Three-dimensional Printing of Shape Memory Alloys

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1. Introduction

Shape memory materials are currently used in medical applications, safety devices, actuators, connectors and fasteners [1]. A common issue is their limited formability. Complex shapes can be obtained by laser cutting and spark machining, but this is usually costly or time consuming. Then, there is a need for the development of alternative cost effective processing routes, with good near-net shape capability.

"Solvent on granule" three dimensional printing: In a previous work [2], a 3D-printer has been designed and built for rapid manufacturing of metal parts. Stainless steel parts have been processed with densities up to 97% of theoretical density and mechanical properties similar to metal injection molding parts. A commercial ink-jet printer head is used to selectively drop solvent on powder-polymer granule beds. The manufacturing process consists in growing a green body by spreading a granule bed on a working table, selective printing solvent on a 2D area, moving down the working table, and repeating the process until consolidation of the final layer (Fig. 1). The size of the printed solvent droplets is about 10 pL. The granule layer thickness can be set between 50 µm and 200 µm. After removing loose powder, the green body is extracted and subjected to conventional debinding and sintering steps. The process provides a great flexibility in the choice of base-materials. Compared with conventional 3D-Printing [3], which drops a binder on a loose powder bed, the novel process has the advantage of reducing risks of obstruction of print-head nozzles.

Base material: The starting material is a commercial Ti-50.5at%Ni pre-alloyed powder produced by gas atomisation (Special Metals Corporation, D_{50} = 59 µm). Polymer-metal powder granules were prepared by wet blending, drying, milling and sieving to -100µm.

Debinding and sintering: After a preliminar outgassing step at 100°C for 2h, thermal debinding was performed at 400°C for 4h under hydrogen, and sintered at 1200°C for 2h under hydrogen protective atmosphere.

Shape memory effect characterization: an apparatus developed in our laboratory was used to measure the strain as a function of temperature under constant tensile stresses. The shape memory effect of near equiatomic Ti-Ni alloys is associated with a thermoelastic martensitic transformation, which lets to a contraction during cooling and an elongation during heating. The intensity of this effect is characterized by the maximum reversible strain measured during thermal cycling.

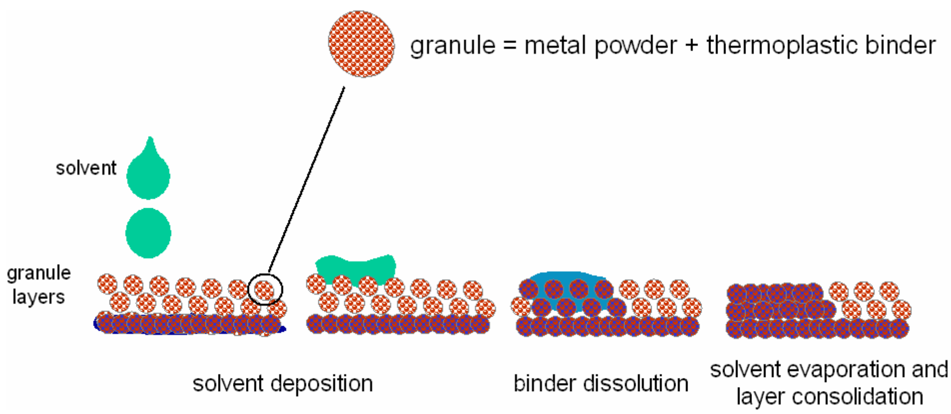
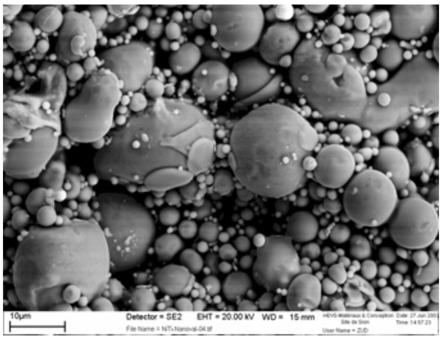


Fig. 1. The principle of the "Solvent on Granule" 3D-Printing process.

Results and discussion: Fig. 2a shows the particle morphology of NiTi prealloyed powder observed by scanning electron microscopy. Differential scanning calorimetry measurements have shown the presence of a reversible martensitic transformation in this powder [4].



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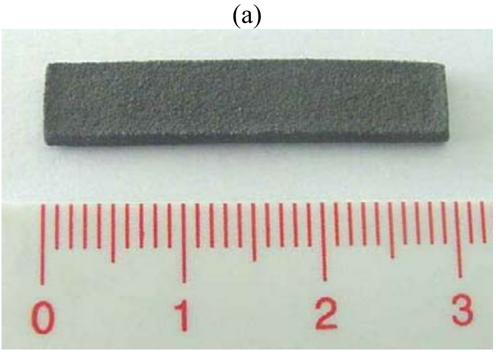
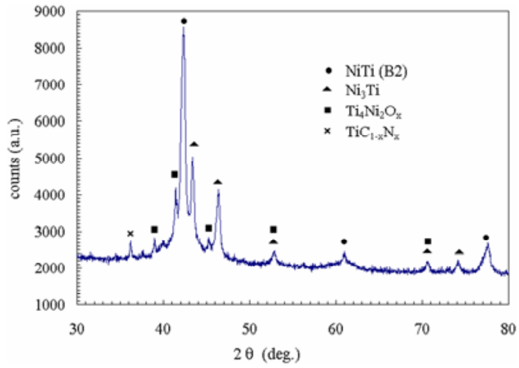


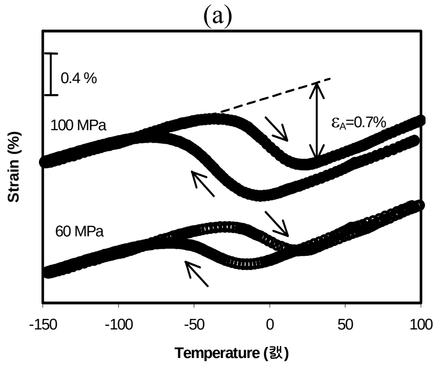
(b)

Fig. 2. (a) Ti-50.5 at% Ni pre-alloyed powder and (b) as sintered NiTi specimen.

Fig. 2b shows a NiTi sintered bar, the phase composition of which was analized by X ray diffraction. The measured density was 95.4% of the theoretical density. The XRD spectrum (Fig. 3a) shows higher and narrower peaks for the B2-NiTi phase and smaller peaks for $Ti_4Ni_2O_x$, Ni_3Ti and $Ti_4Ni_2O_x$ phases. The presence of these additional undesired phases, as well as porosity, is a common issue in powder metallurgy of NiTi, because they reduce both ductility and fatigue resistance. Despite debinding and sintering conditions still need to be improved, the specimen exhibits a sound shape memory effect. The strain versus temperature measurement under a tensile stresss of 100 MPa shows a reversible deformation up to 0.7% (Fig. 3b). A permanent strain of about 0.2% is also observed. Under 60MPa, only a reversible strain is observed. The linear dependent background is related to the thermal expansion of the machine grips and fixtures.



(a)



(b)

Fig. 3. (a) XRD spectrum and (b) tensile strain versus temperature of 3D printed NiTi.

2. Summary

3D printing of NiTi alloys has been successfully achieved. A novel printing process has been developed and used, which consists in selective deposition of a solvent on a granule bed. The granules are composed of metal powders and thermoplastic binder, which are mixed and sieved by conventional methods. A sound green strength is obtained after solvent evaporation. Sintered parts exhibit good density, proper phase composition and shape memory behaviour.

References

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