

## Additive Manufacturing of Ni-Mn-Cu-Ga: Influence of Sintering Temperature on Magnetocaloric Effect and Microstructure

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Cu-doped Ni-Mn-Ga exhibits the magnetocaloric effect (MCE): a sharp isothermal change in magnetic entropy and adiabatic temperature change,  $\Delta T_{ad}$ , associated with a change in magnetic field. This magnetic entropy change arises because of a magneto-structural martensitic phase transformation between the high-temperature cubic austenite and tetragonal or orthorhombic martensite phase [1]. Conventional MCE materials like Ni-Mn-Cu-Ga heat up in an applied magnetic field and can be used in a heat pump for solid-state magnetic refrigerators.

Magnetic refrigeration is achieved through a magnetocaloric material-based heat pump, removing heat via fluid flow. This heat exchange requires a magnetocaloric solid with high surface-to-volume ratio, and a low pressure drop in the fluid across the magnetocaloric material [2]. High efficiency magnetic refrigeration may be achieved by producing magnetocaloric heat exchangers with additive manufacturing (AM), allowing for freedom of internal/external geometries, as well as composition/property gradient structures. Many AM methods utilize full melting, selectively melting powder layer-by-layer. Though these full melting techniques show potential for magnetocalorics [3,4], binder jet printing (BJP) has some distinct advantages. In BJP, binder is selectively deposited layer-by-layer onto a powder bed to bind powder particles together, with subsequent curing and sintering for binder burn-out and densification. This process has been found viable for similar composition Ni-Mn-Ga [5].

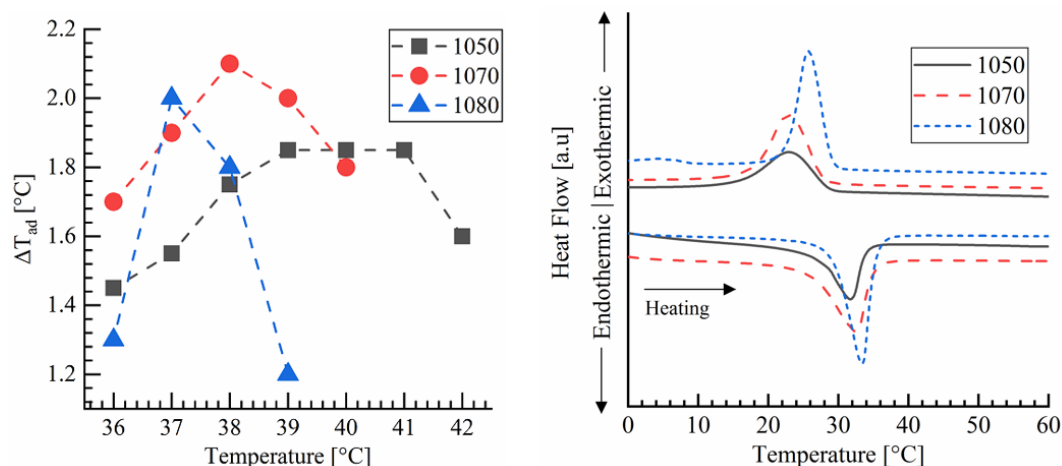
Samples were fabricated from powder using an ExOne Lab binder jetting 3D printer and sintered in an argon-purged vacuum atmosphere at 1050 °C, 1070 °C, and 1080 °C for 2 h then air cooled. Characterization was conducted with a Lakeshore 747 VSM, Pyris 6 DSC, and Zeiss Sigma500 FESEM.

Fig. 1 shows the  $\Delta T_{ad}(T)$  (each point measured at 2 T magnetic field change) and DSC results for the sintered samples.  $\Delta T_{ad}$  results obtained on cooling show a decrease in maximum  $\Delta T_{ad}$  temperature and in transformation hysteresis with increasing sintering temperature. Similarly, in the thermal transformation data, increasing sintering temperature causes the peak to narrow. These two narrowing effects are a result of improved homogenization and grain refinement with the higher sintering temperature.

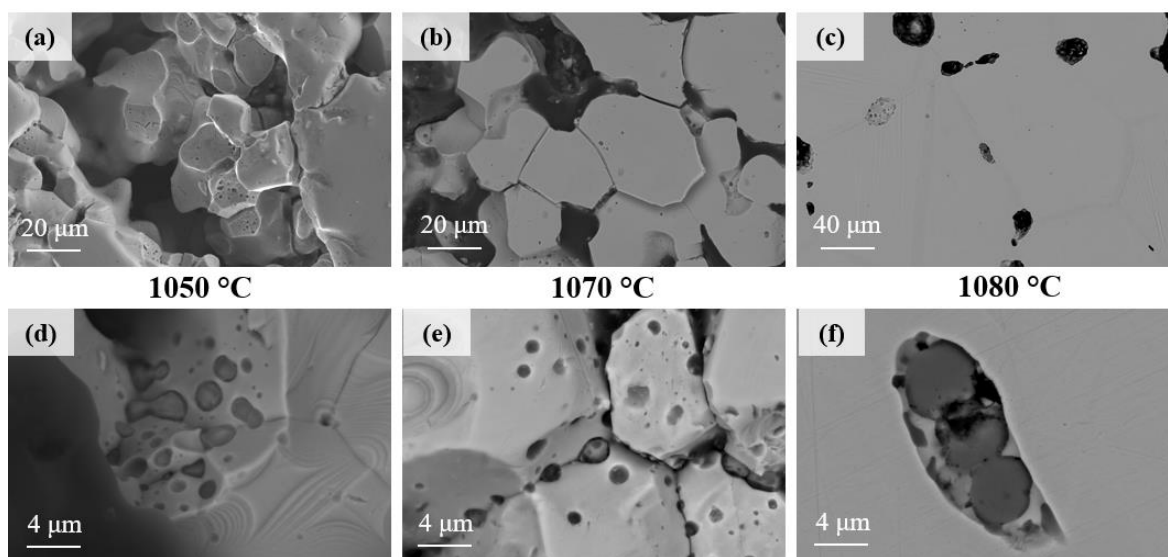
Micrographs from each sintering condition are given in Fig. 2. The 1050 °C sample has low bulk density and limited necking/coalescence between particles (Fig. 2a,d). At this joining of particles, spots are observed that were identified via EDS as Mn-O. The 1070 °C sample (Fig. 2b,e) is similar, with higher bulk density and more coalescence, but still having Mn-O at boundaries. The 1080 °C sample (Fig. 2c,f) is more dense and significant grain growth is observed, yet still shows Mn-O particles and holes. Preliminary EDS and XPS results indicate that these particles are either MnO or Mn<sub>3</sub>O<sub>4</sub> [6]. Despite presence of oxides, MCE results are very encouraging for the further advancement of this material.

## References:

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 [6] The authors acknowledge facilities at the Univ. of Pittsburgh: PINSE NCFE, MMCL, MCL, ANSYS AMRL. E.S. was supported by the DoD through the NDSEG program. K.K. was supported by PPG and SSOE. Project MAT2014-56116-C4-1-3-4-R from MINECO, Spain is acknowledged. A Perez, J Feuchtwanger, A Mostafaei, A Acierno, P Lázpita, and J Toman are acknowledged for their assistance. Research funding was provided by the Mascaro Center for Sustainable Innovation.



**Figure 1.**  $\Delta T_{ad}$  vs. temperature on cooling in a 2 T magnetic field change for samples sintered at 1050 °C, 1070 °C, and 1080 °C (left), and DSC transformation behaviour at zero field (right).



**Figure 2.** (a-c) Low magnification views of microstructures, showing spotted regions where necks formed and powder particles broke away as well as in remnant porosity. (d-f) High magnification micrographs of embedded Mn-O particles at grain boundaries and in remnant porosity.