

# Porous material produced by ceramic injection molding

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## ABSTRACT

**Purpose:** The aim of this research is presented the process of alumina injection molding with a multicomponent binder system based on polymer (polypropylene – PP/polyethylene- HDPE), paraffin wax (PW) and stearic acid (SA). Debinding and sintering process was also studied.

**Design/methodology/approach:** The volume fractions of powder in the feedstocks were 50%vol and the volume of polypropylene and polyethylene were changed from 0-22%vol. The concentrations of SA were kept at 6%vol. The feedstock was heated to melt the binder and injected into a mold. Debinding process was carried out after injection step. The organic part was removed through combination of solvent and thermal debinding. Samples were sintered at 1200-1600°C in one cycle with debinding process.

**Findings:** Thermogravimetric analysis (TGA) was performed to determine decomposition temperatures of polypropylene, polyethylene, paraffin wax and stearic acid. Morphology of alumina powder by scanning electron microscopy (SEM) was disclosed. The microstructure and properties was tested to see how the selected sintering parameter ,as a temperature, affects the structure.

**Originality/value:** The paper presents ceramic injection molding process of alumina parts and sintering to produce porous material which is possible to use as a preform for infiltration by aluminium alloys.

**Keywords:** Powder injection molding; Aluminum oxide; Thermogravimetric analysis; Solvent and thermal debinding; Sintering

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## MATERIALS

### 1. Introduction

Powder injection molding (PIM) is a cost effective production technique derived from polymer injection molding, allowing large scale production of complex geometry. PIM process is a method for ceramics (CIM) and metals (MIM) materials. The properties of products by PIM process are

homogeneous and the microstructure are changeable by applying different parameters during compacting and sintering. PIM process is a combination of the two technologies: polymers injection molding and powder metallurgy. Powder injection molding is made possible by the binding agent which is composed mostly from the thermoplastic polymers. The portion of binder is in the range

30-55% depending of the powder parameters like: shape of grains, wettability. Ceramic injection molding (CIM) allows the manufacturing of complex dimensional parts with narrow dimensional tolerances. Mold design and injection parameters highly influence properties of the finished product [1-8].

Unfavorable parameters of injection molding or mould will lead to products with defects such as voids, cracks etc. CIM uses ceramic powders such as alumina, titania, zirconia, etc. Unique properties of ceramic materials like a good mechanical properties, low specific weight and resistance to high temperature makes them interesting material for a wide variety of applications. These process is generally limited to parts less than 400 g and suitable for the production of parts with complex geometry. Ceramic Injection molding is used in several areas of industry like a automotive, medical and telecommunication industry [11].

Shaping is an approach to form green parts with complex geometry by adding polymeric binders into ceramic powders. It usually contains four steps: forming a feedstock of powder-binder mixture, shaping the feedstock by injection molding machine, degradation the binder and densification in sintering process [13].

In injection molding of ceramic powders the powder is mixed with binder. An ideal binder system for CIM must have some attributes: flow characteristics, interaction with powder, debinding and manufacturing. The perfect binder should have a low viscosity at the molding temperature and it should have low contact angle and adhere to the powder during molding process. During debinding must hold the shape. The binder system has to be full decomposed before sintering. For manufacturing system the binder must be cheap and environmental friendly [14-15].

Usually the binder system is multicomponent. Thermoplastic material like a PP or HDPE in this system is known as the backbone because maintains the shape of the element at high temperature. The second component improves the flowability of the mixture and can be removed in early stages of debinding leaving open pores that allow the gaseous products of the remaining polymer to remove of the structure. The conditions are met for example by paraffin. The third component for example stearic acid must be a bridge between ceramic powder and binder system. Stearic acid as a surfactant decreases the viscosity of the polymer-powder mixture. This multicomponent binder system have good homogeneity of blends and due to the different melting temperature of binder component ensure that when one component has melted the remaining component acts a backbone retaining the shape of the parts. Powder-binder mixture is molded using extruder machine similar to that used for polymer molding. In extruder machine the feedstock is mixed to obtain a homogeneous mixture. The composition of the powder-binder-mixture the feedstock is the most important factor due to the fact that it the

processing conditions i.e. mixing flow and debinding behavior [10-14].

A homogeneous mixture of ingredients known as feedstock is directly inserted into injection molding machine and then injected into a mold. Then binder is removed from component by thermal heating. The result is known as the porous component that still contains its original geometry and size. Injection molding and sintering are the most important steps related to forming the final part.

The sintering step influences the microstructure and property changes and the selection of parameters such as sintering temperature holding time and atmospheres [1-3].

In this paper we have studied the process of alumina injection molding with a binder system based on polymer (polypropylene-PP/polyethylene-HDPE), paraffin wax (PW) and stearic acid (SA). Debinding and sintering process was also studied.

## 2. Experimental

### 2.1. Materials

Alumina powder NABALOX<sup>®</sup> NO-115 used in this study was produced by Nabaltec. The Nabaltec company produces alumina powder for a wide variety of applications in the refractory and ceramics industry. The required product properties are optimized and refined by grinding air separation or granulation. This provides NABALOX<sup>®</sup>-aluminium oxide with a number of advantages [8]:

- optimized packing density,
- wide sintering range,
- low sintering temperature,
- high sintered densities,
- flexible processing,
- optimized flow properties.

According to literature fine powders smaller than 20µm are preferred in PIM process. Particle size determination was performed on the particle size analyzer ANALYSETTE 22 MicroTec plus which showed that particle size is less than 20 µm. The particle size distributions is shown in Fig. 1. The values D (10), D (50), D(90) are respectively 1.93 µm, 6.83 µm and 16.82 µm. D (x) is the diameter below which x% of the particles are found.

Scanning electron microscope (SEM) images have been taken to observe the powders appearances in a micro-scale. The research on SEM shown that the aluminum powder has a tendency to agglomerate. Individual particles has size below 2 µm. The morphology of the alumina powder was irregular in shape as shown in Fig. 2.

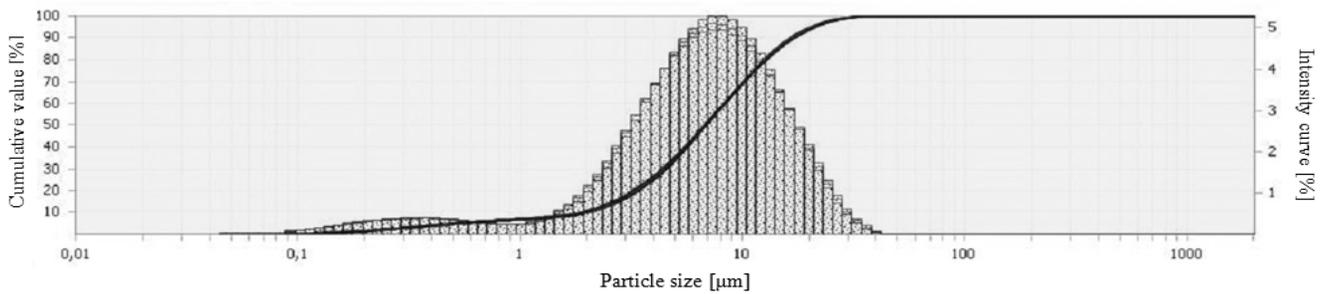


Fig. 1. The particle size distribution

Table 1. Specifications of powder NABALOX® NO-115 [8]

Basic technical parameters of NABALOX® NO-115*		
Chemical composition [%]	Al <sub>2</sub> O <sub>3</sub>	99.5
	Fe <sub>2</sub> O <sub>3</sub>	0.1
	Na <sub>2</sub> O	0.4
Phase composition [%]	α-Al <sub>2</sub> O <sub>3</sub>	98
Theoretical density [g/cm <sup>3</sup> ]		3.98
Particle size distribution [%]	<20μm	85

\* The average results of production batches

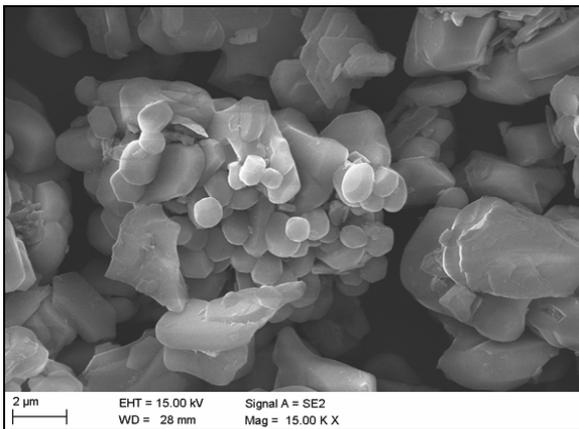


Fig. 2. Morphology of alumina powder by scanning electron microscopy (SEM); Magnification 15000x

The powder density was 3.98 g/cm<sup>3</sup>. To achieve favourable properties the main component of feedstock was polypropylene (PP) or the high density polyethylene (HDPE). The stearic acid was used for dispersion of powder in binder and enhances the miscibility among binder components. Independently of the used main binder (high density polyethylene or polyethylene) the 22% of the

binder volume is of paraffin wax (PW). Characteristics of binder components used in this study are shown Table 2.

Thermogravimetric analysis (TGA) was performed to determine decomposition temperatures of polypropylene, high density polyethylene, paraffin wax and stearic acid. The TGA results were important in the preparation initial proportion of binder components.

## 2.2. Preparation of feedstocks

Three different feedstocks (mixtures of powder and binder) were prepared according to the compositions shown in Table 3. Feedstocks were labelled as A, B and C. The volume fractions of powder in the feedstocks were 50%vol, the volume of polymer and paraffin was 22% vol. The concentrations of SA was 6% vol.

Mixing process of alumina powder and binder was conducted in a Zamak Mercator extruder machine with a pair of rotating screws inside machine. The maximum capacity of the mixing chamber was 15 cm<sup>3</sup>.

Mixing step was optimized using torque measurements in a extruder machine. According to the thermal properties of the mixtures of powder and binder components the extrusion temperature was higher than the highest melting point of the mixture but lower than the lowest degradation temperature of the binder mixture.

In the next step prepared feedstock was injected into a three plate mold as shown in Fig. 3. Three plate mold was applied because of the low shrinkage of the material during injection. By applying three plate mold was easier to remove the sample from the mold. Injection molding process was carried out in an Zamak Mercator injection machine. Processing parameters as a temperature, injection speed pressure and volume were selected to ensure complete filling the mold. The optimization of injection molding parameters was carried out by experimental method.

Table 2.  
Characteristics of binder components used in this study

Binder component	Density (g/cm <sup>3</sup> )	Melting temperature (°C)	Decomposition temperature (°C)
PP	0.89	163	250-450
HDPE	0.94	130	378-500
SA	0.94	73	200-350
PW	0.91	58.3	250-342

Table 3.  
Composition of feedstocks (vol%)

Feedstocks	Alumina		PP		HDPE		PW		SA	
	%vol	%	%vol	%	%vol	%	%vol	%	%vol	%
A	50	81.	22	8	0	0	22	8	6	2
B	50	88.	0	0	22	9	22	9	6	2
C	50	84.	11	4	11	4	22	8	6	2



Fig. 3. Injection molded part in three plate mold

### 2.3. Debinding and sintering

Debinding and sintering process was performed to remove organic part-PW and SA-from sample after injection step. The organic part was removed through combination of solvent and thermal debinding. The solvent debinding was performed by dipping of samples in heptane at 25°C, 45°C and 60°C. Thermal debinding and sintering was performed in air in the furnace for thermal degradation. Samples were sintering during 1h at different temperatures 1200°C, 1300°C, 1400°C, 1500°C, 1600°C. After sintering density of the samples were tested using a hydrostatic method-Archimedes method. Microstructure of the sintered materials was evaluated in a Zeiss Supra 35 Scanning Electron Microscope using SE detector.

## 3. Results and discussion

Independent of main component of the binder, i.e. polypropylene, high density polyethylene or mixtures thereof, prepared feedstock have a low torque which is read during the mixing of all components of the binder at 170°C at 40 rpm. The homogeneity during mixing was predicted through torque curves. The torque value is a measure of the resistance on the rotating screws. Correctly chosen the binder system should wet the powder and achieve homogeneous state in a short time about 30 minutes as shown in Fig. 4.

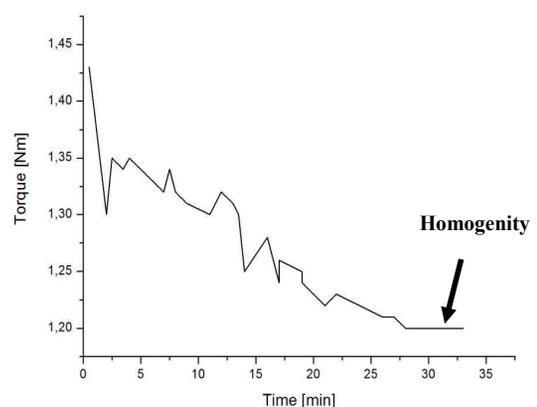


Fig. 4. Torque measurement

Difficulty in feedstock preparation is achievement a homogeneous distribution of powder in the binder system.

Preparing feedstock in the extruder machine relies on the destruction of agglomerates to gain individualized particles in order to improve their mobility under flow.

Unfortunately non agglomerated smaller particles have higher surface area. For that reason the higher amount of binder or surfactant is necessary to use in order to improve the wettability of powder. The adjustment of injection molding parameters was a critical step during the process. This stage was carried out by controlling the main parameters such a pressure, volume and temperature. Injection temperature used in this work was 170°C. This temperature was chosen because is higher than the melting point of polypropylene (163°C) but lower than the degradation temperature of PW (250-342°C). Higher temperature caused some burrs and blisters in the molded parts. The mold temperature also played an important role because when the mold had lower temperature an incomplete mold filling was observed Fig.5. The best results were observed at 40°C.

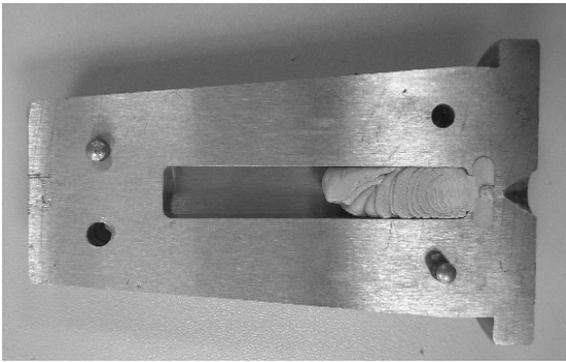


Fig. 5. Incomplete mold filling

Injection molding pressure was varied to determine the optimal injection pressure. Using injection pressure, higher than 4 bars, caused demolding problems of the part and in some cases burrs and blisters inside sample. The optimum injection pressure was between 3 and 4 bar. This is not pressure inside cylinder with feedstock but actuator which press the injection molding machine piston.

After injection step, the organic parts was removed through combination of solvent and thermal debinding. The solvent debinding is used generally to reduce the thermal debinding process and the total time of production cycle. Before thermal removal, samples were immersed in solvent-heptane. During the solvent debinding process heptane diffuses into the sample to dissolve paraffin wax and stearic acid. All specimens were placed together into the solvent (heptane) bath at 25°C, 45°C, 60°C. The solvent debinding was monitored up to 7h. Figures 6 and 7 shows the solvent

binder removal (%) in heptane at different time-temperature combination. It can be observed that the extraction rate is shorter in 60°C than in 25°C and 45°C.

Optimising thermal debinding was performed on the basis of a thermogravimetric analysis of the individual components of the binder. TGA were important to determine decomposition temperatures of polypropylene (Fig. 8) polyethylene (Fig. 9) paraffin wax (Fig. 10) and stearic acid (Fig. 11).

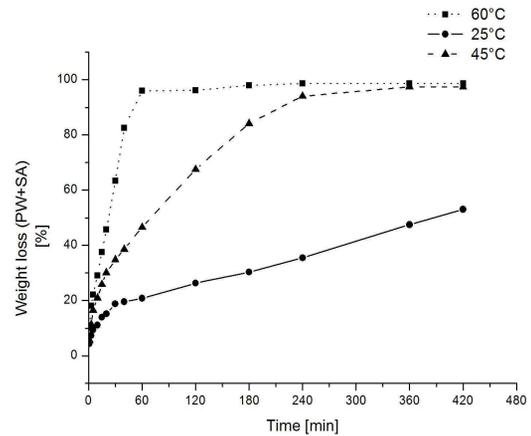


Fig. 6. Solvent binder removal (%) in heptane at different time-temperature combination

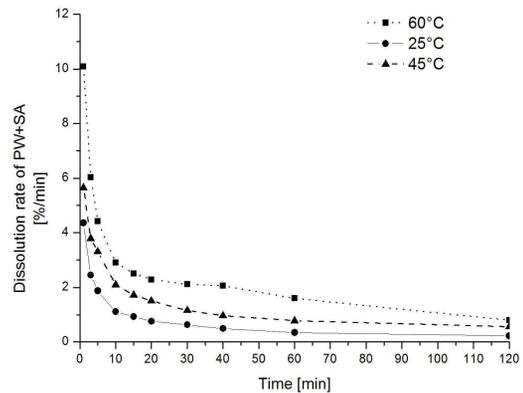


Fig. 7. Effect of dissolution time and temperature on the dissolution rate of paraffin wax and stearic acid

PW and SA start to decompose at 250°C and total evaporation occurs at about 350°C. PE decomposition starts approximately 250°C and finish at 450°C and HDPE decomposition starts around 378°C and finish at 500°C that's why binder degradation occurs in two steps. In the

first step the weight loss to take place between 200-350°C and at this temperature PW and SA degrade. In the second step degradation is faster than in the first step and it occurs from 378°C-500°C. This gradual and wide degradation temperature range is favourable from a technological point because the extant binder component will be used to keep the shape of the part. From 200°C to 350°C the heating rate must be slow to prevent blistering and bloating since the first binder component degradation and the pores are opened.

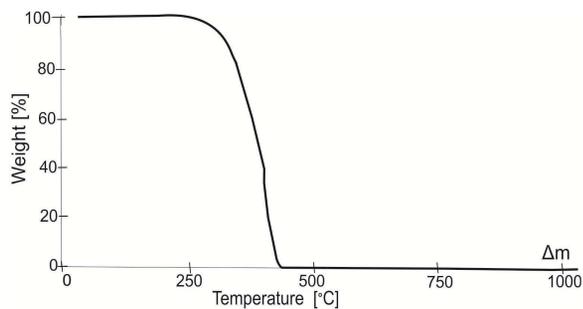


Fig. 8. Thermogravimetric analysis of polypropylene (PP) with heating rate 7.5°C to 1000°C in air

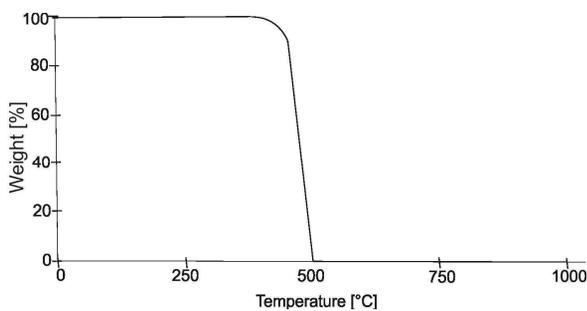


Fig. 9. Thermogravimetric analysis of polyethylene (HDPE) with heating rate 7.5°C to 1000°C in air

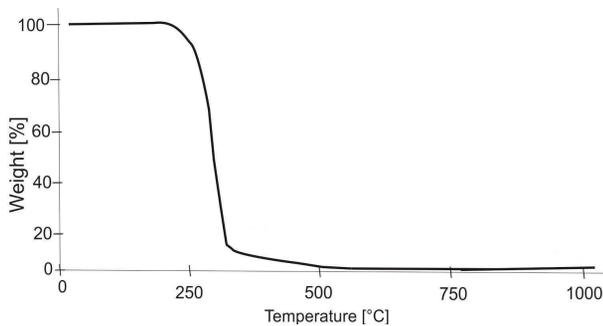


Fig. 10. Thermogravimetric analysis of paraffin (PW) with heating rate 7.5°C to 1000°C in air

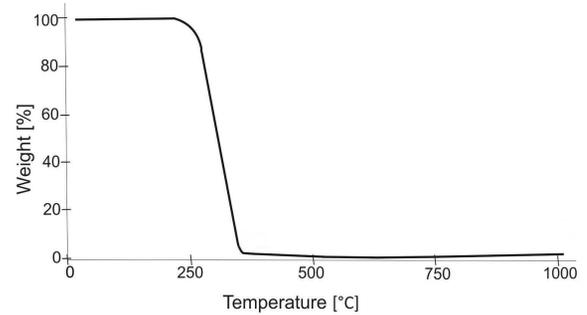
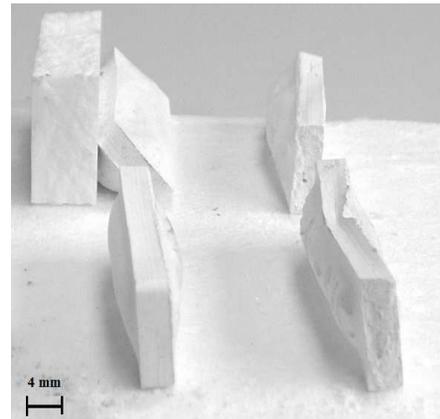


Fig. 11. Thermogravimetric analysis of stearic acid (SA) with heating rate 7.5°C to 1000°C in air

a)



b)

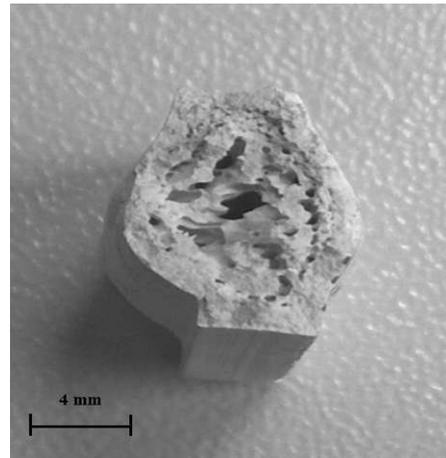


Fig. 12. Blisters into the samples

Higher heating rates, more than 1°C/min, produced defects inside sample. Fast heating rate caused the presence of blisters in the sample as show in Fig. 12. The best results were achieved using heating rates 1°C/min.

Table 4.  
The process of thermal removal of binder components

Thermal debinding (Steps)	Heating rate (°C/min)	Debinding temperature (°C)	Debinding time (min)
1	3	200	60
2	1	250	30
3	1	300	30
4	1	350	60
5	1	400	60
6	1	450	60
7	1	550	30

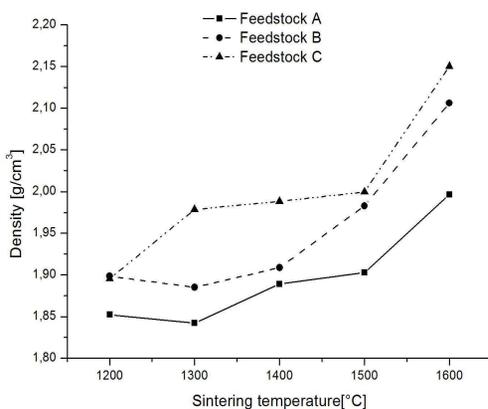


Fig. 13. Effect of sintering temperature on the density

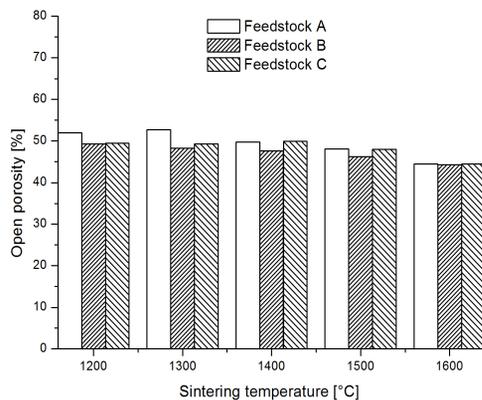


Fig. 14. Effect of sintering temperature for open porosity

Solvent-thermal debinding was carried out without protective gas because the atmosphere applied during debinding and sintering should be able to protect the green part at high temperature by removal oxide from surface, removing binders by burnout and carbon content control.

Sintering process was performed at temperatures between 1200 and 1600°C with step of 100°C for 1h without the protective gas. After sintering the linear shrinkage, porosity and density of the samples were determined. The Fig. 13 and Fig 14 presents the results of density, open porosity and debinding (thermal and solvent-thermal) schedule based on a feedstock C shown in Table 4.

In the case shown in Fig. 13 and Fig. 14 the sintering temperature of 1600°C provided better densification and less porosity by the formation and enlargement of necks between the sintered particles. When the sintering temperature was reduced to 1200°C, 1300°C the density of the sample decreased but the open porosity increased.

This is caused by measurement error in particular that the density of sintered material at 1200°C and 1300°C is comparable. The general rule is that the density increases with increasing sintering temperature and is independent of type of binder. As shown in Fig. 15 at 1400°C the open porosity in feedstock C increased. The reason for this was different arrangement of the sample inside high-temperature furnace.

Shrinkage along the part was in 1200°C and 1300°C approx 1%, in 1400°C approx 4%, in 1500°C approx 6% and in 1600 approx 10%.

## 4. Conclusions

The application of PP or HDPE as a main binder gives the possibility that produce homogeneous feedstock with alumina powder NABALOX® NO-115 for ceramic injection molding process. Fine particles of the Al<sub>2</sub>O<sub>3</sub> powder have high surface area and require a correspondingly higher amount of binder in order to lower the viscosity of the fill and possibilities of injection molding. The selection of conditions like a screw speed and the temperature during a plasticizing and mixing all ingredients in the extruder made it possible in a relatively short time of 30min preparation of the feedstock. Mixing feedstock longer than 30 minutes didn't reduce the torque of the screws, so it can be assumed that the mixture is homogeneous.

The homogenization time for the mixture slightly increased with the powder loading as a consequence of higher resistance on the rotating screws.

The addition of small quantities of SA to binder systems used in PIM is beneficial because substantially reduces the abrasion of the powder. Stearic acid as a surfactant reduces the contact angle by lowering the surface energy of the binder mixtures during injection molding, allowing increase the solid loading and giving a better homogeneity.

Removing the binder was performed by using and a combination of solvent-thermal debinding. The thermal elimination of binder was optimized by means of thermogravimetric analysis of the binder components which provides information about degradation temperature range. Binder components suitable for use in feedstocks for shaping alumina powders by ceramic injection molding has been tested.

Removal of the PW and SA in heptane at 60°C degrees is more rapid than at 25°C and 45°C. The possibility of degradation the both principal components of the binder in heptane permitted to use a solvent and thermal debinding process which reducing considerably the total production cycle time and the formation of defects during debinding process.

The sintering temperature of 1600°C provided better densification and less porosity. When the sintering temperature is reduced to 1200°C, 1300°C the density of the sample decreased but the open porosity increased. It can be seen that longer sintering times made difficult to control grain growth.

## Additional information

Selected issues related to this paper are planned to be presented at the 22<sup>nd</sup> Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10<sup>th</sup> anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

## References

- [1] G. Matula, L.A. Dobrzański, M. Ambroziak, Simulation of powder injection moulding conditions using cadmould program, *Journal of Achievements in Materials and Manufacturing Engineering* 55/2 (2012) 556-560.
- [2] R.E.F.Q. Nogueira, M.J. Edirisinghe, D.T. Gawne, Selection of a powder for ceramic injection molding, *Journal of Materials Science* 27 (1992) 6525-6531.
- [3] G. Matula, Carbide alloyed composite manufactured with the Powder Injection Moulding method and sinterhardened, *Journal of Achievements in Materials and Manufacturing Engineering* 42/1-2 (2010) 164-171.
- [4] R.M. German, A. Bose, *Injection molding of metals and ceramics*, Metal Powder Industries Federation, Princeton, 1997.
- [5] J.M. Torralba, Improvement of mechanical and physical properties in powder metallurgy, *Comprehensive Materials Processing* 3 (2014) 281-294.
- [6] L.A. Dobrzański, G. Matula, Basics of powder metallurgy and sintered materials, *Open Access Library* 8/14 (2012) (in Polish).
- [7] J. Deckers, S. Meyers, J.P. Kruth, J. Vleugels, Direct selective laser sintering/melting of high density alumina powder layers at elevated temperatures, *Journal of the European Ceramic Society* 31/14 (2011) 2551-2558.
- [8] Information brochure from the company Nabaltec (web site: [www.nabaltec.de](http://www.nabaltec.de)).
- [9] V.S. Aigbodion, J. O. Agunsoye, V. Kalu, F. Aduke, S. Ola, Microstructure and mechanical properties of ceramic composites, *Journal of Minerals & Materials Characterization & Engineering* 9/6 (2010) 527-538.
- [10] P. Thomas, B. Levenfeld, A. Várez, Production of alumina microparts by powder injection molding, *International Journal of Applied Ceramic Technology* 8/3 (2011) 617-626.
- [11] A. Salak, *Ferrous Powder Metallurgy*, Cambridge International Science Publishing, Cambridge, 1995.
- [12] M. Trunec, J. Cihlar, Thermal removal of multicomponent binder from ceramic injection mouldings, *Journal of the European Ceramic Society* 22 (2002) 2231-2241.
- [13] M.H. Shaw, M.J. Edirisinghe, Porosity development during removal of organic vehicle from ceramic injection mouldings, *Journal of the European Ceramic Society* 13 (1994) 135-142.
- [14] G. Harranz, B. Levenfeld, A. Varez, J.M. Torralba, Development of a new feedstock formulation based on high density polyethylene for MIM of M2 high speed steel, *Powder Metallurgy* 48/2 (2005) 134-138.
- [15] S.T. Paul Lin, R.M German, The influence of powder loading and binder additive on the properties of alumina injection-moulding blends, *Journal Material Science* 29 (1994) 5367-5373.