S1a) were used. The temperature of the specimen was measured by using a K-type thermocouple attached to the specimen surface. See Supplementary Information for more experimental details.

3. Results and discussion

The as-cast NiCuTiHf$_{0.6}$Zr$_{0.4}$ HEA shows a typical dendritic structure, with the average spanning length and width of the dendrite being 50 and 10 μm, respectively (Figure S1b), which is commonly observed in the as-cast state of HEAs. Energy dispersive spectrometry measurements indicate that the dendritic region is rich in Ni and Hf, while the interdendritic region has higher Cu and Zr concentrations (Figure S1c and Table S1). No nanoprecipitates were observed (Figure S2). DSC measurements reveal that the NiCuTiHf$_{0.6}$Zr$_{0.4}$ HEA shows a reversible thermoelastic martensitic transformation, with martensitic and austenitic transformation start and finish temperatures $M_s$, $M_f$, $A_s$ and $A_f$ being 203, 170, 217 and 254 K, respectively (inset of Figure 1(b)). The thermal hysteresis ($\Delta T_{hys}$), determined by $A_f-M_s$, is 51 K. The latent heat and transformation entropy change are 2.7 J g$^{-1}$ and 11.8 J kg$^{-1}$ K$^{-1}$, respectively.

In order to gain deep insights into the phase transformation from the structural point of view, temperature-dependent in situ HEXRD experiments were performed to trace the crystal structure evolution during cooling and heating (see Figure 1). The main peaks in the diffraction pattern at 303 K (Figure 1(a)) can be well indexed according to the B2 crystal structure with $a_A = 3.134$ Å. In addition, there are also some minor peaks (inset of Figure 1(a)). Comparing the pattern at 123 K (Figure 1(b)) with that at 303 K (Figure 1(a)), one can see that the minor peaks become stronger and new diffraction peaks appear at 123 K. These minor and new peaks can be well indexed according to the B19′ monoclinic structure with $a_M = 3.116$ Å,
$b_M = 4.146 \text{ Å}$, $c_M = 4.855 \text{ Å}$, and $\beta = 100.2^\circ$. As indicated from Figure 1(c), between 303 and 213 K, the phase is predominately austenite. Upon cooling to 203 K, the minor peaks of martensite become much stronger, suggesting that the intensive transformation has already started. Upon further cooling, the intensities of martensitic peaks rapidly increase, implying that the volume fraction of martensite increases. Nevertheless, even at 123 K the martensitic transformation is not completed (the transformation fraction is 40%). During heating, the martensite transforms back to austenite (see Figure 1(d)). When the specimen is heated to 273 K, the martensitic peaks almost disappear except for a few minor peaks, indicating the reverse transformation is nearly completed. Based on the crystal structure information of austenite and martensite, the middle eigenvalue of the transformation stretch matrix is computed \cite{17}. It turns out to be 0.9350, which deviates from 1, indicating the geometric compatibility between austenite and martensite is not good. This may account for the relatively large $\Delta T_{hys}$ and the retained austenite at low temperatures. The above in situ HEXRD experiments clearly demonstrate the reversible transformation between the cubic B2 austenite and the monoclinic B19' martensite during cooling and heating.

To investigate the superelastic properties, the compressive stress–strain response at different temperatures above $A_f$ was examined (see Figure 2). Strikingly, this
NiCuTiHf_{0.6}Zr_{0.4} HEA shows perfect superelasticity in the wide temperature range from 263 to 463 K. The applied strain of about 3% can be fully recovered at all these temperatures (Figure 2 and its inset). The temperature window for the perfect superelasticity is as broad as 200 K, covering the temperature range from subzero temperature, across room temperature, to the temperature region of high-temperature SMAs (above 373 K). This remarkable wide-temperature-range superelasticity has never been achieved before in HEAs. As seen from Figure 2, the superelastic response is dependent on the testing temperature. The critical stress for SIMT increases and the area of hysteresis loop decreases with increasing temperature. It should be noted that, in the present case (Figure 2), the stress at which the stress–strain curve starts to deviate from linearity corresponds to the critical stress for SIMT, not the critical stress for plastic yielding; the plastic yielding occurs at a much higher stress level. The perfect superelasticity can be achieved only if the applied stress is lower than the yield strength, otherwise permanent irrecoverable plastic deformation occurs. Remarkably, even if the applied stress is as high as 1.68 GPa at 443 K, the strain can still be fully recovered upon unloading. This clearly indicates that the yield strength of the present HEA is above 1.68 GPa at this temperature. For comparison, the yield strength of as-cast Ni–Ti SMAs is $\sim 0.85$ GPa [18]. The high yield strength in the present HEA arises from the remarkable solid solution hardening as a result of severe lattice distortion in HEAs.

To reveal the underlying mechanism for the superelasticity, in situ HEXRD experiments during loading and unloading were carried out. The phase is predominately cubic B2 austenite before loading at 303 K (Figure 3(a)). Upon loading to 593 MPa, a new peak with low intensity (at $2\theta$ of $\sim 3^\circ$) appears around the (110)$_A$ peak...
(Figure 3(a)), which corresponds to the (\( \bar{1}11 \))\(_M\) peak of the monoclinic B\( 19' \) martensite. The emergence of this new peak clearly indicates that SIMT occurs. Upon further loading, the intensity of (\( \bar{1}11 \))\(_M\) increases and more peaks of the B\( 19' \) martensite, i.e. (110)\(_M\), (101)\(_M\), (002)\(_M\) and (111)\(_M\), emerge (Figure 3(a)), indicating that the volume fraction of martensite increases. When the stress is increased to 1122 MPa, most of the austenite has transformed to martensite (Figure 3(a)). This is different from the case of temperature-induced transformation for which the transformation fraction is lower. Upon unloading, the intensities of the martensitic peaks become lower while the (110)\(_A\) peak becomes stronger (Figure 3(b)). When the stress is decreased to 430 MPa, the martensitic peaks almost disappear, indicating that all the stress-induced martensite has transformed back to austenite.

![Figure 4](image_url)  
**Figure 4.** (a–h) Adiabatic temperature change (\( \Delta T_{ad} \)) as a function of time during holding, loading to different stresses with a strain rate of 0.125 s\(^{-1}\), holding, unloading with a strain rate of 5.5 s\(^{-1}\) and further holding. The testing temperature is 303 K. The \( \Delta T_{ad} \) values are indicated.
The above *in situ* HEXRD experiments clearly disclose the reversible martensitic transformation process during loading and unloading. Therefore, it is the stress-induced reversible martensitic transformation that is responsible for the perfect superelasticity.

To elucidate the specific reason for the wide temperature window for perfect superelasticity, the crucial factors influencing $\Delta T_{SIMT}$ were scrutinized. It is well acknowledged that the $\Delta T_{SIMT}$ depends on $\sigma_y$, $d\sigma/dT$ and $\Delta T_{hys}$ via the following relation [12,13]:

$$\Delta T_{SIMT} = \sigma_y/(d\sigma/dT) - \Delta T_{hys}$$  \hspace{1cm} (1)

As mentioned above, $\sigma_y$ is at least 1.68 GPa at 443 K; here $\sigma_y = 1.68$ GPa is used to roughly compute $\Delta T_{SIMT}$. In practice, the $d\sigma/dT$ value, which is the inverse of the sensitivity of transformation temperatures to applied stress, is usually determined from the stress vs. temperature phase diagram (Figure S3), which turns out to be 6.97 MPa K$^{-1}$. $\Delta T_{hys}$ is determined from the DSC curves to be 51 K. With these values, $\Delta T_{SIMT}$ is estimated to be $\sim 190$ K. This value is in good agreement with the experimentally observed temperature window (i.e. 200 K). It is clear from Equation (1) that $\Delta T_{SIMT}$ becomes larger if $\sigma_y$ is higher, $d\sigma/dT$ is lower, or $\Delta T_{hys}$ is smaller. Actually, the $d\sigma/dT$ value in the present NiCuTiHf$_{0.6}$Zr$_{0.4}$ HEA is close to or even higher than conventional SMAs [9], and the $\Delta T_{hys}$ of the present alloy is of similar or even higher magnitude as compared with conventional SMAs [19]. Therefore, it is the high yield strength of the present HEA that accounts for the wide temperature window of perfect superelasticity.

Since SIMT occurs in the NiCuTiHf$_{0.6}$Zr$_{0.4}$ HEA, elastocaloric effect is anticipated. Therefore, the elastocaloric effect was examined by monitoring the temperature variation induced by stress changes (see Figures 4 and 5). The loading–unloading procedure for the elastocaloric measurement is illustrated in Figure 5(a) for example and the detailed description can be found in Supplementary Information. The temperature change was determined as the difference between the instant temperature of the specimen and the testing temperature. Considering that the loading and unloading rates are high, this temperature change is approximately taken as the adiabatic temperature change $\Delta T_{ad}$.

Figure 4 shows the $\Delta T_{ad}$ as a function of time for the measurements with different stress levels at 303 K. As can be seen, the $\Delta T_{ad}$ values during both loading and unloading increase monotonically with increasing stress, because the fraction of stress-induced transformation increases. Strikingly, when the applied stress is 1300 MPa, the $\Delta T_{ad}$ during loading reaches +8.8 K and that during unloading is as high as $-9.3$ K (Figure 4(h)). These $\Delta T_{ad}$ values clearly demonstrate a giant elastocaloric effect in
the present NiCuTiHf$_{0.6}$Zr$_{0.4}$ HEA. The magnitude of $\Delta T_{ad}$ during unloading is generally higher than that during loading for all stress levels, because the unloading rate is higher, leading to better adiabatic condition during unloading. The coefficient of performance (COP) of the material, computed from the ratio of $C_p \Delta T_{ad}$ ($C_p$: specific heat capacity) and stress hysteresis loop area, is 4.2, lower than that of Ni–Ti [6]. This is the first time the elastocaloric effect has been achieved in HEAs. The present work opens the avenue for exploring high-performance elastocaloric materials in the vast amount of HEA families.

To examine the temperature range within which the elastocaloric effect occurs, elastocaloric measurements with a maximum stress of 1200 MPa at different temperatures of 303, 323, 343, 363, 383, 403 and 423 K were performed. For clarity, Figure 5 displays the temperature profiles for the measurements at typical temperatures of 303, 363, 403 and 423 K. Under 1200 MPa, the $\Delta T_{ad}$ during loading and unloading at 303 K is +7.3 K and –7.8 K, respectively (Figure 5(a)). As temperature increases, $\Delta T_{ad}$ decreases. This is because under the constant applied stress of 1200 MPa the fraction of SIMT decreases with increasing temperature, since the critical stress for transformation increases. Even at 403 K, $\Delta T_{ad}$ still shows a considerable value of +2.5 K during loading and –2.6 K during unloading (Figure 5(c)). It is worth noting that if a higher stress (e.g. 1500 MPa) is applied at this temperature, a much higher $\Delta T_{ad}$ can be expected. As demonstrated in Figure 5, a considerable elastocaloric effect can be achieved in a wide temperature range at least from 303 to 423 K in the present NiCuTiHf$_{0.6}$Zr$_{0.4}$ HEA. Although the present HEA does not exhibit an elastocaloric effect larger than that of Ni–Ti, its temperature range is at least 40 K wider than that of Ni–Ti SMAs [20] and similar to that of a Cu–Zn–Al SMA with very low $d\sigma/dT$ [21]. This wide temperature range should be quite beneficial for attaining a large refrigeration capacity. The wide $\Delta T_{SIMT}$ mentioned above accounts for the wide temperature range of elastocaloric effect.

4. Conclusions

With the HEA concept, a novel NiCuTiHf$_{0.6}$Zr$_{0.4}$ alloy exhibiting wide-temperature-range superelasticity and giant elastocaloric effect has been developed. This alloy shows perfect superelasticity with fully recoverable strain in a broad temperature range from 263 to 463 K. In situ synchrotron high-energy X-ray diffraction investigation reveals that the superelasticity in this NiCuTiHf$_{0.6}$Zr$_{0.4}$ HEA stems from the stress-induced reversible phase transformation between the cubic B2 austenite and the monoclinic B19' martensite. A giant elastocaloric effect with maximum adiabatic temperature change of 9.3 K is achieved in a wide temperature range at least from 303 to 423 K. The broad temperature window of SIMT is attributed to the core effect of severe lattice distortion in HEAs which leads to remarkable solid solution hardening and high yield strength. This work illuminates the design of novel high-performance superelastic and elastocaloric functional materials with the HEA concept for advanced sensing, actuation and solid-state refrigeration applications.

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