



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

Shaohui Li, Daoyong Cong, Xiaoming Sun, Yong Zhang, Zhen Chen, Zhihua Nie, Runguang Li, Fuqiang Li, Yang Ren & Yandong Wang

To cite this article: Shaohui Li, Daoyong Cong, Xiaoming Sun, Yong Zhang, Zhen Chen, Zhihua Nie, Runguang Li, Fuqiang Li, Yang Ren & Yandong Wang (2019) Wide-temperature-range perfect superelasticity and giant elastocaloric effect in a high entropy alloy, Materials Research Letters, 7:12, 482-489, DOI: [10.1080/21663831.2019.1659436](https://doi.org/10.1080/21663831.2019.1659436)

To link to this article: <https://doi.org/10.1080/21663831.2019.1659436>



© 2019 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group



[View supplementary material](#)



Published online: 27 Aug 2019.



[Submit your article to this journal](#)



Article views: 5434



[View related articles](#)



[View Crossmark data](#)



Citing articles: 52 [View citing articles](#)



ORIGINAL REPORT



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

Shaohui Li ^a, Daoyong Cong ^a, Xiaoming Sun ^a, Yong Zhang ^a, Zhen Chen ^a, Zhihua Nie ^b, Runguang Li ^a, Fuqiang Li ^a, Yang Ren ^c and Yandong Wang ^a

^aBeijing Advanced Innovation Center for Materials Genome Engineering, State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing, People's Republic of China; ^bSchool of Materials Science and Engineering, Beijing Institute of Technology, Beijing, People's Republic of China; ^cX-ray Science Division, Argonne National Laboratory, Argonne, IL, USA

ABSTRACT

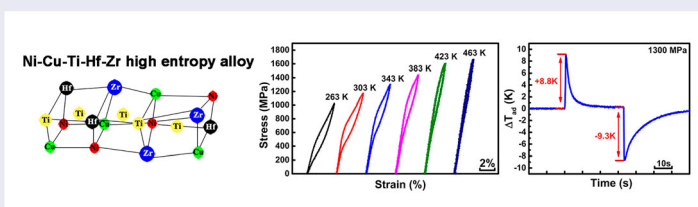
The high entropy alloy concept offers unique opportunities for the design of advanced materials with unprecedented properties. However, hitherto most of the research efforts are focused on structural materials. Here, by employing the core effect of severe lattice distortion in high entropy alloys, a novel functional NiCuTiHf_{0.6}Zr_{0.4} 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.

ARTICLE HISTORY

Received 24 April 2019

KEYWORDS

High entropy alloys; superelasticity; phase transformation; high-energy X-ray diffraction; lattice distortion



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

CONTACT Daoyong Cong dycong@ustb.edu.cn Beijing Advanced Innovation Center for Materials Genome Engineering, State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

Supplemental data for this article can be accessed here. <https://doi.org/10.1080/21663831.2019.1659436>

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 (ΔT_{SIMT}) in SMAs is governed by the yield strength (σ_y) and the sensitivity of critical stress for stress-induced transformation to temperature ($d\sigma/dT$): a higher σ_y or a lower $d\sigma/dT$ leads to a wider ΔT_{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 (ΔT_{hys}), determined by $A_f - M_s$, is 51 K. The latent heat and transformation entropy change are 2.7 J g^{-1} and $11.8 \text{ J kg}^{-1} \text{ K}^{-1}$, 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 $a_A = 3.134 \text{ Å}$. 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 $a_M = 3.116 \text{ Å}$,

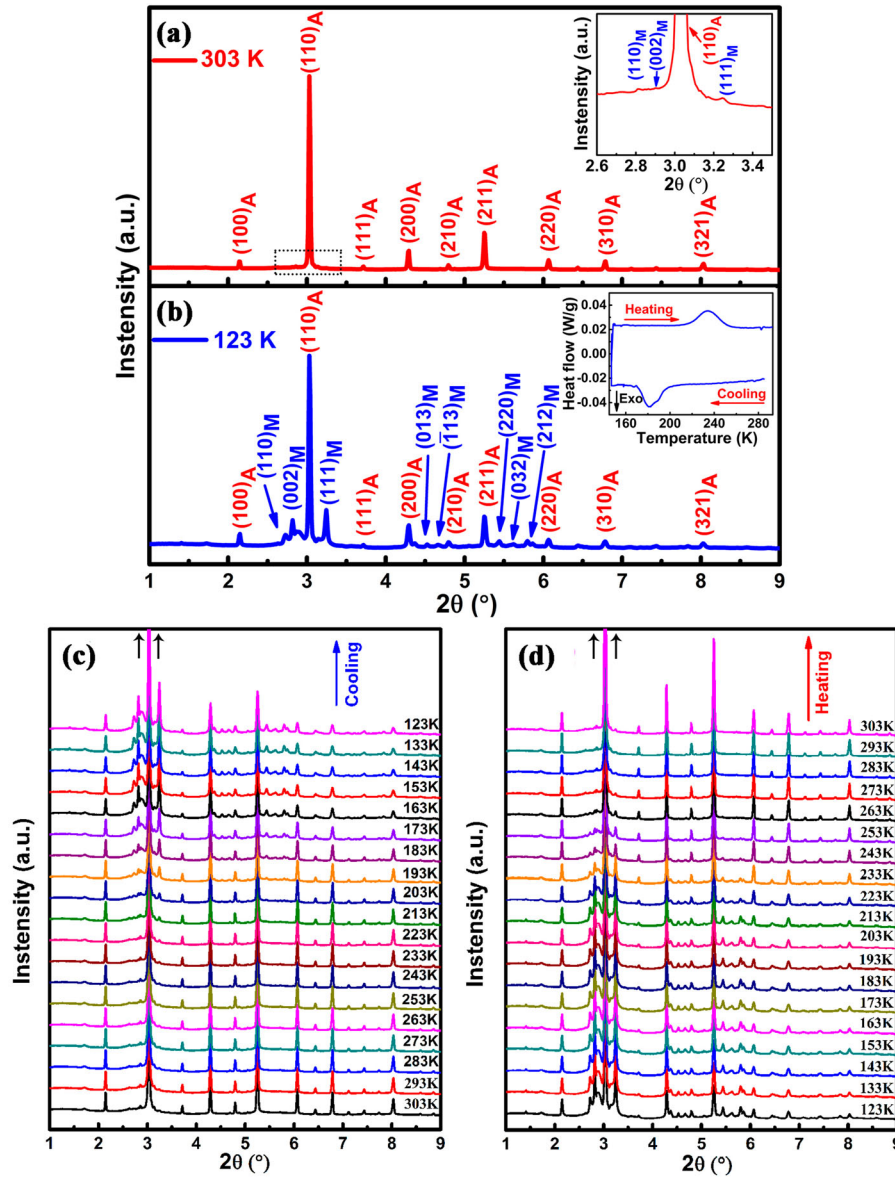


Figure 1. (a, b) HEXRD patterns measured at (a) 303 K and (b) 123 K. The insets of (a) and (b) show the magnified view of the framed zone in (a) and the DSC curves, respectively. 'A' and 'M' in the indices denote austenite and martensite, respectively. (c, d) Evolution of HEXRD patterns during (c) cooling and (d) heating.

$b_M = 4.146 \text{ \AA}$, $c_M = 4.855 \text{ \AA}$, 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 [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 ΔT_{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

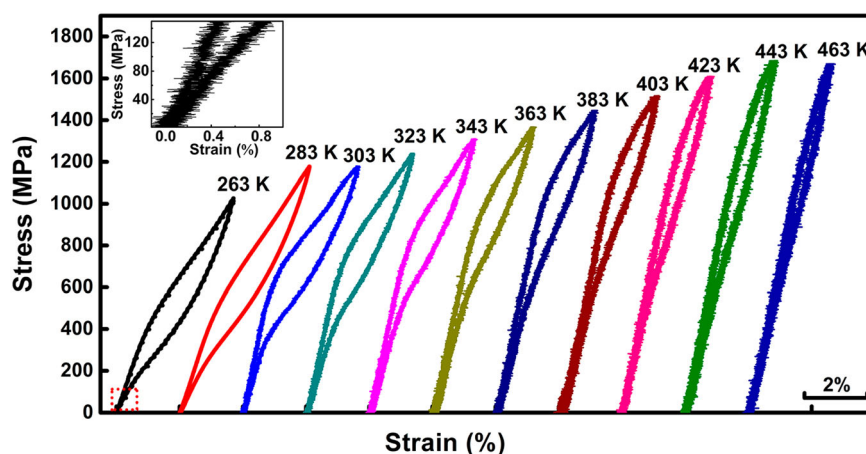


Figure 2. Superelastic stress–strain curves at different temperatures. The inset shows the magnified view of the framed zone.

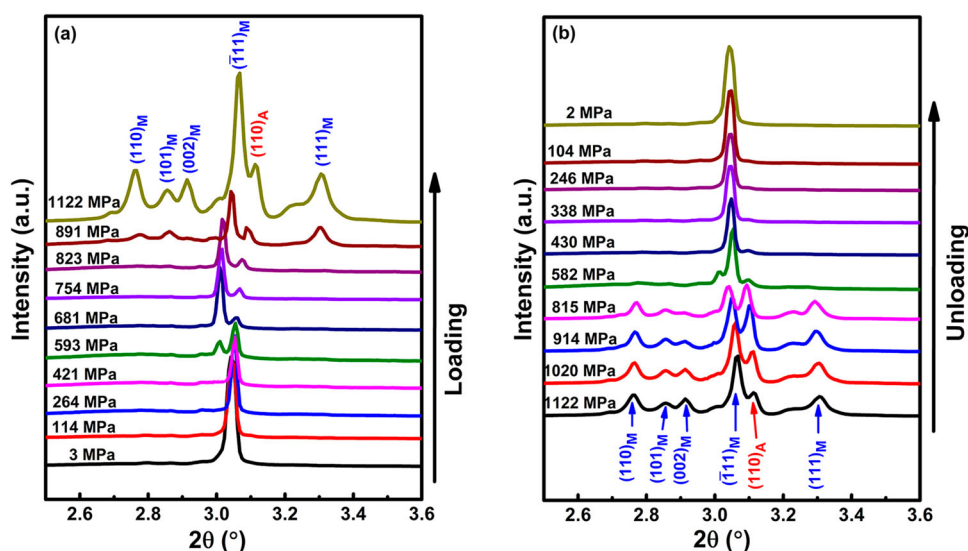


Figure 3. (a, b) Evolution of HEXRD patterns during (a) loading and (b) unloading at 303 K.

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 ~ 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 2θ 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 B19' 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 B19' 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.

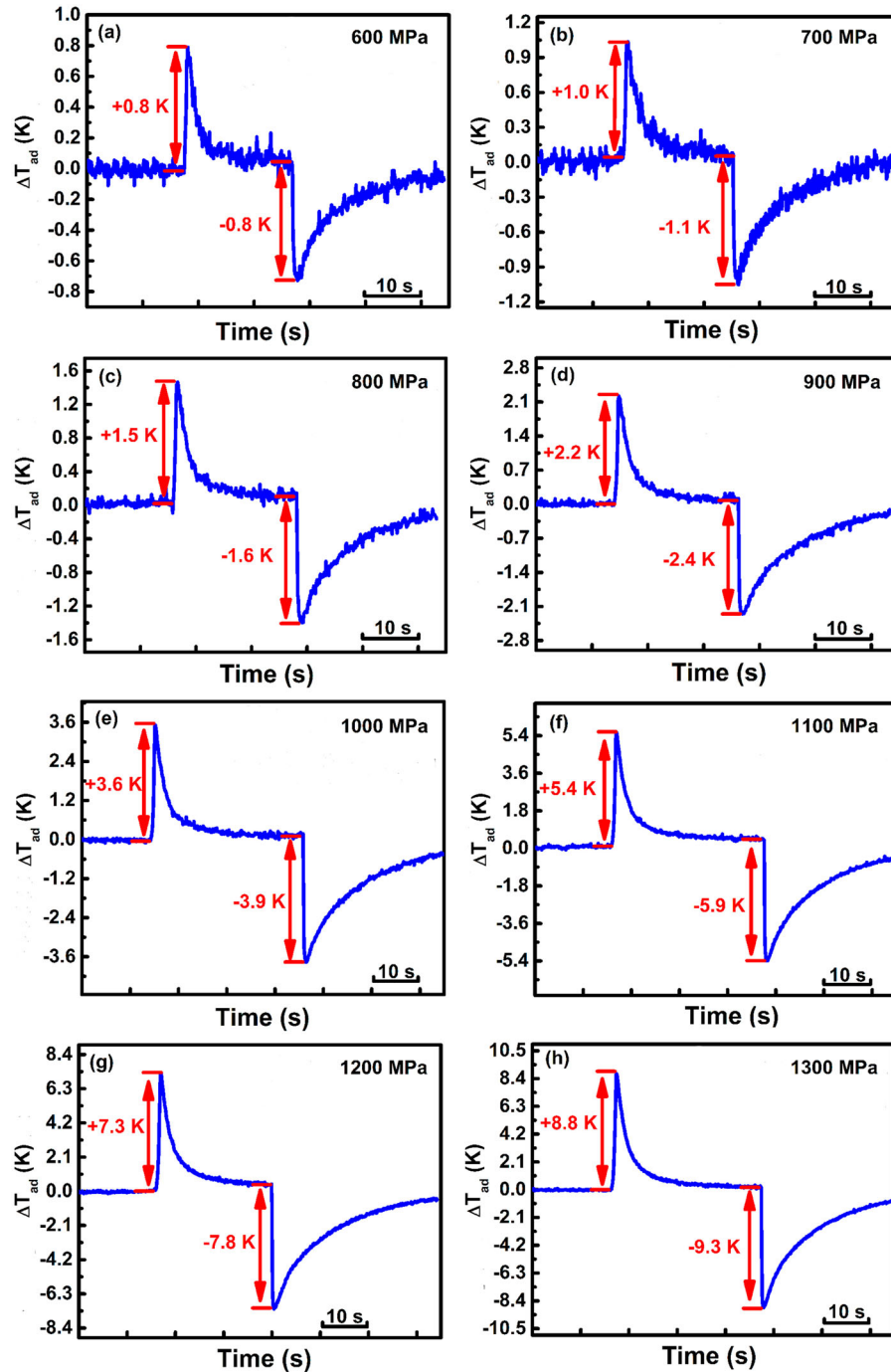


Figure 4. (a–h) Adiabatic temperature change (ΔT_{ad}) as a function of time during holding, loading to different stresses with a strain rate of 0.125 s^{-1} , holding, unloading with a strain rate of 5.5 s^{-1} and further holding. The testing temperature is 303 K. The ΔT_{ad} values are indicated.

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 ΔT_{SIMT} were scrutinized. It is well acknowledged that the ΔT_{SIMT} depends on σ_y , $d\sigma/dT$ and ΔT_{hys} via the following relation [12,13]:

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

As mentioned above, σ_y is at least 1.68 GPa at 443 K; here $\sigma_y = 1.68$ GPa is used to roughly compute ΔT_{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} . ΔT_{hys} is determined from the DSC curves to be 51 K. With these values, ΔT_{SIMT} is estimated to be ~ 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 ΔT_{SIMT} becomes larger if σ_y is higher, $d\sigma/dT$ is lower, or ΔT_{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 ΔT_{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 ΔT_{ad} .

Figure 4 shows the ΔT_{ad} as a function of time for the measurements with different stress levels at 303 K. As can be seen, the ΔT_{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 ΔT_{ad} during loading reaches $+8.8$ K and that during unloading is as high as -9.3 K (Figure 4(h)). These ΔT_{ad} values clearly demonstrate a giant elastocaloric effect in

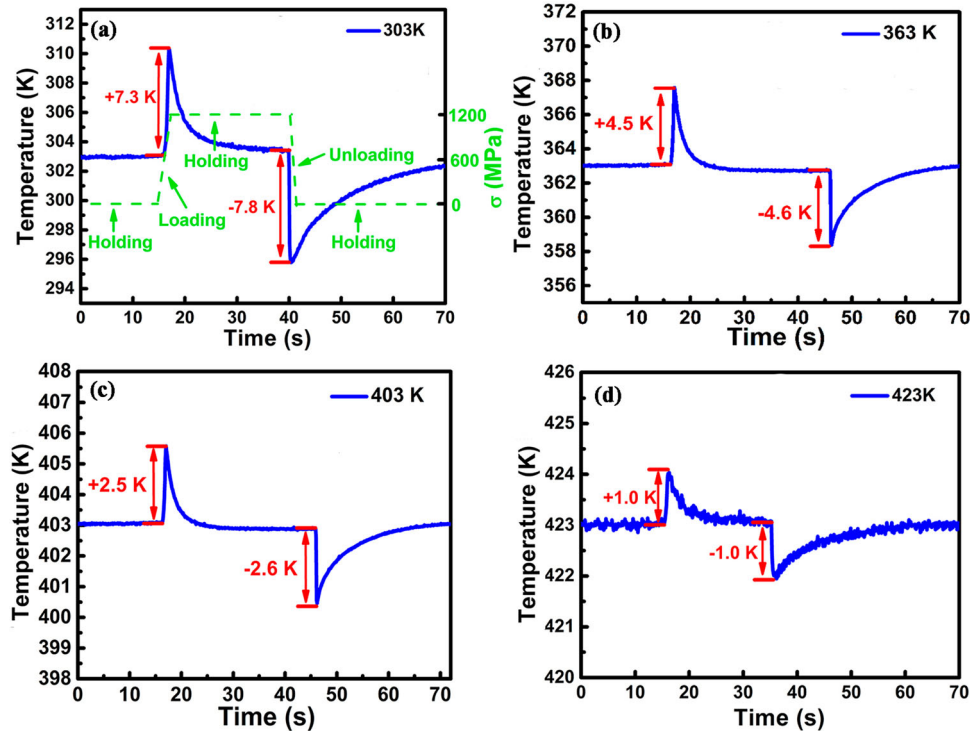


Figure 5. (a–d) Temperature versus time profiles measured during holding, loading with a strain rate of 0.125 s^{-1} to 1200 MPa, holding, unloading with a high strain rate of 5.5 s^{-1} and further holding, at different temperatures. The loading–unloading procedure for (a) is illustrated. The ΔT_{ad} values are indicated.

the present NiCuTiHf_{0.6}Zr_{0.4} HEA. The magnitude of ΔT_{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 ΔT_{ad} during loading and unloading at 303 K is +7.3 K and −7.8 K, respectively (Figure 5(a)). As temperature increases, ΔT_{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, ΔT_{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 ΔT_{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 ΔT_{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.

Acknowledgments

The use of the advanced photon source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science, under Contract No. DE-AC02-06CH11357.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the National Natural Science Foundation of China [grant numbers 51822102, 51731005, and 51831003] and the Fundamental Research Funds for the Central Universities (No. FRF-TP-18-008C1).

ORCID

Shaohui Li  <http://orcid.org/0000-0003-3078-0338>

Runguang Li  <http://orcid.org/0000-0001-5395-0470>

References

- [1] Yeh JW, Chen SK, Lin SJ, et al. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. *Adv Eng Mater.* 2004;6:299–303.
- [2] Cantor B, Chang ITH, Knight P, et al. Microstructural development in equiatomic multicomponent alloys. *Mater Sci Eng A.* 2004;375-377:213–218.
- [3] Miracle DB, Senkov ON. A critical review of high entropy alloys and related concepts. *Acta Mater.* 2017;122:448–511.
- [4] Zou Y, Ma H, Spolenak R. Ultrastrong ductile and stable high-entropy alloys at small scales. *Nat Commun.* 2015;6:7748.
- [5] Lin CM, Tsai HL. Evolution of microstructure, hardness, and corrosion properties of high-entropy Al_{0.5}CoCrFeNi alloy. *Intermetallics.* 2011;19:288–294.
- [6] Energy savings potential and RD&D opportunities for Non-Vapor-Compression HVAC technologies. Report of the U.S. Department of Energy; March 2014. Available from: <https://energy.gov/eere/buildings/downloads/non-vapor-compression-hvac-technologies-report>.
- [7] Mañosa L, Planes A. Materials with giant mechanocaloric effects: cooling by strength. *Adv Mater.* 2017;29:1603607.
- [8] Chluba C, Ge W, de Miranda RL, et al. Ultralow-fatigue shape memory alloy films. *Science.* 2015;348:1004–1007.

- [9] Omori T, Ando K, Okano M, et al. Superelastic effect in polycrystalline ferrous alloys. *Science*. [2011](#);333:68–71.
- [10] Ahadi A, Kawasaki T, Harjo S, et al. Reversible elastocaloric effect at ultra-low temperatures in nanocrystalline shape memory alloys. *Acta Mater*. [2019](#);165:109–117.
- [11] Smith A, Bahl CRH, Björk R, et al. Materials challenges for high performance magnetocaloric refrigeration devices. *Adv Energy Mater*. [2012](#);2:1288–1318.
- [12] Saghaian SM, Karaca HE, Tobe H, et al. Effects of aging on the shape memory behavior of Ni-rich $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ single crystals. *Acta Mater*. [2015](#);87:128–141.
- [13] Liu Y, Galvin SP. Criteria for pseudoelasticity in near-equiatomic NiTi shape memory alloys. *Acta Mater*. [1997](#);45:4431–4439.
- [14] Firstov GS, Kosorukova TA, Koval YN, et al. High entropy shape memory alloys. *Mater Today: Proceedings*. [2015](#);2:S499–S503.
- [15] Canadinc D, Trehern W, Ma J, et al. Ultra-high temperature multi-component shape memory alloys. *Scr Mater*. [2019](#);158:83–87.
- [16] Chen CH, Chen YJ. Shape memory characteristics of $(\text{TiZrHf})_{50}\text{Ni}_{25}\text{Co}_{10}\text{Cu}_{15}$ high entropy shape memory alloy. *Scr Mater*. [2019](#);162:185–189.
- [17] Song Y, Chen X, Dabade V, et al. Enhanced reversibility and unusual microstructure of a phase-transforming material. *Nature*. [2013](#);502:85–88.
- [18] Jiang S, Zhang Y. Microstructure evolution and deformation behavior of as-cast NiTi shape memory alloy under compression. *Trans Nonferrous Met Soc China*. [2012](#);22:90–96.
- [19] Otsuka K, Ren X. Physical metallurgy of Ti–Ni-based shape memory alloys. *Prog. Mater. Sci*. [2005](#);50:511–678.
- [20] Wu Y, Ertekin E, Sehitoglu H. Elastocaloric cooling capacity of shape memory alloys–role of deformation temperatures, mechanical cycling, stress hysteresis and inhomogeneity of transformation. *Acta Mater*. [2017](#);135:158–176.
- [21] Mañosa L, Jarque-Farnos S, Vives E, et al. Large temperature span and giant refrigerant capacity in elastocaloric Cu–Zn–Al shape memory alloys. *Appl Phys Lett*. [2013](#);103:211904.