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Nickel-free P558 Austenitic Steel Parts Processed from Metal Powder – PHA Biopolymer Feedstocks

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Abstract

In this work, the feasibility of a novel processing route for high-nitrogen content austenitic steels is explored. Feedstock for powder injection moulding was prepared with gas atomized P558 stainless steel powder and binder containing a natural polymer as backbone polymer. Binders consisting of 45 wt% P(3HB-co-3HV) processed by bacterial fermentation, 45 wt% paraffin wax and 10 wt% stearic acid were employed. The solids loading was 60 vol.%. Tensile test specimens were injection moulded and subsequently subjected to solvent debinding in heptane, thermal debinding at 500°C and sintering at 1270°C under nitrogen. The microstructure was characterized by metallographic observation and X-ray diffraction. Yield stress values of 600 MPa, ultimate tensile strength of 900 MPa and elongation of 25% were achieved.

INTRODUCTION

Stainless steels for surgical and dental prosthetics must meet several requirements, among which are good biocompatibility, absence of ferromagnetism, high corrosion resistance and good combination of strength, ductility, fatigue endurance and wear resistance. In addition, the use of nickel-free stainless steels is important to avoid the harmful effect of nickel-ion release in the human body [1]. Several development works and production from the 90's have shown that nitrogen combined with molybdenum and manganese can effectively replace nickel as austenite formation element and increase the corrosion resistance [2-3]. In high-nitrogen austenitic stainless steels processed by powder metallurgy, nitrogen can be added via the sintering atmosphere [4]. A feedstock with polyacetal binder is commercially available, the application of which under different sintering and solid state nitriding conditions has been extensively studied [5].
Compared with polymers derived from oil, natural polymers offer the advantage of better biocompatibility, biodegradable character and sustainability. Polyhydroxyalkanoates (PHAs) are natural polyesters synthesised by a large number of microorganisms under nutrient-limiting condition and excess of carbon source. Several applications of PHAs including bioplastics, fine chemicals, implant biomaterials and biofuels have been developed in the last decades.
In this work, the feasibility of using short chain length PHA natural polymers produced by bacterial fermentation as backbone binder constituent for the powder injection moulding of nickel-free P558 steel is explored.

EXPERIMENTAL

The starting powder (Fig. 1) was gas atomized P558 steel (P.A.N.A.C.E.A., Sandvik Osprey Ltd, UK). The particle size distribution was determined by laser diffractometry in a Malvern Mastersizer 2000 apparatus: Dv10 = 3.01 µm, Dv50 = 6.05 µm, Dv90 = 9.56 µm, D[4,3] = 6.22 µm.

Table 1. Chemical composition of P.A.N.A.C.E.A powder (Sandvik Osprey Ltd)

Cr wt.%	Mn wt.%	Mo wt.%	Si wt.%	Ni wt.%	C wt.%	others wt.%
16-18	11.8-12.5	3.0-4.0	1	≤ 0.05	≤ 0.3	≤ 0.5

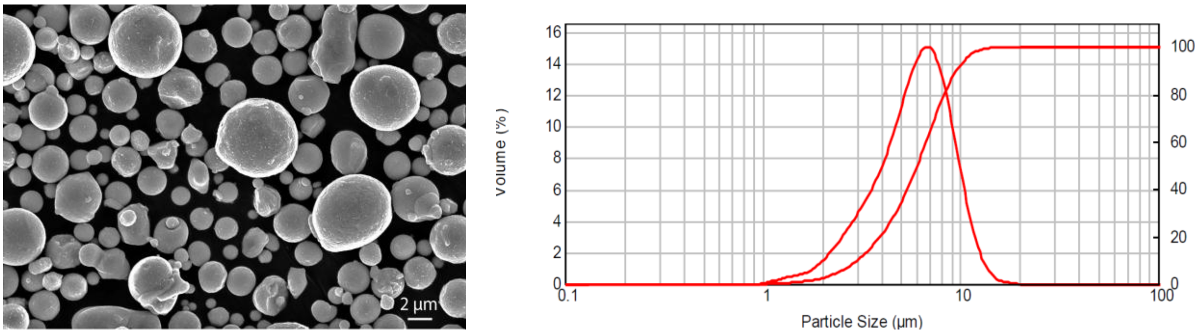

Figure 1: P558 steel gas atomized powder and its particle size distribution

Short chain length PHA polymers, in particular a PHBV copolymer, have been synthesized [6-7] by cultivating *Ralstonia eutropha* DSM 428 in a chemostat at a dilution rate of D = 0.1 ± 0.01 h^{-1} under the conditions of simultaneous limitation by carbon (butyric and/or valeric acid) and nitrogen (ammonium). Polymer solutions were extracted directly from dry biomass with CH_2Cl_2 and recovered using a pressure-filtration unit. After further steps of distillation, recrystallization and purification, the polymer was characterized by NMR in a Bruker 400 MHz spectrometer (Bruker, Billerica, MA, USA). The thermal properties were determined by DSC measurements.

Feedstocks for PIM were prepared with a binder consisting of 45 wt% P(3HB-co-3HV), 45 wt% paraffin wax and 10 wt% stearic acid. The solids loading was 60 vol.%. Tensile test specimens were shaped using a Boy XS injection moulding machine with a two-half mould thermalized at 40°C and a nozzle temperature of 120°C. Green parts were solvent debinded in heptane at 50°C for 20h, then thermal debinded at 500°C for 1h and sintered at 1270°C for 3h under nitrogen in a Nabertherm VHT08-16MO MIM furnace (Fig. 3). Selected samples were annealed at 1150°C for 1h and water quenched. Density measurements were made by the Archimedes method. Metallographic samples for SEM observation were polished and etched with Glyceregia etchant (15cc HCl, 10cc glycerol, 5cc HNO_3) at room temperature during 2 minutes. The constituent phases were determined by X-ray diffractometry (X'Pert Pro PANalytical) using a Cu K_α source (λ=0.154060 nm). Tensile tests were performed according to DIN EN ISO 6892-1 method B in a Zwick 1445 machine.

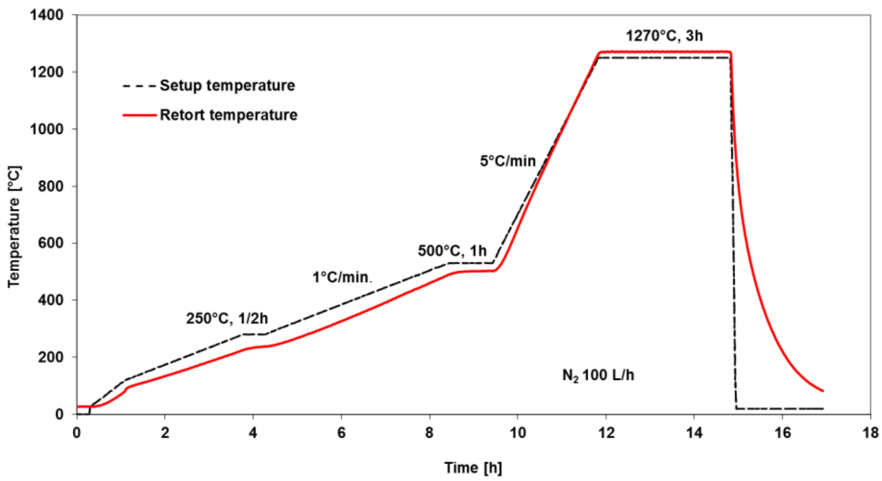

Figure 2. Thermal cycle for thermal debinding and sintering of P558 steel

RESULTS AND DISCUSSION

NMR spectroscopy (Fig. 3) allows to identify the synthesized PHBV copolymer as Poly-(3-hydroxybutyrate-co-3-hydroxyvalerate), named P(3HB-co-3HV). It is constituted of two monomers: 3-hydroxybutyrate (20 mol.%) and 3-hydroyvalerate (80 mol.%). The measured values for glass transition temperature and melting point temperatures were -12°C and 96°C respectively. Compared with the PHB homopolymer, PHBV confers good injectability to the multicomponent binder. Due to its stiffness PHBV provides good strength to both green and brown parts.

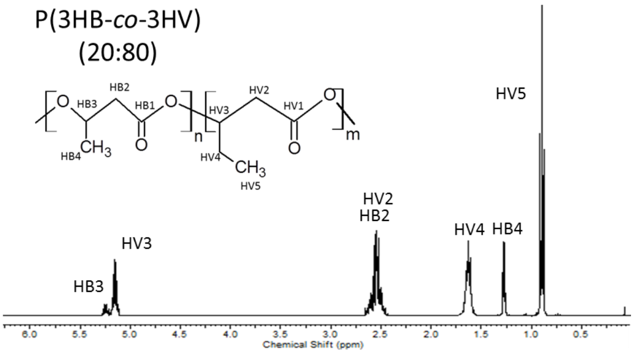

Figure 3: P(3HB-co-3HV)natural polymer structure and NMR characterization

Sintered P558 parts (Fig. 4) exhibit a density of 7.45 ± 0.05 g/cm^3 and a linear shrinkage of about 15%. The specimens are non-magnetic and the metallographic observation reveals a microstructure of austenitic equiaxed grains with some visible twins, and rounded porosity typical of PIM materials (Fig. 5). The measured X-ray diffraction patterns showed only peaks originating from the austenite γ phase, confirming the fully austenitic character of the sintered steel (Fig. 6).

Figure 4: PIM P558 austenitic steel green (top) and sintered (bottom) specimens.

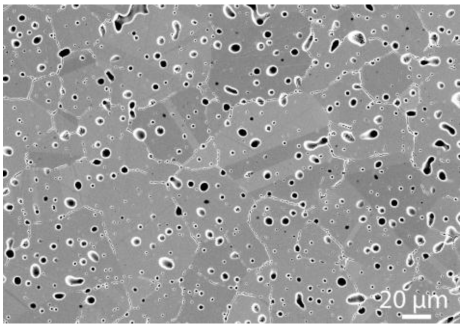

Figure 5: SEM observation of as-sintered PIM P558 austenitic steel

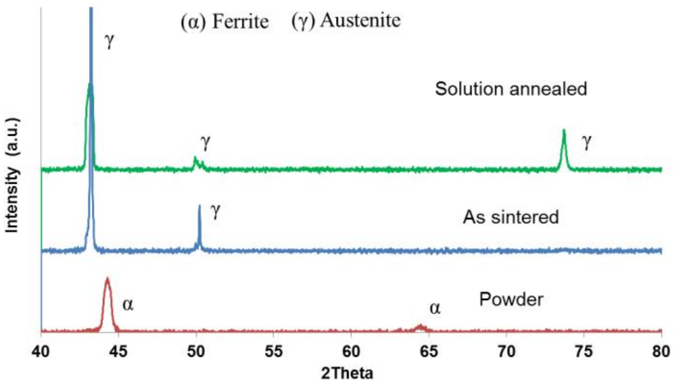

Figure 6: X-ray diffraction pattern of as-sintered and heat-treated PIM P558 steel

The mechanical properties for both as sintered and solution annealed specimens were evaluated by tensile tests. Measured values for yield stress (YS), ultimate tensile strength (UTS) and elongation (A5) are summarized in Table 2 and compared with reference P558 commercial steel [1]. Solution annealing improves mechanical properties by a solution hardening mechanism due to a large amount of interstitial nitrogen. Optimal quench rates are needed to prevent nitride precipitation, which has little influence on the yield and ultimate strength, but significantly reduces plasticity [8-9]. The strength of PIM P558 meets the values of the reference steel, but the ductility needs improvement, which could be achieved by optimizing both mixing conditions during feedstock processing and injection moulding parameters. These results are a preliminary step in the development of a feedstock fully-made of natural polymer, for which paraffin wax and stearic acid substitutes should be found and tested.

Table 2: Mechanical properties of P558 steel

	YS [MPa]	UTS [MPa]	A5 [%]
PIM P558 as sintered	640	800	16
PIM 558 solution annealed	600	900	25
Böhler P558 solution annealed	≥ 520	≥ 850	≥ 45

CONCLUDING REMARKS

Short chain length PHA natural polymers have been processed by bacterial fermentation, then characterized and used in the formulation of feedstock for powder injection moulding.
Nickel-free austenitic stainless steel with good mechanical properties has been processed. The feasibility of using P(3HB-co-3HV) natural polymer as a backbone binder constituent has been assessed. The optimization of the processing conditions to improve the material ductility is in progress.

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