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Direct Laser Deposition and Homogenization of Ni-Co-Mn-Sn Magnetocaloric Material

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Heusler type Ni-Mn-based metamagnetic shape memory materials exhibit an inverse magnetocaloric effect (IMCE) as a result of magnetic field induced martensitic transformation (MT) [1]. A large magnetic entropy change is obtained since MT in these materials is accompanied by a large change of magnetization between austenitic and martensitic phases [2]. Materials exhibiting IMCE belong to so-called negative MCE materials (cool down with an applied field), whereas materials with a conventional MCE are positive ones (heat up with an applied field). Both types of materials are important for solid state refrigeration with great potential to replace liquid-gas cooling technologies. A negative MCE material cooling cycle proceeds as follows: (1) a field is applied and the material cools down, (2) heat is introduced from the system to be cooled and the temperature of the material increases while the field is still applied, (3) the field is removed, allowing the material to spontaneously heat further, (4) an external fluid flows over the material to remove the heat and return the material to its original temperature.

Critical to the MCE cooler performance is step (3), the removal of heat via a fluid. To achieve high rates of heat exchange, the surface area must be large. This can be achieved by designing thin fins which can be readily obtained by additive manufacturing (AM). Through AM, MCE materials could potentially be produced with specially designed cooling channels at low costs. For both MCE materials the refrigeration capacity depends on the MT and Curie temperature spreads which are controlled by the composition [3]. A structure that has a wide range of available MT temperatures or Curie temperatures is necessary to achieve a useful operating temperature range. AM can provide the opportunity for gradient structures with a variety of transformation temperatures without special assembly.

Direct laser deposition (DLD) was used in the present work to produce samples from $Ni_{43}Co_7Mn_{39}Sn_{11}$ melt spun and mechanically ground powder, then samples were homogenized for 4 hours at 1000 °C in an argon atmosphere. Microstructure, magnetic properties, and thermal properties are compared between the as-printed and homogenized samples.

As-printed samples were in a mixed austenite-martensite state, as indicated by minimal twinning observed with scanning electron microscopy (SEM), a high saturation magnetization measured with vibrating sample magnetometry (VSM), broad transformation peaks measured by differential scanning calorimetry (DSC), and phase analysis from x-ray diffraction (XRD). Homogenization promoted the growth of martensite and led to an increase in twinning observed with SEM, a lower saturation magnetization with VSM, sharper transformation peaks in DSC, and more prominent martensitic peaks in XRD (see Figs. 1 and 2). Results from the homogenized sample are promising for enhancing the functionality and may lead to practical usage of additive manufacturing for magnetocaloric materials.

References:

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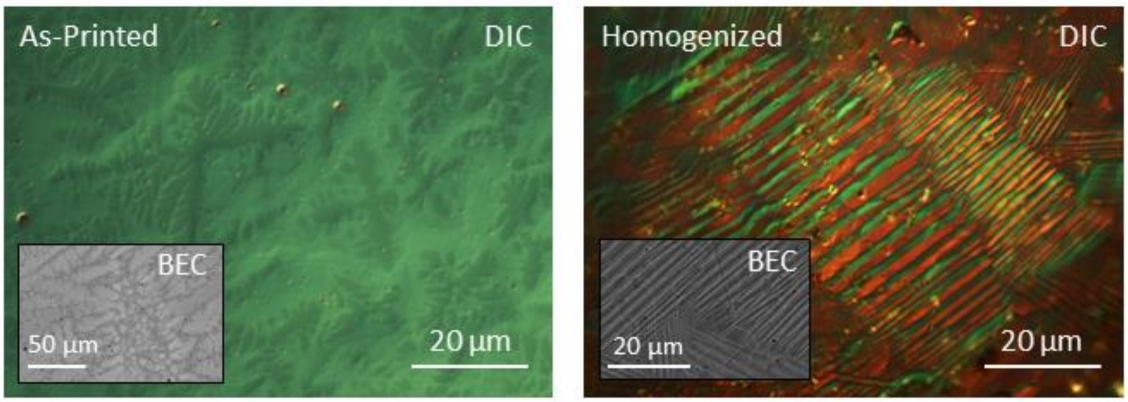

Figure 1. Comparison of as-printed and homogenized microstructures. As-printed sample (left) showed minimal twinning and prominent dendrites in both the differential interference contrast (DIC) and backscattered electron contrast (BEC) micrographs. Homogenized sample (right) showed clear twinning in both DIC and BEC micrographs, indicating a marked presence of martensite.

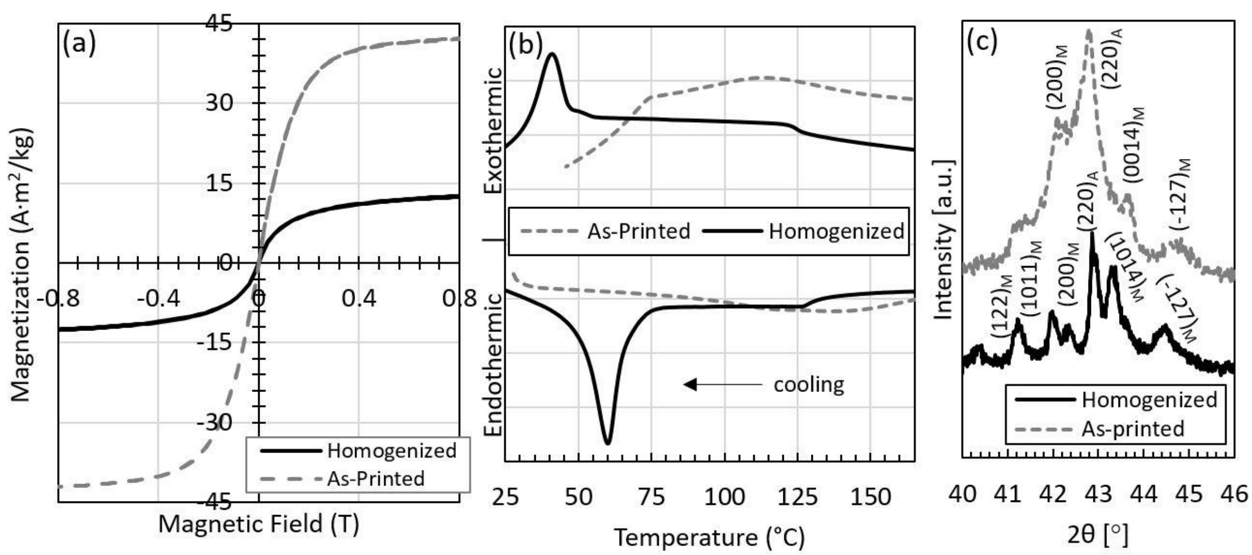

Figure 2. (a) Magnetization vs. magnetic field, showing a drop in saturation magnetization after homogenization, which is interpreted as an increase in the weakly magnetic martensite. (b) Heat flow vs. temperature of the as-printed and homogenized samples, where homogenization led to more distinct phase transformations both on heating and on cooling, attributed to a formation of a more uniform martensitic microstructure. (c) XRD data collected from homogenized and as-printed samples.