

SINTERING-DISSOLUTION PROCESS FOR MANUFACTURING NI-625 SUPERALLOY FOAMS¹

*Ismail Unver²
Hamit Özkan Gulsoy²
Bulent Aydemir³*

Abstract

In this work, porous Ni-625 superalloy was produced by use of a water soluble pore forming agent prior to sintering. Carbamide particles were used as the space holder material. After mixing and compaction the space holder particles were extracted using warm water leaching over a range of temperatures. The porous green parts were subsequently thermally debound to remove the paraffin wax under a pure Argon atmosphere, and subsequently sintered at high vacuum. The effects of volume fraction of space holder particles on density (porosity) and elastic modulus were investigated. Microstructures were captured using optical and scanning electron microscopy (SEM). Pore size was quantified using image analysis software integral to the SEM. In addition, compression tests were conducted on the sintered samples.

Key words: Superalloys; Metal foam; Sintering.

¹ *Technical contribution to 67th ABM International Congress, July, 31th to August 3rd, 2012, Rio de Janeiro, RJ, Brazil.*

² *Ph.D., Assoc.Prof., Marmara University, Technology Faculty, Metallurgy and Materials Eng. Göztepe, Istanbul; Tubitak-MRC, Materials Institute, Gebze-Kocaeli, Turkey.*

³ *Tubitak- National Metrology Institute, Gebze-Kocaeli, Turkey.*

1 INTRODUCTION

Metallic materials with controlled porosity are widely used in filtration, wicks, heat pipes, spargers, sound attenuation, abradable seals, and flow control devices. Even lower densities are being promoted for energy absorption and applications requiring tailored mechanical, thermal, acoustic, and conduction properties.^(1,2) Open cell structures are most useful for thermal management in the form of heat exchangers and heat sinks, as well as aerospace devices, filters. Foamed materials are still expensive so their use is restricted to aerospace applications.⁽¹⁻³⁾ Unlike foaming approaches, where precision and uniformity are unknown, here we investigate a Ni-625 superalloy with inclusion of a polymer pore former. With proper development the strength to weight ratio of these higher superalloys foams could be an alternative to other superalloy parts and composite materials.⁽⁴⁻⁶⁾

Pore former and space holders techniques have previously been demonstrated in the fabrication of other metallic and ceramic parts as well as stainless steel and low strength steel.^(7,8) Similar approaches are useful for higher strength materials, including titanium. Here the fabrication process consists of adding a pore forming sacrificial large polymer particle to the powder prior to compaction and then after compaction removing the pore former from the compact to leave behind the desired pores prior to sintering.⁽⁸⁻¹⁰⁾ With proper selection of the sintering cycle the small particles will bond but the large intentional pores will remain. Thus, the process is composed of four sequential steps; (i) mixing of the powder, polymeric molding binder, and space holder particles; (ii) compacting or shaping the mixture, for example by axial compression; (iii) removing the binder phase and dissolving the space holder particles without damaging the particle structure usually by a thermal step; and (iv) sintering the structure to induce strong particle bonding without densification of the pores remaining from the space holder particles. In the approach, the initial size and content of the space holder particles provides the key control over the porosity, pore size, and pore connectivity.^(11,12)

Several pore forming agents have been used in the past, including ice, salt, polymers, and volatile compounds such as camphor and ammonium bicarbonate $((\text{NH}_4)\text{HCO}_3)$.⁽⁷⁻¹⁰⁾ These have been combined with several metallic powders including aluminum, titanium, stainless steel, and nickel superalloys. A problem arises since residuals from some additives, such as NaCl, contaminate the material and either increase corrosion rates or decrease mechanical properties. Both carbamide $((\text{NH}_2)_2\text{CO}$ also known as urea) and ammonium bicarbonate have been used with thermal extraction by heating below 200°C; however, there are negative factors from the vapor release from these pore forming species.^(6,8)

In this work, porous Ni-625 superalloy was produced by use of a water soluble pore forming agent prior to sintering. Carbamide particles were used as the space holder material. After compaction the space holder particles were extracted using warm water leaching over a range of temperatures. The porous green parts were subsequently thermally debound to remove the paraffin wax, and subsequently sintered under vacuum. The effects of volume fraction of space holder particles on density (porosity) and elastic modulus were investigated. Microstructures were captured using optical and scanning electron microscopy (SEM). Pore size was quantified using image analysis software integral to the SEM. In addition, compression tests were conducted on the sintered samples.

2 EXPERIMENTAL PROCEDURE

A schematic illustration of the manufacturing process is given in Figure 1. The powder was gas atomized Ni-625 superalloy. It was obtained from Sandvik Osprey Metals Ltd. with a reported chemistry of 64.0Ni-20.9Cr-2.6Fe-3.2Nb-8.4Mo-0.01Al-0.01Co-0.029C-0.31Si-0.39Mn. The cumulative size distribution at the 10%, 50% and 90% points corresponds to particle sizes of $D_{10} = 3.7 \mu\text{m}$, $D_{50} = 11.1 \mu\text{m}$, $D_{90} = 26.7 \mu\text{m}$ based on laser light scattering. Carbamide had a density of 1.34 g/cm^3 , melting temperature of 133°C , and solubility in water at 20°C of more than 1,000 g per liter. It was prepared as an irregular particle in a size range from $1,200 \mu\text{m}$ to $1,400 \mu\text{m}$. Figure 2 shows a SEM image of the Ni-625 superalloy powder, carbamide particles and coated carbamide particles with Ni-625 powder.

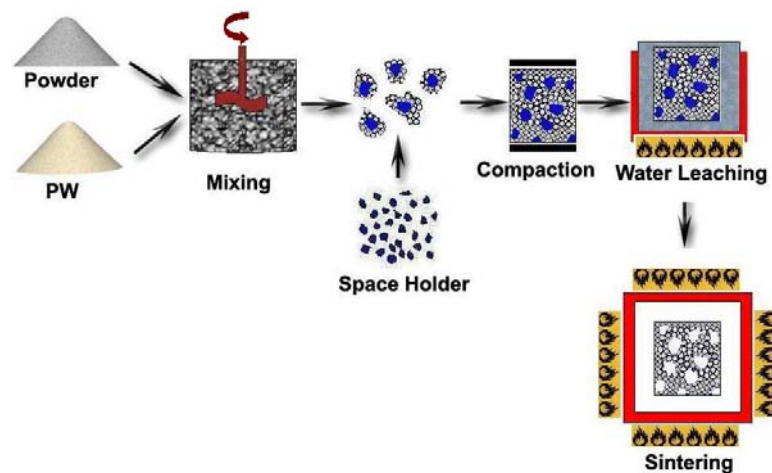


Figure 1. Processing steps of production of porous Ni-625 superalloy containing intentionally large pores.

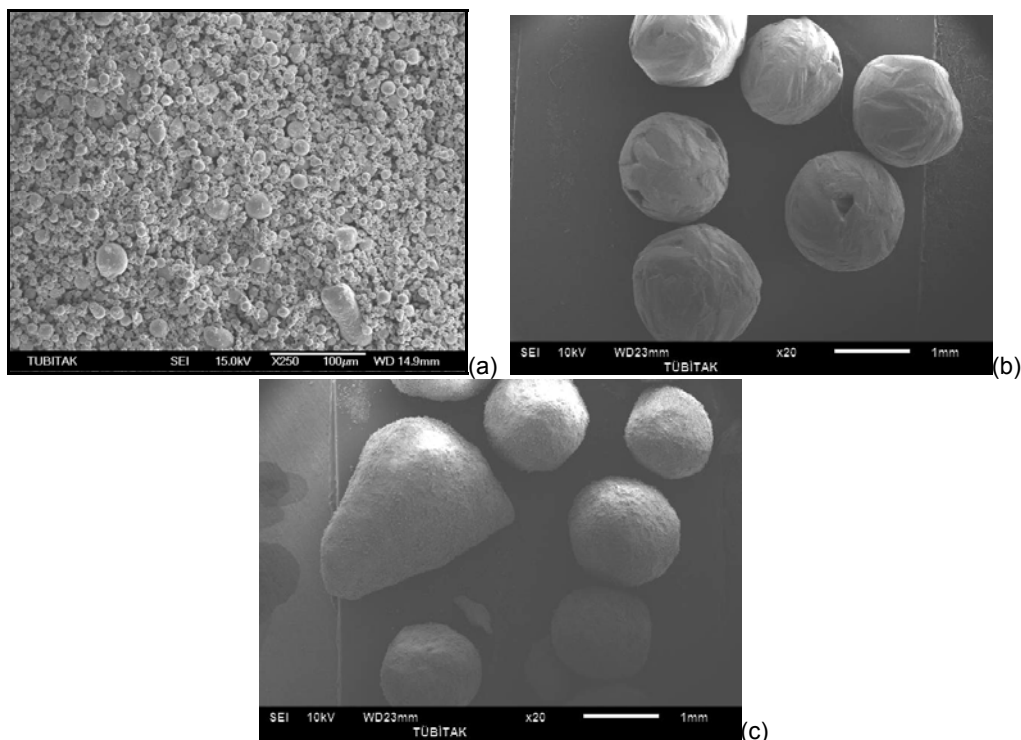


Figure 2. Scanning electron micrograph of (a) Ni-625 superalloy powder; (b) carbamide particles and (c) coated carbamide particles with Ni-625 powder.

The binder ingredient for green strength was paraffin wax with a melting range from 96 to 98°C. It was used at 2 wt.% based on the Ni-625 superalloy mass. Initially, the Ni-625 powder and paraffin wax were mixed for 45 min. using a double-cone mixer heated to 100°C to melt the wax. The mixture was deagglomerated by passing through a sieve. The Ni-625 and carbamide particle ratios were adjusted to give 50 vol.% and 80 vol.% carbamide particles and paraffin wax in the samples. Mixing of the waxed Ni-625 and carbamide powders was performed in a Turbula mixer for 1 h. The mixes were compacted at 150 bar into cylinders with a diameter of 19 mm and height of 20 mm.

The green samples were held at 30°C and 50°C for times ranging from 1 h to 6 h. in distilled water. The specimens were supported on perforated stainless steel plate to enable carbamide leaching from both the top and bottom surfaces. Samples were removed from the water immersion at regular intervals, dried in air at 50°C for 6 h and weighed to determine the amount of carbamide extracted.

The paraffin wax was thermally removed as part of the sintering cycle, which consisted of heating step-by-step at 1°C/min to 600°C with a 6 h hold, followed by heating at 5°C/min to 700°C for 1 h to present the compacts. This was performed in high purity Argon. Subsequent final sintering relied on a heating rate of 10°C/min to 1,300°C for 1 h. under vacuum (10^{-4} mbar). The density was calculated by dividing the mass of the compact by its volume, which was calculated from physical dimensions. Microstructures were obtained via optical and scanning electron microscopy. Pore size was estimated using image analysis software on the SEM. Compression tests were performed at a crosshead speed of 1 mm/min (Zwick, Roel-Z250 materials testing system). At least three specimens were tested under the same conditions to assess repeatability.

3 RESULTS and DISCUSSION

Figure 3 shows the effect of leaching time and temperature on carbamide (≈ 80 vol%) removal from the compacts. As expected based diffusion, the removal rate (the slope of the curve) decreased as leaching time increased; removal slowed as the water diffusion distance into the porous structure increases, while a higher temperature improved diffusion and gave a faster removal rate.⁽⁶⁻⁸⁾ Faster leaching results from a higher temperature, but a high temperature softened the paraffin wax and resulted in compact slumping. Nearly 99% removal was obtained at 50°C in about 6 h for a compact of 20 mm cross-section.

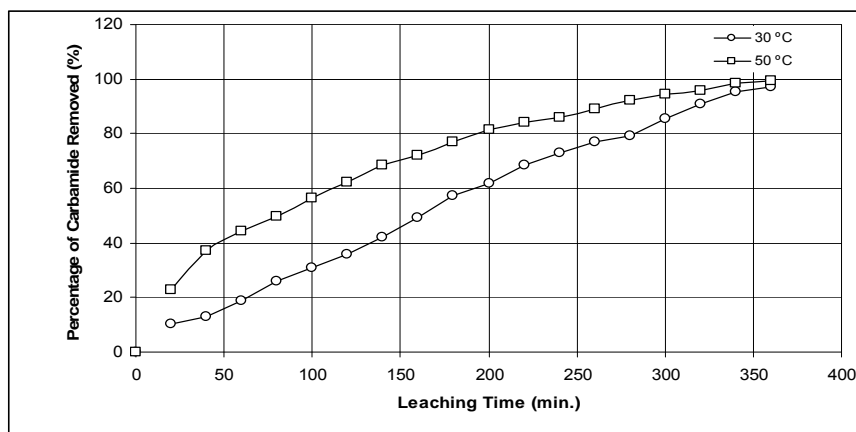


Figure 3. Percentage of carbamide removed during water leaching at temperatures ranging from 30°C to 50°C for sample contain 80 vol.% porosity.

SEM images of the sintered samples are provided in Figure 4 showing a relatively uniform distribution of pores. Figure 4a to 4d images correspond to 50 vol.% to 80 vol.% added carbamide, respectively. The open pore structures formed in the green compacts after water leaching facilitated removal of the paraffin wax during the heating cycle. In the sintering stage, in spite of strong sintering shrinkage between the Ni-625 particles, the large pore framework remained with little shrinkage or densification. In all samples, the morphology of the final pores was similar to that of the carbamide powder particles. This suggests that novel pore structures might be designed by proper size, shape, and content selection in the added carbamide particles. Figure 5 shows macro photographs of Ni-625 superalloy samples, after sintering, with a porosity of 50%-80% and their related pore size distributions. All samples differ with regard to shape and size distribution of the space-holder carbamide. In both cases the appearance of the pores is directly related to the space-holder particles, considering insignificantly decreased pore sizes due to the sintering shrinkage.

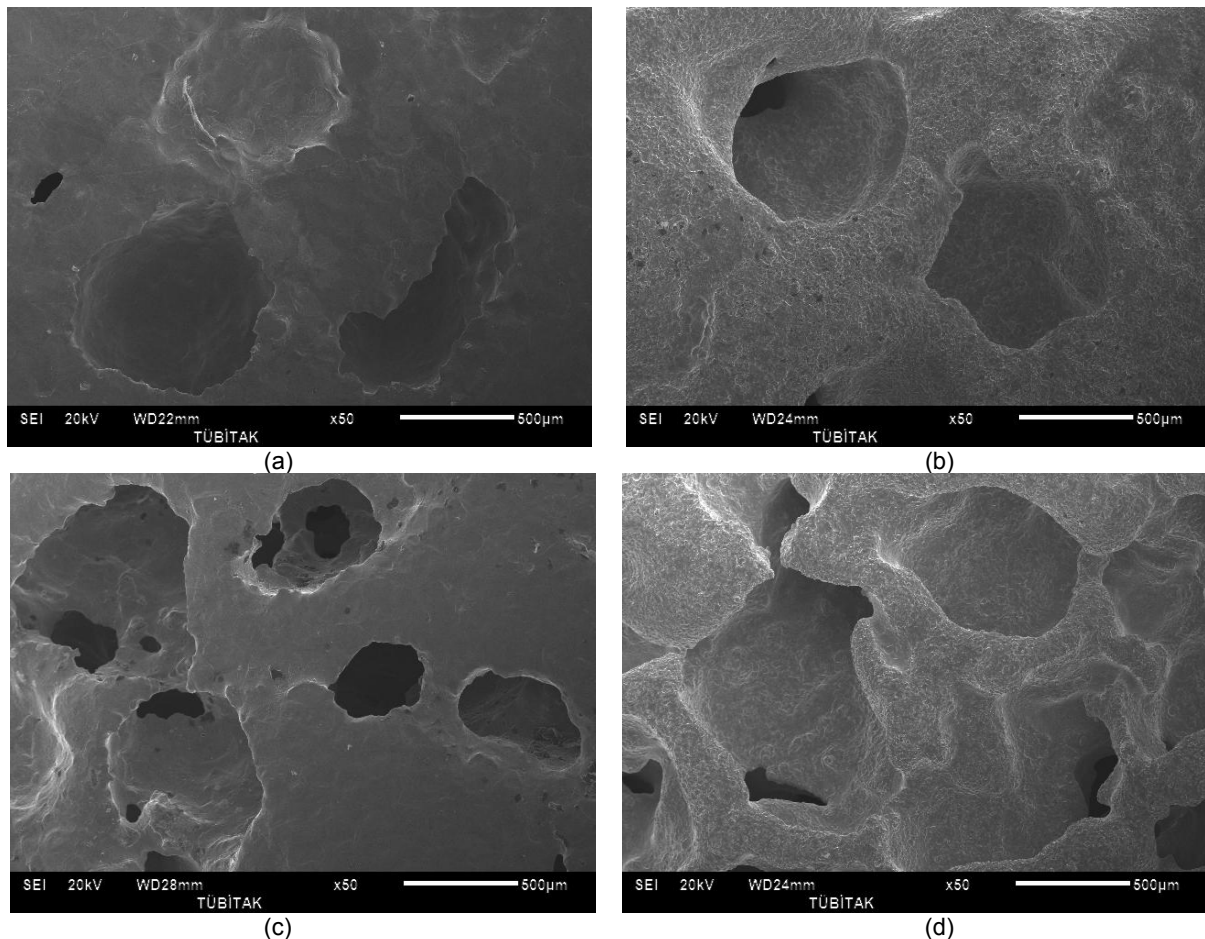


Figure 4. SEM images of the surface of porous Ni-625 superalloy samples (a) 50 vol.% porosity; (b) 60 vol.% porosity; (c) 70 vol.% porosity; and (d) 80 vol.% porosity.

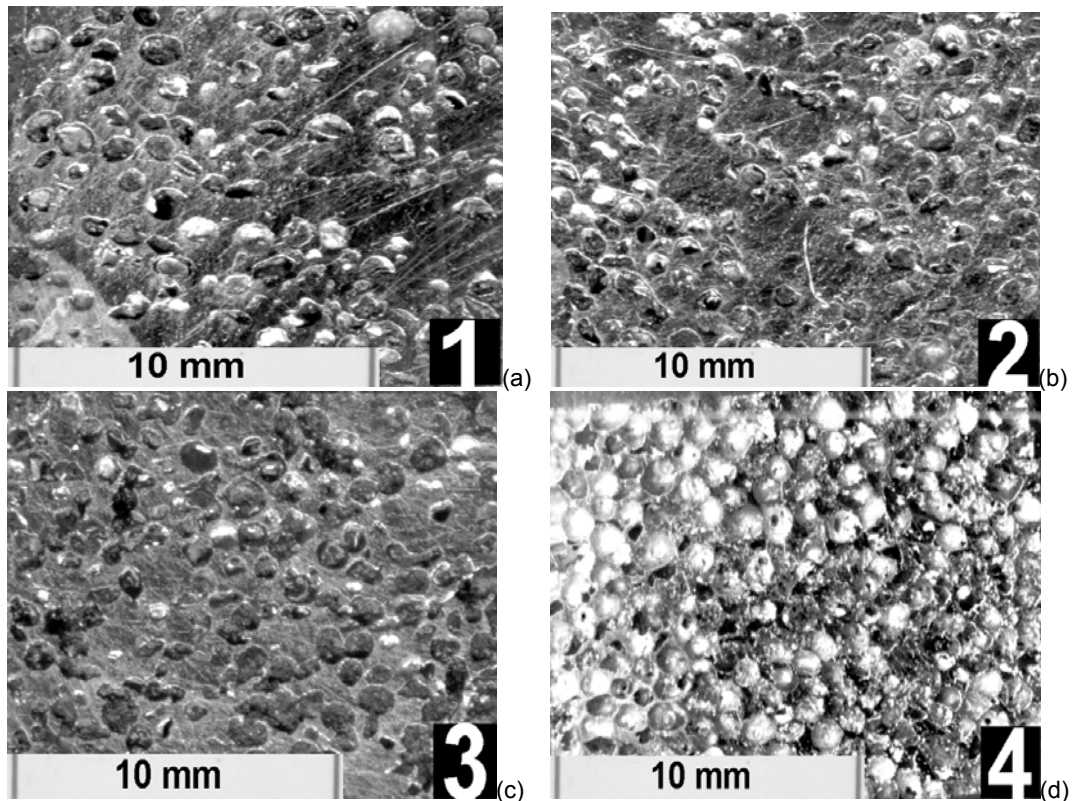


Figure 5. Photographs of pore structure of Ni-625 superalloy samples; (a) 50 vol.% porosity; (b) 60 vol.% porosity; (c) 70 vol.% porosity; and (d) 80 vol.% porosity.

Figure 6 shows the compressive stress-strain curves of base and porous Ni-625 samples with different fractions carbamide. The corresponding strengths for carbamide added samples at 50% and 80% are 874 MPa and 174 MPa for 17% strain. Lower compression stresses and a decrease in the Young's modulus are obtained with the increment in porosity.⁽¹³⁾ The fraction of carbamide particles decreased the sintered density and stress of porous samples. The stress of samples increased with a decrease in porosity. Figure 6 shows that a common stress-strain behavior characterized by three distinct regions (i.e., stress rising linearly with strain at low stresses (elastic deformation), followed by a strong plastic yielding for strains and then a progressive densification regime where the cell walls come in contact one with another, causing an abrupt rise in the flow stress).⁽⁸⁾

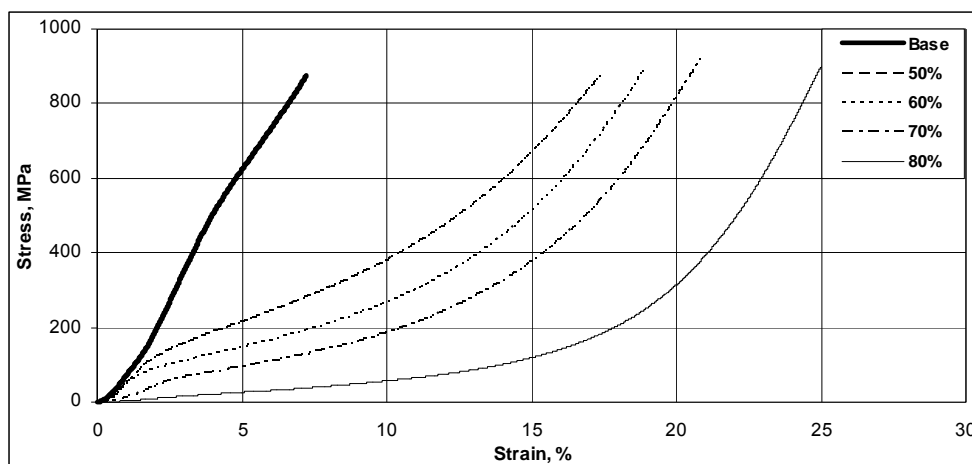


Figure 6. Compressive stress-strain curves of porous Ni-625 samples with 50 vol.% and 80 vol.% carbamide space holders.

4 CONCLUSIONS

Experimental results show that a carbamide pore former, nearly 100-fold larger than the Ni-625 superalloy particles, provides a means to retain large pores in the sintered body. By extraction of the carbamide by water leaching after compaction but prior to sintering, intermediate density Ni-625 superalloy foams are realized by a traditional powder metallurgy route. The green compact had sufficient strength for handling after water leaching at sintering stages. No distortion or other visible reduction in part quality or surface finish was observed at 1,300°C for 1 h under vacuum.

Acknowledgements

This work was supported by the Scientific Research Project Program of Marmara University.

REFERENCES

- 1 ASHBY MF, EVANS A, FLECK NA, GIBSON LJ, HUTCHINSON JW, WADLEY HNG, Metal Foams A Design Guide, Elsevier Science, 2000.
- 2 BANHART J, Manufacture, characterisation and application of cellular metals and metal foams, Progress in Materials Science, 46, p 559, 2001.
- 3 DUNAND DC, Processing of titanium foams, Adv. Eng. Mater., 6, p 369, 2004.
- 4 CHOE H, DUNAND DC, Synthesis, structure, and mechanical properties of Ni-Al and Ni-Cr-Al superalloy foams, Acta Materialia, 52, p 1283, 2004.
- 5 RAJ SV, GHOSH LJ, Failure maps for rectangular 17-4PH stainless steel sandwiched foam panels, Mater. Sci. Eng. A, 474, p 88, 2008.
- 6 GULSOY HO, GERMAN RM, Sintered foams from precipitation hardened stainless steel powder, Powder Metallurgy, 51, p 350, 2008.
- 7 ZHAO YY, SUN DX, A novel sintering-dissolution process for manufacturing Al foams, Scripta Mater. 44, p 105, 2001.
- 8 BAKAN HI, A novel water leaching and sintering process for manufacturing highly porous stainless steel, Scripta Mater. 55, p 203, 2006.
- 9 JIANG B, ZHAO NQ, SHI CS, LI JJ, Processing of open cell aluminum foams with tailored porous morphology, Scripta Mater: 53, p 781, 2005.
- 10 BRAM M, STILLER C, BUCHKREMER HP, STOVER D, BAUR H, High-porosity titanium, stainless steel, and superalloy parts, Adv. Eng. Mater. 2, P 196, 2000.
- 11 LAPTEV A, BRAM M, BUCHKREMER HP, STOVER D, Study of production route for titanium parts combining very high porosity and complex shape, Powder Metall. 47, p 85, 2004.
- 12 BANSIDDHI A, DUNAND DC, Processing of NiTi Foams by Transient Liquid Phase Sintering, Journal of Materials Engineering and Performance, 20, p 511, 2011.
- 13 KOHL M, HABIJAN T, BRAM M, BUCHKREMER HP, STOVER D, KOLLER M, Powder metallurgical near-net-shape fabrication of porous NiTi shape memory alloys for use as long-term implants by the combination of the metal injection molding process with the space-holder technique, Adv. Eng. Mater., 11, p 959, 2009.