Investigation and optimization of homogeneity of ceramic injection molding raw material to improve crack toughness of end product

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Abstract

This study used capillary rheometer, gas densimeter and injection molding pressure measurement to quantitatively analyze the homogeneity of alumina based injection molding feedstock, and presents the report of the relationship between material homogeneity and kneading parameters, and the ration of different raw components. The researchers found as main result that the flux material has the highest effect on the homogeneity, since increasing the amount of this material can help in the equable mixing of alumina powder and paraffin wax. Furthermore, increasing the mixing time has positive effect on the homogeneity of the material, but much less than the amount of flux.

Keywords: alumina powder, paraffin wax, ceramic injection molding, densimeter, capillary rheometer, feedstock

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1. Introduction

The procedures of ceramic injection molding (CIM) include four steps: kneading process, injection molding, debinding, and sintering. The CIM technology offers the opportunity to make complex and near-net-shape of ceramic parts. The kneading process is an important step in ceramic injection molding. The kneading stress offered by a sigma-blade kneader is quite enough, but in special cases with other kneaders it may be not enough to break down the powder agglomerates in the ceramic feedstock, especially, if the agglomerates are consisted of ultra-fine powder. The agglomerates are retained until sintering and become the fracture origin if the effective size of the defects is too large to withstand fracture stress [1, 2, 3]. Evans [4] reported a result of zirconia, which was fractured in a defect size greater than 10 μm. The fracture strength is not affected, if the agglomerates are smaller than 10 μm [4]. Recently, the fundamental and application issues of nanotechnology and micro-electromechanical system (MEMS) have evoked the interest toward ceramists. The precision microinjection molding makes the manufacturing of small parts possible for many advanced applications. The powder size must be reduced to produce thin and complex parts. The nanopowder tends to agglomerate due to van der Waal force. However, little attention for the kneading behavior of ceramic feedstock have been given in literature by using ultra-fine or nanopowder [5].

For producing ceramic arc tube parts (plugs), there are three different major components used for producing injection molding raw material (hereinafter *feedstock*): high purity alumina powder as the main component, an organic paraffin wax as a binder material, and flux material as surfactant.

After selecting a suitable powder and a binder system, the first processing step in CIM is to mix them to prepare an appropriate feedstock for molding and subsequent processing. A homogeneous feedstock having high powder content is required to achieve a low shrinkage during binder removal and sintering. The feedstock should have the particles separated with a very thin layer of binder. To achieve this, powder agglomerates have to be dispersed in the binder [1, 2, 6].

With a homogeneous feedstock, in this experiment the main goals were to improve the quality of end product and to avoid the cracks and material discontinuities in the sintered ceramic parts (*Fig. 1*).

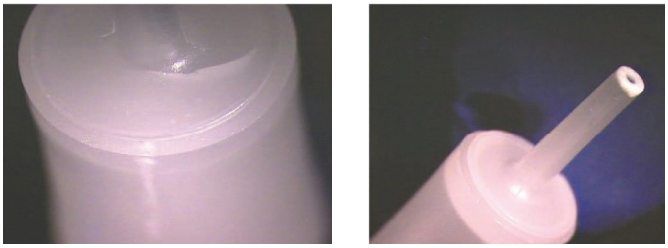

Fig. 1. Cracked (left) and intact (right) sintered alumina ceramic
1. ábra Repedt kerámia (balra) és ép kerámia (jobbra)

1.1. Possible options to determine the homogeneity of ceramic feedstock

In the case of the present experiments, the following measurement methods were chosen as output parameters of the grade of homogeneity: capillary rheometry, densiometry and pressure during injection molding. Literature mentions viscosity as a tool to determine the grade of homogeneity [7, 8, 9], but regarding the other two measurements it was not found to be advantageous for the determination of homogeneity during the present studies.

In the case of all three methods (described below) the same evaluation principle was followed: several samples were taken from the prepared material cell, and the standard deviation of

the measured values were investigated as an output parameter that can show the picture about the grade of material homogeneity and internal diversity [10].

1.1.1 Capillary rheometry

The shape of material is changing by the effect of external forces. Two ideal cases of deformation are known: elastic and viscous, which states can be mathematically well described by rheological state equations (constitutive equations) [11,12]. The Ostwald de Waele power law can follow the behaviour of injection molding feedstock, where the raising tension (τ) and the deformation speed (γ) are proportional to a power of n>0 natural number; see Eq. (1). Generally, in most of the cases n<1, so the viscosity of molten material decreases with the increasing deformation speed, at constant temperature (*Fig. 2*). This kind of material behaviour is pseudo-plastic: in this case the material is thinning by the shear stress.

$$\tau = K \cdot \dot{\gamma}^n \qquad (n<1) \tag{1}$$

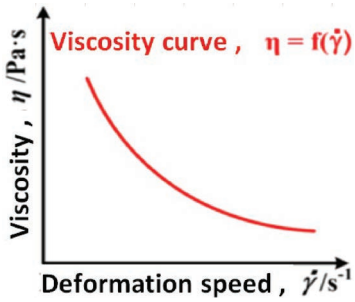

Fig. 2. Typical viscosity curve of pseudo-plastic materials
2. ábra A pszeudo-plasztikus anyagok tipikus viszkozitás ábrája[13]

The principle of capillary rheometry is the following: the measured material flows through a small diameter tube with relative small flowing velocity. Knowing the amount of material flow over given time, the pressure difference, and the geometry of the capillary (radius, length) the viscosity can be defined according to the Hagen - Poiseuille law; see Eq. (2) [13,14].

$$v = \frac{\pi(p_1 - p_2)}{8\eta l} r^4 t \tag{2}$$

where:
v: velocity of flow
p_1 and p_2: the pressure on the two ends of the capillary
η: viscosity
l: length of capillary
r: capillary radius
t: time

Considering the theory of determining homogeneity using viscosimetry, if the homogeneity of the material is increasing then the standard deviation of the viscosity values of samples is decreasing under constant temperature.

1.1.2 Densiometry

To determine the real density of ceramic feedstock a Quantachrome Ultrapyc 1200e densitometer (*Fig. 3*) was used with He gas system. The He gas for density measurements is used due to its small atomic size and high diffusion ability since it is able to penetrate into the smallest pores, even up to 0.2 nm. The densiometry is based on pycnometer volume determination, which is equal to the volume of displaced gas by the feedstock material (Archimedes law) and to the gas expansion technique (Boyle law). The volume of open pores can be defined with this method, but the closed or impenetrable pores can not be measured [15,16].

Fig. 3. Quantachrome 1200e type densiometer (left) and measuring cells (right)
3. ábra Quantachrome 1200e típusú sűrűségmérő berendezés (balra) és a hozzá tartozó mérőcellák (jobbra)

The standard deviation of measured density values can refer to the grade of homogeneity of feedstock since the mixed injection molding raw material consists of several components of different density. Namely, if some component did not mixed properly in the feedstock, then there can be a local enrichment from it, and so the measured density can be comparable with other samples, where there is no component enrichment; that may be considered a properly mixed raw material [16].

1.1.3 Injection molding pressure

The injection molding pressure is a parameter, which arises when the injection switches to holding pressure. In other words, this parameter is the maximum injection molding pressure during the injection process, which is needed for the filling of molding tool with a given quantity of material. The maximum speed of the material is defined by the gate between the injection unit and the injection tool, as a minimum cross-section (bottle-neck) [17,18].

Since the temperature, the minimum cross-section and the amount of material are constant, only the properties of material has influence on the flow of molten material, the change of the resistant force and so the injection molding pressure depends only on the flow behaviour of the material. In this way, one can get a similar capillary viscosimeter, in which the viscosity from the pressure against to the material flow can be estimated. And thus, from the standard deviation of pressure values, the homogeneity of feedstock can be determined as well.

The relationship between the two parameters is linear (*Fig. 4*).

The describing equation of the relationship with 92% probability is given by Eq. (3):

$$y=2.2488x+56.287 \tag{3}$$

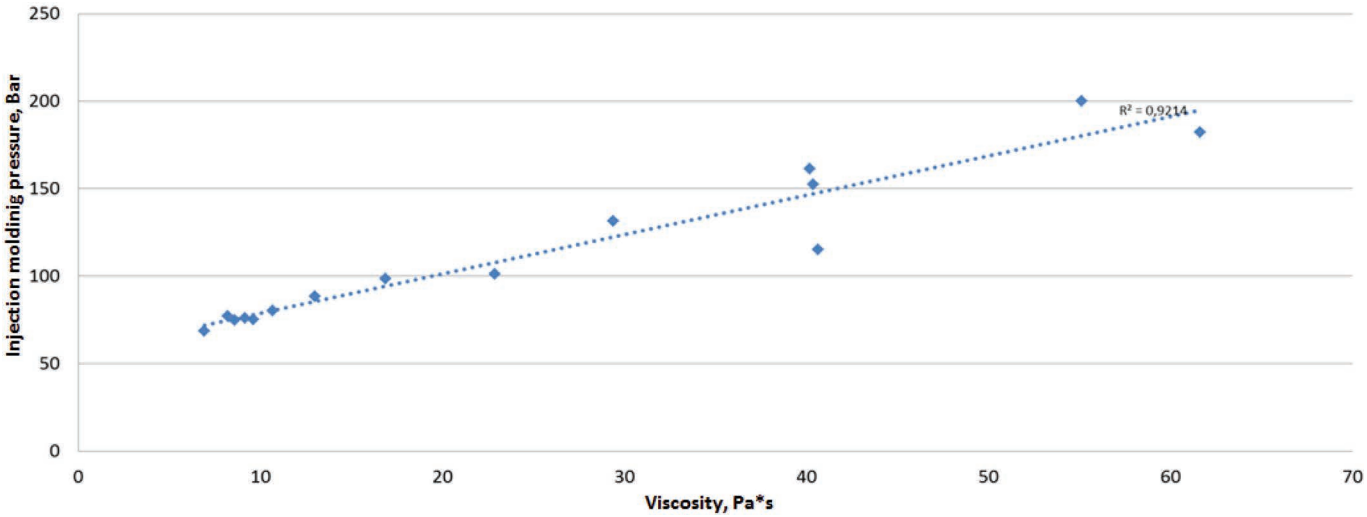

Fig. 4. The determined relationship between the capillary viscosity and injection molding pressure
4. ábra A meghatározott lineáris kapcsolat a kapilláris viszkozitásmérés és a fröccsnyomás értékei között

This linear relationship between the two outputs shows, that one can get data about the homogeneity with the standard deviation of injection molding pressure of the feedstock produced with the given mixing parameters.

2. Experimental

The primary standpoint of the experiment is to discover the connection between the homogeneity of feedstock and the quality of end product, and to determine the homogeneity at all. To reach this goal, different mixtures were made with different processes and amounts of components.

To research the properties of homogenous feedstock, a design of experiment was made, using the MINITAB statistical software.

To analyse the main effects, the Plackett-Burman III resolution fractional factorial design of experiment was used [19,20,21]. Considering this, 4 factors were investigated at two levels: amount of flux material, mixing time, mixing temperature and the dosage of alumina powder during mixing.

In favor of control of reproducibility, repeatability and linearity, the centre point was repeated three times according to the design of experiment, and the full test was consisted of 15 different runs.

There were constant mixing volumes and weights run by run. The determination of the factor values was made by the operating levels and literature research. After the mixings, 5 samplings were carried out for each run.

3. Results and discussion

3.1 Determination of homogeneity

3.1.1 Results of capillary viscosimetry

The most important properties of an injection molding feedstock are the viscosity and homogeneity. According to the literature review, the high quality feedstock has low viscosity, and the viscosity does not change within manufacturing batch, that means the viscosity has low fluctuation, it was homogenously mixed [22,23].

The capillary viscosimetry measurements were carried aout by a laboratory Dynisco LMI 4000 type capillary rheometer, the measuring temperature was set to 68 °C, and the melting time was 360 seconds (*Fig. 5*). The measuring temperature was chosen to that of the temperature of injection molding of the test materials, to help the comparison of different test results. For the measurements, 3700 g pressing weight and 1.042 mm capillary diameter were chosen.

Fig. 5. Dynisco capillary rheometer (left) and the viscosity measurement of feedstock (right)
5. ábra Dynisco kapilláris viszkoziméter (balra) és a feedstock viszkozitás mérése (jobbra)

After the measurement, the equipment automatically displays the viscosity value based on the MFR (Melt Flow Rate). The measurements were repeated on five sapmles per batch, in this way the standard deviation values were possible to be determined. *Fig. 6* shows the influences of input parameters on the standard deviation of viscosity – so the dependence of homogeneity on the input parameters of mixing.

It can be seen, that the flux material has the strongest effect on the homogeneity, so if more flux is added into the feedstock, the standard deviation of viscosity becomes lower. The flux is

a surfactant in the system, so if the amount of alumina powder and paraffin wax is increased, then the components can be mixed with each other more effectively. Consequently, the wax can be able to coat the alumina more, and this can decrease the powder-powder friction, and the focus is placed to the wax-wax friction [24].

In addition, it can be observed, that the homogeneity is decreased with the increasing mixing time, but not so strong effect can be observed with the narrow variation intervals chosen, however, it is visible that with the increase of mixing time the components can mixed better with each other.

The dosage of alumina shows weak negative effect, however, it would be logical that the homogeneity is increasing if the dosage of powder is increasing. It can be noticed that the results are probably distorted by the noise of applied dosage method, namely, if there were more steps of dosage then more stops appeared in the mixing process and it would have a negative effect on the homogeneity and the efficiency of mixing. Nevertheless, it can be concluded that the continuous mixing is more important than the dosage in more steps. The dosage in more portions with continuous mixing together can improve quality.

3.1.2 Results of density measurements

The method of density measurement was the following. Sample was placed into the sample holder with constant weight, measurement was performed with 20 psi constant He gas pressure. Before the test 90 cleaning rinse were applied to eliminate the stuck air particles in the pores and on the surface of feedstock.

The equipment records 3 density values, and calculates the average of those. Five samples were taken and measured from the different feedstock runs, to be able to study the homogeneity of the composition of material from the standard deviation of the measurements. *Fig. 7* shows the dependence of the standard deviation of density on the input parameters of mixing.

It can be seen in case of this measurement method as well that the increase of flux material amount and mixing time results the standard deviation of density values to decrease, so the homogeneity of the feedstock increases. However, it can be seen here as well, that more steps of dosage does not result positive effect in the homogeneity, due to the same reasons mentioned above.

3.1.3 Evaluation of injection molding pressure measurements

The value of pressure during injection molding would be theoretically equal to the other two measurements before, since this measurement is an alternative capillary viscosimetry on account of constant and fixed cross-section, temperature, material velocity and material properties. In this case, the resistance of material was also measured during forcing trough the capillary. As it was expected, the pressure results are comparable to the results of the other two measurements (*Fig. 8*).

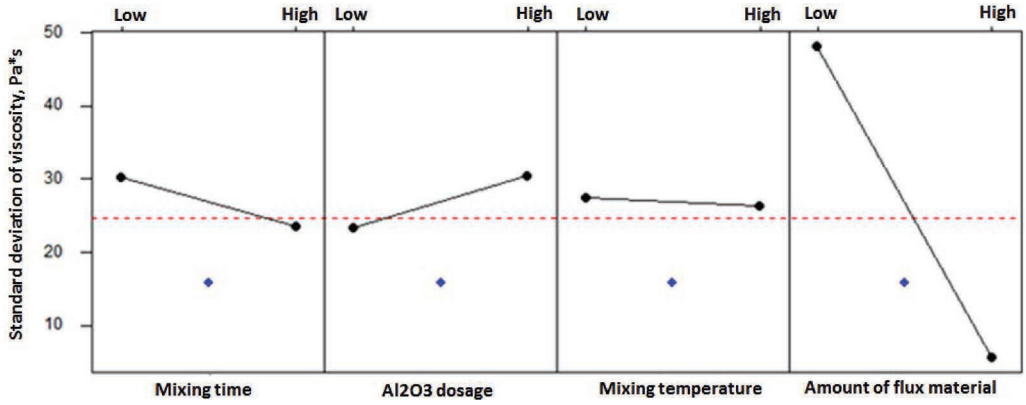

Fig. 6. Influences of input parameters on the standard deviation of viscosity
6. ábra A feedstock viszkozitás szórásának függése az egyes bemenő paraméterektől

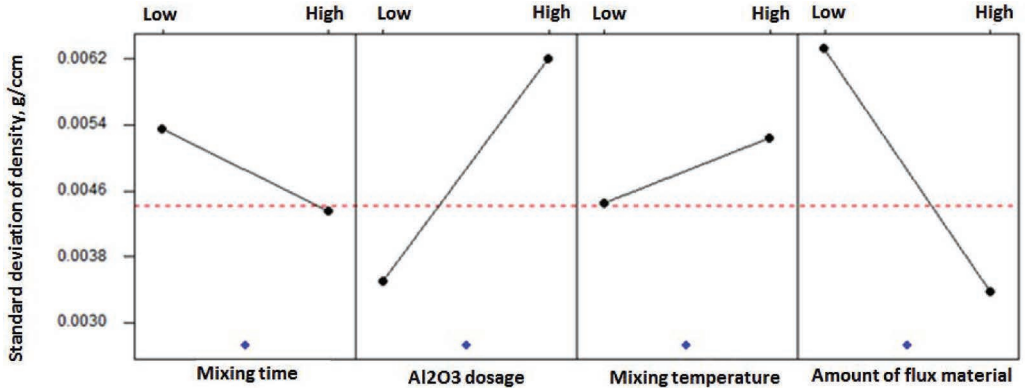

Fig. 7. Influences of input parameters on the standard deviation of density
7. ábra A mért sűrűség értékek szórása az egyes bemenő paraméterek függvényében

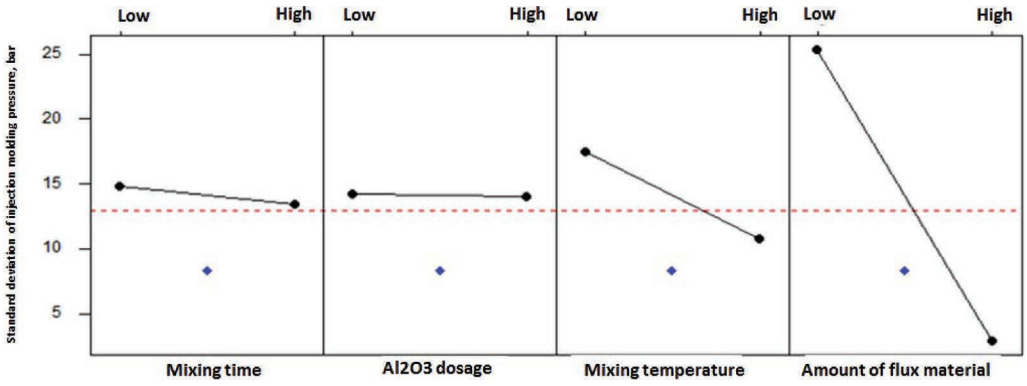

Fig. 8. Influences of input parameters on the standard deviation of injection molding pressure
8. ábra A fröccsöntési nyomás az egyes bemenő paraméterek függvényében

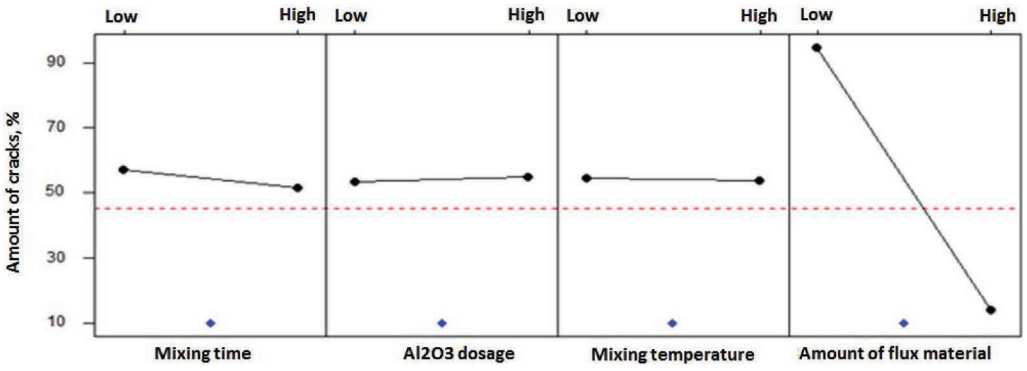

Fig. 9. Susceptibility to cracking, depending on the input mixing parameters
9. ábra Repedésre való hajlamosság az egyes bemenő paraméterek függvényében

In this case as well, the amount of flux dominates, although in this case one could observe the highest positive effect of the mixing temperature on homogeneity. However, this effect is not significant enough to enunciate that the mixing temperature has an influential role on the homogeneity within the interval variation studied.

3.2 Results of injection molding experiments

As a second step, after the determination of the homogeneity of different feedstocks, the injection molding was carried out. In this case the main question was the effect of homogeneity on the quality of the sintered end product, especially on the occurrence of cracks in the ceramic.

The samples of different runs were classified after the presintering and sintering processes, which results can be seen in *Fig. 9*.

In this case as well, the positive effect of the amount of flux is noticeable. The explanation is the same as before: the homogeneity of feedstock was improved, hereby less separated component remained in the mixture (whether powder or paraffin wax), which can cause cracks, voids or any heterogeneity in the sintered end product [25,13,14]. The other three factors did not have any significant effect on the amount of cracked products within the variation interval studied, except for the weak positive effect of mixing time.

4. Conclusions

The introduced test methods can be suitable to determine the grade of homogeneity of the ceramic injection molding raw materials.

With the defined mixing settings the homogeneity of raw material can be improved.

The flux material has the strongest effect on the homogeneity, since increasing the amount of this component can help homogeneous mixing of alumina powder and paraffin wax.

Increasing the mixing time has positive effect on the homogeneity of the material, but in a much less pronounced fashion than the amount of flux.

In the decrease of the amount of cracked ceramics, the mixing time and the amount of flux material were found to be the most effective input parameters.

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Kerámia fröccsöntési alapanyag homogenitásának vizsgálata és optimalizálása a végtermék repedési szívósságának fokozása érdekében

Jelen kutatásban a szerzők ahhoz, hogy meghatározzák az adott keverési feltételekkel és különböző bemenő komponens mennyiségekkel előállított kerámia fröccsöntési alapanyag homogenitásának fokát, kapilláris viszkozimetriát, sűrűségmérést, valamint fröccsöntési nyomásmérést alkalmaztak. Legfőbb megállapításképpen elmondható, hogy a folyósító anyag mennyiségének változtatása volt a legnagyobb hatással a homogenitás növelésére, mivel ez az adalék tudja elősegíteni az alumínium-oxid por és a paraffin viasz minél egyenletesebb elkeveredését. Továbbá, a keverési idő növelésének pozitív hatása van az anyag homogenitására, de sokkal kisebb mértékben, mint a folyósító szernek.

Kulcsszavak: alumínium-oxid por, paraffin wax, kerámia fröccsöntés, kapilláris viszkozitás, sűrűségmérés, feedstock