Supplementary Information

Ultrahigh cyclability of a large elastocaloric effect in multiferroic phase-transforming materials

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S1. Effect of B microalloying and Fe substitution on martensitic transformation temperature

Figure S1 shows the DSC curves of the Ni-Mn-In-based alloys. As can be seen, B microalloying leads to the decrease of the transformation temperature. To compensate the effect of B microalloying on transformation temperature, Fe was substituted for both In and Ni to controllably increase the transformation temperature. By deliberately tuning the amount of B microalloying and Fe substitution, a (Ni\(_{51}\)Mn\(_{33}\)In\(_{14}\)Fe\(_2\))\(_{99.4}\)B\(_{0.6}\) alloy with an austenite transformation finish temperature (\(A_f\)) slightly below room temperature was obtained.

Figure S1. DSC curves for the Ni\(_{51.5}\)Mn\(_{33}\)In\(_{15.5}\), (Ni\(_{51.5}\)Mn\(_{33}\)In\(_{15.5}\))\(_{99.4}\)B\(_{0.6}\), Ni\(_{51}\)Mn\(_{33}\)In\(_{14}\)Fe\(_2\), and (Ni\(_{51}\)Mn\(_{33}\)In\(_{14}\)Fe\(_2\))\(_{99.4}\)B\(_{0.6}\) alloys, recorded with a heating and cooling rate of 10 K min\(^{-1}\). The Curie temperature \(T_c\) can be determined from the inflection point on the DSC curves, as indicated by the arrow.
S2. Effect of B microalloying on mechanical properties.

Figure S2 shows the stress-strain curves recorded at a strain rate of $10^{-3}$ s$^{-1}$. To avoid the effect of stress-induced martensitic transformation, the testing temperature was selected to be 60 K higher than $A_f$ for each alloy. While the Fe substitution leads to slight improvement of mechanical properties, the B microalloying remarkably enhances the mechanical properties. As can be seen, the (Ni$_{51}$Mn$_{33}$In$_{14}$Fe$_2$)$_{99.4}$B$_{0.6}$ alloy shows very good mechanical properties.

Figure S2. Compressive stress-strain curves for the Ni$_{51.5}$Mn$_{33}$In$_{15.5}$, Ni$_{51}$Mn$_{33}$In$_{14}$Fe$_2$, and (Ni$_{51}$Mn$_{33}$In$_{14}$Fe$_2$)$_{99.4}$B$_{0.6}$ alloys, respectively, measured at $A_f + 60$ K ($A_f$: austenitic transformation finish temperature) with a strain rate of $10^{-3}$ s$^{-1}$. 
S3. Effect of B microalloying on microstructure

Figure S3 demonstrates the scanning electron microscopy (SEM) images for the boron-free and boron-microalloyed samples. Clearly, boron microalloying is very effective in grain refinement. The Ni$_{51.5}$Mn$_{33}$In$_{15.5}$ and Ni$_{51}$Mn$_{33}$In$_{14}$Fe$_2$ alloys show a coarse-grained microstructure, with a grain size of ~100 μm. In contrast, the grains in the boron-microalloyed (Ni$_{51.5}$Mn$_{33}$In$_{15.5}$)$_{99.4}$B$_{0.6}$ and (Ni$_{51}$Mn$_{33}$In$_{14}$Fe$_2$)$_{99.4}$B$_{0.6}$ alloys are remarkably refined, and the average grain size is only ~15 μm. In addition, boron microalloying results in the formation of precipitates, mainly at grain boundaries. Energy dispersive spectroscopy (EDS) analysis demonstrates that these precipitates are rich in Ni and lean in In, as shown in Table S1.

Figure S3. Room-temperature SEM secondary electron images for the (a) Ni$_{51.5}$Mn$_{33}$In$_{15.5}$, (b) Ni$_{51}$Mn$_{33}$In$_{14}$Fe$_2$, (c) (Ni$_{51.5}$Mn$_{33}$In$_{15.5}$)$_{99.4}$B$_{0.6}$ and (d) (Ni$_{51}$Mn$_{33}$In$_{14}$Fe$_2$)$_{99.4}$B$_{0.6}$ alloys, respectively. Note the different scale bars in (a-c) and (d). The dashed frame in (d) denotes the region from which the 3D-APT tip specimen was taken.
Table S1. Compositions of the matrix and precipitates obtained from EDS analysis.

| Composition       | Matrix (at.%) | Second phase (at.%) |
|-------------------|---------------|---------------------|
|                   | Ni  | Mn  | In  | Fe  | Ni  | Mn  | In  | Fe  |
| Ni\textsubscript{51.5}Mn\textsubscript{33}In\textsubscript{15.5} | 51.17 | 32.36 | 16.47 | -  | -   | -   | -   | -   |
| (Ni\textsubscript{51.5}Mn\textsubscript{33}In\textsubscript{15.5})\textsubscript{99.4}B\textsubscript{0.6} | 48.04 | 34.20 | 17.76 | -  | 81.08 | 15.59 | 3.33 | -   |
| Ni\textsubscript{51}Mn\textsubscript{33}In\textsubscript{14}Fe\textsubscript{2} | 49.84 | 33.53 | 14.60 | 2.03 | -   | -   | -   | -   |
| (Ni\textsubscript{51}Mn\textsubscript{33}In\textsubscript{14}Fe\textsubscript{2})\textsubscript{99.4}B\textsubscript{0.6} | 47.73 | 32.68 | 16.64 | 2.95 | 71.94 | 18.97 | 2.85 | 6.24 |
S4. Characterization of the precipitates in the boron-microalloyed samples

Figure S4a and S4b shows the room-temperature TEM bright field images for the (Ni$_{51}$Mn$_{33}$In$_{14}$Fe$_2$)$_{99.4}$B$_{0.6}$ alloy. The selected area electron diffraction patterns of the matrix and the precipitates are demonstrated in the insets of Figure S4a and S4b, respectively. It is revealed that the precipitates exhibit a face-centered-cubic structure. Figure S4c shows the high-resolution TEM image of the interface area, which reveals that the interface between the precipitates and the matrix is incoherent with a large lattice misfit. Therefore, it is expected that the precipitates have little contribution to the strengthening of the alloys.

\[ \text{Figure S4. (a) TEM bright field image, showing the precipitates and matrix, for the (Ni$_{51}$Mn$_{33}$In$_{14}$Fe$_2$)$_{99.4}$B$_{0.6}$ alloy. The inset shows the selected area electron diffraction pattern of the matrix (indexed according to the cubic L2$_1$ Heusler structure of austenite). (b) TEM bright field image focusing on a single precipitate. The insets show the selected area electron diffraction patterns of the precipitate, from the zone axes $[\bar{1}12]$ and $[\bar{1}23]$, respectively. (c) High-resolution TEM image showing the interface between the precipitate and the matrix. The inset shows the inverse Fast Fourier Transforms (FFT) pattern corresponding to the area enclosed in the red frame.} \]
S5. Cyclability of elastocaloric effect in (Ni_{51.5}Mn_{35}Sn_{12.5}Fe_{1})_{99.4}B_{0.6} alloy

Figure S5. Temperature variation during cyclic loading, holding, and unloading, shown as a function of time for the (Ni_{51.5}Mn_{35}Sn_{12.5}Fe_{1})_{99.4}B_{0.6} alloy. The testing temperature is 317 K, the maximum applied stress is 400 MPa and the strain rate is $2.8 \times 10^{-2}$ s$^{-1}$. The whole experiment was conducted by three consecutive tests each consisting of 1000 cycles (denoted by 1st, 2nd and 3rd, respectively, in the figure), and for each test the measurement was interrupted after every 300 cycles to save the data while the sample temperature was still being monitored during that time period.
S6. Magnetic-filed-induced phase transformation in the (Ni\textsubscript{51}Mn\textsubscript{33}In\textsubscript{14}Fe\textsubscript{2})\textsubscript{99.4}B\textsubscript{0.6} alloy

Figure S6a shows the temperature dependence of magnetization ($M$-$T$ curve) under different magnetic fields for the (Ni\textsubscript{51}Mn\textsubscript{33}In\textsubscript{14}Fe\textsubscript{2})\textsubscript{99.4}B\textsubscript{0.6} alloy. As can be seen, the high-temperature austenite shows ferromagnetic feature, while the low-temperature martensite is in a weak magnetic state. Consequently, there is a large magnetization difference ($\Delta M$) between the two phases across transformation. It is clear that application of magnetic fields drastically decreases the phase transformation temperatures. This indicates that if a magnetic field is applied at a constant temperature close to $A_s$ (austenitic transformation start temperature), there will be a magnetic-filed-induced transformation from martensite to austenite. To confirm this, we performed isothermal magnetization ($M$-$H$ curve) measurements, as shown in Figure S6b. Evidently, magnetic-field-induced transformation from the low-magnetization martensite to high-magnetization austenite occurs in the temperature range 230-250 K.

**Figure S6.** (a) $M$-$T$ curves measured under magnetic fields of 0.05 T, 5 T, and 14 T, respectively, for the (Ni\textsubscript{51}Mn\textsubscript{33}In\textsubscript{14}Fe\textsubscript{2})\textsubscript{99.4}B\textsubscript{0.6} alloy. (b) $M$-$H$ curves measured at 223 K, 230 K, 237 K, and 250 K, respectively, for the (Ni\textsubscript{51}Mn\textsubscript{33}In\textsubscript{14}Fe\textsubscript{2})\textsubscript{99.4}B\textsubscript{0.6} alloy.