

Elastocaloric Cooling: State-of-the-art and Future Challenges in Designing Regenerative Elastocaloric Devices

Parham Kabirifar – Andrej Žerovnik – Žiga Ahčin – Luka Porenta – Miha Brojan – Jaka Tušek*
University of Ljubljana, Faculty of Mechanical Engineering, Slovenia

Table S1 shows the basic elastocaloric properties for the most interesting elastocaloric materials published to date. In addition to adiabatic temperature changes (and their corresponding applied stress/strain), which are the most important elastocaloric parameters, Table S1 also shows other parameters such as sample preparation, microstructure and geometry of the sample, sample's history (stabilization and training), loading mode (tension or compression) and measuring technique (thermocouples or IR camera) that can all significantly affect the eCE. In Table S1, ΔT_{ad+} and ΔT_{ad-} stand for adiabatic temperature changes upon loading and unloading the elastocaloric material, respectively, and A_f stands for austenitic finish temperature of the material.

Table S1. Overview of the most interesting elastocaloric materials

Alloy (at. %)	Sample/ microstructure	Training	Mechanical / Thermal / characterization	Stress ¹ [MPa]	Strain %	A_f [°C]	ΔT_{ad+} [K]	ΔT_{ad-} [K]	Ref.
Shape-memory alloys (SMA)									
<i>Ni-Ti based</i>									
$Ni_{50.38}Ti_{49.62}$	[112] Single crystal aged sheets with 400 nm precipitates / Prepared by Bridgman technique [148] Single crystal aged sheets with 400 nm precipitates / Prepared by Bridgman technique	-	IR camera / RT ² tension	-	-	0	-	13.3 (largest of first 3 cycles) 14.2 (largest of first 4 cycles)	[1]
Ni-Ti	Polycrystalline wires of different diameters and lengths / manufactured by NDC ³	-	Thermocouple (K-type) / RT tension	~<600 ⁴	8.5	-	25.5	17	[2]
$Ti_{51.1}Ni_{48.9}$	Commercial grade polycrystalline wire	400 cycles at different temperatures	Thermocouple (K-type) / RT compression	~750	6.0	-	~7 (assuming RT:22 °C)	~13 (assuming RT:22 °C)	[3]
$Ni_{50.4}Ti_{49.6}$	Heat treated DC magnetron sputtered film (20 μm thick)	-	IR camera / RT tension	-	-	20	17	16	[4]
$Ni_{50.5}Ti_{49.1}Fe_{0.4}$	Heat treated cold-rolled foil (30 μm thick)	-	IR camera / RT tension	-	-	6	22	17	[5]
$Ti_{47.25}Ni_{45}Cu_{5}V_{2.75}$	Polycrystalline ribbon (0.3 to 0.8 mm thick) / prepared by arc melting	40 cycles	IR camera / RT Tension	-	-	-	22 (at 40th cycle)	21 (at 40th cycle)	[6]
$Ni_{50}Ti_{45.3}V_{4.7}$	Polycrystalline square prism with large columnar grains and no texture / prepared by arc melting under Ar	30 cycles (5000 fatigue cycles)	IR camera / RT compression	-	-	14.7	-	~>10 (after training) ~<10 (after fatigue cycles)	[7]
$Ti_{59.4}Ni_{32.5}Cu_{12.6}$	Heat treated sputtered film (20 μm thick) with a grain size of 200 nm	1502 cycles	IR camera / tension at different temperatures	-	-	-	4.1 (cycle 1 at 73 °C) 4.6 (cycle 1502 at 73 °C)	6.1 (cycle 1 at 73 °C) 6.2 (cycle 1502 at 73 °C)	[8]
$Ni_{50.4}Ti_{49.6}$	Heat treated DC magnetron sputtered film (20 μm thick) with a grain size of 2.5 μm	-	IR camera / tension at different temperatures	-	-	-	9.0 (cycle 1 at 25 °C) 5.1 (cycle 27 at 25 °C)	7.4 (cycle 1 at 25 °C) 4.4 (cycle 27 at 25 °C)	[8]

$Ti_{55}Ni_{29.6}Cu_{12.6}Co_{2.8}$ $Ni_{50.4}Ti_{49.6}$	Heat treated DC magnetron sputtered films (20 μm thick)	-	-	-	9	12	[9]
$TiNi_{44}Cu_{5}Al$	VIMs / hot-rolled, then cold-rolled and finally heat treated / sheet of 40 nm grain size	5000 cycles at 44.8 °C	-	-	~17	16	
$Ni_{50.8}Ti$	Cold-rolled and heat treated as above	10 cycles at 64.9 °C	-	-	-	17.4 (cycle 1 at 44.9 °C) 16.9 (cycle 5000 at 44.9 °C) 25.3 (cycle 1 at 64.9 °C) 19.8 (cycle 10 at 64.9 °C)	[10]
$TiNi_{44}Cu_{5}Al_1$	VIM / hot-rolled, then cold-rolled and finally heat treated / sheet of 40 nm grain size	-	-	-	-	25.7 (at 53.9 °C)	[11]
<i>Cu-based</i>							
$Cu_{88.13}Zn_{15.7}Al_{16.13}$	Heat treated [100] single crystal sheet	-	-	-	-	15	[12]
$Cu_{88}Zn_{16}Al_{16}$	Aged polycrystalline sheet / prepared by induction melting under N_2	100 cycles	-	-	-	6	[13]
$Cu_{64.6}Zn_{33.7}Sn_{1.7}$	Single crystal sheet	-	-	-	12	12	[14]
$Cu_{83}Al_{14}Ni_3$	<001> Single crystal sheet	-	-	-	14	~>14	[15]
$Cu_{71.5}Al_{17.5}Mn_{11}$	Directionally solidified sheet with columnar grains and strong <100> texture as-quenched Above sample after aging	-	-	-	-	12.8 (at RT) 13 (at 41.9 °C)	[16]

<i>Fe-based</i>						
$Fe_{68.8}Pd_{31.2}$	[001] single crystal square prism prepared by floating zone method from arc melted ingots	-	200	-43.2	$\sim > 3.0$ (at -33.2 °C)	$\sim > 3.0$ (at -33.2 °C)
$Fe_{99}Rh_{51}$	0.27 mm thick heat treated polycrystalline	-	-	-	-	5.17 (at 38 °C)
Magnetic shape-memory alloys (MSMA)						
$Ni_{54}Fe_{46}Ga_{27}$	[001] Single crystal sheet / Prepared by Bridgman technique [011] Single crystal sheet / Prepared by Bridgman technique	-	-	22	-	8.4 (av. of 1 st 5 cycles) 7.6 (av. of 1 st 3 cycles)
$Ni_{54.9}Mn_{17.9}Ga_{27.2}$	Directionally solidified polycrystalline rectangular parallelepiped with columnar grains and <001> _A texture	19 cycles	-	7.9	-	10.7 (1 st cycle) 8.5 (cycle 19, before sample's fracture)
$Co_{40}Ni_{33.17}Al_{26.83}$	[115] Single crystal sheet / Prepared by Bridgman technique	-	-	45	-	3.1 (4 measurements at 100 °C) 3.9
$Ni_{50}Mn_{32}In_{16}Cr_2$	Textured polycrystalline parallelepipeds with columnar grains prepared by arc melting under Ar	-	100	-	4.8 Along [001] of austenite	2.0 Along [001] of austenite
$Ni_{50}Mn_{32}In_{16}Cr_2$	Textured polycrystalline parallelepipeds with columnar grains prepared by arc melting under Ar	-	100	21.9	2.0 Along [111] of austenite	1.3 Along [111] of austenite
$Ni_{50}Mn_{31.5}Ti_{18.5}B_{0.2}$	Heat treated polycrystalline columnar grained samples with <001> _A texture / prepared by arc melting	-	700	-	26.9	31.5
$Ni_{45}Mn_{37}In_{13}Co_5$	Square prism / polycrystalline without precipitates / prepared by induction melting under Ar	-	80	52.9	2.1 (at 59.9 °C)	1.9 (at 59.9 °C)
$Ni_{45}Mn_{36}In_{13}Co_5Cr$	Square prism / polycrystalline with precipitates along grain boundary / prepared by induction melting under Ar	-	300	39.9	6.7 (at 49.9 °C)	5.8 (at 49.9 °C)

Shape-memory polymers (SMP)						
Natural rubber (NR)	Commercial grade film of 100 μm thickness	Several cycles to 600 % strain	Thermocouple / tension at different temperatures	n/a	-	12 (at 10 °C) [23]
Poly(cyclooctene) PCO	sheet	-	IR camera / tension at 70 °C	n/a	2.8 (at 70 °C)	2.8 (at 70 °C) [24]
Polyvinylidene di-fluoride based PVDF	0.3 mm thick hot-pressed sheet (for tensile test)	-	Calculated based on the results of tension at different temperatures (indirect)	n/a	-	1.8 (at 24.9 °C) [25]
Poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) terpolymer P(VDF-TrFE-CrFE)	40 μm thick solution casted annealed film	-	IR camera / RT tension	n/a	-	2.15 [26]

- 1 Stress and strain values which are mentioned are reached under adiabatic loading. Values reached by isothermal loading are not mentioned.
- 2 RT stands for room temperature.
- 3 Nitinol Devices and Components, Inc.
- 4 The values which are marked by “~” are the ones which are estimated from the graphs and figures of the cited references and are not directly mentioned by the authors of the cited references.
- 5 Heat treatment might have been referred to as annealing by the authors of the cited references.
- 6 Prepared by Vacuum Induction Melting (VIM).

REFERENCES OF SUPPLEMENTARY DATA

- [1] Pataky, G.J., Ertekin, E., Sehitoglu, H. (2015). Elastocaloric cooling potential of NiTi, Ni₂FeGa, and CoNiAl. *Acta Materialia*, vol. 96, p. 420-427, DOI:10.1016/j.actamat.2015.06.011.
- [2] Cui, J., Wu, Y., Muehlbauer, J., Hwang, Y., Radermacher, R., Fackler, S., Wuttig, M., Takeuchi, I. (2012). Demonstration of high efficiency elastocaloric cooling with large ΔT using NiTi wires. *Applied Physics Letters*, vol. 101, no. 7, ID 073904, DOI:10.1063/1.4746257.
- [3] Tušek, J., Engelbrecht, K., Mikkelsen, L.P., Pryds, N. (2015). Elastocaloric effect of Ni-Ti wire for application in a cooling device. *Journal of Applied Physics*, vol. 117, no. 12, DOI:10.1063/1.4913878.
- [4] Ossmer, H., Lambrecht, F., Gültig, M., Chluba, C., Quandt, E., Kohl, M. (2014). Evolution of temperature profiles in TiNi films for elastocaloric cooling. *Acta Materialia*, vol. 81, p. 9-20, DOI:10.1016/j.actamat.2014.08.006.
- [5] Ossmer, H., Miyazaki, S., Kohl, M. (2015). The elastocaloric effect in TiNi-based foils. *Materials Today: Proceedings*, vol. 2, p. S971-S974, DOI:10.1016/j.matpr.2015.07.443.
- [6] Schmidt, M., Ullrich, J., Wiczorek, A., Frenzel, J., Schütze, A., Eggeler, G., Seelecke, S. (2015). Thermal stabilization of NiTiCuV shape memory alloys: Observations during elastocaloric training. *Shape Memory and Superelasticity*, vol. 1, no. 2, p. 132-141, DOI:10.1007/s40830-015-0021-4.
- [7] Kim, Y., Jo, M.-G., Park, J.-W., Park, H.-K., Han, H.N. (2018). Elastocaloric effect in polycrystalline Ni₅O_{145.3}V_{4.7} shape memory alloy. *Scripta Materialia*, vol. 144, p. 48-51, DOI:10.1016/j.scriptamat.2017.09.048.
- [8] Bechtold, C., Chluba, C., Lima De Miranda, R., Quandt, E. (2012). High cyclic stability of the elastocaloric effect in sputtered TiNiCu shape memory films. *Applied Physics Letters*, vol. 101, no. 9, p. 1-5, DOI:10.1063/1.4748307.
- [9] Ossmer, H., Chluba, C., Güeltig, M., Quandt, E., Kohl, M. (2015). Local evolution of the elastocaloric effect in TiNi-based films. *Shape Memory and Superelasticity*, vol. 1, no. 2, p. 142-152, DOI:10.1007/s40830-015-0014-3.
- [10] Chen, H., Xiao, F., Liang, X., Li, Z., Jin, X., Fukuda, T. (2018). Stable and large superelasticity and elastocaloric effect in nanocrystalline Ti-44Ni-5Cu-1Al (at%) alloy. *Acta Materialia*, vol. 158, p. 330-339, DOI:10.1016/j.actamat.2018.08.003.
- [11] Chen, H., Xiao, F., Liang, X., Li, Z., Li, Z., Jin, X., Fukuda, T. (2019). Giant elastocaloric effect with wide temperature window in an Al-doped nanocrystalline Ti-Ni-Cu shape memory alloy. *Acta Materialia*, vol. 177, p. 169-177, DOI:10.1016/j.actamat.2019.07.033.
- [12] Bonnot, E., Romero, R., Mañosa, L., Vives, E., Planes, A. (2008). Elastocaloric effect associated with the martensitic transition in shape-memory alloys. *Physical Review Letters*, vol. 100, no. 12, p. 1-4, DOI:10.1103/PhysRevLett.100.125901.
- [13] Mañosa, L., Jarque-Farnos, S., Vives, E., Planes, A. (2013). Large temperature span and giant refrigerant capacity in elastocaloric Cu-Zn-Al shape memory alloys. *Applied Physics Letters*, vol. 103, no. 21, DOI:10.1063/1.4832339.
- [14] Brown, L.C. (1981). The thermal effect in pseudoelastic single crystals of β -CuZnSn. *Metallurgical and Materials Transactions A*, vol. 12, no. 8, p. 1491-1494, DOI:10.1007/BF02643695.
- [15] Rodriguez, C., Brown, L.C. (1980). The thermal effect due to stress-induced martensite formation in β -CuAlNi single crystals. *Metallurgical and Materials Transactions A*, vol. 11, no. 1, p. 147-150, DOI:10.1007/BF02700450.
- [16] Xu, S., Huang, H.-Y., Xie, J., Takekawa, S., Xu, X., Omori, T., Kainuma, R. (2016). Giant elastocaloric effect covering wide temperature range in columnar-grained Cu_{71.5}Al_{17.5}Mn₁₁ shape memory alloy. *APL Materials*, vol. 4, no. 10, ID 106106, DOI:10.1063/1.4964621.
- [17] Xiao, F., Fukuda, T., Kakeshita, T. (2013). Significant elastocaloric effect in a Fe-31.2Pd (at. %) single crystal. *Applied Physics Letters*, vol. 102, no. 16, p. 161914, DOI:10.1063/1.4803168.
- [18] Nikitin, S.A., Myalikgulyev, G., Annaorazov, M.P., Tyurin, A.L., Myndyev, R.W., Akopyan, S.A. (1992). Giant elastocaloric effect in FeRh alloy. *Physics Letters A*, vol. 171, no. 3-4, p. 234-236, DOI:10.1016/0375-9601(92)90432-L.
- [19] Li, D., Li, Z., Yang, J., Li, Z., Yang, B., Yan, H., Wang, D., Hou, L., Li, X., Zhang, Y., Esling, C., Zhao, X., Zuo, L. (2019). Large elastocaloric effect driven by stress-induced two-step structural transformation in a directionally solidified Ni₅₅Mn₁₈Ga₂₇ alloy. *Scripta Materialia*, vol. 163, p. 116-120, DOI:10.1016/j.scriptamat.2019.01.014.
- [20] Hernández-Navarro, F., Camarillo-García, J.P., Aguilar-Ortiz, C.O., Flores-Zúñiga, H., Ríos, D., González, J.G., Álvarez-Alonso, P. (2018). The influence of texture on the reversible elastocaloric effect of a polycrystalline Ni₅₀Mn₃₂In₁₆Cr₂ alloy. *Applied Physics Letters*, vol. 112, no. 16, ID 164101, DOI:10.1063/1.5018732.
- [21] Cong, D., Xiong, W., Planes, A., Ren, Y., Mañosa, L., Cao, P., Nie, Z., Sun, X., Yang, Z., Hong, X., Wang, Y. (2019). Colossal Elastocaloric effect in ferroelastic Ni-Mn-Ti Alloys. *Physical Review Letters*, vol. 122, no. 25, ID 255703, DOI:10.1103/PhysRevLett.122.255703.
- [22] Shen, A., Sun, W., Zhao, D., Liu, J. (2018). Influence of Cr on microstructure and elastocaloric effect in Ni-Mn-In-Co-Cr polycrystalline alloys. *Physics Letters A*, vol. 382, no. 39, p. 2876-2879, DOI:10.1016/j.physleta.2018.06.022.
- [23] Xie, Z., Sebald, G., Guyomar, D. (2017). Temperature dependence of the elastocaloric effect in natural rubber. *Physics Letters A*, vol. 381, no. 25-26, p. 2112-2116, DOI:10.1016/j.physleta.2017.02.014.
- [24] Hong, S.B., An, Y., Yu, W.-R. (2019). Characterization and modeling of elastocaloric effects of shape memory poly(cyclooctene). *Applied Physics Letters*, vol. 114, no. 1, p. 013904, DOI:10.1063/1.5082357.
- [25] Patel, S., Chauhan, A., Vaish, R., Thomas, P. (2016). Elastocaloric and barocaloric effects in polyvinylidene difluoride-based polymers. *Applied Physics Letters*, vol. 108, no. 7, DOI:10.1063/1.4942000.
- [26] Yoshida, Y., Yuse, K., Guyomar, D., Capsal, J.-F., Sebald, G. (2016). Elastocaloric effect in poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) terpolymer. *Applied Physics Letters*, vol. 108, no. 24, ID 242904, DOI:10.1063/1.4953770.