

Electron Microscopy Investigation of Binder Saturation and Microstructural Defects in Functional Parts Made by Additive Manufacturing

¹Matthew Caputo, ²C. Virgil Solomon, ³Phi-Khanh Nguyen, and ³Ami E. Berkowitz

¹Materials Science & Engineering Program, Youngstown State University, Youngstown, Ohio, USA

²Mechanical & Industrial Engineering Department, Youngstown State University, Youngstown, USA

³Center for Memory and Recording Research, University of California San Diego, La Jolla, USA

Metallic foams of ferromagnetic Ni-Mn-Ga Heusler alloy show an 8.7% magnetic field induced strain (MFIS) [1]. The large MFIS in foams are orders of magnitude higher compared to bulk polycrystalline Ni-Mn-Ga, revealing that porosity is responsible for the increase in MFIS. Additive manufacturing (AM) techniques such as powder-bed binder-jet technique, known as 3D printing, are suitable for producing near-net shaped parts with controlled porosity. AM is a relatively new method of engineering that produces near-net shape components, one layer at a time, based on a computer aided design (CAD). The purpose of this work is to manufacture functional near-net shape parts with predetermined porosity from pre-alloyed ferromagnetic Ni-Mn-Ga powders using powder-bed binder-jet 3D printing technique. 3DP resemble ink-jet printing, but with multiple passes to build the materials upwards into a three-dimensional form. This method has been proved successful in additive manufacturing near-net shape parts made from pre-alloyed Ti-Ni-Hf powders [2]. Bulk Ti-Ni-Hf alloy is a known high-temperature shape memory alloy [3].

Pre-alloyed spherical Ni-Mn-Ga powders used in this experiment have been produced by spark-erosion in argon and nitrogen dielectrics. Recommended printing parameters (layer thickness, binder saturation, spread speed) for metallic powders by 3D printer manufacturer (ExOne, North Huntington, PA) did not prove successful for Ni-Mn-Ga spark-eroded powders. Binder saturation is a major parameter in the printing process. Binder saturation level affects both the breaking strength, as well as the dimensional tolerance of the green printed part. Insufficient binder reduces the mechanical strength of the green part, which can affect the integrity of the part when removed from the printer, or manipulated in between the printer and curing oven. A higher binder saturation level can produce lateral spreading, therefore affecting the dimension and surface quality of the final product. A water-based binder, provided by ExOne, was used in the experiment. In order to find the optimum binder saturation for Ni-Mn-Ga powders, a method similar to the bench top test was used [4]. Cured samples impregnated with various amounts of binder were investigated using SEM, Figure 1. The 2.0 μ L of binder impregnation seemed to provide an adequate amount of binder for the printing process. Using the optimized printing parameters, green Ni-Mn-Ga parts were obtained. Figure 2(a) shows a green part after binder curing at 463K for 4 h.

The green Ni-Mn-Ga parts were sintered in controlled atmosphere at various temperatures for varying periods of time. Figure 2(b) shows a low magnification SEM micrograph of the sintered part. It can be easily notice, voids are visible and the part is porous. The martensitic transformation behavior of sintered Ni-Mn-Ga parts has been analyzed by XRD, DSC, SEM, FIB, and TEM. The XRD investigation shows that the printed material displays Ni₂MnGa Heusler phase. Based on the DSC investigation the sintered material shows reversible martensitic transformation. Figure 3(a) shows a cross-section SE ion micrograph of two sintered particles. The martensitic phase twins are clearly visible due to ion channeling contrast. The twins have been also observed during high resolution TEM investigation, Figure 3(b). In conclusion, additive manufacturing was used to produce porous near-net shape Ni-Mn-Ga parts that display reversible martensitic transformation behavior after post processing.

References

- [1] M. Chmielus, *et al*, *Nature Materials* **8** (2009), p. 865.
 [2] K. Lu, W. Reynolds, *Powder technology*. **187** (2008), p. 1118.
 [3] G.S. Firstov, *et al*, *Materials Science and Engineering A* **378** (2004) p.2.
 [4] B. Utela, *et al*, *Journal of Manufacturing Processes* **10** (2008) p. 97.
 [5] The use of the Electron Microscopy and Additive Manufacturing Facilities within the Center for Excellence in Advanced Materials Analysis, STEM College at Youngstown State University is gratefully acknowledged. This work was supported by NSF, DMR grant 1229129.

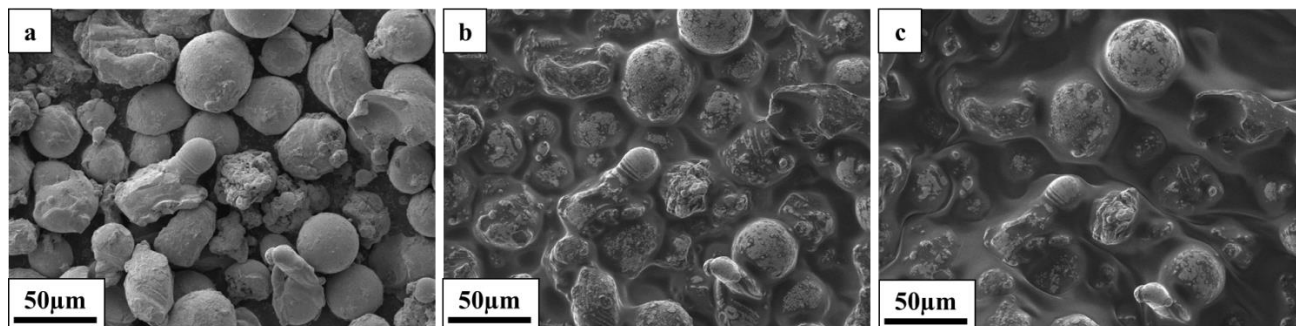


Figure 1: SE images: (a) as-sparked Ni-Mn-Ga powders; and printed powders with (b) 2 μL and (c) 4 μL of binder impregnation.

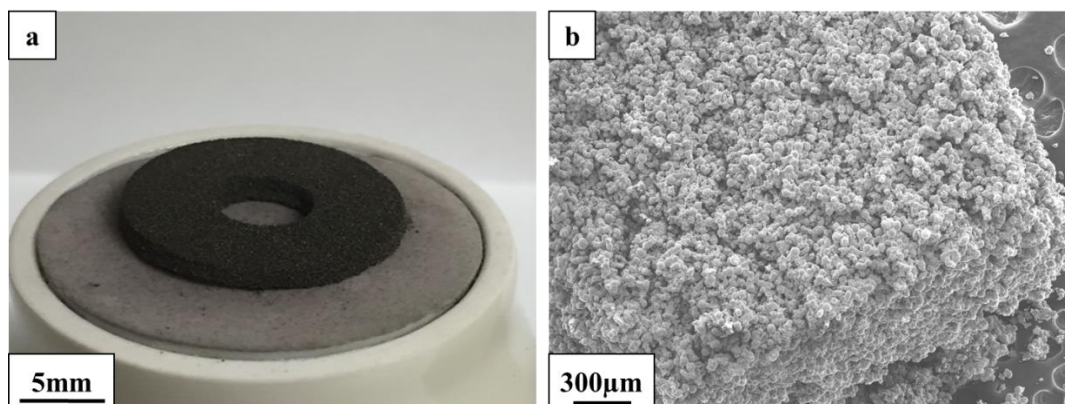


Figure 2: (a) Cured 3D printed Ni-Mn-Ga part; (b) SE micrograph of sintered part.

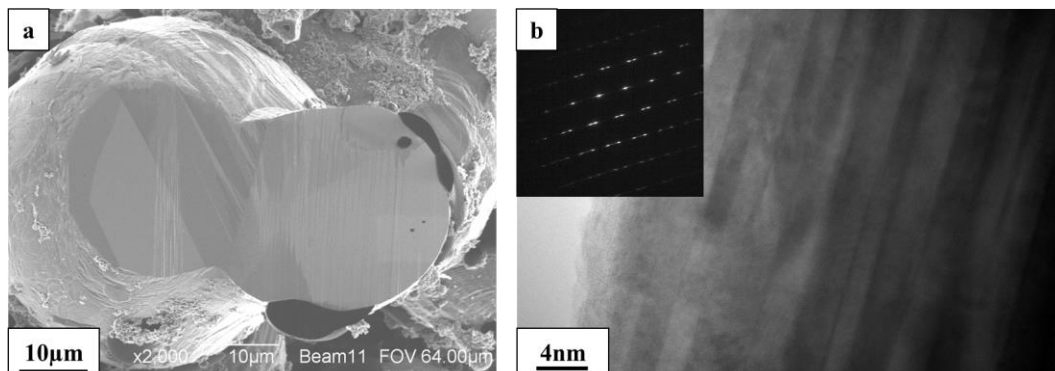


Figure 3: (a) SE ion image of a cross-section into two sintered particles; (b) BF-TEM micrograph of twin variants and SADP.