Preparation and characterization of high-porosity titanium, stainless steel, and superalloy parts

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Abstract

Light-weight structures with good corrosion resistance and high strength are of increasing interest for technical applications. Titanium and Ti-based alloys, stainless steel and Ni-based superalloys fulfil these requirements. Highly porous parts made of these alloys with porosities of up to 80 % were produced using a suitable powder metallurgical production process that includes the adding of space holder materials to the starting powders. To avoid a high increase of impurities during the process the space holder should be removed completely at temperatures lower than 200°C. The present investigation recommends carbamide (urea) and ammonium hydrogen carbonate as suitable space holders. The pore size distribution and the shape of the pores are directly related to the space holder particles that are commercially available in spherical and angular shapes. The highly porous samples were characterised using optical microscopy and scanning electron microscopy, chemical analysis of the remaining impurities and strength tests.

1 Introduction

Titanium, stainless steel and Ni-based super alloys combine good corrosion resistance with sufficient strength. The production of highly porous parts from these alloys is of increasing interest in light-weight constructions. Established techniques like the foaming of metals with a low melting point (Al, Zn, Pb) are not useful because the well-known foaming agents (for example TiH_2) decompose far below the required temperatures [1,2]. On the other hand, the application of conventional high-melting organic space holders is limited by the strong reaction of titanium, stainless steel and nickel-based alloys with the cracking products of these compounds in a temperature range of 350 – 600°C [3]. In this case high concentrations of impurities remain in the samples. Similar problems occur if alkali salts or low-melting metals like Mg, Sn or Pb are used.

An optimal space holder should be completely removed at temperatures lower than 200°C. In this temperature range the reactivity of the interesting metals due to the cracking products is almost negligible. Carbamide (urea) and ammonium hydrogen carbonate were successfully used to produce samples from titanium, stainless steel (316 L) and nickel-based super alloys (Hastelloy C, Hastelloy X, Inconel 600, Inconel 625) with porosities between 60 and 80 %. Depending on the shape and the size distribution of the space holder, spherical and angular pores in the range of 0.1 to 2.5 mm were obtained.

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2 Experimental

Fig. 1 shows schematically the processing steps of the space holder method. Tab. 1 gives the composition and the particle size of the starting powders (titanium, stainless steel (316 L), Hastelloy C, Hastelloy X, Inconel 600, Inconel 625). Carbamide (urea) particles with a spherical or angular shape and ammonium hydrogen carbonate with an angular shape were used as space holder materials. The particle size of these compounds varied between 0.8 and 6 mm and 0.1 and 0.9 mm. Narrow particle size distributions of the space holder particles were achieved by sieving. The weight ratios of the metal powder to the amount of the space holder were calculated to obtain defined porosities of 60, 70 and 80 % in the sintered compact.

First of all, the space holder was moistened with a suitable solvent by mixing on a rolling bench. The metal powder was added to the mixture after 3 minutes still continuing the mixing process. The powder particles adhered to the surface of the space holder. The agglomerates were uni-axially pressed at 166 MPa into cylindrical compacts (∅ = 30 mm, h = 10 mm) and flat plates (∅ = 70 mm, h = 5 mm). The space holder material was removed by a thermal treatment below 200°C. The debindered green compacts had to be handled with care. The sintering temperature of the compacts varied between 1200 and 1400°C, and the sintering time between 1 and 2 hours. All sintering procedures were performed in a vacuum furnace (p = 10^{-3} Pa). The sintering parameters of the different alloys have still not been optimised and are the subject of further investigations. The oxygen, carbon and nitrogen contents were analysed for the starting powders, for the green compact after removal of the space holder and for the sintered compact. The microstructures were determined by optical microscopy and scanning electron microscopy (SEM). The pore size distribution was measured by quantitative image analysis. Finally, compression and bending tests were carried out depending on the apparent porosity. The samples for the strength tests were machined to cylinders (∅ = 10 mm, h = 10 mm) for the compression test and rectangular bars (45 x 10 x 8 mm^3) for the bending test. Three-point bending tests were carried out with a span width of 40 mm.

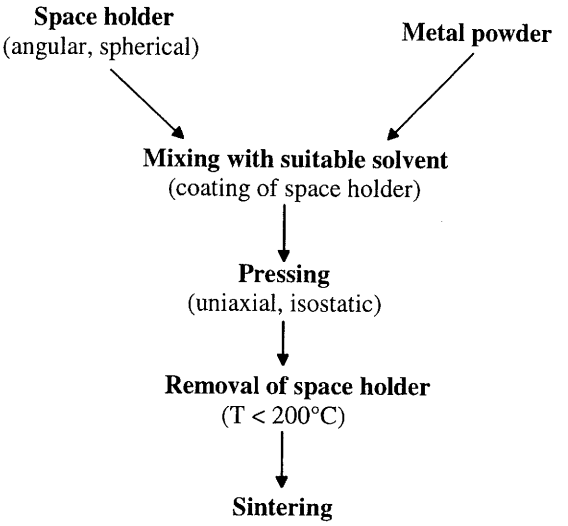

Fig. 1: Processing steps of the space holder method.

Tab. 1: Composition and grain size of metal powders used in this investigation.

	Manufacturer	Composition	Grain size
Titanium	GFE, Germany	Ti-0.25O-0.01N-0.01C	< 45 µm
Stainless steel 316L	Anval, France	Fe-17.9Cr-12.9Ni-2.6Mo-0.9Si-0.02C	< 16 µm
Hastelloy X	Höganäs, Sweden	Ni-21.8Cr-21.6Fe-8.7Mo-1.3Co-1.3Si-0.02C	100 - 200 µm
Hastelloy C	Höganäs, Sweden	Ni-17.2Cr-16.4Mo-4.8W-3.2Fe-0.8Co-0.6Si-0.02C	75 - 100 µm
Inconel 600	Höganäs, Sweden	Ni-15.6Cr-6.9Fe-2.0Si-0.04Cu-0.01C	100 - 200 µm
Inconel 625	Höganäs, Sweden	Ni-21.0Cr-9.0Mo-3.7Nb-2.9Fe-1.8Si-0.4O-0.2Mn-0.02C	100 - 200 µm

3 Results

The preparation of highly porous parts using the space holder method requires a particle size distribution of the metal powders that is lower than the diameter of the space holders. In this case a homogeneous coating of the space holder particles is expected. Additionally, a high ductility of the powders is advantageous to achieve the stability of the green compacts after the removal of the space holder. The use of brittle powders like TiAl as starting materials seems to be problematic without additional binder systems.

Fig. 2 and 3 show the microstructures of titanium samples after sintering with a porosity of 70 % and the related pore size distributions. The two samples differ regarding the shape and the 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. Fig. 4 and 5 demonstrate the influence of the particle size of the starting powders on the microstructure after sintering. Stainless-steel powders with a grain size below 16 µm showed a skeleton with almost theoretical density regarding the higher sintering activity of the smaller particles. In comparison to this behaviour, the powder particles of the Inconel 600 sample (particle size 100 – 200 µm) are still visible after the sintering step connected by the well-known sintering necks. In this case the density of the network could be increased by reducing the particle sizes of the starting powders or by increasing the sintering time. A higher sintering temperature should be avoided with respect to the increasing evaporation tendency of the alloying elements and partial melting.

Titanium has the highest susceptibility of the investigated alloys for oxygen, nitrogen and carbon. Fig. 6 gives the results of the chemical analysis of these elements in the titanium sample after the different processing steps. The carbon content increases from 100 ppm in the starting powder to 600 – 700 ppm in the green body after removing the space holder carbamide. The contents of nitrogen and oxygen remain nearly unchanged. After the sintering process the C-, O- and N-impurities were distinctly increased. The reason for this behaviour is probably a contaminated furnace atmosphere and does not seem to be related to the removal of the space holder material. The improvement of the sintering parameters for the stainless steel and nickel-based alloys is still in progress.

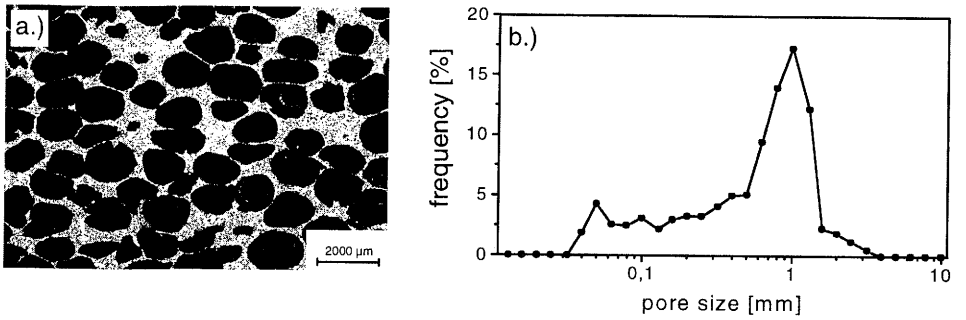

Fig. 2: Titanium sample with spherical space holder carbamide (0.8-2.4 mm), porosity 70 %, 1400°C, 1 h. **a.)** microstructure **b.)** pore size distribution.

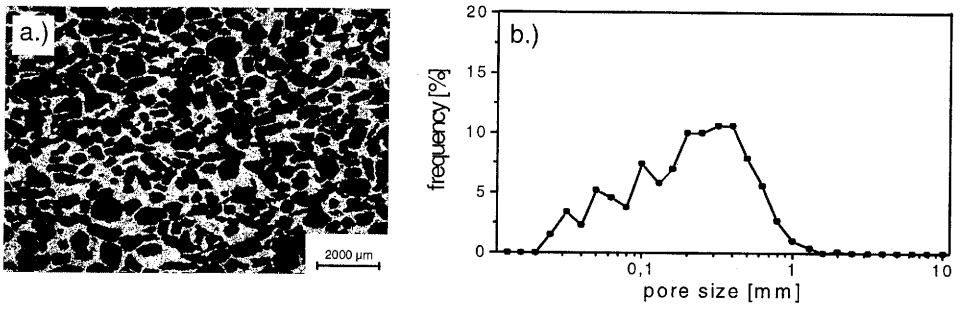

Fig. 3: Titanium sample with angular space holder carbamide (0.1-0.9 mm), porosity 70 %, 1400°C, 1 h. **a.)** microstructure **b.)** pore size distribution.

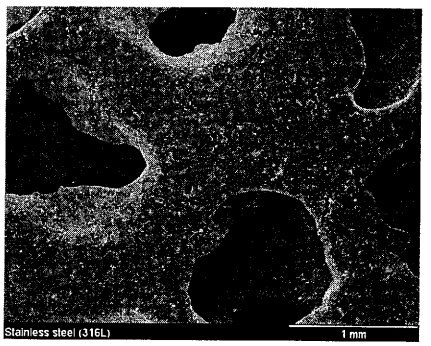

Fig. 4: Highly porous microstructure of stainless steel (316L), powder < 16 µm, space holder carbamide (1 – 1.4 mm), 70 % porosity, 1200°C, 1 h.

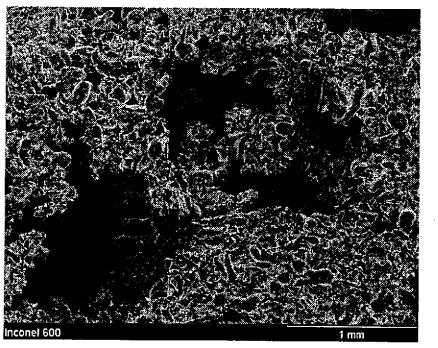

Fig. 5: Highly porous microstructure of Inconel 600, powder 100 – 200 µm, space holder carbamide (1 –1.4 mm), 70 % porosity, 1300°C, 1 h.

Fig. 7 shows the upsetting of titanium samples with different porosities depending on the compressive stress. The apparent porosities were 7, 60 and 80 %. The first porosity value resulted from carrying out the processing route without a space holder. The geometry of the samples differed from the DIN standard (aspect ratio ≥ 2), so the tests were stopped after an upsetting of 50 %. Up to this value the deformation behaviour of the highly porous titanium parts was comparable to that of aluminium foams [2]. In the first stage of the compression tests an almost linear increase of the compressive stress was observed. This increase was followed by an area with small changes of the compressive stress. At higher upsetting rates a further increase of the stress is expected regarding the complete consolidation of the porous structure. In this case a plastic deformation of the almost dense microstructure takes place. Similar to the aluminium foams, highly porous titanium parts seem to be promising candidates for energy absorption applications. Lowering the porosity from 77 % to 60 % leads to a shift of the compression curve by a factor of 10 to higher stresses. A further distinct increase is observed when the porosity is reduced to 7 %. Tab. 2 gives the bending strength of the titanium samples depending on porosity. Lowering the porosity from 77 % to 60 % leads to an increase of the bending stress by a factor of 10 again. The stress-strain behaviour of highly porous stainless steel (316 L) and nickel-based superalloys (Hastelloy C, Hastelloy X, Inconel 600, Inconel 625) will be published in the near future.

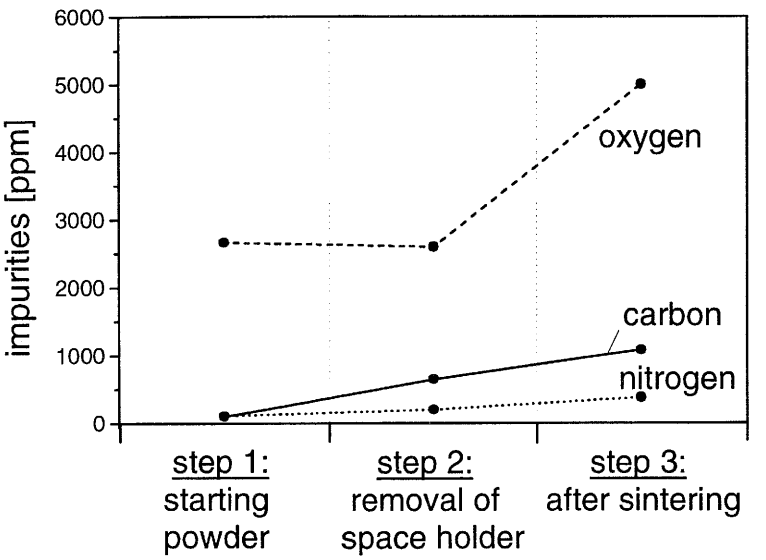

Fig. 6: Chemical analysis of oxygen, carbon and nitrogen contents in titanium samples depending on the processing steps.

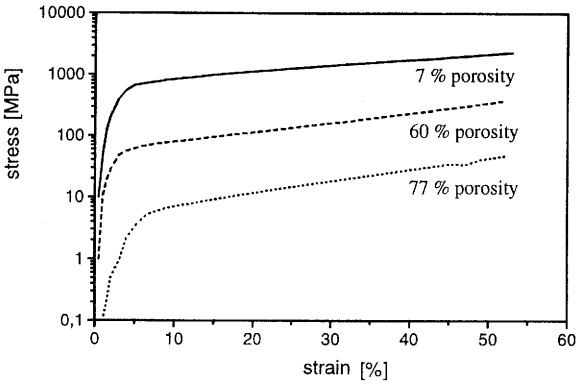

Fig. 7: Compressive stress curves of titanium samples with different porosities, sintered at 1400°C for 1 h.

Tab. 2: Bending strength of titanium samples depending on the porosity. Sintering conditions 1400°C for 1 h.

porosity	7 %	60 %	77 %
bending strength [MPa]	759	68	5.6

4 Conclusions

- Production of highly porous PM-parts using suitable space holder materials (carbamide (urea) and ammonium hydrogen carbonate) was sucessfully applied for titanium, stainless steel (316L) and different nickel-based superalloys (Hastelloy X, Hastelloy C, Inconel 600, Inconel 625).
- Porosities of 60 to 80 % were achieved.
- Depending on the shape and the size distribution of the space holder particles angular and spherical pores in the range from 0.1 to 2.5 mm with a homogeneous distribution were produced. Smaller pores down to 20 µm could be achieved by milling the space holders, larger pores by using coarser particles.

References

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