Contributed Papers from Materials Science and Technology 2017 (MS&T17)
October 8 – 12, 2017, David L. Lawrence Convention Center, Pittsburgh, Pennsylvania USA

DOI 10.7449/2017/MST_2017_430_432

CHARACTERIZATION OF DIRECT LASER DEPOSITED MAGNETOCALORIC Ni-Co-Mn-Sn

Erica Stevens[1], Katerina Kimes[1], Volodymyr Chernenko[2,3], Anna Wojcik[4], Wojciech Maziarz[4], Jakub Toman[1], Markus Chmielus[1]

[1] Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15261, USA
[2] BCMaterials & University of Basque Country (UPV/EHU), 48080 Bilbao, Spain
[3] Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain
[4] Polish Academy of Science, Institute of Metallurgy and Materials Science, Krakow, Poland

Keywords: Metamagnetic, Laser Metal Deposition, Additive Manufacturing

Introduction

Ni-Mn-based Heusler alloys have been investigated for a number of different multifunctional applications, including shape memory and caloric effects under the influence of a magnetic field [1]. Ni-Mn-Sn alloys with small amount of Co have been found to exhibit a giant magnetocaloric effect (MCE) due to a large entropy change at the magnetic field-induced martensite → austenite phase transition [2]. This entropy change corresponds to a large change in magnetization, leading these alloys to be designated as the metamagnetic shape memory alloys (MMSMAs).
One of the attractive applications for MMSMAs is in refrigeration, replacing vapor compression technology to increase efficiency and decrease environmental impact [3]. Ni-Co-Mn-Sn is an inverse MCE material – it cools with an applied magnetic field – and an example of a refrigeration cycle using such a material is shown in Figure 1.

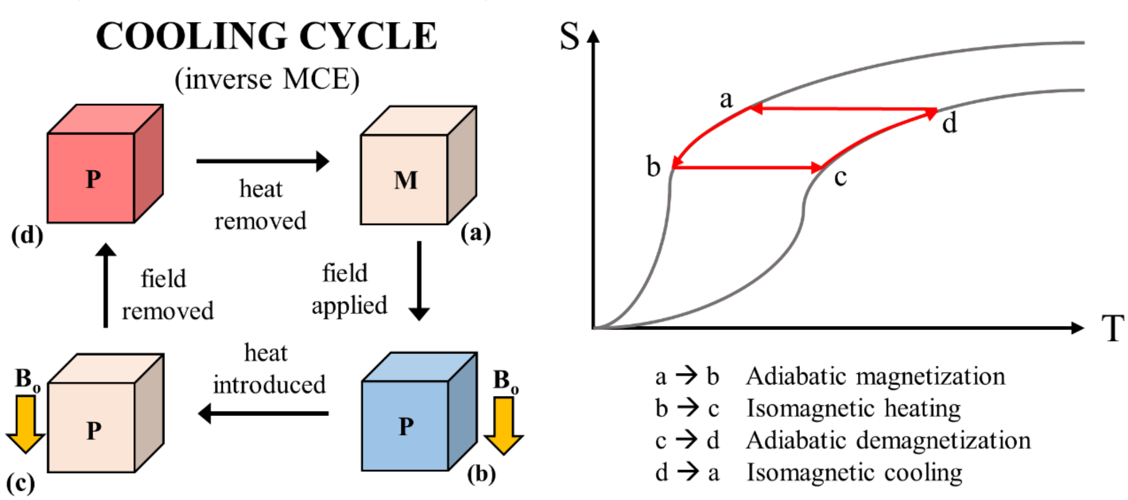

Figure 1. An example cooling cycle with an inverse magnetocaloric material, with a thermodynamic representation shown to the right. (a) The material begins in the martensite phase (M) at room temperature. (b) Applying a field (B_o) lowers the transformation temperature and causes the parent austenite (P) to form. (c) Introduction of heat drawn from the device to be cooled returns the material to near its nominal temperature. (d) When the field is removed, the material heats up again. This excess heat is removed by a heat sink and the cycle can repeat.

Additive manufacturing (AM) is the process of fabricating parts by strategic addition of material. Though additive manufacturing has crept into the production of many structural materials, its use for functional materials is still limited, especially for magnetocaloric materials. The only available study on AM of magnetocaloric materials was published by Moore et al. on $La(Fe, Co, Si)_{13}$ in 2013 using selective laser melting [4]. The current work aims to advance the knowledge of how AM affects Ni-Mn MMSA using direct laser deposition and characterization of structure and magnetic properties of as-printed $Ni_{43}Co_7Mn_{39}Sn_{11}$.

Experimental Methods

Samples were fabricated with five layers of two neighboring parallel beads using an Optomec LENS® 450 direct laser deposition system with powder that had been melt spun and crushed in a vibration Fritsch mill using one ball. Two types of samples resulted from using laser powers between 200 and 300 W, layer height and hatch spacings 0.25 or 0.5 mm, and powder feed rates 4-6 rpm: properly built (PB) and overbuilt (OB). These samples types did not correspond to machine parameter changes and will therefore not be correlated with them.

Powder observation was conducted on both loose and mounted powder. A Keyence VHX-600 was used for optical microscopy (OM) and a Zeiss Sigma 500 for scanning electron microscope (SEM) of both powder and samples. Structure was investigated using a Bruker B8 Discover X-ray diffractometer (XRD) with a Cu-K_α source. Magnetic properties were measured with a Lakeshore 7407 vibrating sample magnetometer (VSM) from -2 T to 2 T with a ramp cycle as follows: 0 T → 2 T → -2 T → 2 T with 410 total data points.

Results and Discussion

<u>Morphology and Structure</u>

PB and OB samples had profiles as shown in Figure 2, which were taken after the sample was cut in half lengthwise (parallel to the laser travel direction), mounted, and polished.

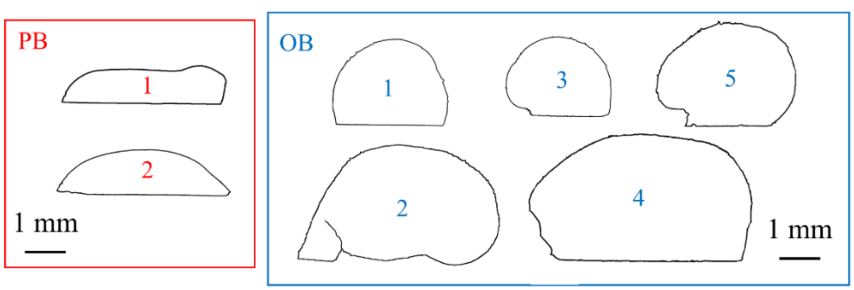

Figure 2. Outlines of the center profile after length-wise cutting of all samples, divided into properly-built (PB) and overbuilt (OB) categories.

SEM analysis of the length-wise cross-sections revealed a difference in microstructure between PB and OB areas, even within the same sample. For example, the right-hand side of sample PB1 was considered OB, while the bottom edge of sample OB3 was considered PB. This determination was based on the shape and locations of the melt pool boundaries seen in backscatter electron imaging. In PB areas, there was less visible twinning than in OB areas.

XRD measurements showed a difference in phase composition between PB and OB samples. This phase difference can be seen primarily through peak splitting in the pattern since austenite is cubic and martensite has lower symmetry.

Magnetic Properties

Saturation magnetization (M_S) and the coercivity were measured and observed using VSM and the plots are shown in Figure 3. The M_S values for OB samples were around 25-45 Am^2/kg, while M_S for PB samples were higher, from 45-55 Am^2/kg. This difference indicates a difference in magnetic structure, likely through phase distribution.

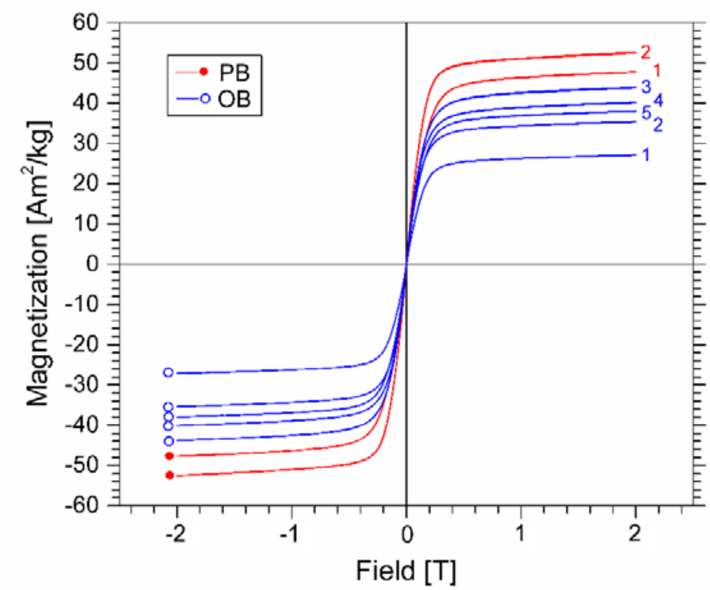

Figure 3. VSM plots for all samples, showing a higher saturation magnetization for PB samples, and a small coercivity for all samples.

Conclusions

There are observable and measurable differences between the properly-built and overbuilt samples of $Ni_{43}Co_7Mn_{39}Sn_{11}$ made with direct laser deposition, including microstructure, phase distribution, and magnetic properties. These characterizations are the first step in determining how additive manufacturing can be used to advance the fabrication platform of magnetocaloric materials. The second step would be related to an understanding of the transformation behavior of sample, which is needed to elaborate a strategy for direct MCE measurements.

Acknowledgements

This work was performed in part at the Nanoscale Fabrication and Characterization Facility, a laboratory of the Gertrude E. and John M. Petersen Institute of NanoScience and Engineering, and at the Materials Micro-Characterization Laboratory, both housed at the University of Pittsburgh. Partial funding was provided by the Mascaro Center for Sustainable Innovation.

References

[1] G.-H. Yu et al., "Recent progress in Heusler-type magnetic shape memory alloys," *Rare Met.*, vol. 34, no. 8, pp. 527–539, 2015.

[2] C. Jing et al., "Martensitic transition and inverse magnetocaloric effect in Co doping Ni-Mn-Sn Heulser alloy," *Eur. Phys. J. B*, vol. 67, no. 2, pp. 193–196, 2009.

[3] S. Fähler et al., "Caloric Effects in Ferroic Materials: New Concepts for Cooling," *Adv. Eng. Mater.*, vol. 14, no. 1–2, pp. 10–19, Feb. 2012.

[4] J. D. Moore et al., "Selective laser melting of La(Fe,Co,Si)$_{13}$ geometries for magnetic refrigeration," *J. Appl. Phys.*, vol. 114, no. 4, pp. 1–9, 2013.