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Nb-Si intermetallic composites for high-temperature applications produced by MIM

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Abstract

Refractory alloys such as Nb-Si intermetallic composites exhibit low density and high strength above the operating temperature of currently applied nickel-based superalloys. Due to these advantageous properties they offer a potential to replace superalloys in structural components for high-temperature applications, such as aircraft or land-based turbines. In this study, gas atomised powder as well as high-energy mechanically alloyed powder of the recently developed alloy composition Nb-20Si-23Ti-6Al-3Cr-4Hf (at%) was produced to evaluate the feasibility for processing by MIM. A feedstock consisting of a wax-polymer based binder was successfully moulded into simple shapes. Sintering at 1500°C for 3 hours at high vacuum showed promising results for the fine powder fraction of gas atomised powder concerning residual porosity, homogeneity of the multiphase microstructure and interstitial elements contamination. Compared to other processing technologies, the processed MIM samples reveal a very fine-grained microstructure with more homogeneously distributed silicide particles.

Introduction

The efficiency of turbine engines can be further improved by increasing the operating temperature in the high-pressure section. To fulfil these requirements innovative materials are necessary that withstand temperatures beyond the operating conditions of currently used nickel-based superalloys. Refractory alloys such as niobium-based silicide intermetallic composites (Nb-Si) are a promising material group for these applications. Besides high strength at elevated temperatures, they reveal a low density of around 7 g/cm³ compared to nickel-based superalloys with a density of about 9 g/cm³ [1,2]. Nb-Si alloys consist of a ductile niobium solid solution (Nb_{ss}) matrix which provides toughness at room temperature while an intermetallic silicide phase based on Nb₅Si₃ particles provides high-temperature strength and oxidation resistance. Alloying elements such as titanium, chromium and aluminium are added to improve the corrosion resistance, while hafnium should strengthen the niobium matrix. Until now, the utilized processing technologies to develop and process Nb-Si alloys were mainly casting, directional solidification, arc melting plus subsequent extrusion, physical vapour deposition and hot extrusion of gas atomised powders [3]. Processing the material in large batch sizes aiming at a good homogeneity of the dual phase microstructure and to prove its feasibility in industrial scale is still a challenge [2,3].

Metal Injection Moulding (MIM) is known as a near-net-shape manufacturing technology that is industrially applied to produce technical parts with a homogeneous microstructure [4]. A wide range of materials can be processed provided that certain requirements are taken into account for the utilized powders. Whereas nickel-based superalloys have already been processed by MIM in research and industry [5,6,7], Nb-Si alloys are a new material group processed by MIM.

The aim of this project is to find a suitable feedstock composition and preparation conditions for MIM of Nb-Si powders of the alloy composition Nb-20Si-23Ti-6Al-3Cr-4Hf (at%) that were produced by gas-

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atomisation as well as high energy mechanical alloying of elemental powders. The feedstock development includes a comprehensive characterisation of the feedstock properties for one of the feedstocks, the production of simple MIM shapes and appropriate conditions for debinding and sintering. The porosity, the multiphase microstructure, the residual carbon, nitrogen and oxygen content as well as the density of the sintered MIM samples are analysed to determine the influence of the powder source and to assess MIM of Nb-Si alloys with regard to other processing technologies.

Experimental procedure

Powder production

Two different powder production techniques were utilized to prepare Nb-Si powder of the nominal composition Nb-20Si-23Ti-3Cr-6Al-4Hf (at%). On the one hand, the alloy was gas atomised (GA) starting with plasma melting element pieces and casting them into a 100 mm die that was double melted to produce a 150 mm diameter billet. To meet the requirements for atomisation the billet was subsequently wire eroded (EDM) into seven 44 mm diameter rods. These rods as well as the remaining ingot were gas atomised by electrode induction melting (EIGA) in argon atmosphere. The powder was subsequently classified into several size fractions. The fractions with a nominal particle size of <25 μm and <45 μm were utilized. The powder particles are spherical and show a smooth particle surface providing a good flowability for MIM (Figure 1). A particle size distribution (PSD) was determined with a laser diffractometer (type LS, Beckmann Coulter). It reveals a d_{90} value of 32 μm for the GA <25 μm powder and a d_{90} value of 40 μm for the GA <45 μm powder fraction (Figure 2). Usually, MIM requires fine powders with a particle size below 20 μm [4]. The GA <25 μm powder fraction reveals some coarse agglomerates with a size of about 100 μm . These agglomerates are expected to be deagglomerated during feedstock preparation by the shearing forces of the mixer.

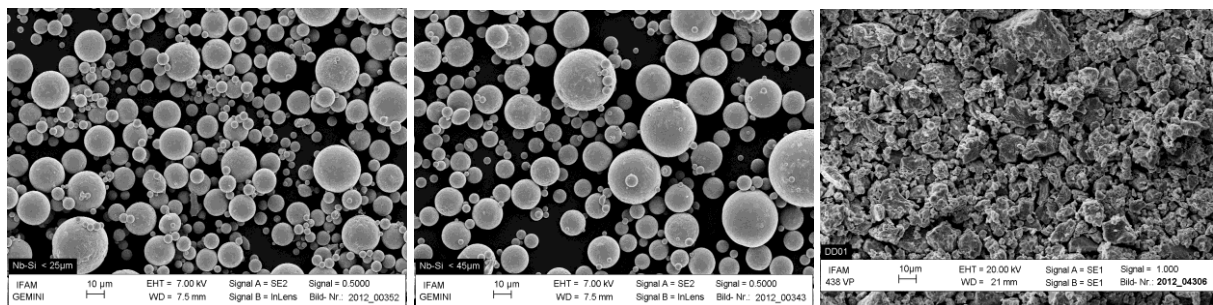


Figure 1: SEM image of the Nb-Si powder fractions GA <25 μm (l.), GA <45 μm (m.) and the MA powder (r.)

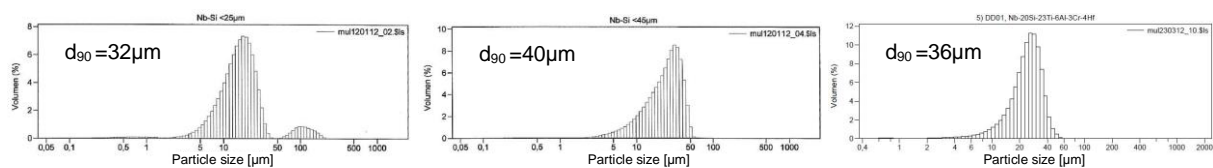


Figure 2: Particle size distribution of the powder fractions GA <25 μm (l.), GA <45 μm (m.) and the MA powder (r.)

Another Nb-Si powder of the same nominal composition Nb-20Si-23Ti-3Cr-6Al-4Hf was produced by mechanical alloying of elemental powders with hardened steel balls (diameter 5 mm) in a Zoz CM01 Simoloyer attritor. The ball-to-powder weight ratio (BPR) was 10:1. During milling the attritor was cooled to -15°C to prevent sticking of the powder to the balls and the walls of the attritor. The total milling time of 10 h was reached by cycling 30 s of milling at 1200 rpm and 30 s of milling break for cooling. The alloyed powder was subsequently sieved to a nominal fraction of <25 μm . The PSD measurement shows a d_{90} value of 36 μm (Figure 2).

Feedstock development

The powder fractions were mixed with a wax-polymer based binder with a suitable powder load providing adequate feedstock flowability (Table 1). The multi-component binder system contains a mixture of polyethylene (PE), waxes and stearic acid. Due to the very spherical particles and a high content of wax and stearic acid the powder load could be defined at 70 vol% for both GA powder fractions. The mixing was done at 120°C for 2 hours in a 50 ml double-sigma mixer (Brabender Plastograph).

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Table 1: Nb-Si powder and feedstock characteristics

Feedstock	Powder source	Nominal particle size	Actual particle size (d_{90})	Powder load
GA <25 μm	Gas atomisation	<25 μm	32 μm	70 vol%
GA <45 μm	Gas atomisation	<45 μm	40 μm	70 vol%
MA	Mechanical alloying	<25 μm	36 μm	52 vol%

A larger amount of feedstock of about 1600 ml (7.8 kg) of the fine GA <25 μm powder fraction was prepared using the same powder load of 70 vol%. It was mixed in a high speed laboratory mixer (type TGHK 5, Lödige) at 120°C for 2 hours and subsequently homogenised and granulated on a shear roll extruder (type BSW 135-1000, Bellaform). This feedstock was used to determine the feedstock properties. Due to the angular and irregular shaped particles the powder load for the MA powder feedstock was defined at 52 vol%. Due to its affinity to oxygen the powder was handled under inert gas atmosphere (argon) during mixing at 120°C for 2 hours in a 100 ml mixer (type PMS, FEMIX).

Feedstock characterisation

A comprehensive feedstock characterisation was only carried out for the GA <25 μm feedstock. The feedstock viscosity, the specific volume, the thermal conductivity and the specific heat capacity were determined. The viscosity was evaluated at the temperatures 100°C, 110°C and 120°C and shear rates between 10 and 4000 s^{-1} which are expected during moulding. The analysis was carried out on a high pressure capillary rheometer (Rheograph 2002, Göttfert) using a slit nozzle with a nozzle clearance of 0.5×10 mm. The specific volume was evaluated against pressure (200 – 1600bar) and temperature (40 – 120°C) measured with isobaric cooling of 6 K/min on a pvT-analyser (type PVT100, SWO Polymertechnik, according to ISO 17744). The thermal conductivity was measured at temperatures between RT and 120°C at ambient pressure with a linear heat source according to ASTM D5930-09 (K-System II, Advanced CAE Technology). The specific heat capacity c_p was determined in the temperature range from 0°C to 120°C by DSC (type DSC1, Mettler Toledo, according to ISO 11357-4) with a linear heating rate of 10 K/min at N_2 gas atmosphere.

Injection moulding, debinding and sintering

The feedstocks were moulded into disk-shaped samples of 30 mm in diameter and 4 mm in thickness on a piston injection moulding machine (HEK). The feedstock temperature was 100°C with an injection pressure of 6 bar without any packing pressure. The green samples were solvent extracted in hexane for 20 hours at room temperature to remove the wax ingredients of the binder. The mass loss was monitored to assure that at least 95 % of the waxes were extracted. The polymeric backbone of PE was removed by thermal debinding previous to the sintering in a combined debinding-sintering furnace (ELNIK MIM 3001). The thermal debinding was carried out with a low heating rate of 3 K/min in argon atmosphere at 600 mbar. To ensure a residue-free binder removal at 600°C a holding step for 1 hour was implemented. The sintering was performed with a heating rate of 5 K/min and sintering temperature of 1500°C for 3 hours at high vacuum as shown in Figure 3. The samples were placed on an Y_2O_3 coated plate and surrounded by titanium sponge getters to prevent oxidation on the surface of the samples. Further they were covered by another plate to provide an argon gas flow along the getter material during debinding.

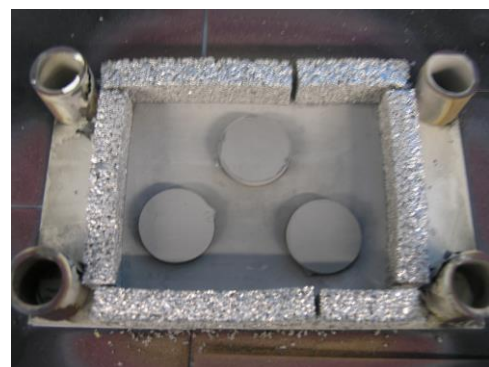
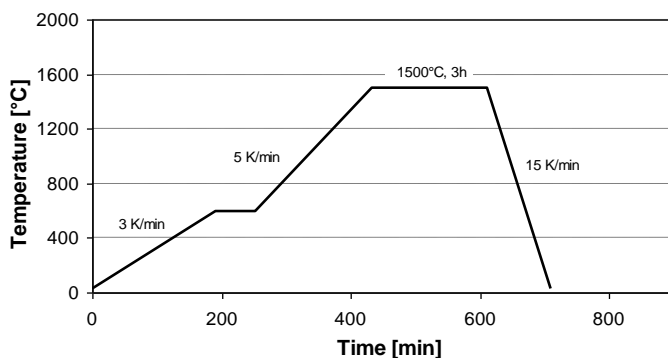


Figure 3: Thermal debinding and sintering cycle (l.) and Nb-Si disk-shaped samples after sintering (r.)

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Characterisation methods for sintered material

The sintered samples were prepared according to the common method of grinding and polishing with diamond paste. Optical light microscopy and scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray analysis (EDX) were performed to evaluate the microstructure. The contamination by carbon, oxygen and nitrogen was assessed for the gas atomised powders and the sintered MIM samples by melt extraction method (TC-436, Leco). All the values of phase analyses and interstitial elements are average values of three measurements. The density was measured by fluid displacement method in ethanol by Archimedes' principle on a precision balance (type XS603S Delta Range, Mettler Toledo).

Results and discussion

Feedstock properties

The properties of the feedstock that was prepared with the Nb-Si GA <25 μm powder are shown in Figure 4. For the relevant processing temperatures and shear rates the feedstock reveals a viscosity in the range of 15 to 80 Pa*s. The pvT data of the feedstock confirms an expected pressure-volume-temperature correlation suitable for injection moulding. The thermal conductivity and specific heat capacity c_p at processing temperature are about 1.205 W/mK and 450 J/kg°C, respectively. Altogether, these characteristics are typical for standard MIM feedstocks [4] and reveal an adequate flowability and good processability for injection moulding.

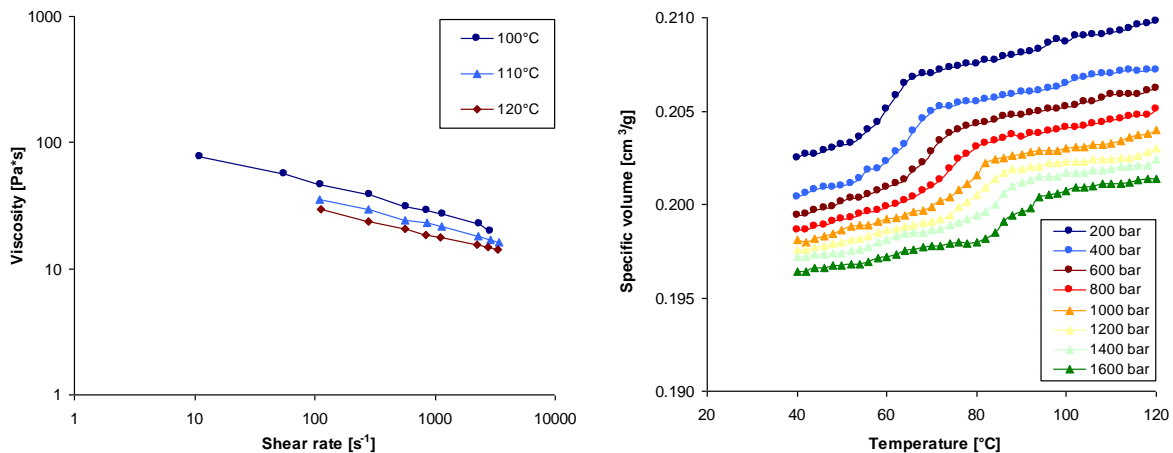
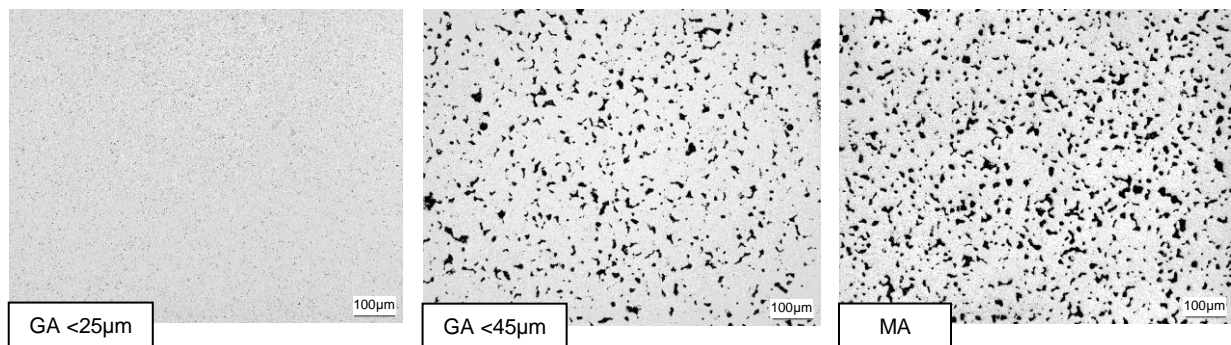


Figure 4: Properties of the Nb-Si GA <25 μm powder feedstock including viscosity (l.) and pvT data (r.)

Microstructure

Optical micrographs of the sintered MIM samples of the GA <25 μm , GA <45 μm and the MA powder are shown in Figure 5. The sintered GA <25 μm material seems to have almost full density revealing an optical residual porosity much lower than that of the GA <45 μm and the MA samples. The sintered GA <45 μm and the MA samples show a closed porosity with pores of up to 15 μm in diameter. Optical microscopy reveals a fine-grained and homogeneous dual phase microstructure in all processed materials. The agglomerates that were noticed in the GA <25 μm powder by PSD analysis (Figure 2) were obviously deagglomerated during mixing and did not interfere the sintering.



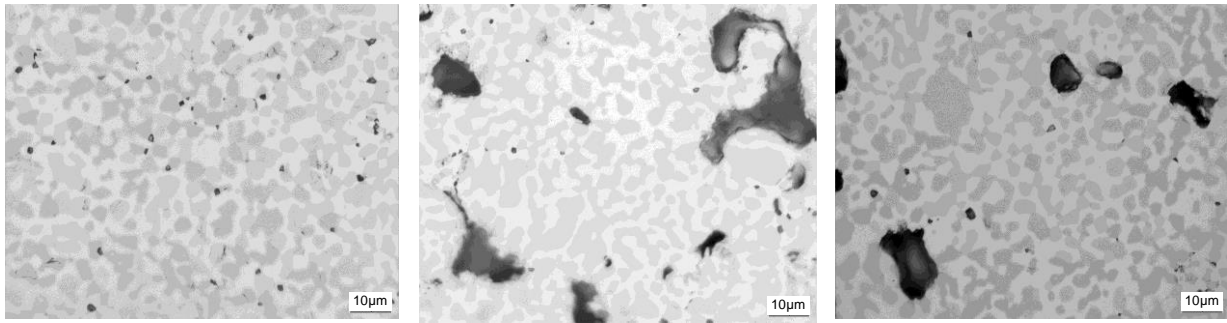
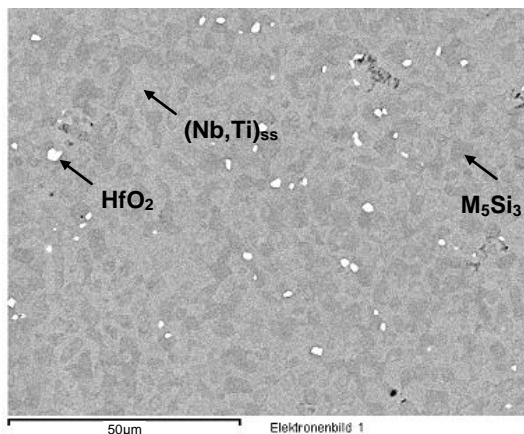


Figure 5: Optical micrographs of the sintered MIM samples of GA <25µm (l.), GA <45µm (m.) and MA powder in two magnifications

The SEM/EDX analysis on the sintered GA <25 µm material shows the phases in detail (Figure 6). The dual phase microstructure consists of a light grey (Nb,Ti)_{ss} phase and a dark grey M₅Si₃ phase of intermetallic silicide particles. The composition of the observed phases is given in the table. The niobium solid solution (Nb,Ti)_{ss} consists mainly of Nb and Ti but also Cr, Al and Hf. The intermetallic silicide particles M₅Si₃ consist of a mixture of Nb, Ti, Hf silicide. The size of the silicide particles seem to be homogeneous and in the range of some micrometers, not exceeding a diameter of 10 µm. It is comparable for all sintered powders. The SEM micrograph also reveals tiny, white spots that are evenly distributed among the dual-phase microstructure. These can also be noticed in the optical micrographs as dark spots (Figure 5) and consist of hafnium oxide (HfO₂). Obviously, part of the Hf present in the solid solution reacts with the dissolved oxygen to yield hafnia particles during powder processing.



	Nb [at%]	Ti [at%]	Hf [at%]	Cr [at%]	Al [at%]	Si [at%]	O [at%]
(Nb,Ti) _{ss}	54.5	26.4	2.4	5.1	8.1	3.6	---
M ₅ Si ₃	42.9	16.0	3.6	---	2.4	35.1	---
HfO ₂	7.6	2.1	29.1	0.2	1.4	---	59.6

Figure 6: SEM micrograph (l.) and phase analysis by EDX (r.) for the sintered GA <25 µm powder

The microstructure that was achieved by MIM reveals a much finer grained microstructure with more homogeneously distributed silicide particles compared to Nb-Si alloys with slightly different chemical composition that were processed via directional solidification, hot isostatic pressing (HIP) and hot extrusion of gas atomised powders [3]. Obviously, MIM of fine gas atomised Nb-Si powders is a promising process route to produce an adequate homogeneous dual phase microstructure especially if a very fine-grained microstructure is required.

Interstitial elements

The carbon, nitrogen and oxygen content of the utilized gas atomised powders and the corresponding sintered MIM samples are shown in Figure 7. The carbon and nitrogen content did not change significantly during the MIM process. While the oxygen content of the GA <25 µm and GA <45 µm powder is comparable, the sintered MIM samples of the fine GA <25 µm material show an increase in oxygen although both were sintered in the same sintering cycle. Probably, due to the larger specific surface of the finer particles, the GA <25 µm fraction picks up more oxygen during MIM processing than the coarse GA <45 µm powders.

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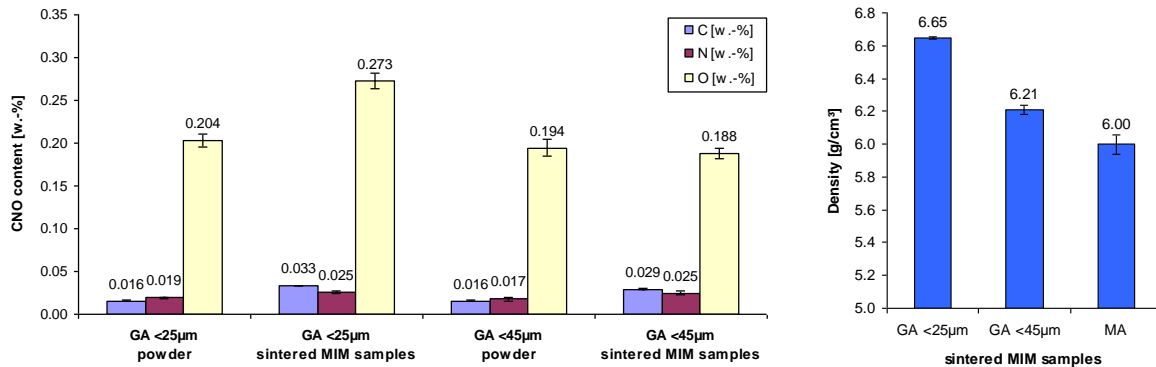


Figure 7: Interstitial elements carbon, nitrogen and oxygen in the gas atomised powders and the corresponding sintered MIM samples (l.); density of the sintered MIM samples (r.)

Density

The sintered MIM samples reveal a density of 6.65 g/cm³ for the GA <25 µm material, 6.21 g/cm³ for the GA <45 µm material and 6.00 g/cm³ for the MA material. The density measurements correspond to the micrographs that reveal very low porosity for the GA <25 µm material and higher porosities for the GA <45 µm and the MA material. A relative density of 97 % was reached for the GA <25 µm powder according to the pycnometry density (6.85 g/cm³) of fully dense samples gained by HIPing of a coarse gas atomised powder fraction. To increase the density of the MIM parts even further, a post-HIP processing could be a possibility.

Conclusions

In this study, a Nb-Si intermetallic composite was processed by MIM using gas atomised as well as mechanically alloyed powder. The developed MIM process included a feedstock development, a comprehensive feedstock analysis for one of the feedstocks, the debinding and the sintering conditions as well as a characterisation of the sintered MIM samples. The following conclusions can be noted:

- A processable feedstock was developed using a wax-polymer based binder system with an adequate powder load that was adapted to the powder characteristics.
- The feedstock characterisation with the GA <25 µm powder feedstock showed homogeneous properties with adequate qualities for successful MIM processing. The chosen powder load revealed an adequate flowability to produce MIM parts with simple shape.
- The GA <25 µm powder fraction allows to produce MIM samples with low residual porosity and a homogeneous fine-grained dual phase microstructure compared to other processing technologies. Powder agglomerates were deagglomerated during mixing. The oxygen content increased only slightly during MIM processing.
- The acquired knowledge provides a solid basis to develop the injection moulding, debinding and sintering process for geometrically complex technical components.
- Further characterisations as the mechanical properties at elevated temperatures still have to be evaluated. The sufficient oxidation resistance at application temperature can not be reached by the Nb-Si material itself and must be provided by an adequate coating.

Acknowledgement

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