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THE INFLUENCE OF MIM AND SINTERING-PROCESS PARAMETERS ON THE MECHANICAL PROPERTIES OF 316L SS

VPLIV PROCESNIH PARAMETROV BRIZGANJA IN SINTRANJA NA MEHANSKE LASTNOSTI NERJAVNEGA JEKLA 316L

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Metal injection moulding (MIM) is a relatively new and promising technology for the mass production of small, complex near-net-shape products. The dimensions, tolerances and mechanical properties of MIM products are influenced by the process parameters of injection moulding, as well as by the sintering. The mechanical properties primarily depend on the sintering density and microstructure. However, the process parameters of the injection moulding must not be neglected. This investigation showed that the appropriate mechanical properties of MIM products can be obtained. However, they are drastically reduced if inappropriate injection moulding and sintering conditions are selected. An incomplete debinding process results in residual carbon, which hinders the sintering. High-temperature vacuum sintering causes the evaporation of volatile elements (chromium, manganese), resulting in an increased near-surface porosity. The formation of a hard and brittle sigma phase is controlled by the cooling rate after sintering. The ceramic supports can react with the sintered steel. In this paper the influence of injection-moulding and sintering parameters on the mechanical properties of sintered material is presented and discussed.

Keywords: metal injection moulding, stainless steel, mechanical properties, microstructure, influence of process parameters

Povzetek: Tehnologija brizganja kovinskih prašnatih materialov (MIM) je relativno nova in je primerna predvsem za masovno izdelavo kompleksnih izdelkov visoke natančnosti. Tako na dimenzije (tolerance) kot na mehanske lastnosti izdelkov MIM imajo vpliv procesni parametri brizganja in sintranja. Mehanske lastnosti so predvsem odvisne od gostote po sintranju in mikrostrukture. Hkrati pa se ne sme zanemariti vpliva procesnih parametrov brizganja. Raziskave so pokazale, da se lahko z MIM-postopkom dosežejo primerne mehanske lastnosti izdelkov, ki pa se izrazito poslabšajo, če so izbrani neprimerni pogoji sintranja in brizganja. Rezultat nedokončanega procesa odstranjevanja veziva je zaostali ogljik, ki zavira sintranje. Visokotemperaturno vakuumsko sintranje povzroči izhlapevanje nekaterih elementov (kroma, mangana) in posledični povečano podpovršinsko poroznost. Nastanek krhke sigma-faze se lahko nadzoruje s hitrostjo ohlajanja po sintranju. Keramične podpore lahko reagirajo s sintranim jeklom. V tem prispevku je prikazan in pojasnjen vpliv parametrov brizganja in sintranja na mehanske lastnosti.

Ključne besede: brizganje kovinskih prašnatih materialov, nerjavno jeklo, mehanske lastnosti, mikrostruktura, vpliv procesnih parametrov

1 INTRODUCTION

Powder injection moulding (PIM) or metal injection moulding (MIM) is a combination of four sequential technological processes – mixing, injection moulding, debinding and sintering – all of which have an effect on the characteristics of the final parts. **Figure 1** presents schematically the whole process. The feedstock, which has to be as homogeneous as possible, is made by intensive mixing of the metal powder and the binder. In the next phase a green part is made by injection moulding. Then the binder is removed from the green part in various debinding processes. The brown part produced retains its shape due to the friction between the metal powder particles. This part is very brittle and needs to be sintered carefully to achieve its final sintered density and the desired mechanical, chemical and dimensional properties. The final properties of the product can be further improved with additional heat and mechanical treatments.

The mechanical properties of PIM products depend mainly on the sintering conditions. Injection moulding has a minor effect if it is performed at the normal (prescribed) temperature/pressure conditions for the selected feedstock. However, the sintering process is relatively difficult to control because of the relatively large number of influencing parameters. Namely, the properties of the sintered products depend not only on controllable factors but also on factors that are difficult

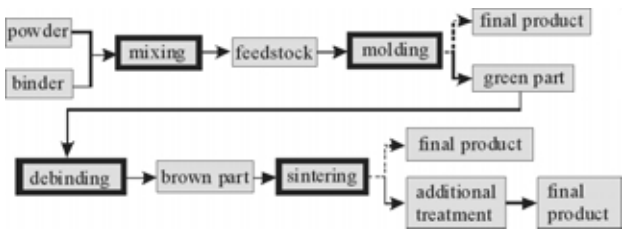


Figure 1: Schematic representation of the PIM process
Slika 1: Shematski prikaz procesa brizganja prašnatih materialov

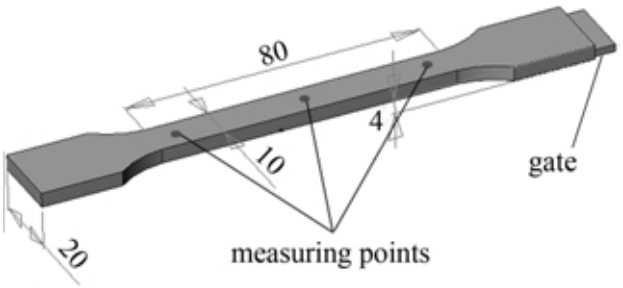
to control. This is a characteristic of high-temperature sintering, especially where there are a small amount of impurities, sintering temperature deviations and inappropriate atmospheres, causing a significant deterioration of the products' quality.

Our investigations were focused on the influence of the main injection-moulding parameters (pressure, temperature etc.) and the sintering conditions – debinding, sintering atmosphere and temperature – on the mechanical properties of the sintered material.

2 EXPERIMENTAL

2.1 PIM feedstock characterization

A standardized tensile-test specimen (**Figure 2a**) for the testing of polymer materials (ISO 3167) was used for our PIM experiments. The selected feedstock for PIM was a commercial product, ADVAMET(R), from Advanced Metalworking Inc., USA. It is a mixture of polymer binder, wax and 316L type of stainless-steel (SS) powder. The chemical composition of the 316L SS powder is given in **Table 1**, and the microstructure of the powder particles is shown in **Figure 2b**.



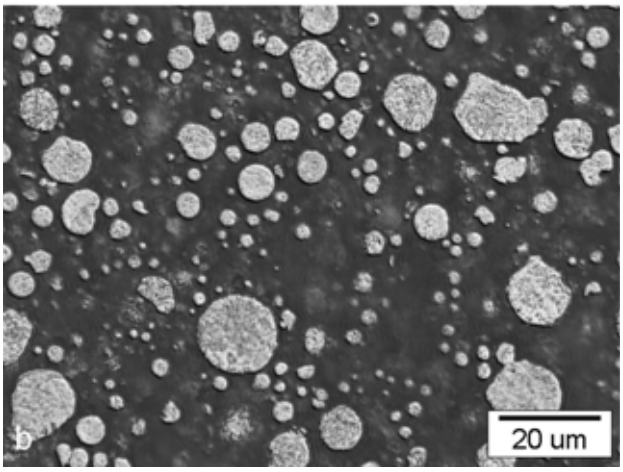


Figure 2: a) Standardized tensile-test specimen and b) micrograph of MIM feedstock (SS powder particles and binder) at magnification 500x

Slika 2: a) Standardiziran preizkušanec za natezni preizkus in b) mikroposnetek MIM-mešanice (delci nerjavnega jekla in vezivo) pri 500-kratni povečavi

The PIM feedstock has approximately mass fraction 6 % and approximately volume fraction 50 % of binder. The density of the mixture is approximately 5.3 g/cm^3. The SS powder consisted of spherical particles (Figure 2b) and was probably manufactured by inert gas atomization. The particle size is smaller than 45 μm, with $d_{80} \leq 16$ μm. The PIM feedstock has a viscosity of about 827 Pa s at 175 °C (ASTM D1238).

For the design of experiments of the injection moulding process the Taguchi approach [1] was selected because it is commonly used in the industrial environment, but it can also be used for scientific research. The selected and analyzed injection-moulding parameters are given in **Table 2**.

Table 2: Injection-moulding parameters and considered interactions among the individual parameters (designated as A-F and 1-2)

Tabela 2: Parametri brizganja in interakcije med posameznimi parametri (označeni z A-F in 1-2)

Parameter	1	2
Injection speed – v_b (A)	20 mm/s	40 mm/s
Die temperature – T_o (B)	20 °C	40 °C
Melt temperature – T_t (C)	180 °C	200 °C
Holding pressure – p_n (D)	10 MPa	50 MPa
Time of holding pressure – t_n (E)	3 s	7 s
Cooling time – t_o (F)	15 s	30 s

The actual pressure of the injection moulding varied between 95 MPa and 110 MPa. The filling time of the die was 1.6 s at the lower, and 1.0 s at the higher, injection moulding rate.

2.2 Debinding and sintering

A thermal debinding process in a nitrogen atmosphere or in vacuum can be used for the ADVAMET 316L feedstock. In our case the latter was selected simultaneously with sintering in the same industrial furnace. Ceramic sandwich Al_2O_3/SiC plates were used as a support for the sintered material. They are much more stable during high-temperature sintering (1360 °C) in comparison with metallic supports. This prevents distortion of the sintered material during the sintering. The pressure was lower than 100 Pa and the heating rate was approximately 0.7 °C/min during debinding. The sintering was performed at 1360 °C for 30 min at an absolute pressure of approximately 1 Pa. The sintering process for stainless steels is usually

Table 1: Nominal chemical composition of 316L SS powder in mass fraction *w*%

Tabela 1: Kemična sestava prašnatih delcev iz nerjavečega jekla v masnih deležih *w*%

Material	Cr	Ni	Mo	C	Mn	Si	P	N	S	O	Fe
w/%	16.8	10.5	2.2	0.03	1.4	0.5	<0.01	0.18	<0.01	0.08	68.7

performed by either super-solidus liquid-phase sintering (SLPS) or liquid-phase sintering (LPS) [2,3]. Our thermodynamic calculations showed that in general a solid-state sintering process occurred because the liquid starts to form only above 1390 °C. The small additions of B or Cu enhance the densification, increasing in this way the sintering density and the improving the mechanical properties [4,5].

For the metallographic analysis a Microphot FXA (Nikon) optical microscope equipped with a 3CCD camera Hitachi HV-C20AMP and software AnalySIS PRO 3.1 was used. For the microanalysis a JEOL JSM-6500F field-emission scanning electron microscope with an EDS (energy-dispersive spectroscopy) analyzer was used. It was also used for fractographic examinations of fractured surfaces from the tensile-test specimens.

3 RESULTS AND DISCUSSION

3.1 Mechanical properties

The sintering density of stainless steel is usually higher than 95 % [2]. The theoretical density of SS 316L is 8.0 g/cm^3, while the average sintered density achieved during our experiments was 7.81 g/cm^3, or 97.6 % of the theoretical density. The highest density achieved was 7.86 g/cm^3 or 98.3 % of the theoretical density. The achieved density is relatively high due to the sintering in vacuum, where the densification and pore shrinkage are not hindered by internal gas pressure, as is the case in a reductive hydrogen atmosphere. The experimental standard deviation of the sintered density was 0.1%. This means that the influence of the injection-moulding parameters on the sintered density was negligible.

The tensile strength of the sintered parts of SS 316L is up to 510 MPa [3], and this was achieved when the optimal parameters were used. The yield strength was in all cases approximately the same – 165 MPa. In **Figure 3a** the dependence of the tensile strength on the sintering conditions is presented. It is evident that the tensile strength decreases from the first to the last sintering batch. This implies that despite the fact that the setup of the sintering process parameters was always the same, the real conditions during sintering were not. The average difference between the highest (sintering batch 1) and lowest (sintering batch 7) tensile strength was more than 30 MPa, or about 6 %. This can be either due to the contamination of parts with elements (Si, C, alkalis, etc.) that diffused from support plates or because the binder was not properly removed from the parts, and so it disintegrated into the retained carbon. The contamination of parts could be avoided by the replacement of the sandwich plates or by powdering the support plates with Al_2O_3 powder particles.

The tensile strength of sintered PIM parts is also influenced by the injection-moulding parameters, especially the holding pressure, the melt temperature and the injection speed. The combination of injection-moulding parameters 7, 8, 15 and 16, when the injection speed and holding pressure were the highest, also gives the highest tensile strength (**Figure 3b**). The higher these parameters are the bigger is the increase in the mass and the tensile strength. This is especially evident when the best (experiment 15 and 16) and the worst (experiment 1 and 2) injection-moulding parameters are compared. In addition to this the deviation of the tensile strength is bigger for badly moulded parts (±20 MPa), while for good parts it is only ±5 MPa.

The σ-ε diagram in **Figure 4** presents the tensile stress-strain curves for different moulding and sintering conditions. It is evident that the tensile strength is the highest when the moulding and the sintering parameters are optimal (1) and the lowest when the parameters are

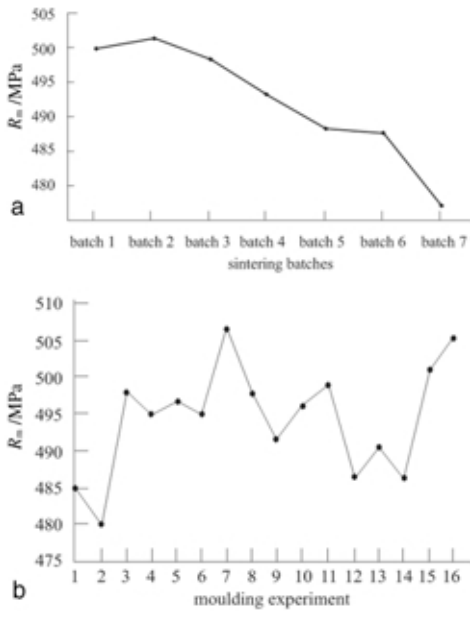


Figure 3: a) The dependence of the average tensile strength on the sintering conditions and b) the dependence of the tensile strength on the injection-moulding parameters

Slika 3: a) Povprečna natezna trdnost v odvisnosti od pogojev sintranja in b) natezna trdnost v odvisnosti od parametrov brizganja

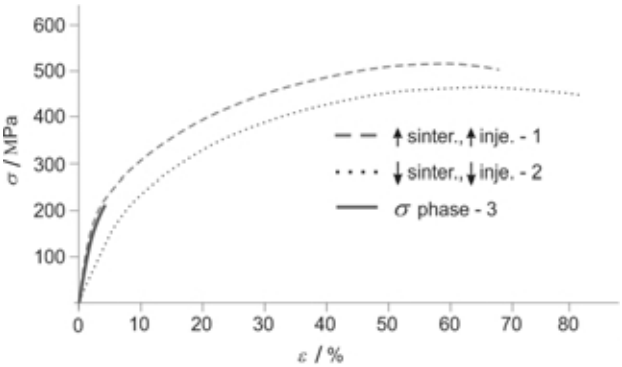


Figure 4: Tensile strength of sintered specimens made ubder different conditions

Slika 4: Natezna trdnost sintranih vzorcev pri različnih pogojih

the worst (2). For a comparison, the curve of the tensile-test specimen with the σ phase is added. The presence of a brittle phase was detected with the SEM/EDS analysis. In this case the tensile strength is very low, practically the same as the yield strength, and also the elongation and the contraction of the specimen are minimal (3). The differences in the microstructures were also confirmed using a fractographic examinations of the fractures.

The mechanical properties of the specimens are presented in **Table 3**. It is clearly evident that the manufacturing conditions affected the tensile strength and elongation, while the effect on the hardness, the yield strength and the contraction is negligible.

Table 3: The properties of specimens produced using the best and the worst conditions

Tabela 3: Lastnosti preizkušancev, narejenih pri najboljših in najslabših pogojih

Moulding and sintering parameters	R_m MPa	$Rp_{0.2}$ MPa	ε %	Ψ %	*HB*
best mould., best sinter.	508	167	62	60	109
worst mould., best sinter.	497	167	60	58	112
best mould., worst. sinter.	490	165	69	60	108
worst mould., worst. sinter.	455	156	67	60	110

In **Figures 5 to 7**, typical fractures of tensile-test specimens made under different moulding and sintering conditions are presented. **Figure 5** presents an SEM micrograph of a typical fractured surface of a specimen made with the best moulding and sintering conditions. In **Figure 5a**, good ductility and a distinctive contraction of sintered steel are clearly visible. The porosity of the specimen seems to be bigger than the actual porosity because the initiation and the propagation of the fracture proceeded with the pore growth.

In **Figure 6a**, the SEM micrograph of a fracture of a specimen made in the worst moulding and sintering conditions is presented. It is clear that also here a good ductility with distinctive contraction was achieved. But in this case during the tensile test the thin contaminated specimen's surface layer flaked off. The porosity of this specimen (**Figure 6b**) was greater than the porosity of the specimen in **Figure 5b**.

In **Figure 7** the fracture of a specimen with sigma phase under the surface is presented. The appearance of the fracture (**Figure 7a**) is of mixed micro-morphology. In **Figure 7b** it is clear that an unwanted reaction and over-sintering occurred, which results in a brittle fracture.

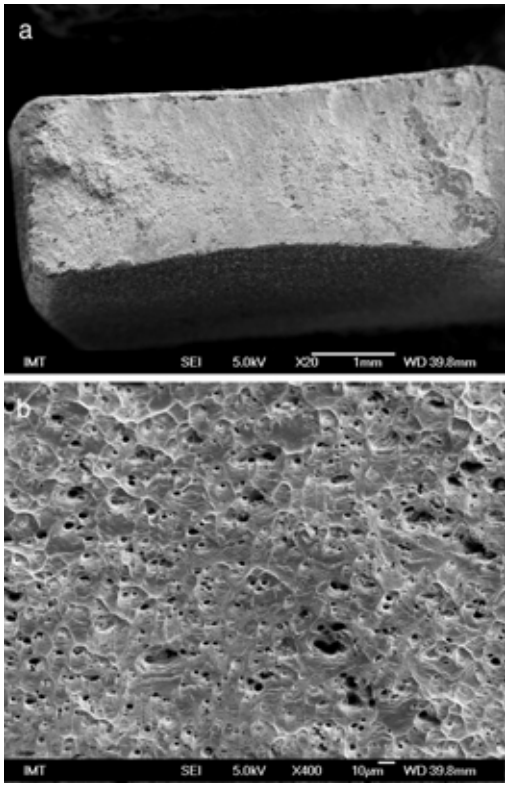


Figure 5: The SEM micrograph of a sintered specimen's fractured surface: a) macro shot (magnification 20x) and b) the mid-part of the specimen made with the optimal sintering and moulding conditions (magnification 400x)

Slika 5: SEM-posnetek loma sintranega vzorca: a) makroposnetek (povečava 20-kratna) in b) sredina sintranega vzorca, izdelanega pri najboljših pogojih sintranja in brizganja (povečava 400-kratna)

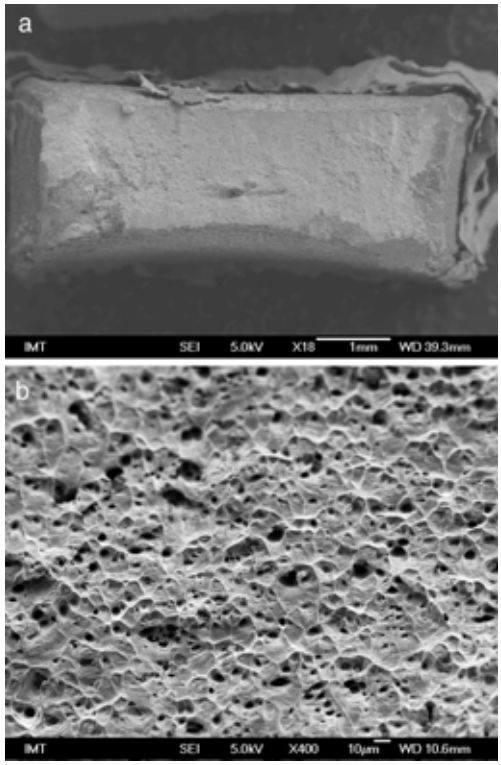


Figure 6: The SEM micrograph of a sintered specimen's fractured surface: a) macro shot (magnification 20x) and b) the mid-part of the specimen made with the worst sintering and moulding conditions (magnification 400x).

Slika 6: SEM posnetek loma sintranega vzorca: a) makroposnetek (povečava 20-kratna) in b) sredina sintranega vzorca, izdelanega pri najslabših pogojih sintranja in brizganja (povečava 400-kratna)

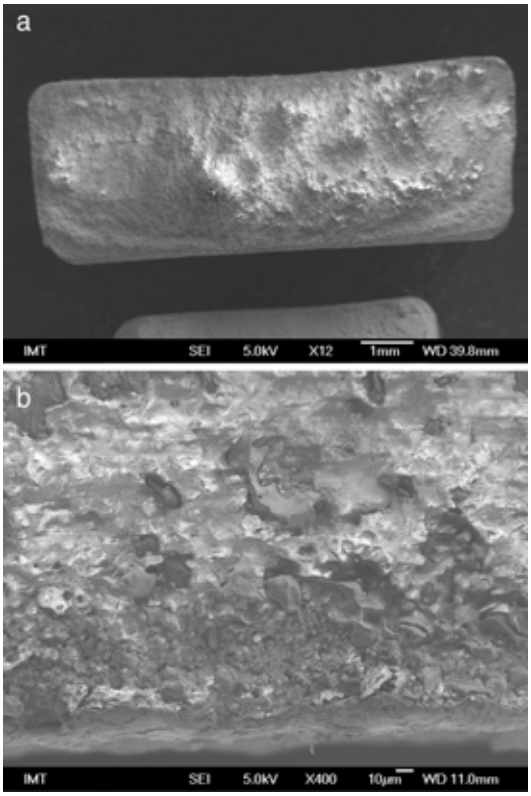


Figure 7: The SEM micrograph of a sintered specimen's fractured surface: a) macro shot (magnification 20x) and b) the mid-part of the sintered part with sigma phase (magnification 400x).
Slika 7: SEM-posnetek loma sintranega vzorca: a) makroposnetek (povečava 20-kratna) in b) sredina sintranega vzorca s sigma-fazo (povečava 400-kratna)

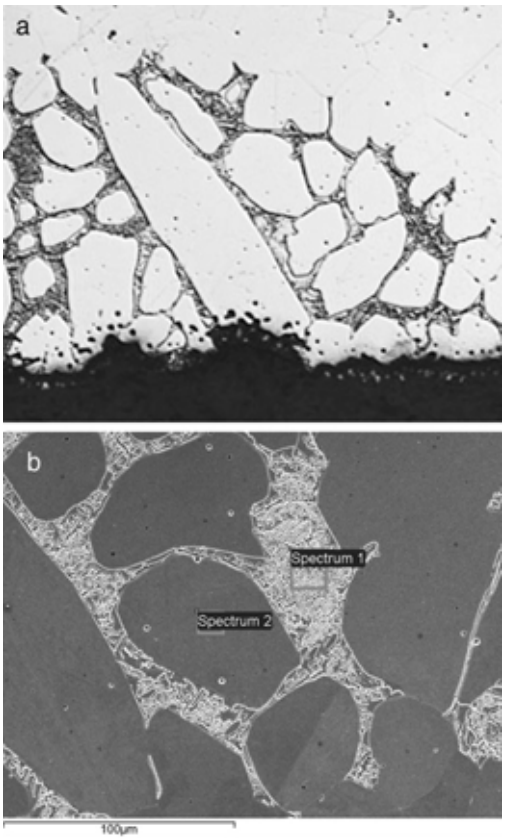


Figure 8: a) Sigma phase (LM micrograph, magnification 100x, etched), b) EDS analysis of sigma phase (magnification 500x, etched)
Slika 8: a) Sigma-faza (mikroposnetek, povečava 100-kratna, jedkano), b) EDS-analiza sigma-faze (povečava 500-kratna, jedkano)

The sigma phase is typical for stainless steels and it is usually formed when the cooling rate is too slow in the temperature range from 600 °C to 800 °C. The presence of the sigma phase was proved by an SEM/EDS analysis. The EDS microanalysis showed (**Figures 8a, 8b**) that the bright spots are richer in Cr, Mn, Si and O and poorer in Ni. The sigma phase is brittle and hard, and the consequence is a lower tensile strength and deformability.

Therefore, the presence of the sigma phase in the MIM/sintered SS can present a serious problem. The right chemical composition, appropriate cooling rate after sintering or subsequent quenching of the sintered parts reduce the possibility of its occurrence. The formation of the sigma phase could be also connected with the inhomogeneity of the feedstock.

The sintering of brown PIM parts can cause other defects that may influence the mechanical properties. The defects occurring during the feedstock preparation and injection moulding can become more distinctive, while inappropriate sintering conditions can cause the formation of new ones. The most frequent defect is the formation of voids, which can be the consequence of trapped gas during debinding or they occur during injection moulding in the thicker areas of the parts because of shrinkage of the binder.

The mechanical properties of sintered parts can differ greatly, even though the same material is used. The main reasons are inappropriate sintering conditions, the size of the pores and grains, impurities, chemical composition, defects after sintering and sintering density [6,7]. The Weibull distribution indicates the cumulative fracture distribution according to the equation:

$$P(\sigma) = 1 - \mathrm{e}^{\left[-\left(\frac{\sigma}{\sigma_0}\right)^M\right]} \quad (1)$$

where $P(\sigma)$ is the probability of material fracture at a stress of σ, σ_0 is the characteristic material strength, and m is the Weibull modulus. This modulus is an effective measure of the width of the failure distribution. The higher the value, the lower is the probability of material fracture at a stress lower than the characteristic one. Typically, the Weibull modulus is between 8 and 14, but with special effort 20 and even 25 can be achieved. In our case because of the relatively small number of specimens a statistical analysis was not carried out.

3.2 Analysis of the microstructure

EDS microchemical analyses were performed to check the chemical composition of the specimens on the fractured surfaces and in the middle of the samples, as

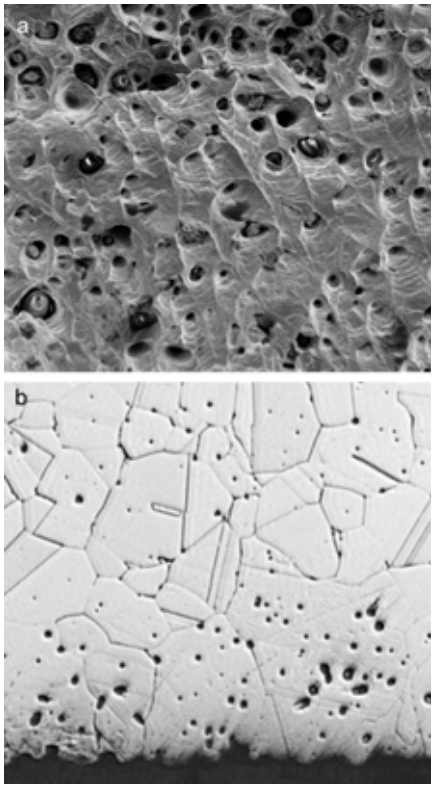


Figure 9: a) SEM micrograph of inclusions in pores close to the surface (magnification 400x) and b) increased porosity close to the surface (LM micrograph, magnification 100x, etched).

Slika 9: a) SEM-mikroposnetek vključkov v porah blizu površine (povečava 400-kratna) in b) povečana poroznost blizu površine (povečava 100-kratna, jedkano)

well as for the explanation of the differences in the mechanical properties among the sintering batches. It was established that the silicon content and the oxidation level increase from the middle to the surface. The increased silicon content in the surface layer indicates that the specimens were enriched (contaminated) by the Si, which probably originated from the supports. Partly the silicon diffused from the matrix because of selective oxidation, which is more intensive on the surfaces. The silicon content at the bottom surface was higher than at the upper one (difference 1–2 %).

The content of chromium and manganese in the surface layer is lower than in the middle of the specimen, and this suggests the evaporation of these elements, because of their high vapour pressure. The lower content of these elements caused higher porosity (approximately 2 %) close to the surface, while the porosity in the middle of the specimens was only approximately 0.5 %. The deficiency of the chromium and the manganese caused differences in the microstructure and the sinterability of the surface layer. The sintering of SS in vacuum is therefore problematic, but on the other hand, the sintering densities are higher in vacuum than with hydrogen sintering. The increased porosity near the surface was caused by the high temperature near the supports, too high heating rates, the formation of oxides and the enrichment (contamination) of the surface layer with Si. The porosity was more distinctive in the lower (bottom) surface layer, which was also more enriched with silicon, forming complex oxides with other elements. In **Figure 9a** inclusions, formed especially in the surface layers, are presented. With the SEM/EDS analysis it was established that these are complex oxides based on silicon and other metals (chromium, manganese, aluminium). The heating rate has an influence on pore movement during densification. Faster heating rates cause the separation of pores from the grain boundaries. The separated pores remain in the grains and their shrinkage is stopped (**Figure 9b**).

4 CONCLUSIONS

It was established that the mechanical properties of parts manufactured with PIM are influenced by the sintering conditions as well as by injection moulding. Besides the controlled parameters also uncontrolled ones are important, and they proved to be crucial in our experiments. An inappropriate choice of material for the supports, incorrect disintegration of the binder into residual carbon, the atmosphere, too high a heating rate and sintering temperatures (evaporation of Cr, Mn and Si), impurities, and too slow a cooling rate, enhancing the formation of the sigma phase, drastically reduce the mechanical properties of the sintered parts.

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