Stable elastocaloric effect under tensile stress of iron-palladium alloy and its *in situ*

X-ray observation

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Abstract

The elastocaloric effect under tensile stress along the [001] direction has been investigated in an Fe-31.2Pd (at%) alloy, which exhibits a weak first-order martensitic transformation at 230 K from a face-centered cubic structure to a face-centered tetragonal ($c/a < 1$) structure. A stable temperature variation of 1.9 K was observed at room temperature (~ 288 K) up to 10000 cycles of sinusoidal tensile stress (200 MPa). The stress-strain curve shows **a macroscopic strain of 1.2% under 200 MPa with a negligible stress hysteresis**. The macroscopic strain coincides with the lattice strain obtained by *in situ* X-ray diffraction. A significant extension of the 200 reflection, perpendicular to the tensile direction, was observed. This peak extension could be the way the specimen realizes a high elastic strain, even under tensile stress.

Keywords: Elastocaloric effect; Elastic behavior; Martensitic phase transformation; Shape memory alloy

1. Introduction

Due to their high efficiency and environmental friendliness, solid-state cooling systems hold great potential to replace conventional vapor-compression cooling systems [1]. The refrigerant of a solid-state cooling system uses one of the following caloric effects: magnetocaloric [2,3], electrocaloric [4,5], barocaloric [6,7], or elastocaloric [8,9], depending on the type of external field. Recently, elastocaloric effects in shape memory alloys (SMAs) have been attracting increasing attention due to the pronounced release and absorption of latent heat associated with stress-induced martensitic transformations (MTs) [10,11].

However, the use of first-order MTs in SMAs has several drawbacks for solid-state refrigeration. One is the hysteresis loss, which appears in the stress-strain curves [12–14]. The hysteresis loss directly deteriorates the coefficient of performance of the material (COP), which is defined as the ratio between cooling power and input power [15,16]. Another drawback is the accumulation of defects due to the repeating stress-induced MTs. The accumulation of defects could severely deteriorate the elastocaloric effect and result in fracture of the material. As an example, the adiabatic temperature variation caused by the elastocaloric effect of a $\text{Ni}_{50}\text{Fe}_{19}\text{Ga}_{27}\text{Co}_4$ (at%) single crystal has been reported to decrease by approximately 30% after a fatigue test of up to 3000 cycles [17]. Hence, it is extremely important to reduce the hysteresis loss and accumulation of defects of refrigerant materials.

One solution to reduce both the hysteresis loss and accumulation of defects is to use materials with a weak first-order MT. Recently, a significant elastocaloric effect has

been observed for an Fe-31.2Pd (at%) alloy [18,19], which exhibits a weak first-order MT from a face-centered cubic (FCC) structure to a face-centered tetragonal (FCT) structure with tetragonality (c/a) smaller than one [20,21]. This alloy shows a significant softening of the elastic constant C' due to the band Jahn-Teller effect; therefore, the elastic strain along the [001] direction depends strongly on temperature, which causes significant elastocaloric effect. Since the elastocaloric effect of the Fe-31.2Pd (at%) alloy under compressive stress is mainly caused by elastic strain, the hysteresis loss is negligible and the accumulation of defects is negligible as well, unless the stress exceeds the yield stress. Due to these characteristic features, an Fe-Pd alloy exhibiting FCC-FCT transformation could be a potential refrigerant material for solid-state cooling systems.

Recently, several devices using elastocaloric effects in SMAs have been proposed. Since a larger surface-to-volume ratio enables faster heat transfer, these devices use tensile stress instead of compressive stress to induce MTs [22–24]. Although Fe-Pd alloys exhibit excellent elastocaloric effects under compressive stress, the caloric effects under tensile stress have yet not been examined. Since the FCT phase is contracted along the [001] direction compared with the FCC phase [25], both the elastic behavior and elastocaloric effect under tensile stress could be significantly different from those under compressive stress.

The present study was carried out to reveal the elastocaloric effect and elastic deformation behavior of a single crystal of Fe-31.2Pd (at%) alloy under tensile stress. We focused on the stability of the elastocaloric effect. For this purpose, up to 10000

cyclic tests were carried out. In addition, to understand the deformation behavior under tensile stress, *in situ* high-energy X-ray diffraction (HE-XRD) experiments were carried out under tensile stress.

2. Experiments

An ingot of an Fe-31.2Pd (at%) alloy was prepared by arc melting using a Fe rod (99.998%) and a Pd sheet (99.99%) as starting materials. A single-crystalline boule was grown using a floating zone method at a growth rate of 3 mm h⁻¹ and its orientation was determined by the back-reflection Laue method. After homogenization at 1375 K for 24 h, the boule was quenched in ice water to retain the disordered parent phase. From the boule, two single-crystalline sheets were cut by electrical discharge machining, with the dimensions of 0.2 mm × 4.2 mm × 25.2 mm (Specimen A) and 0.2 mm × 3.8 mm × 28.0 mm (Specimen B). All the edges were parallel to one of the <001> directions.

The stress-strain curves were measured using an Instron-5966 testing machine at a strain rate of 10⁻³ s⁻¹ at room temperature (RT), and the strain was recorded using an advanced video extensometer.

The temperature variation during stress application and removal was measured using a stress-controlled dynamic testing machine (BOSE 3510) at RT in a stress range of 12–200 MPa and frequencies of 0.02, 0.05, 0.1, and 0.2 Hz. These frequencies correspond to the average strain rates of 8×10⁻⁴, 3.2×10⁻⁴, 1.6×10⁻⁴, and 8×10⁻³ s⁻¹, respectively. One side of the specimen was coated with a thin black paint,

and the temperature of this side was monitored using a multi-detector infrared (IR) camera FLIR SC7700M.

In situ HE-XRD experiments (photon energy = 105.7 keV) were performed at the beam line of 11-ID-C, Advanced Photon Source, Argonne National Laboratory. Uniaxial tensile stress was applied at RT along the [001] direction of the single crystal sheet, and the incident beam was close to the [010] direction. A PerkinElmer α -Si flat-panel large-area detector was used to collect two-dimensional (2D) diffraction patterns. At each stress state, the sample was oscillated $\pm 5^\circ$ around the [001] or [100] axes in order to obtain the Bragg reflections. The software package FIT2D was used for the diffraction data analysis.

3. Results

3.1 Elastic deformation and elastocaloric effect

Figure 1 shows the stress-strain curve of the Fe-31.2Pd (at%) single crystalline sheet (Specimen A) at RT. In the measurement, a maximum tensile stress of 200 MPa was applied along the [001] direction. There is no detectable hysteresis between stress applying and removing processes. The elastic strain under 200 MPa reached 1.2%.

In order to detect the elastocaloric effect under tensile stress, the spatial-resolved temperature variation was measured. Figure 2(a) shows a representative IR image obtained during the test. The dashed white rectangle in Figure 2(a) represents the specimen. Figure 2(b) shows a series of thermal images of the white rectangle area monitored during the unloading process from 200 MPa at a frequency of 0.02 Hz. The

time interval between two adjacent images is ~ 4 s. As the stress varies at a rate of $\sim 8 \text{ MPa s}^{-1}$, the stress difference between two adjacent panels is $\sim 32 \text{ MPa}$. It is observed in Figure 2(b) that the temperature of the specimen decreases with decreasing stress. We notice a slight difference in temperature between the center and near the edge of the specimen. This difference is due to the heat transfer between the specimen and the surroundings. If we ignore the heat transfer effect, the temperature of the specimen is almost homogeneous through the stress-removal process. Such a homogeneous temperature variation is due to a macroscopically homogeneous strain in the specimen. In the case of a typical first-order MT in Ti-Ni SMAs, a distinct inhomogeneity in temperature appears between the transformed and untransformed regions as reported by Shaw et al. [26]. We have confirmed that the reverse temperature variation during the stress-application process is also homogeneous. Details of the thermal images during the loading and unloading processes at different frequencies (0.02, 0.05, 0.1, and 0.2 Hz) can be observed in the supplementary Videos 1–4.

We evaluated the average temperature within the rectangular areas marked in Figure 3(a) with R_S and R_A . The former represents the temperature of the specimen T_S and the latter represents the ambient temperature T_A . Figures 3(a)–(d) show the evaluated temperature of the specimen T_S as a function of time. The measurements were carried out by applying a cyclic tensile stress with a maximum tensile stress of 200 MPa. The ambient temperature T_A is indicated by a dashed red line in each panel. It is observed that T_S oscillates sinusoidally around T_A . This implies that the energy

dissipation during the cyclic stress application is negligible for this specimen.

The maximum temperature variation ($\Delta T_{\max}$) is indicated on the right side of each panel, and is plotted as a function of frequency in Figure 3(e). It is noted that $\Delta T_{\max}$ increases with increasing frequency and is ~ 2 K under a frequency of 0.2 Hz. The increase of $\Delta T_{\max}$ with frequency is due to time dependence of heat transfer to the surroundings.

During the measurement of the temperature variation, we also monitored the stress-strain curves, and the result is shown in Figure 4. We noticed that the deformation behavior is quite insensitive to the frequency. This behavior is different from that of stress-induced first-order MT, where the stress required for the transformation tends to increase with increasing strain rate [27,28].

In order to determine the long-term stability of the elastic strain and elastocaloric effect, a fatigue test (up to 10000 cycles) was conducted at a frequency of 0.2 Hz at RT using Specimen B. The stress-strain curves recorded after steps of 2000 cycles are presented in Figure 5(a). As expected, no significant change in the stress-strain characteristics is observed even after 10000 cycles. Figure 5(b) shows the temperature variation during the cycles (5 cycles for every 1000 cycles are shown). The ambient temperature varied slightly due to the long testing time as indicated by the dashed curve. It should be noted that the temperature variation ($\Delta T_{\max} \approx 2.1$ K) in the 10000th cycle is the same as that in the first cycle. Considering the elastic-like deformation of this specimen, we may expect an even longer stability.

3.2 Structural change under tensile stress

From the stress-strain curves shown in [Figure 1](#), we may speculate that the deformation is mainly caused by lattice strain. In addition, based on the homogeneity of the temperature observed in the spatially resolved temperature image, we may also speculate that the lattice strain is almost homogeneous in the specimen. To confirm these speculations, we performed *in situ* HE-XRD.

[Figure 6\(a\)](#) shows a representative 2D XRD pattern obtained under the lowest tensile stress of 1.5 MPa (this stress was applied to hold the specimen). The tensile direction is indicated by an arrow. The regions around the 002 and 202 reflections are obtained by oscillating [around](#) the [100] axis, while the region around the 200 reflection is obtained by oscillating [around](#) the [001] axis. [Figures 6\(b\)–\(d\)](#) are the magnification of the highlighted areas in [Figure 6\(a\)](#). We notice streaks along the [101] and $[\bar{1}01]$ directions around the Bragg reflections. These streaks have been reported in electron microscope observation, and are related to the tweed microstructure of the Fe-Pd alloys [\[29,30\]](#). The change in the profile of the 002 reflection by the application of tensile stress can be observed in [Figures 6\(b'\) and \(b''\)](#). The 002 peak moves towards the origin of the reciprocal space as stress increases. This is due to the lattice distortion under tensile stress. In addition, we notice that the intensity of the streaks around this peak decreases [as the stress increases](#). The hardening of the elastic constants under stress could be the reason for the weakening of the streaks, which will be discussed in section 4.2. A significant change of the shape occurs for the 200 and 202 reflections, as observed in [Figures 6\(c'\), \(c''\), \(d'\), and \(d''\)](#). The peaks are

extended perpendicular to the tensile axis. The extension of the Bragg reflections suggests a broadening of the lattice spacing under tensile stress. When the stress is removed, the peak profiles return to the original state ((a), (b), and (c)). Details of the pattern evolution as a function of the applied stress are provided in the supplementary [Videos 5–7](#).

The integrated 1D diffraction profile of the 002 and 200 reflections is shown in [Figures 7\(a\) and \(b\)](#), respectively. These profiles vary continuously during the loading and subsequent unloading processes. Since tensile stress is applied along the [001] direction, we may consider that the specimen has a tetragonal symmetry **with** a tetragonality $c/a > 1$ under the stress. Therefore, we take the lattice **parameter** in the tensile direction as c and that perpendicular to it as a . [Figure 7\(c\)](#) shows stress dependence of the lattice parameters evaluated by fitting the peak profiles shown in [Figure 7\(a\)](#). They vary continuously as stress increases. There is no hysteresis between the loading and unloading processes, which is a typical elastic behavior. The tetragonality, c/a , also varies continuously from 1 to 1.014 as shown in [Figure 7\(d\)](#). The volume of the unit cell, which is evaluated as ca^2 , increases monotonically with increasing stress, as shown in [Figure 7\(e\)](#); the slope divided by the volume, $(dV/d(\sigma))/V$, is approximately $2.18 \times 10^{-11} \text{ Pa}^{-1}$. The change in the shape of the Bragg reflections mentioned in [Figure 6](#) appears as a variation of the full-width at half-maximum (FWHM) in the 1D peak profile ([Figure 7\(f\)](#)): the decrease in diffuse streaks along the $\langle 110 \rangle$ directions around the 002 reflection appears as a slight decrease in FWHM (green curve), while the extension of the 200 reflection appears as

an increase in FWHM (blue curve).

4. Discussion

4.1 Correlation between lattice and elastic strains

From the lattice parameters shown in [Figure 7](#), we can evaluate the lattice strain along the [001] direction using the formula $(c - c_0)/c_0$, where c_0 is the value of c under a stress of 0 MPa. The open (red) symbols in [Figure 1](#) are the lattice strain thus evaluated from the lattice parameter c . The lattice strain coincides with the elastic strain obtained by macroscopic measurements. Therefore, it is concluded that the temperature variation shown in [Figures 3](#) and [5](#) results mainly from an elastic deformation. Hence, the main reason for the stable elastocaloric effect shown in [Figure 6](#) is due to this elastic behavior. Since there is no hysteresis for both the macroscopic strain and lattice strain, we can consider that energy dissipation is negligible. Hence, an ultra-high COP is expected for Fe-Pd alloys compared with other conventional SMAs [\[12,13,17\]](#).

4.2 Difference between tensile and compressive stresses

Although the elastic-like strain in [Figure 1](#), which is induced by applying tensile stress along the [001] direction, is large compared with that of conventional metals and alloys, the strain is ~40% [of](#) that induced by compressive stress [\[21,31\]](#). There should be a large difference in the elastic-like deformation for the tensile and compressive cases. We compare the deformation behaviors for these two cases below.

The black curve in Figure 8 shows the slope $d\sigma/d\varepsilon$ as a function of the applied stress (obtained from Figure 1). In this figure, the value under compressive stress evaluated from the stress-strain curve reported in [21] is also shown. The initial value of $d\sigma/d\varepsilon$, which is considered as the Young's modulus, is similar for both cases (nearly 10 GPa). The slight difference at zero stress is due to either a difference in experimental procedure or an unavoidable difference in composition between the two specimens. The slope increases monotonically as tensile stress increases, while it decreases as compressive stress increases. This tendency is consistent with the behavior of shear moduli reported by Seiner *et al* [32]. They reported that the shear modulus of the (110) plane along the $[1\bar{1}0]$ direction increased, while that of the (101) plane along the $[10\bar{1}]$ direction decreased by the application of compressive stress along the [001] direction. As the FCT martensite phase is contracted along the [001] direction, the alloy shows a lower $d\sigma/d\varepsilon$ value under compressive stress than under tensile stress.

The Poisson's ratio (ν), which is defined as $\nu = -\{c_0(a-a_0)\}/\{a_0(c-c_0)\}$, can be also evaluated from the lattice parameters shown in Figure 7(c). The average Poisson's ratio under tensile stress is ~ 0.34 , which is close to the value of aluminum (0.35) but is smaller than that under compressive stress (0.42, which is calculated from the stress-strain curves along the [001] and [100] directions [21]). The relatively small Poisson's ratio further confirms the lattice hardening for the Fe-31.2Pd (at%) single crystal under the tensile test.

4.3 Change in the XRD profile

We observed a significant broadening of the XRD pattern in the direction perpendicular to the tensile axis as shown in [Figure 6\(c''\)](#). Considering that the change in the profile is reversible, we can consider that it is not related to a defect introduction. We discuss the reason for this behavior below.

While analyzing the 1D diffraction patterns, we used the tensile direction as the c -axis, and the direction perpendicular to the tensile direction as the a -axis, considering the symmetry from a macroscopic point of view. The tetragonality based on this analysis is larger than one as shown in [Figure 7\(d\)](#). However, the tetragonality of the thermally induced FCT martensite for this specimen is lower than one [\[25\]](#). This indicates that if the FCT martensite is induced by tensile stress, the variants with its a -axis (longer axis) being parallel to the tensile direction ($[001]$) should be selected. There are two such variants: in one variant (V1), the c -axis corresponds to $[100]$ and the remaining a -axis corresponds to $[010]$; in the other variant (V2), the c -axis corresponds to $[010]$ and a -axis to $[100]$. Therefore, if the FCT martensite phase is induced under tensile stress, we may expect the 200_{FCC} reflection to separate into 002_{FCT} of V1 and 200_{FCT} of V2. The broadening of the 200 reflection in [Figure 6\(c''\)](#) suggests that part of the specimen is transformed to FCT martensite with $c/a < 1$, even under tensile stress. Presumably, the specimen is composed by the two variants of FCT martensite mentioned above and the elastically deformed FCC phase with $c/a > 1$. Because of this mixture, the strain under a uniaxial tensile stress will not be homogeneous at the microscopic scale, although the temperature variation appears

macroscopically homogeneous as shown in [Figure. 2](#). Such an inhomogeneity in strain could be one important reason for the high elastic strain, resulting in a stable elastocaloric effect of the Fe-Pd alloy, even under tensile stress.

5. Summary

In summary, the elastic-like strain of the Fe-31.2Pd (at%) single crystalline sheet reaches 1.2% under **tensile stress** of 200 MPa, and the corresponding temperature variation (1.9 K) is stable even after 10000 stress cycles. This large elastic-like deformation results from the continuous and reversible lattice **deformation** under tensile stress, which has been confirmed by *in situ* HE-XRD. **Application of the stress suppresses** the diffuse streaks in the $\langle 110 \rangle$ direction. The 200 reflection extends significantly in the direction perpendicular to the tensile direction as the applied stress increases. Presumably, the high elastic strain of the specimen under tensile stress is related to this peak extension. The ultra-stable mechanical behavior and elastocaloric effect indicate that Fe-Pd alloys could be a potential elastocaloric material.

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References

- [1] X. Moya, S. Kar-Narayan and D. Mathur, Caloric materials near ferroic phase transitions, Nat. Mater. 13 (2014) 439–450, <http://dx.doi.org/10.1038/NMAT3951>
- [2] V. K. Pecharsky and K. A. Gschneidner Jr., Giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$, Phys. Rev. Lett. 78 (1997) 4494–4497, <http://dx.doi.org/10.1103/PhysRevLett.78.4494>
- [3] J. Liu, T. Gottschall, K. P. Skokov, J. D. Moore and O. Gutfleisch, Giant magnetocaloric effect driven by structural transitions, Nat. Mater. 11 (2012) 620–626, <http://dx.doi.org/10.1038/NMAT3334>
- [4] A. S. Mischenko, Q. Zhang, R. W. Whatmore, J. F. Scott and N. D. Mathur, Giant electrocaloric effect in the thin film relaxor ferroelectric $0.9\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - 0.1\text{PbTiO}_3$ near room temperature, Appl. Phys. Lett. 89 (2006) 242912, <http://dx.doi.org/10.1063/1.2405889>
- [5] A. S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore and N. D. Mathur, Giant electrocaloric effect in thin-film $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$, Science 311 (2006) 1270–1271, <http://dx.doi.org/10.1126/science.1123811>
- [6] S. Yuce, M. Barrio, B. Emre, E. Stern-Taulats, A. Planes, J. Tamarit, Y. Mudryk, K. Gschneidner, Jr., V. Pecharsky and L. Mañosa, Barocaloric effect in the magnetocaloric prototype $\text{Gd}_5\text{Si}_2\text{Ge}_2$, Appl. Phys. Lett. 101 (2012) 071906,

<http://dx.doi.org/10.1063/1.4745920>

[7] L. Mañosa, D. González-Alonso, A. Planes, M. Barrio, J. Tamarit, I. Titov, M. Acet, A. Bhattacharyya and S. Majumdar, Inverse barocaloric effect in the giant magnetocaloric La–Fe–Si–Co compound, *Nat. Commun.* 2 (2011) 595,

<http://dx.doi.org/10.1038/ncomms1606>

[8] E. Bonnot, R. Romero, L. Manosa, E. Vives and A. Planes, Elastocaloric effect associated with the martensitic transition in shape-memory alloys, *Phys. Rev. Lett.* 100, (2008) 125901, <http://dx.doi.org/10.1103/PhysRevLett.100.125901>

[9] J. Tušek, K. Engelbrecht, L. P. Mikkelsen and N. Pryds, Elastocaloric effect of Ni-Ti wire for application in a cooling device, *J. Appl. Phys.* 117 (2015) 124901, <http://dx.doi.org/10.1063/1.4913878>

[10] L. Mañosa, A. Planes, E. Vives, E. Bonnot and R. Romero, The use of shape-memory alloys for mechanical refrigeration, *Funct. Mater. Lett.* 2 (2009) 73–78, <http://dx.doi.org/10.1142/S1793604709000594>

[11] L. Mañosa, S. Jarque-Farnos, E. Vives and A. Planes, Large temperature span and giant refrigerant capacity in elastocaloric Cu-Zn-Al shape memory alloys, *Appl. Phys. Lett.* 103 (2013) 211904, <http://dx.doi.org/10.1063/1.4832339>

[12] S. Miyazaki, K. Otsuka and Y. Suzuki, Transformation pseudoelasticity and deformation behavior in a Ti-50.6at%Ni alloy, *Scripta Metall.* 15 (1981) 287–292, [http://dx.doi.org/10.1016/0036-9748\(81\)90346-X](http://dx.doi.org/10.1016/0036-9748(81)90346-X)

[13] K. Otsuka, H. Sakamoto and K. Shimizu, Successive stress-induced martensitic transformations and associated transformation pseudoelasticity in Cu-Al-Ni alloys,

- Acta Metall. 27 (1979) 585–601, [http://dx.doi.org/10.1016/0001-6160\(79\)90011-7](http://dx.doi.org/10.1016/0001-6160(79)90011-7)
- [14] Y. Tanaka, K. Himuro, R. Kainuma, Y. Sutou, T. Omori and K. Ishida, Ferrous polycrystalline shape-memory alloy showing huge superelasticity, Science 327 (2010) 1488–1490, <http://dx.doi.org/10.1126/science.1183169>
- [15] J. Cui, Y. Wu, J. Muehlbauer, Y. Hwang and R. Radermacher, Demonstration of high efficiency elastocaloric cooling with large ΔT using NiTi wires, Appl. Phys. Lett. 101 (2012) 073904, <http://dx.doi.org/10.1063/1.4746257>
- [16] J. Tušek, K. Engelbrecht, R. Millán-Solsona, L. Mañosa, E. Vives, L. Mikkelsen and N. Pryds, The elastocaloric effect: a way to cool efficiently, Adv. Energ. Mater. 5 (2015) 150036, <http://dx.doi.org/10.1002/aenm.201500361>
- [17] F. Xiao, M. Jin, J. Liu and X. Jin, Elastocaloric effect in $\text{Ni}_{50}\text{Fe}_{19}\text{Ga}_{27}\text{Co}_4$ single crystals, Acta Mater. 96 (2015) 292–300, <http://dx.doi.org/10.1016/j.actamat.2015.05.054>
- [18] F. Xiao, T. Fukuda and T. Kakeshita, Significant elastocaloric effect in a Fe-31.2Pd (at%) single crystal, Appl. Phys. Lett. 102 (2013) 161914, <http://dx.doi.org/10.1063/1.4803168>
- [19] F. Xiao, T. Fukuda, T. Kakeshita and X. Jin, Elastocaloric effect by a weak first-order transformation associated with lattice softening in an Fe-31.2Pd (at%) alloy, Acta Mater. 87 (2015) 8–14, <http://dx.doi.org/10.1016/j.actamat.2015.01.004>
- [20] J. Cui, T. W. Shield and R. D. James, Phase transformation and magnetic anisotropy of an iron–palladium ferromagnetic shape-memory alloy, Acta Mater. 52 (2004) 35–47, <http://dx.doi.org/10.1016/j.actamat.2003.08.024>

- [21] F. Xiao, T. Fukuda and T. Kakeshita, On the physical nature of high reversible strain in Fe–Pd single crystals exhibiting lattice softening, *Acta Mater.* 61 (2013) 4044–4052, <http://dx.doi.org/10.1016/j.actamat.2013.03.025>
- [22] H. Ossmer, S. Miyazaki and M. Kohl, Solid-State Sensors, Elastocaloric heat pumping using a shape memory alloy foil device, *Actuators and Microsystems (TRANSDUCERS)*, 2015 Transducers, 21–25 June 2015, Anchorage, Alaska, USA: IEEE Press 726–729, <http://dx.doi.org/10.1109/TRANSDUCERS.2015.7181026>
- [23] C. Bechtold, C. Chluba, R. Lima de Miranda and E. Quandt, High cyclic stability of the elastocaloric effect in sputtered TiNiCu shape memory films, *Appl. Phys. Lett.* 101 (2012) 091903, <http://dx.doi.org/10.1063/1.4748307>.
- [24] H. Ossmer, F. Lambrecht, M. Gültig, C. Chluba, E. Quandt and M. Kohl, Evolution of temperature profiles in TiNi films for elastocaloric cooling, *Acta Mater.* 81 (2014) 9–20, <http://dx.doi.org/10.1016/j.actamat.2014.08.006>
- [25] T. Kakeshita, T. Fukuda and T. Takeuchi, Magneto-mechanical evaluation for twinning plane movement driven by magnetic field in ferromagnetic shape memory alloys, *Mater. Sci. Eng. A* 438–440 (2006) 12–17, <http://dx.doi.org/10.1016/j.msea.2006.02.193>
- [26] J. A. Shaw and S. Kyriakides, On the nucleation and propagation of phase transformation fronts in a NiTi alloy, *Acta Mater.* 45 (1997) 683–700, [http://dx.doi.org/10.1016/S1359-6454\(96\)00189-9](http://dx.doi.org/10.1016/S1359-6454(96)00189-9)
- [27] H. Tobushi and Y. Shimeno, T. Hachisuka and K. Tanaka, Influence of strain rate on superelastic properties of TiNi shape memory alloy, *Mech. Mater.* 30 (1998) 141–

150, [http://dx.doi.org/10.1016/S0167-6636\(98\)00041-6](http://dx.doi.org/10.1016/S0167-6636(98)00041-6)

[28] W. W. Chen, J. H. Kang and N. A. Winfree, Compressive superelastic behavior of a NiTi shape memory alloy at strain rates of $0.001\text{--}750\text{ s}^{-1}$, *Int. J. Solids Struct.* 38 (2001) 8989–8998, [http://dx.doi.org/10.1016/S0020-7683\(01\)00165-2](http://dx.doi.org/10.1016/S0020-7683(01)00165-2)

[29] S. Muto, S. Takeda, R. Oshima and F. E. Fujita, High-resolution electron microscopy of the tweed microstructure in an Fe-Pd alloy, *Jpn. J. Appl. Phys.* 27 (1988) L1387–L1389, <http://dx.doi.org/10.1143/JJAP.27.L1387>

[30] M. Mitsuka, T. Ohba, T. Fukuda, T. Kakeshita and M. Tanaka, Martensitic transformation in FePd alloy revealed by synchrotron radiation, *Mater. Sci. Eng. A* 438–440 (2006) 332–335, <http://dx.doi.org/10.1016/j.msea.2005.12.050>

[31] F. Xiao, T. Fukuda and T. Kakeshita, Elastic limit of Fe–Pd alloys exhibiting lattice softening, *ISIJ International* 54 (2014) 1374–1378, <http://dx.doi.org/10.2355/isijinternational.54.1374>

[32] H. Seiner, P. Stoklasová, P. Sedlák, M. Ševčík, M. Janovská, M. Landa, T. Fukuda, T. Yamaguchi and T. Kakeshita, Evolution of soft-phonon modes in Fe–Pd shape memory alloy under large elastic-like strains, *Acta Mater.* 105 (2016) 182–188, <http://dx.doi.org/10.1016/j.actamat.2015.12.025>

Figure Captions

Figure 1. Stress-strain curve of the Fe-31.2Pd (at%) single crystalline sheet under a tensile stress along the [001] direction up to 200 MPa at RT. The open red circles represent the strains calculated from *in situ* XRD.

Figure 2. (a) Typical temperature image of the Fe-31.2Pd (at%) single crystalline sheet during the tensile test at RT. The specimen and ambient temperatures are averaged over the representative areas in the red rectangles R_S and R_A , respectively. (b) Temperature images of the specimen in the white rectangular area during the unloading process at a frequency of 0.02 Hz.

Figure 3. Calculated average temperature of the Fe-31.2Pd (at%) single crystalline sheet as a function of time at different frequencies: (a) 0.02, (b) 0.05, (c) 0.1, and (d) 0.2 Hz at RT. The red dashed lines indicate the ambient temperature at each test. (e) Maximum temperature variation as a function of frequency.

Figure 4. Stress-strain curves of the Fe-31.2Pd (at%) single crystalline sheet for the tensile stress range of 12–200 MPa and frequencies of 0.02, 0.05, 0.1, and 0.2 Hz at RT.

Figure 5. (a) Stress-strain curves of the Fe-31.2Pd (at%) single crystalline sheet at the 1st, 2000th, 4000th, 6000th, 8000th, and 10000th cycles during the long-term fatigue test

for the tensile stress range of 12–200 MPa and a stress-frequency of 0.2 Hz at RT. (b) Specimen temperatures of five cycles at individual stages indicated in the figure as a function of the cycle number. The dashed curve indicates the ambient temperature variation during the long-term test.

Figure 6. (a) Representative 2D XRD patterns for the Fe-31.2Pd (at%) single crystalline sheet under a tensile stress of 1.5 MPa. Magnified areas of the main Bragg reflections (b–b'') 002, (c–c'') 200, and (d–d'') 202 under the tensile stresses of 1.5 MPa (b, c, and d), 92.5 MPa (b', c', and d'), 190.4 MPa, (b'', c'', and d'') during the loading process. The tensile direction is indicated by an arrow.

Figure 7. Evaluated 1D diffraction patterns of the (a) 002 and (b) 200 Bragg reflections for the Fe-31.2Pd (at%) single crystalline sheet under different tensile stresses at RT. Stress dependencies of (c) lattice parameters c and a , (d) tetragonality, (e) unit cell volume, and (f) FWHM of the diffraction peaks during the loading (black symbols) and unloading (red symbols) processes. The variation tendencies of FWHM for the 200 and 002 reflections are fitted by the blue and green curves, respectively.

Figure 8. $d\sigma/d\varepsilon$ slope as a function of the applied stress in this study (black line) and in the compressive case at 300 K [21] (red line).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Graphical Abstract