A strategy of designing high-entropy alloys with high-temperature shape memory effect

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Shape memory effect, the ability to recover a pre-deformed shape on heating, results from a reversible martensitic transformation between austenite and martensite phases. Here, we demonstrate a strategy of designing high-entropy alloys (HEAs) with high-temperature shape memory effect in the CrMnFeCoNi alloy system. First, we calculate the difference in Gibbs free energy between face-centered-cubic (FCC) and hexagonal-close-packed (HCP) phases, and find a substantial increase in thermodynamic equilibrium temperature between the FCC and HCP phases through composition tuning, leading to thermally- and stress-induced martensitic transformations. As a consequence, the shape recovery temperature in non-equiatomic CrMnFeCoNi alloys can be increased to 698 K, which is much higher than that of conventional shape memory alloys (SMAs) and comparable to that of B2-based multi-component SMAs containing noble metals (Pd, Pt, etc.) or refractory metals (Zr, Hf, etc.).

This result opens a vast field of applications of HEAs as a novel class of cost-effective high-temperature SMAs.

The concept of high-entropy alloys (HEAs) and complex, concentrated alloys (CCAs), which consist of multi-principal elements with near equiatomic composition, have generated substantial interest for the exploration of immense composition space offered by multiple principal elements and the development of new materials with exceptional properties. Cr20Mn20Fe20Co20Ni20 alloy (in at.%) with a simple lattice of FCC crystal structure, is one of the most extensively studied single-phase HEAs. At low temperatures, this alloy exhibits excellent fracture toughness and tensile properties due to deformation-induced nano-twinning, which is favored in low stacking fault energy materials. Theoretical approaches predict that Gibbs free energy between the FCC and HCP phases ($\Delta G_{\text{HCP-FCC}}$) in the CrMnFeCoNi alloy system can be widely changed through tuning of the alloy composition. For example, the $\Delta G_{\text{HCP-FCC}}$ calculation has been used to design metastable dual-phase HEAs with an excellent combination of strength and ductility, which benefit from the massive solid solution strengthening of a HEA and transformation-induced plasticity effect of a metastable FCC phase. Other metastable alloys like FeMn-based alloys, β-Ti alloys, or Mg alloys, have shown their potential for the shape memory effect and superelasticity, which are attributed to reversible martensitic transformations. Although these types of functional applications were recently investigated in B2-based multi-component alloys with increased configurational entropy, very little attention has been paid to the shape memory effect in 3d transition metal-based HEAs (3d HEAs), which generally exhibit better deformability and lower processing cost compared to previously developed shape memory alloys (SMAs).

Here, we develop 3d HEAs exhibiting an appreciable shape memory effect in a wide composition range and characterize their shape memory properties. First, we calculate $\Delta G_{\text{HCP-FCC}}$ and thermodynamic equilibrium
temperature, \( T_0 \), in the various non-equiatomic CrMnFeCoNi HEAs and evaluate the composition dependence of \( \Delta G_{\text{HCP-FCC}} \) using CALPHAD methodology with the TCHEA3 database. Second, we carefully reveal the reversible martensitic transformation between the FCC and HCP phases in the compositionally tuned 3d HEAs using in situ X-ray diffraction (XRD) and thermal analyses. Third, we confirm the shape recovery on heating after pre-deformation in the developed non-equiatomic CrMnFeCoNi HEAs. Indeed, we can manipulate the shape memory effect of the HEAs to have exceptionally wide range of transformation temperatures such as reverse transformation finish temperature from 435 to 698 K. These findings suggest that non-equiatomic CrMnFeCoNi HEAs are promising candidates for cost-effective shape memory actuators even at elevated temperatures.

**Results**

**Design of high-entropy alloys with shape memory effect.** Figure 1a shows the predicted \( \Delta G_{\text{HCP-FCC}} \) at 300 K using CALPHAD methodology with the TCHEA3 database in five hypothetical alloy systems of 3d HEAs: (MnFeCoNi)\(_{100-x}\)Cr\(_x\), (CrFeCoNi)\(_{100-x}\)Mn\(_x\), (CrMnCoNi)\(_{100-x}\)Fe\(_x\), (CrMnFeNi)\(_{100-x}\)Co\(_x\), and (CrMnFeCo)\(_{100-x}\)Ni\(_x\). To evaluate the relative influence of each principal element on \( \Delta G_{\text{HCP-FCC}} \), the atomic fraction of the fifth element was modified between 10 and 30 at.% while that of other four elements was kept in equimolar ratio. The CALPHAD prediction showed that \( \Delta G_{\text{HCP-FCC}} \) can be significantly reduced when the Ni content decreases or the Co content increases from the equiatomic composition, suggesting that \( \Delta G_{\text{HCP-FCC}} \) is significantly reduced by the replacement of Ni with Co. Figure 1b shows \( \Delta G_{\text{HCP-FCC}} \) for a series of non-equiatomic CrMnFeCoNi alloys with different Cr/Mn ratios from 0.6 to 3, which were predicted to form a single-phase FCC solid solution. All the alloy series exhibited a pronounced decrease in \( \Delta G_{\text{HCP-FCC}} \) as the Ni content was replaced with Co. With an increase in the Cr/Mn ratio up to 3, a more drastic decrease in \( \Delta G_{\text{HCP-FCC}} \) was predicted in the alloys with a lower Ni/Co ratio. Compared with \( \text{Cr}_{30}\text{Mn}_{20}\text{Fe}_{20}\text{Co}_{20}\text{Ni}_{30} \) alloy, the value of \( \Delta G_{\text{HCP-FCC}} \) in several compositions was calculated to be negative. These results imply that the HCP phase can be favored over the FCC phase at 300 K in a wide composition range of non-equiatomic CrMnFeCoNi HEAs.

Figure 1c shows the temperature dependence of \( \Delta G_{\text{HCP-FCC}} \) in the \( \text{Cr}_{30}\text{Mn}_{20}\text{Fe}_{20}\text{Co}_{20}\text{Ni}_{30} \) alloy system (x = 0, 5, 10, and 20 at.%). The \( \text{Cr}_{30}\text{Mn}_{20}\text{Fe}_{20}\text{Co}_{20}\text{Ni}_{30} \) alloy showed a positive value of \( \Delta G_{\text{HCP-FCC}} \) at lower temperatures. By replacing Ni with Co, the atomic fraction of the fifth element was increased up to 30 at.% while that of other four elements was kept in equimolar ratio. The CALPHAD prediction showed that \( \Delta G_{\text{HCP-FCC}} \) is significantly reduced by the replacement of Ni with Co. With an increase in the Cr/Mn ratio up to 3, a more drastic decrease in \( \Delta G_{\text{HCP-FCC}} \) was predicted in the alloys with a lower Ni/Co ratio. Compared with \( \text{Cr}_{30}\text{Mn}_{20}\text{Fe}_{20}\text{Co}_{20}\text{Ni}_{30} \) alloy, the value of \( \Delta G_{\text{HCP-FCC}} \) in several compositions was calculated to be negative. These results imply that the HCP phase can be favored over the FCC phase at 300 K in a wide composition range of non-equiatomic CrMnFeCoNi HEAs.
with Co in the Cr$_{20}$Mn$_{20}$Fe$_{20}$Co$_{30}$Ni$_{10}$ system, system, $T_0^{CAL}$ increased from 102 K for the Cr$_{15}$Mn$_{25}$Fe$_{20}$Co$_{30}$Ni$_{10}$ alloy and to 666 K for the Cr$_{30}$Mn$_{10}$Fe$_{20}$Co$_{40}$ alloy. The range of $T_0^{CAL}$ was wider than the range of the experimentally measured $T_0$ in conventional SMAs such as TiNi (227–359 K)\textsuperscript{29}, CuAlNi (241–407 K)\textsuperscript{30}, and FeMnSi (363–493 K)\textsuperscript{31,32}. These predictions suggest the possibility of developing non-equiautomatic CrMnFeCoNi HEAs for functional applications employing the shape memory effect (or pseudoelasticity) since the martensitic transformation from the FCC to HCP phase could occur by undercooling below $T_0^{CAL}$.

To understand the relationship among the increase in $T_0^{CAL}$, microstructure, and martensitic transformation behavior in the non-equiautomatic CrMnFeCoNi HEAs, we prepared Cr$_{30}$Mn$_{10}$Fe$_{20}$Co$_{40}$ alloy. The range of $T_0^{CAL}$ was wider than the range of the experimentally measured $T_0$ in conventional SMAs such as TiNi (227–359 K)\textsuperscript{29}, CuAlNi (241–407 K)\textsuperscript{30}, and FeMnSi (363–493 K)\textsuperscript{31,32}. These predictions suggest the possibility of developing non-equiautomatic CrMnFeCoNi HEAs for functional applications employing the shape memory effect (or pseudoelasticity) since the martensitic transformation from the FCC to HCP phase could occur by undercooling below $T_0^{CAL}$.

Reversible martensitic transformation. Figure 3a shows the XRD patterns of the Ni5 alloy collected in the temperature range from 100 to 700 K. The alloy was initially heated to 700 K under vacuum, then the XRD patterns were obtained during cooling to 100 K and then subsequent heating to 700 K. Compared to the Ni10 alloy, which was a single-phase FCC solid solution during cooling down to 100 K (Figure S1), the Ni5 alloy exhibited diffraction peaks of the HCP phase when the temperature decreased to 200 K. With further cooling to 100 K, the Ni5 alloy exhibited a dual-phase FCC-HCP structure with an average grain size of ~100 μm, while the as-annealed Ni0 alloy exhibited a dual-phase FCC–HCP structure with a thermally induced HCP phase fraction of ~20 vol. %.

These results reveal a reversible martensitic transformation between the FCC and HCP phases in the Ni5 alloy.

A similar phase transition was observed in the Ni0 alloy (Fig. 3b). The alloy showed higher onset temperatures, where the HCP phase appears (300 K) and disappears (700 K), than the Ni5 alloy, indicating an enhanced HCP phase stability, as predicted in Fig. 1c. The unit cell parameters were determined from the XRD pattern at 300 K to be $a = 3.58747 \pm 0.00001$ Å for the FCC phase and $a = 2.5369 \pm 0.0004$ Å and $c = 4.0944 \pm 0.0018$ Å for the HCP phase. The Ni5 alloy cooled by liquid nitrogen exhibited a dual-phase FCC–HCP structure with a thermally induced HCP phase fraction of ~20 vol. % from EBSD analysis and a homogeneous elemental distribution confirmed by electron probe microanalysis (Figure S2). These results reveal a reversible martensitic transformation between the FCC and HCP phases in the Ni5 alloy.

Figure 4a shows the results of thermal analysis of the Ni10, Ni5, and Ni0 alloys measured by differential scanning calorimetry (DSC). An exothermic peak during cooling and an endothermic peak during heating were observed for the Ni5 and Ni0 alloys, indicating forward and reverse martensitic transformations, respectively. The martensitic transformation start temperature ($M_s$), martensitic transformation finish temperature ($M_f$), reverse transformation start temperature ($A_s$), and reverse transformation finish temperature ($A_f$) obtained from the DSC

![Figure 2](image-url)
with a decrease in the Ni/Co ratio, and an increasing trend was also seen in the experimentally determined forward (~9.0 J·g\(^-1\)L\(^-1\)) and reverse transformation (~6.0 J·g\(^-1\)L\(^-1\)) were very stable as compared to Co-32Ni alloy where the transformation peak rapidly decayed by thermal cycling\(^{34}\). Thus, the martensitic transformation is highly reversible in the present alloys.

We compared the characteristic temperatures of martensitic transformation measured by DSC and a thermo-mechanical analyzer (Figure S3) with \(T_{o}^{CAL}\) as a function of Ni content in the Cr\(_{20}\)Mn\(_{20}\)Fe\(_{20}\)Co\(_{20}\)Ni\(_{20}\) HEA system (Fig. 4c). The thermodynamic equilibrium temperature \(T_{o} = (M_{s} + A_{f})/2\) was calculated from the DSC results to be 366 and 509 K for the Ni5 and Ni0 alloys, respectively. The predicted \(T_{o}^{CAL}\) monotonically increased with a decrease in the Ni/Co ratio, and an increasing trend was also seen in the experimentally determined \(T_{o}\). In addition to the Ni5 and Ni0 alloys, the Cr\(_{20}\)Mn\(_{20}\)Fe\(_{20}\)Co\(_{20}\)Ni\(_{20}\) alloy, which was predicted to show the lowest \(\Delta G_{HCP-FCC}^{CAL}\) (Fig. 1b) and the highest \(T_{o}^{CAL}\) (Fig. 1d), exhibited higher \(M_{s}(479 K), A_{f}(698 K),\) and \(T_{o}(589 K)\) than the Ni0 alloy (Fig. 4d). These results validate the CALPHAD prediction in Fig. 1 that the HCP phase stability as well as \(T_{o}\) can be tailored through composition tuning in 3d HEAs.

Shape memory effect. Figure 5a–c shows the relative change in the specimen length (\(\Delta L/L_{0}\), where \(\Delta L\) is the change in length and \(L_{0}\) is the initial length) of the as-annealed Ni10, Ni5, and Ni0 alloys measured by a thermo-mechanical analyzer. The as-annealed Ni10 and Ni5 alloys exhibited thermal expansion curves similar to the single-phase Cr\(_{20}\)Mn\(_{20}\)Fe\(_{20}\)Co\(_{20}\)Ni\(_{20}\) HEA\(^{35}\), indicating that no phase transformation occurred during heating to 1000 K and cooling to room temperature. However, the as-annealed Ni0 alloy displayed a dilation during heating and a contraction during cooling. The onset temperatures of the dilation and contraction were 531 and 399 K, respectively.

Figure 5d–f shows the thermal expansion and contraction curves of the pre-strained Ni10, Ni5, and Ni0 alloys deformed with a compressive strain of about 1% at room temperature. In contrast to the pre-strained Ni10 alloy, the pre-strained Ni5 and Ni0 alloys exhibited a significant dilation during heating and a pre-strained Ni0 alloy showed a contraction during cooling. The onset temperatures of the dilation for Ni5 and Ni0 alloys and the contraction for Ni0 alloy were 402, 542, and 397 K, respectively. The three as-annealed alloys and the pre-strained Ni0 alloy exhibited thermal expansion curves similar to the single-phase Cr\(_{20}\)Mn\(_{20}\)Fe\(_{20}\)Co\(_{20}\)Ni\(_{20}\) HEA system (Fig. 4c). The thermodynamic equilibrium temperature \(T_{o} = (M_{s} + A_{f})/2\) was calculated from the DSC results to be 366 and 509 K for the Ni5 and Ni0 alloys, respectively. The predicted \(T_{o}^{CAL}\) monotonically increased with a decrease in the Ni/Co ratio, and an increasing trend was also seen in the experimentally determined \(T_{o}\). In addition to the Ni5 and Ni0 alloys, the Cr\(_{20}\)Mn\(_{20}\)Fe\(_{20}\)Co\(_{20}\)Ni\(_{20}\) alloy, which was predicted to show the lowest \(\Delta G_{HCP-FCC}^{CAL}\) (Fig. 1b) and the highest \(T_{o}^{CAL}\) (Fig. 1d), exhibited higher \(M_{s}(479 K), A_{f}(698 K),\) and \(T_{o}(589 K)\) than the Ni0 alloy (Fig. 4d). These results validate the CALPHAD prediction in Fig. 1 that the HCP phase stability as well as \(T_{o}\) can be tailored through composition tuning in 3d HEAs.
The onset temperatures of the dilation and contraction in the dual-phase alloys (Fig. 5c,e,f) agreed well with $A_s$ and $M_s$ measured by DSC analysis, indicating that the dilation and contraction are associated with the reverse and forward martensitic transformations between the FCC and HCP phases, respectively.

The dilation observed during heating was stronger in the pre-strained Ni5 and Ni0 alloys than the as-annealed Ni0 alloy. The small dilation in the as-annealed Ni0 alloy was due to the reverse martensitic transformation of the thermally induced HCP phase. The significant dilation in the pre-strained Ni5 and Ni0 alloys originated from the reverse martensitic transformation of the stress-induced HCP phase. When the initial FCC phase of the Ni5 and Ni0 alloys was strained, the HCP phase was stress-induced by the movement of Shockley partial dislocations preferentially in the direction of the applied shear stress. The reverse martensitic transformation of the stress-induced HCP phase was achieved by the reverse motion of the partial dislocations along this direction. Thus, the shape recovery of the Ni5 and Ni0 alloys can be attributed to the formation of the stress-induced HCP phase during a shape change and the reverse martensitic transformation of the stress-induced HCP phase on heating.
Recovery strain. Figure 6a–c shows the recovery strain in the Ni10, Ni5, and Ni0 alloys measured by bending rectangular specimens with dimensions of 3 × 0.6 × 40 mm³ at two different deformation temperatures, room (293 K) and liquid-nitrogen (77 K) temperatures. The Ni10 alloy deformed at 293 K exhibited no recovery strain, while the alloy deformed at 77 K showed a recovery strain with a maximum value of ~1.8%. The Ni5 and Ni0 alloys at both temperatures exhibited recovery strain with maximum values of ~2.0% and ~1.1% when deformed at 293 K and ~1.4% and ~1% when deformed at 77 K, respectively. The Ni5 alloy deformed at 293 K displayed the largest recovery strain among the alloys (Fig. 6d and Supplementary Video 1). The recovery strain in the alloys increased with an increase in the pre-strain, but remained stable after reaching a pre-strain of ~3.0%.

With a decrease in deformation temperature from 293 to 77 K, the recovery strain decreased by ~30% for the Ni5 alloy. The alloy showed a dual-phase structure with an HCP fraction of ~20 vol.% after cooling to 77 K (Figure S2). Since the thermally induced HCP phase suppresses the stress-induced martensitic transformation and the stress-induced HCP phase interacts with the pre-existing phase boundaries during pre-straining, the stress-induced martensitic transformation and the reverse martensitic transformation of the stress-induced HCP phase are interrupted in the dual-phase alloys. Thus, the Ni5 alloy exhibited a smaller recovery strain when deformed at 77 K. The reason why the recovery strain is almost the same in the Ni0 alloy deformed at both temperatures is unclear, but the smaller recovery strain in the Ni0 alloy than the Ni5 alloy may be associated with the higher fraction (~40 vol.%) of the thermally induced HCP phase at room temperature (Fig. 2d).

The Ni10 alloy exhibited the largest recovery strain among the alloys deformed at 77 K. The pre-strained Ni10 alloy at 77 K exhibited distinct dilation during heating in the thermo-mechanical analysis (Figure S3), indicating a reverse martensitic transformation from the HCP to FCC phase. However, a forward martensitic transformation was not observed in the in situ XRD (Figure S1), DSC analysis (Fig. 4a), and the XRD pattern of the alloy cooled by liquid nitrogen (not shown), implying that the Ni10 alloy did not undergo any transformation.
HCP phase, which is one of the reasons why the Ni10 alloy deformed at 77 K exhibited a similar recovery strain as the Ni5 alloy deformed at 293 K.

**Discussion**

In this work, we have developed novel shape memory alloys in the CrMnFeCoNi alloy system using the CALPHAD methodology by calculating the $\Delta G_{\text{HCP-FCC}}$ variation for a wide composition range of 3d HEAs. In comparison with the previously reported SMAs with martensitic transformation between the FCC and HCP phases, the recovery strain in the Ni5 alloy deformed at 293 K was found to be much larger than that in CoNi$_{34.38-40}$, FeMn$_{41}$, and FeMnC$_{42}$ alloys (less than 0.3%$^{38,42}$) and comparable to that in polycrystalline FeMnSi-based alloys ($\sim 2.0\%^{43}$) containing Si up to about 11 at.%$^{43,44}$, used for industrial applications like pipe joining and seismic damping$^{44,45}$. For CoNi and FeMn binary alloys with a poor shape memory effect, the addition of a significant amount of Si led to a remarkable improvement in the recovery strain. The roles of Si in the shape memory effect have been determined to be$^{41-46}$ 1) suppressing the magnetic transition from paramagnetism to anti-ferromagnetism, which inhibits the martensitic transformation due to magnetic ordering, 2) enhancing the reversibility of the martensitic transformation by decreasing the volume change between the FCC and HCP phases, and 3) solid-solution strengthening of the FCC phase to suppress the glide motion of dislocations.

The Cr$_{20}$Mn$_{20}$Fe$_{20}$Co$_{20}$Ni$_{20}$ alloy was predicted to show a very low magnetic transition temperature of 23 K by the addition of Cr and Mn$^{47}$, implying that the martensitic transformation is not strongly affected by the magnetic transition in the non-equiatomic CrMnFeCoNi HEAs. The volume changes between the FCC and HCP phases calculated from the lattice constants$^{46}$ were 1.15 $\pm$ 0.07% and 1.05 $\pm$ 0.2% for the Ni5 and Ni0 alloys, respectively. These values are much lower than the values of 2.26% for the Fe$_{74.5}$Mn$_{24.5}$ alloy and 1.42% for the Fe$_{65.5}$Mn$_{25.1}$Si$_{9.4}$ alloy$^{46}$, which indicates an enhanced reversibility of the martensitic transformation in the Ni5 and Ni0 alloys without the addition of Si. The yield strengths of the Cr$_{20}$Mn$_{20}$Fe$_{20}$Co$_{20}$Ni$_{20}$ alloy (from 160 MPa$^{48}$ to 260 MPa$^{49}$ for a grain size from 140 to 16 $\mu$m, respectively) and the Ni5 alloy (218 MPa for a grain size of 18 $\mu$m, not shown) were comparable to that of the Fe$_{71.1}$Mn$_{10}$Si$_{11.1}$C$_{1.1}$ alloy (200 MPa$^{46}$) but much higher than that of the Fe$_{75.7}$Mn$_{24.3}$ (80 MPa$^{43}$) and Co$_{68.8}$Si$_{31.1}$ (85 MPa$^{48}$) alloys. The higher yield strength resulted from the enhanced solid solution strengthening of the HEA, which contributes to the stress-induced martensitic transformation as a predominant deformation mode in the pre-straining. Therefore, the large recovery strain in non-equiatomic CrMnFeCoNi HEAs with shape memory effect can be attributed to the reduced volume change between the FCC and HCP phases and the improved yield strength of the FCC phase.

**Figure 6.** Recovery strain of 3d HEAs. (a–c) Recovery strain in (a) Ni10, (b) Ni5, and (c) Ni0 alloys measured by a bending test at 293 and 77 K, respectively. All three alloys clearly exhibit a shape memory effect when deformed at both temperatures except for the Ni10 alloy deformed at 293 K. (d) Appearance of the deformed Ni5 alloys at 293 K before and after heating to 873 K for 10 min. The pre-strain and recovery strain of each specimen are marked in the figure.
Cr$_{30}$Mn$_{10}$Fe$_{20}$Co$_{40}$ alloys, 1 kg in weight, were produced by high frequency vacuum induction melting. The as-cast ingots were homogenized at 1473 K for 24 h under Ar atmosphere followed by water quenching. The homogenized ingots were subjected to multi-pass caliber rolling at 673 K to form squared bars. The phase constitutions in the temperature ranges 100–700 K for Ni$_{10}$ alloy, Ni$_{5}$ alloy, Ni$_{0}$ alloy, Cr$_{30}$Mn$_{10}$Fe$_{20}$Co$_{40}$ Ni$_{x}$ alloys (x = 0, 5, 10, and 20 at.%), and Cr$_{30}$Mn$_{10}$Fe$_{20}$Co$_{40}$ Ni$_{x}$ alloys, 1 kg in weight, were produced by high frequency vacuum induction melting. The as-cast ingots with cross-sections of $30 \times 30$ mm$^2$ were homogenized at 1473 K for 24 h under Ar atmosphere followed by water quenching. The homogenized ingots were subjected to multi-pass caliber rolling at 673 K to form squared bars, with cross-sections of $14 \times 14$ mm$^2$, then annealed at 1373 K for 1 h.

**Microstructural characterization.** The phase constitutions in the temperature ranges 100–700 K for the Ni$_{10}$ alloy and 100–873 K for the Ni$_{0}$ alloy were confirmed by low- and high-temperature XRD experiments. The as-cast ingots were polished after heat treatment to a mirror-like finish. The XRD patterns were recorded using a Siemens D5000 diffractometer with Cu K$_\alpha$ radiation at 40 kV and 30 mA. The XRD patterns were analyzed using the Rietveld method to determine the lattice parameters and the volume fraction of each phase. The microstructure was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

**Methods**

**Materials processing.** Ingots of a series of Cr$_{30}$Mn$_{10}$Fe$_{20}$Co$_{40}$Ni$_{x}$ alloys (x = 0, 5, 10, and 20 at.%) and Cr$_{30}$Mn$_{10}$Fe$_{20}$Co$_{40}$Ni$_{x}$ alloys, 1 kg in weight, were produced by high frequency vacuum induction melting. The as-cast ingots with cross-sections of $30 \times 30$ mm$^2$ were homogenized at 1473 K for 24 h under Ar atmosphere followed by water quenching. The homogenized ingots were subjected to multi-pass caliber rolling at 673 K to form squared bars, with cross-sections of $14 \times 14$ mm$^2$, then annealed at 1373 K for 1 h.

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JEOL, Tokyo, Japan) equipped with EBSD. The EBSD analysis was performed at an accelerated voltage of 20 kV and step size of 1 μm. Electron probe microanalysis (JXA-8500F, JEOL Ltd, Tokyo, Japan) was conducted to analyze the elemental distribution of the alloys.

**Evaluation of the shape memory effect.** A thermal expansion test of the as-annealed and pre-strained specimens was performed using a thermo-mechanical analyzer (TMA; Q400, TA Instruments, New Castle, DE, USA) at a constant heating/cooling rate of 5 K-min⁻¹ with a specimen dimension of 4 × 4 × 10 mm³. The pre-strained specimens with a strain of about 1% were prepared by compressive tests at a strain rate of 1 × 10⁻³ s⁻¹. The recovery strain was evaluated by a bending test at room and liquid-nitrogen temperatures. Specimens with dimensions of 3 × 0.6 × 40 mm³ were bent using steel pieces with different radii. For the bending test at liquid-nitrogen temperature, the specimens were immersed in liquid nitrogen for 10 min and bent using stainless steel tweezers. The bending strains in the deformed specimens before and after heating to 873 K for 10 min were calculated from the radius of curvature (\( r = t/2r \times 100 \), where \( r \) is the specimen thickness and \( r \) is the radius of curvature) measured by an optical microscope with image analysis software (Figure S4).

**Data Availability**
The data that support the findings of this study are available from the corresponding authors, at jilee@pusan.ac.kr or Tsuchiya.Koichi@Nims.go.jp, upon reasonable request.

**References**
1. Senkov, O., Miller, J., Miracle, D. & Woodward, C. Accelerated exploration of multi-principal element alloys with solid solution phases. Nat. Commun. 6, 7529 (2015).
2. Senkov, O. N., Wilks, G. B., Miracle, D. B., Chuang, C. P. & Liaw, P. K. Refractory high-entropy alloys. Intermetallics 18, 1758–1765 (2010).
3. Zhang, Y. et al. Influence of chemical disorder on energy dissipation and defect evolution in concentrated solid solution alloys. Nat. Commun. 6, 8736 (2015).
4. Gludovatz, B. et al. Exceptional damage-tolerance of a medium-entropy alloy CrCoNi at cryogenic temperatures. Nat. Commun. 7, 10602 (2016).
5. Miracle, D. B. & Senkov, O. N. A critical review of high entropy alloys and related concepts. Mater. Sci. Eng. A 575, 213–218 (2004).
6. Tracy, C. L. et al. High pressure synthesis of a hexagonal close-packed phase of the high-entropy alloy CrMnFeCoNi. Nat. Commun. 8, 15634 (2017).
7. Zhang, F. et al. Polymorphism in a high-entropy alloy. Nat. Commun. 8, 15687 (2017).
8. Lee, J. I., Oh, H. S. & Park, E. S. Manipulation of \( S \) and \( A \) temperatures. Appl. Phys. Lett. 109, 061906 (2016).
9. Oh, H. S. et al. Lattice distortions in the FeCoNiCrMn high entropy alloy studied by theory and experiment. Entropy 18, 321 (2016).
10. Laplanche, G., Kostka, A., Horst, O. M., Figge, G. & George, E. P. Microstructure evolution and critical stress for twinning in the CrMnFeCoNi high-entropy alloy. Acta Mater. 118, 152–163 (2016).
11. Gludovatz, B. et al. A fracture-resistant high-entropy alloy for cryogenic applications. Science 345, 1153–1158 (2014).
12. Otto, F. et al. The influences of temperature and microstructure on the tensile properties of a CoCrFeMnNi high-entropy alloy. Acta Mater. 61, 5743–5755 (2013).
13. Huang, S. et al. Temperature dependent stacking fault energy of FeCrCoNiMn high entropy alloy. Scr. Mater. 108, 44–47 (2015).
14. Zaddach, A. J., Niu, C., Koch, C. C. & Irving, D. L. Mechanical properties and stacking fault energies of NiFeCrCoMn high-entropy alloy. JOM 65, 1780–1789 (2013).
15. Li, Z., Körmann, F., Grabowski, B., Neugebauer, J. & Raabe, D. Ab initio assisted design of quinary dual-phase high-entropy alloys with transformation-induced plasticity. Acta Mater. 136, 262–270 (2017).
16. Wei, D. et al. Novel Co-rich high performance twinning-induced plasticity (TWIP) and transformation-induced plasticity (TRIP) high-entropy alloys. Scr. Mater. 165, 39–43 (2019).
17. Li, Z., Pradeep, K. G., Deng, Y., Raabe, D. & Tasan, C. C. Metastable high-entropy dual-phase alloys overcome the strength–ductility trade-off. Nature 534, 227 (2016).
18. Li, Z., Tasan, C. C., Pradeep, K. G. & Raabe, D. A TRIP-assisted dual-phase high-entropy alloy: grain size and phase fraction effects on deformation behavior. Acta Mater. 131, 323–335 (2017).
19. Otsuka, H. et al. Effects of alloying additions on Fe-Mn-Si shape memory alloys. ISIJ Int. 30, 674–679 (1990).
20. Omori, T. et al. Superelastic effect in polycrystalline ferrous alloys. Science 333, 68–71 (2011).
21. Kim, H., Ikehara, Y., Kim, J., Hosoda, H. & Miyazaki, S. Martensitic transformation, shape memory effect and superelasticity of Ti-Nb binary alloys. Acta Mater. 54, 2419–2429 (2006).
22. Ogawa, Y., Ando, D., Sutou, Y. & Koike, J. A lightweight shape-memory magnesium alloy. Science 353, 368–370 (2016).
23. Firstov, G. S., Kosorukova, T. A., Koval, Y. N. & Odinov, V. V. High entropy shape memory alloys. Mater. Today: Proc. 2S, S499–S503 (2015).
24. Canadine, D. et al. Ultra-high temperature multi-component shape memory alloys. Scr. Mater. 158, 83–87 (2019).
25. Kim, W. et al. Correlation between the thermal and superelastic behavior of Ni50-xTi5xZr15Cu3 shape memory alloys. Intermetallics 107, 24–33 (2019).
26. Hong, S. H. et al. Influence of Zr content on phase formation in the Co-Cr-Fe-Mn-Ni multi-component system. Acta Mater. 128, 327–336 (2017).
27. Frenzel, J. et al. Influence of Ni on martensitic phase transformations in NiTi shape memory alloys. Acta Mater. 58, 3444–3458 (2010).
28. Recarte, V. et al. Thermodynamics of thermally induced martensitic transformations in Cu−Al−Ni shape memory alloys. Acta Mater. 52, 3941–3948 (2004).
29. Cotes, S., Guillermiet, A. F. & Sade, M. Phase stability and fcc/hcp martensitic transformation in Fe−Mn−Si alloys: Part I. Experimental study and systematics of the \( A_1 \) and \( A_2 \) temperatures. J. Alloy Compd. 278, 231–238 (1998).
30. Wen, Y. H. et al. Large recovery strain in Fe−Mn−Si-based shape memory steels obtained by engineering annealing twin boundaries. Nat. Commun. 5, 4964 (2014).
31. Laplanche, G., Volkert, U. F., Eggeler, G. & George, E. P. Oxidation behavior of the CrMnFeCoNi high-entropy alloy. Oxid. Met. 85, 629–645 (2016).
32. Liu, Y. et al. Thermally induced fcc ↔ hcp martensitic transformation in Co-Ni. Acta Mater. 53, 3625–3634 (2005).
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Author Contributions

J.I.L. and K.T. processed the research, J.I.L. and W.T. processed the alloys with help from T.S. and H.M., thermodynamic calculation was performed by J.I.L., H.S.O. and E.S.P., in situ X-ray diffraction measurement was conducted by T.H. and Y.M., all authors analyzed and interpreted the data, and J.I.L. and K.T. wrote the paper.

Additional Information

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