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EFFECT OF SINTERING PARAMETERS ON THE DENSITY, MICROSTRUCTURE AND MECHANICAL PROPERTIES OF THE NIOBIUM-MODIFIED HEAT-RESISTANT STAINLESS STEEL GX40CrNiSi25-20 PRODUCED BY MIM TECHNOLOGY

VPLIVI PARAMETROV SINTRANJA NA GOSTOTO, MIKROSTUKTURO IN MEHANSKE LASTNOSTI Z NIOBIJEM LEGIRANGA NERJAVNEGA OGNJEVZDRŽNEGA JEKLA GX40CrNiSi25-20, IZDELANEGA Z MIM-TEHNOLOGIJO

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Properties of heat-resistant, stainless-steel parts produced by the metal-injection-molding (MIM) process depend mostly on the sintering parameters. The effect of these sintering parameters on the densification, microstructure, hardness and tensile properties of the niobium-modified, heat-resistant stainless steel GX40CrNiSi25-20 were investigated. The prepared feedstock was injection molded to obtain tensile test specimens (ISO 2740). The debinding of the molded parts was performed using the catalytic debinding method, while the residual binder was removed by thermal debinding. The sintering was performed at 1200 °C and 1310 °C, in argon (Ar), hydrogen (H_2) and nitrogen (N_2) atmospheres, with the sintering times between 3 h and 6 h. It was found that sintering in a nitrogen atmosphere increased the strength and reduced the ductility. The mechanical properties were also enhanced by a higher sintering temperature (1310 °C), due to the positive effects of the pore rounding and increased density. The prolonged sintering time caused changes in the grain size, but had little effect on the density. Faster sintering and improved ductility was observed for the samples sintered in hydrogen and argon atmospheres.

Keywords: metal injection molding, heat-resistant stainless steel, sintering parameters, density, microstructure, mechanical properties, metal powder

Lastnosti izdelkov iz ognjevzdržnega nerjavnega jekla, izdelanih s tehnologijo brizganja praškastih materialov (MIM) so v največji meri odvisne od parametrov sintranja. Vplivi parametrov sintranja na zgoščevanje, mikrostrukturo, trdoto in trdnostne lastnosti z niobijem legiranega nerjavnega ognjevzdržnega jekla GX40CrNiSi25-20 so opisani v tem članku. Iz pripravljenega surovega materiala so bili nabrizgani vzorci za preizkuse z injekcijskim ulivanjem. Sintranje je bilo izvedeno pri temperaturah 1200 °C in 1310 °C v argonski (Ar), vodikovi (H_2) in dušikovi (N_2) atmosferi v trajanju med 3 h in 6 h. Ugotovljeno je bilo, da sintranje v dušikovi atmosferi povzroči utrjevanje materiala in zmanjšanje duktilnosti. Mehanske lastnosti so bile povečane tudi pri višji temperaturi sintranja (1310 °C) zaradi zaokroževanja por in povečanja gostote. Podaljšan čas sintranja je povzročil spremembe v velikosti zrn, vendar je imel majhen vpliv na gostoto sintranih delov. Hitrejše sintranje in izboljšana plastičnost je bila pri vzorcih, ki so bili sintrani v vodikovi in argonski atmosferi.

Ključne besede: praškasti materiali, ognjvzdržno nerjavno jeklo, sintranje, gostota, mikrostruktura, mehanske lastnosti

1 INTRODUCTION

The metal-injection-molding (MIM) process combines the advantages of polymer injection molding with the material flexibility of powder metallurgy. MIM technology enables the mixing of different metal powders with different binders and allows the processing of materials with complex mechanical, thermal, wear and magnetic properties. It is a cost-effective process in the high-volume production of small and complex-shaped parts.[1–3] The application of MIM technology in the production of complex-shaped components from heat-resistant stainless steel represent a very attractive solution to reduce manufacturing costs and overcome the machinability problems.

Heat-resistant stainless steels are selected for a wide range of applications because of their superior resistance to creep, corrosion and oxidation. Heat-resistant stainless steel GX40CrNiSi25-20 modified with niobium belongs to the group of precipitation-hardened steels. This high-temperature alloy provides strength and oxidation resistance at temperatures up to 1200 °C and it is generally used in the presence of combustion gases that may be generated from exhaust and pollution-control equipment.

There are four main steps that make up the MIM process: preparation of feedstock (mixing of metal powder with binder), injection molding, solvent/chemical debinding and sintering.[4] The most complex step of MIM technology in producing stainless-steel parts is sintering. Sintering parameters, such as, heating and

cooling rate, sintering time, sintering atmosphere, sintering temperature, partial pressure of sintering atmosphere, affect the mechanical and physical properties, as well as corrosion and the heat resistance of sintered parts.[5] The wrong sintering parameters can lead to a low density, the absorption and desorption of some elements, deteriorated mechanical properties, reduced corrosion and oxidation resistance and a reduced service time.[5] Also, if the optimal parameters are not selected, increased sintering costs can be expected.

In this regard, the effect of sintering temperature, time and atmosphere on the physical and mechanical properties of metal-injection-molded heat-resistant stainless steel GX40CrNiSi25-20 modified with niobium was investigated in this work.

2 EXPERIMENTAL WORK

2.1 Material

Niobium-modified GX40CrNiSi25-20 is a heat-resistant stainless steel with a high resistance to creep and oxidation. A higher percent of chromium provides superior oxidation resistance, while a higher percent of carbon, compared to ordinary austenitic stainless steel, provides high strength and creep resistance.[6,7] The niobium addition gives structural stability and precipitation hardening. The austenitic structure provides the strength and structural stability at elevated temperatures. This steel is intended for high-temperature applications, up to 1200 °C, e.g., turbine blades or furnace parts. The production of feedstock involved the mixing of pre-alloyed metal powder with a suitable binder. The typical chemical composition after sintering is presented in **Table 1**.

Table 1: Typical chemical composition after sintering niobium-modified GX40CrNiSi25-20 in mass fractions, *w*/%
Tabela 1: Tipična kemična sestava sintranega jekla GX40CrNiSi25-20 s povišanim niobijem v masnih deležih, *w*/%

C	Cr	Ni	Si	Nb	Fe
0.2–0.5	24–26	19–22	0.75–1.3	1.2–1.5	Bal

2.2 Injection molding

The injection molding of the prepared feedstock was made in a machine for the injection molding of metal powders type ALLROUNDER 320 C 600–100. The shape of the mold cavity corresponds to a standard specimen for tensile tests used in powder metallurgy (ISO 2740).

At the beginning of the injection-molding process the material is heated to 185 °C at the nozzle of the barrel and with a screw rotation transported at the barrel top. The back pressure of the accumulated material was 30 bar. After the accumulation of a sufficient quantity of material, the screw stops rotating and moves forward, pushing the melted material into the tool cavity at a tool temperature of 110–115 °C. The holding pressure of 900 bar and its duration of 3 s provide for complete cavity filling. After the injection molding, the parts were cooled for 27 s.

The average density of the injection-molded parts was 5.5 g/cm^3.

2.3 Catalytic debinding

After the injection molding the parts were debound by a catalytic debinding method. Polyacetal, as a main component of the feedstock, was decomposed by nitric acid at a temperature below the melting point of polyacetal, preventing the parts from deformation during the debinding. Usually, a small concentration of a backbone polymer, that is unaffected by the catalyst, is included to hold the particles together until the material is ready to start forming necks between the particles by diffusion (often polyethylene).

The debinding was performed at 120 °C, where vaporized acid exists in the atmosphere. A nitrogen flow rate of 50 L/min was used to spread the nitric acid over the debinding furnace chamber. The nitric acid flow rate was 3.4 mL/min. The preheating time and the debinding time used during the debinding were 30 min and 4 h, respectively. A purging time of 30 min was used to remove the residual acid to the combustion chamber, where it was burned by propane gas.

2.4 Thermal debinding and sintering

The thermal debinding and sintering were performed in the same furnace type MIM 3045. The parts were gradually heated to 600 °C, where the residual binder starts to degrade and annealed for 2 h. After the residual binder was totally removed the parts were heated to the sintering temperature. The sintering is a process with the temperature, time and sintering atmosphere as influential factors. The thermal cycle of the debinding was the same for all the experiments (**Figure 1**). The sintering temperatures were 1200 °C and 1310 °C and the sintering

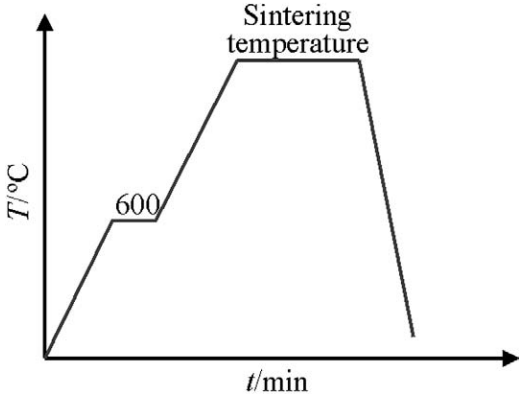

Figure 1: Thermal cycle of sintering and debinding
Slika 1: Termalna cikla sintranja in odstranjevanja veziva

times were 3 h and 6 h. The atmospheres used during the experiments were hydrogen, nitrogen, and argon.

3 RESULTS AND DISCUSSION

3.1 Density

The density of the sintered parts was measured by Archimedes' immersion method. The influence of the sintering atmosphere, temperature and time on the density of the investigated material was performed and analyzed using a general full factorial experiment. Analysis of variance (ANOVA) was used to demonstrate the significance level of the variables, as well as the effect of the sintering variables on the sintered density. The influential factors, their levels and average density for a selected set of parameters are presented in **Table 2**.

Table 2: Sintering conditions and density of sintered alloy
Tabela 2: Pogoji sintranja in gostota sintrane zlitine

Atmosphere (A)	Temperature, °C (B)	Time, h (C)	Average density, g/cm^3
Ar	1 200	3	6.89
H_2	1 200	3	7.27
N_2	1 200	3	6.59
Ar	1 310	3	7.71
H_2	1 310	3	7.80
N_2	1 310	3	7.75
N_2	1 310	6	7.66
H_2	1 310	6	7.77
Ar	1 310	6	7.72
N_2	1 200	6	7.16
H_2	1 200	6	7.44
Ar	1 200	6	7.17

Generally, all the sintering variables have a significant effect on the sintered density. The ANOVA (**Table 3**) showed that the sintering temperature has the highest influence on the sintered density (72.6 %), followed by the sintering atmosphere (9.3 %), the sintering time (4.1 %) and the two-factor and three-factor interactions. The influence of the sintering temperature, time and atmosphere on the density of the sintered parts is shown in **Figure 2**. It was found that sintering time has a significant effect on the sintered density only at 1200 °C, increasing the average sintered density from 6.91 g/cm^3 to 7.26 g/cm^3. A longer sintering time at 1310 °C caused insignificant changes to the density, which has to be taken into account during the sintering-costs analysis.

Higher sintering temperatures caused a more intensive atomic diffusion, resulting in faster sintering and higher resulting densities. Increasing the sintering temperature from 1200 °C to 1310 °C resulted in the average density increasing from 7.09 g/cm^3 to 7.73 g/cm^3 (average of all runs). Statistical data indicated that the sintering atmosphere also has a significant effect on the sintered density. Sintering in hydrogen gave a density higher than the sintered densities achieved in the nitrogen and argon atmospheres. This difference is particularly emphasized at a temperature of 1200 °C and a time of 3 h, where sintering in hydrogen gave a density of 7.27 g/cm^3, while sintering in nitrogen and argon gave densities of 6.59 g/cm^3 and 6.89 g/cm^3, respectively. Small hydrogen atoms diffuse into the metal lattice and do not inhibit the elimination of final porosity[1]. Argon and nitrogen remains in the final pores and build the internal pressure, whereby the elimination of the porosity in the final stage of sintering is inhibited.

For the nitrogen samples the sintering activity was probably impeded by the absorbed nitrogen, which

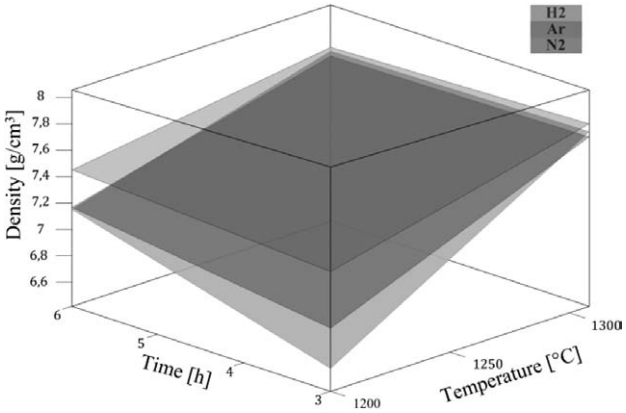

Figure 2: Influence of sintering temperature, time and atmosphere on the density of the sintered parts
Slika 2: Vpliv temperature, časa in atmosfere sintranja na gostoto sintranih delov

Table 3: Analysis of Variance for density
Tabela 3: Analiza variance za gostoto

Term	DOF	SumSqr	MeanSqr	P	F	Contribution, %
A	2	0.324213	0.162106	< 0.0001	111.5602	9.355652
B	1	2.516833	2.516833	< 0.0001	1732.064	72.62707
C	1	0.142913	0.142913	< 0.0001	98.35132	4.123965
AB	2	0.159606	0.079803	< 0.0001	54.9198	4.605679
AC	2	0.032124	0.016062	0.0019	11.05376	0.92699
BC	1	0.211313	0.211313	< 0.0001	145.4236	6.097752
ABC	2	0.060982	0.030491	0.0001	20.98351	1.759717
Pure Error	12	0.017437				0.503171
Residuals	12	0.017437	0.001453			

obviously reduces the mass-transport mechanism during sintering.[5] Also, it is well known that hydrogen is the most effective reducing atmosphere causing effective oxide removal, which results in a longer sintering dwell time. The highest density of 7.8 g/cm^3, which is 98.7 % of theoretical density, was achieved using a hydrogen atmosphere and a temperature of 1310 °C.

3.2 Mechanical properties

Parameters of sintering at the final stage of the MIM (Metal Injection Molding) process have a decisive influence on the mechanical properties of the produced parts. The characteristics of the residual porosity, chemical composition, structure after sintering and the density of the sintered parts are factors that make heat-resistant stainless steel very sensitive to the sintering parameters. Tensile tests were made on standard tensile tests samples used in powder metallurgy.

Table 4 shows the tensile and elongation results of the samples sintered in nitrogen, hydrogen and argon atmospheres at 1200 °C and 1310 °C. All the samples were sintered for 3 h in an atmosphere with 400 mbar of partial pressure.

It was found that the tensile and yield strengths increased with an increase of the temperature. The average tensile strength for parts sintered in argon and nitrogen was increased from 317 MPa to 680 MPa with a change of the sintering temperature from 1200 to 1310 °C. The tensile strength increase is the result mainly of increased density and a significant reduction of porosity. Also, a reduction of porosity by increasing the temperature caused a substantial improvement in the elongation of the sintered parts (**Figure 3**).

The reduction of the temperature leads to a large drop in the elongation and strength of the material. It is evident that sintering at a temperature of 1200 °C and in a nitrogen atmosphere gives an elongation of 2.2 %, while sintering in argon achieved a maximum elongation of 3.5 %. A slight improvement was observed for the samples sintered in hydrogen atmospheres (5.3 %), because of the higher density compared to the densities of samples sintered in argon and nitrogen. The low density and the sharp edges of the residual porosity of the parts sintered at lower temperatures caused a stress concentration during the tensile test, making the material very brittle. Analyzing and comparing the tensile test results, it is evident that the samples sintered in a nitrogen atmosphere experienced strengthening during the sintering. The best tensile strength of 777 MPa and yield strength of 412 MPa were achieved using a nitrogen atmosphere and a sintering temperature of 1310 °C

Sintering in a nitrogen atmosphere caused the absorption of nitrogen, resulting in the solid solution strengthening of the material. Also, based on previous research, the formation of NbCrN and precipitation strengthening were also possible[8]. The strengthening of the material was avoided using an argon atmosphere, where the average tensile strength and yield strength of 583 MPa and 223 MPa were achieved, respectively. A substantial elongation improvement was also observed on samples sintered in an argon atmosphere and temperature 1310 °C.

In order to see the effect of nitrogen absorption on the mechanical properties of the sintered parts, additional experiments were made. The main condition for intensifying the absorption and increasing the nitrogen content in the steel is to increase the partial pressure of the nitrogen atmosphere. In this regard, the partial pressure of nitrogen in the sintering furnace chamber was increased from 400 mbar to 600 mbar. After sintering, the hardness was measured and the results are presented in **Table 5**. The increasing of the partial pressure of nitrogen caused an increasing of the hardness of the sintered parts (**Figure 4**). A higher nitrogen level contained in the steel after sintering, as a result of the increased partial pressure of the nitrogen atmosphere, caused a more intensive strengthening of steel. It can be concluded that the change in the mechanical properties of the sintered heat-resistance stainless steel is possible through the partial pressure of the nitrogen atmosphere.

It was also observed that the sintering temperature has a very significant effect on the hardness of the sintered parts. The hardness increased with a higher sintering temperature and the average hardness increased

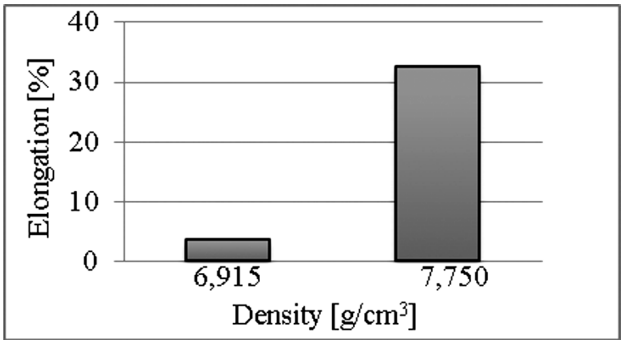

Figure 3: Influence of density on the elongation of the sintered parts
Slika 3: Vpliv gostote na raztezek sintranih kosov

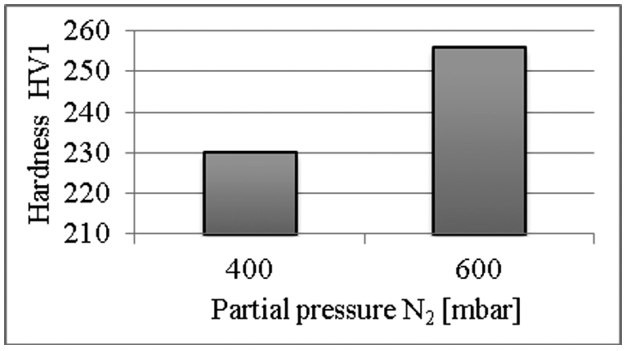

Figure 4: Influence of nitrogen partial pressure on the hardness of the sintered parts
Slika 4: Vpliv parcialnega tlaka dušika na trdoto sintranih delov

from 180 HV1 to 230 HV1 with a temperature increase from 1200 °C to 1310 °C.

Table 4: Mechanical properties after sintering
Tabela 4: Mehanske lastnosti po sintranju

Temperature /°C	Atmosphere	Partial pressure /mbar	Average tensile strength R_m/MPa	Average yield strength R_e/MPa	Average elongation A/%
1310	Ar	400	583	223	38
1310	N_2	400	777	412	27
1200	H_2	400	359	245	5.3
1200	N_2	400	292	–	2.2
1200	Ar	400	291	217	3.5

Table 5: Comparison of the hardness for different partial pressures of the nitrogen atmosphere and temperatures
Tabela 5: Primerjava trdote za različne parcialne tlake dušika in temperature

Partial pressure /mbar	Temperature /°C	Hardness /HV1
400	1200	180
400	1310	230
600	1310	255

3.3 Microstructure

The microstructure of the samples sintered at a temperature of 1200 °C and an argon atmosphere (**Figure 5a**) reveals an insufficient degree of sintering with a noticeable residual porosity and a very small grain size with a density of 6.89 g/cm^3. Insufficient connection between the grains caused a tensile and yield strength reduction and the elongation of parts sintered at 1200 °C. Micrograph of the parts sintered at a temperature of 1310 °C (**Figures 5b, d** and **e**) reveal grain growth and a fully austenitic microstructure with a minimal residual porosity and a density of 7.71 g/cm^3. A small percent of residual porosity indicates that the material reached almost theoretical density with well connected grains and better mechanical properties.

The parts sintered in hydrogen and argon experienced a more intensive grain growth compared to the parts sintered in nitrogen. Clean grain boundaries facilitate grain-boundary movement, resulting in effective pore absorption, higher density and larger grains compared to the parts sintered in nitrogen. Impeded sintering activity and reduced mass transport caused slower motion of the grain boundaries of the parts sintered in nitrogen, resulting in a reduced sintering density. The microstructure of parts sintered at 1310 °C is comparable to the microstructure of the wrought material.

A prolonged sintering time caused a slight grain coarsening (**Figures 5c** and **f**). Also, some of the pores observed on the samples sintered for 6 h coarsened maybe as a consequence of an extended sintering time and vacancy diffusion from smaller to bigger pores.[9,10] The micrographs of parts sintered in nitrogen reveal an austenitic microstructure with Cr_2N regions created as a consequence of nitrogen absorption.

4 CONCLUSION

The density of the heat-resistant stainless steel GX40CrNiSi 25–20 produced by the MIM process depends mostly on the sintering temperature. Increasing the average density from 7.09 g/cm^3 to 7.73 g/cm^3 was achieved by increasing the sintering temperature from 1200 °C to 1310 °C. Sintering in hydrogen and argon resulted in higher densities and better ductility of the sintered parts compared to the nitrogen atmosphere.

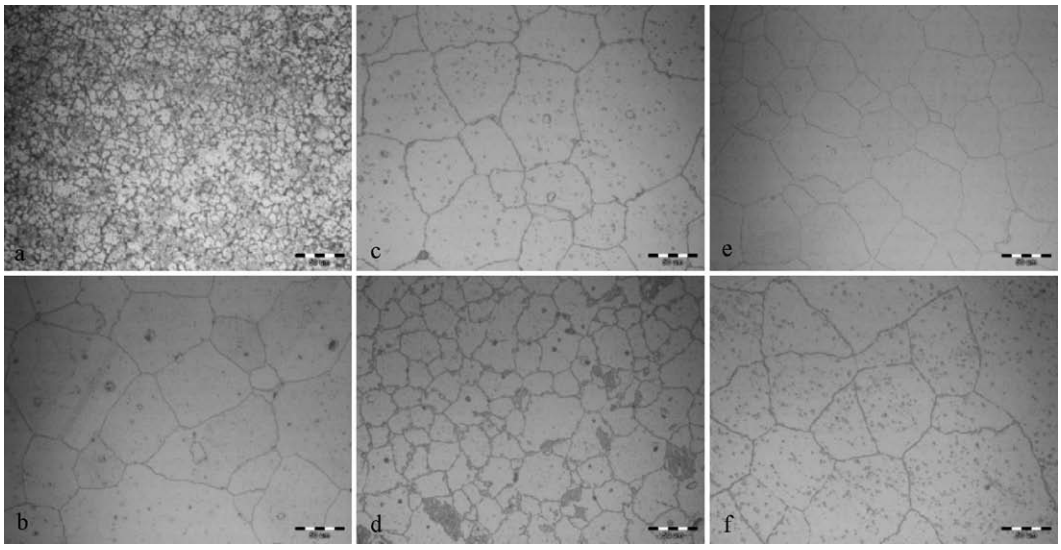

Figure 5: Microstructure of sintered parts for different conditions: a) argon, 1200 °C, 3 h, b) argon, 1310 °C, 3 h, c) argon, 1310 °C, 6 h, d) nitrogen, 1310 °C, 3 h, e) hydrogen, 1310 °C, 3 h, f) hydrogen, 1310 °C, 6 h, glyceregia
Slika 5: Mikrostruktura sintranih kosov pri različnih razmerah: a) argon, 1200 °C, 3 h, b) argon, 1310 °C, 3 h, c) argon, 1310 °C, 6 h, d) dušik, 1310 °C, 3 h, e) vodik, 1310 °C, 3 h, f) vodik, 1310 °C, 6 h, glyceregia

Insufficient density of parts sintered at a temperature of 1200 °C caused brittleness of the steel with a maximum elongation of 5.3 %. A superior tensile and yield strength were obtained by sintering in a nitrogen atmosphere. The maximum tensile strength of 777 MPa and yield strength of 412 MPa were achieved using a nitrogen atmosphere with 400 mbar of partial pressure and a temperature of 1310 °C. Strengthening also depended on the nitrogen partial pressure. The hardness was increased by 10 % when the nitrogen partial pressure was changed from 400 mbar to 600 mbar. It was found that a longer sintering time at a temperature of 1310 °C had a minor effect on the density of the sintered parts. Also, it is very important to emphasize that the prolongation of the sintering time at a temperature of 1200 °C, from 3 h to 6 h, increased the sintered density from 6.91 g/cm^3 to 7.26 g/cm^3, which is still much less than the density achieved at a temperature of 1310 °C. This is very important during the optimization of the sintering profile and indicates the importance of using a higher temperature to reduce the sintering time and the sintering costs.

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