MIM of nickel–free nitrogen strengthened austenitic stainless steel from biopolymer based feedstock

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MIM of nickel-free nitrogen strengthened austenitic stainless steel from biopolymer based feedstock

Nickel-free stainless steels are of high interest for medical and dental applications, as well as consumer goods where contact with the skin is a consideration. In this paper Prof Efraín Carreño-Morelli and colleagues from the University of Applied Sciences and Arts Western Switzerland evaluate the MIM processing of the high-nitrogen content austenitic stainless steel P558. This is processed using a novel environmentally friendly binder that incorporates a polymer produced by bacterial fermentation.

Stainless steels for surgical and dental prosthetics must meet several requirements, among which are good biocompatibility, absence of ferromagnetism, high corrosion resistance and a 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 effects of nickel-ion release in the human body [1-2]. Similar requirements are of interest also for the jewellery and watch industries. Several development studies and production from the 1990s have shown that nitrogen combined with molybdenum and manganese can effectively replace nickel as the austenite formation element and increase the corrosion resistance [3-5]. In high-nitrogen austenitic stainless steels processed by Powder Metallurgy, nitrogen can be added via the sintering atmosphere [3,6]. A wrought alloy grade (P558, Böhler) and a MIM feedstock with polyacetal binder, which is removed by catalytic debinding (Panacea, BASF), are commercially available. For the latter, different sintering and solid state nitriding conditions have been extensively studied [7-8].

Cost issues and market considerations have limited the use of PM nickel-free steels until now. In the case of MIM, the development of new environmentally friendly systems can offer new opportunities for widespread use of nitrogen strengthened stainless steels. Compared with polymers derived from oil, natural polymers offer the advantage of better biocompatibility, biodegradable character and sustainability. MIM binders are usually multi-component, composed

Fig. 1 MIM is a key production process for precision components in a wide range of industries, from watchmaking, jewellery and consumer electronics to critical applications in the automotive, medical and aerospace sectors. Many of these markets have an interest in the development of cost-effective nickel free stainless steel alloys

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

Table 1 Chemical composition of P558 stainless steel powder

of a filler phase (which provides good flowability), a surface active phase (to ensure good wettability of the powder by the binder), and a backbone phase (which provides green part strength). Among the natural polymers which can be used as filler phase, there are natural waxes such as carnauba wax. Castor oil, seed oil and stearic acid are biosourced surfactants. Finally, as a backbone phase, one can notably cite polyhydroxyalkanoates, bio-derived polyethylene, polylactic acid and polysaccharides.

Polyhydroxyalkanoates (PHAs) are natural polyesters synthesised by a large number of microorganisms under nutrient-limiting conditions and excess of carbon source. Several applications of PHAs, including bioplastics, fine chemicals, implant biomaterials and biofuels, have been developed in recent decades.

In this reported work, biosourced PHA polymers are used as backbone phase (removed by thermal debinding) for the powder injection moulding of nickel-free P558 stainless steel.

Fig. 2 P558 stainless steel gas atomised powder and its particle size distribution

Experimental

The selected backbone polymer was a PHBV copolymer, which is a polyhydroxyalkanoate-type polymer. It has been synthesised [9-10] by cultivating Ralstonia eutropha DSM 428 soil bacteria 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, recrystallisation and purification, the polymer was characterised by NMR in a Bruker 400 MHz spectrometer (Bruker, Billerica, Massachusetts, USA). The thermal properties were determined by DSC measurements. Paraffin wax (PW, Sigma Aldrich Chemie GmbH, Buchs, Switzerland) and two polyethylene glycol grades with different molecular weight were used as a second feedstock component: PEG 4000 (Alfa Aesar GmbH & Co KG, Karlsruhe, Germany) and PEG 8000 (Sigma Aldrich Chemie GmbH). The third component was stearic acid (SA, Sigma Aldrich Chemie GmbH).

The starting powder (Fig. 2) was a gas atomised nickel-free steel (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.

Feedstocks for MIM were prepared with the following binder formulations:

- 45 wt.% PHBV, 45 wt.% PW, 10 wt.% SA
- 45 wt.% PHBV, 45 wt.% PEG 4000, 10 wt.% SA
- 45 wt% PHBV, 45 wt.% PEG 8000, 10 wt.% SA

The solids loading was 60 vol.%. The PHBV-PW based feedstock was compounded in a laboratory mixer followed by extrusion in the injection moulding machine. Compounding
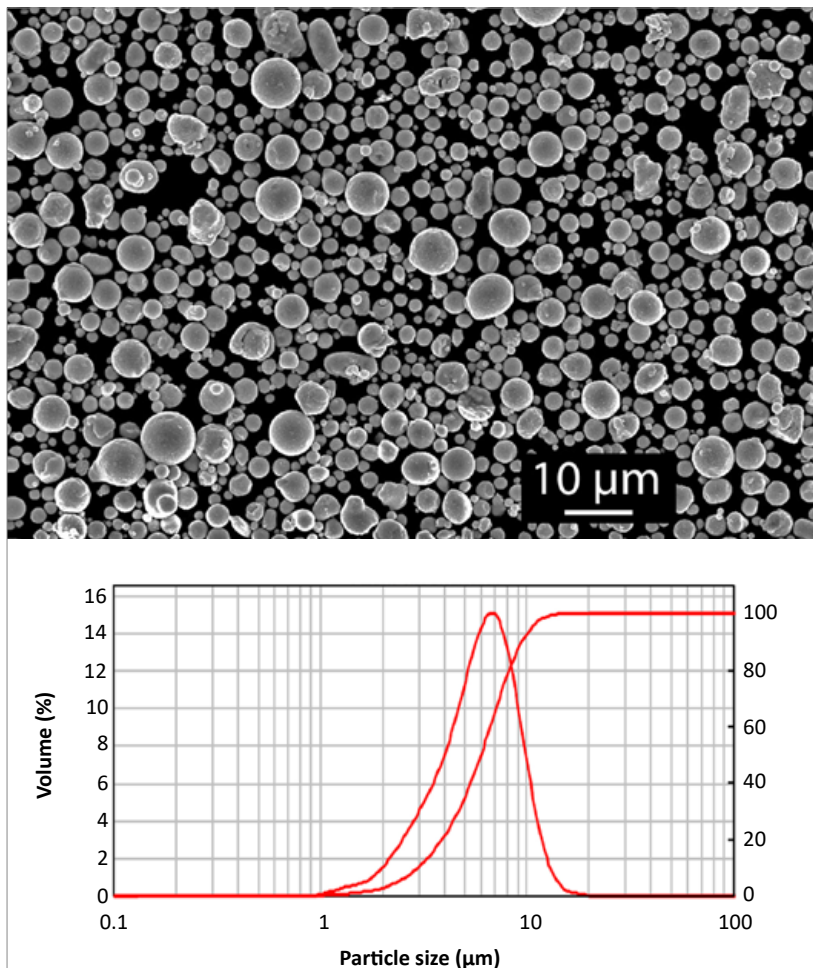
of PHBV-PEG based feedstocks was performed in a modular system Thermoscientific Polylab OS, with a Rheomix 600 mixer driven by a Rheodrive 7 torque rheometer, which allowed the production of small batches of feedstock. Tensile test specimens were shaped with a Boy XS injection moulding machine (maximum stroke volume 8 cm³), into a two-half mould thermalised at 40°C. The nozzle temperature was set up at 120°C. Green parts were solvent debound in water at 50°C for 20 h, then thermally debound at 500°C for 1 h and sintered at 1270°C for 3 h under nitrogen in a Nabertherm VHT08-16MO MIM furnace (Fig. 3). Selected samples were annealed at 1150°C for 1 h and water quenched. Density measurements were made by the Archimedes method. Metallographic samples for SEM observation were polished and etched with Glyceregia etchant (15 cm³ HCl, 10 cm³ glycerol, 5 cm³ HNO₃) at room temperature for 2 min. The constituent phases were determined by X-ray diffractometry (X'Pert Pro PANalytical) using a Cu K$_\alpha$ source (λ = 0.154060 nm). The mechanical properties for both as-sintered and solution annealed specimens were evaluated by tensile tests, which were performed according to DIN EN ISO 6892-1 method B in a Zwick 1475 machine. The carbon and nitrogen contents were measured by melt extraction with LECO devices.

Results and discussions

NMR spectroscopy (Fig. 4) allows the identification of the synthesised 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 temperature were -12°C and 96°C respectively. PHBV confers good injectability to the multicomponent binder. Moreover, its stiffness provides good strength to both green and brown parts.
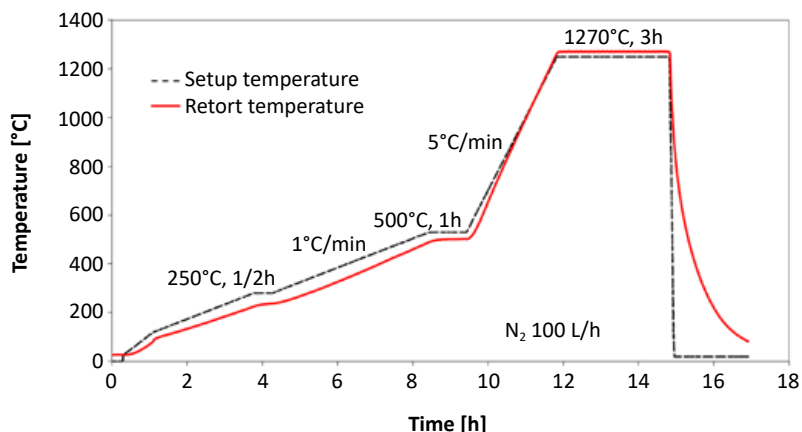

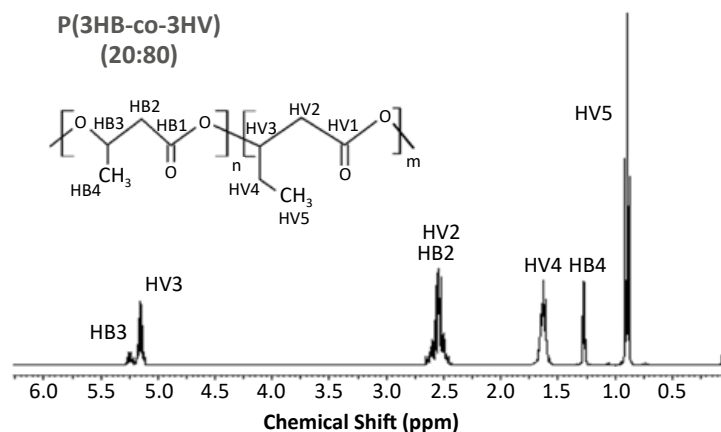*Fig. 3 Thermal cycle for thermal debinding and sintering of P558 steel*

Fig. 4 P(3HB-co-3HV) natural polymer structure and NMR characterisation

Fig. 5 MIM P558 austenitic stainless steel green (top) and sintered (bottom) specimens

Green parts from PHBV-PW based feedstocks exhibited better green strength than those moulded from PHBV-PEG based feedstocks (among which the use of PEG 8000 led to the best results).

Sintered P558 parts (Fig. 5) exhibit a density of 7.46 ± 0.08 g/cm³ and a linear shrinkage of about 15%. The measured X-ray diffraction patterns showed only peaks originating from the austenite γ phase, confirming
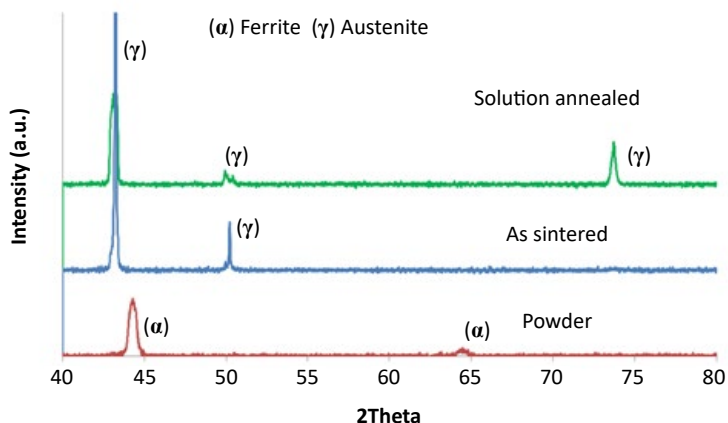
Fig. 6 X-ray diffraction patterns of as-sintered and heat-treated MIM P558 stainless steel
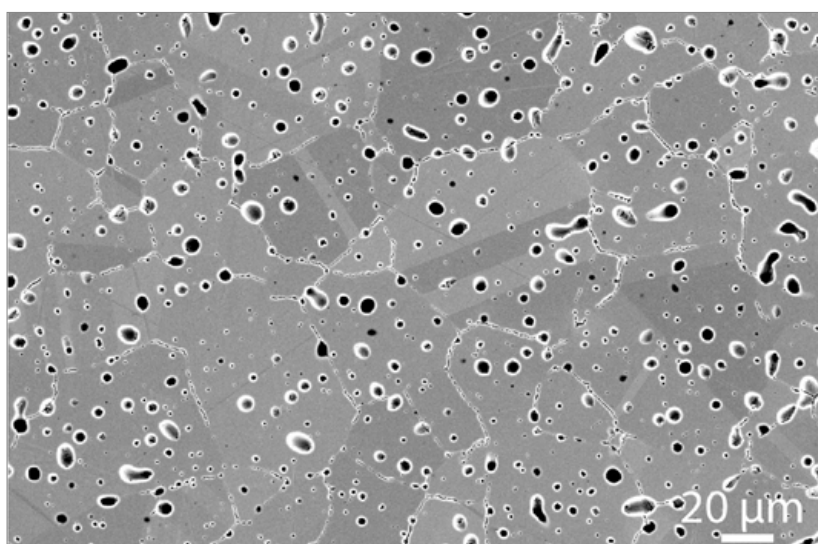

Fig. 7 SEM observation of as-sintered MIM P558 austenitic stainless steel
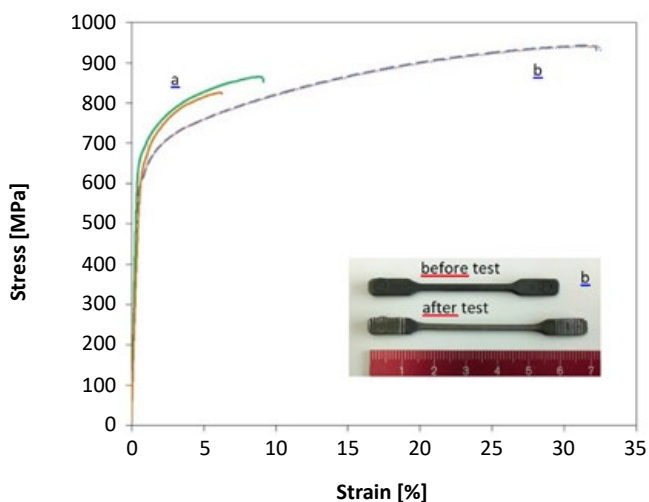

Fig. 8 Tensile behaviour of MIM P558 austenitic steel (from PHBV - PEG 8000 - SA - steel feedstock) for as sintered (a) and solution treated (b) conditions

the fully austenitic character of the sintered steel (Fig. 6). The specimens are non-magnetic, with a total absence of attraction by strong NdFeB magnets, which is also a confirmation of the fully austenitic character of the sintered steel. The metallographic observation reveals a microstructure of austenitic equi-axed grains with some visible twins and rounded porosity typical of MIM materials (Fig. 7).

Measured values for yield stress (YS), ultimate tensile strength (UTS) and elongation (A) for both as-sintered and solution annealed parts are summarised in Table 2 and compared with the reference P558 commercial steel [1]. Sintering under nitrogen atmosphere is a key step for improving mechanical properties by a solution hardening mechanism due to a large amount of interstitial nitrogen. However, limited cooling rates achieved during furnace cooling can lead to the precipitation of chromium nitride precipitates, which has little influence on the yield and ultimate strength, but significantly reduces ductility [11-12]. Then, a solution annealing treatment followed by quenching is needed. The carbon and nitrogen contents were 0.15% and 0.90% respectively, with no significant increase between the as-sintered and annealed conditions. It has been suggested that the nitrogen level must be kept below 0.95% to avoid a ductile-to-brittle transition [3]. The tensile behaviour of both as-sintered and solution treated parts, processed from PHBV - PEG 8000 - SA - steel feedstock, are shown in Fig. 8. This feedstock formulation has led to the best mechanical performance. Both tensile strength and ductility are improved after solution annealing and quenching, which is due to the effective dissolution of Cr_2N precipitates present in the as-sintered material [8]. The strength of MIM P558 meets the values of the reference steel. Ductility values of about 30% are lower than the reference value of 45% for wrought steel, but good enough for a large variety of potential applications (e.g., watch cases and bracelet segments).

steel	processing details	YS [MPa]	UTS [MPa]	A [%]
MIM P558 as sintered	from PHBV-PW-SA-steel feedstock	640	800	16
	from PHBV-PEG4000-SA-steel feedstock	620	814	9
	from PHBV-PEG8000-SA-steel feedstock	643	846	7
MIM P558 solution annealed	from PHBV-PW-SA-steel feedstock	600	900	25
	from PHBV-PEG4000-SA-steel feedstock	541	905	30
	from PHBV-PEG8000-SA-steel feedstock	587	942	32
Böhler P558 solution annealed	wrought, reference material	≥ 520	≥ 850	≥ 45

Table 2 Mechanical properties of MIM P558 stainless steel compared with a reference wrought steel

Concluding remarks

Biosourced P(3HB-co-3HV) co-polymer has been processed by bacterial fermentation, then characterised and used in the formulation of MIM feedstock in combination with stearic acid and paraffin wax (heptane soluble) or polyethylene glycol (water soluble).

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.

Despite PEG being produced from ethylene coming from the petrochemical industry, its use as a second feedstock constituent to replace paraffin wax is a more environmentally friendly option, because of its water soluble character. The development of fully biosourced MIM binder is in progress.

Acknowledgments

Authors

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[13] E Carreño-Morelli, M Zinn, M Rodriguez-Arbaizar, M Bassas, Proc. of European Powder Metallurgy Conference Euro PM2015, Reims, France, October 4-7, 2015, pp. 1-4.

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