Turk J Engin Environ Sci
25 (2001) , 315 – 319.

Preparation of Homogeneous Feedstocks for Injection Moulding of Zirconia-Based Ceramics

Hüseyin Ş. SOYKAN, Yılmaz KARAKAŞ
Department of Metallurgical and Materials Engineering,
Sakarya University, Esentepe, 54187, Adapazarı - TURKEY

Received 04.09.1999

Abstract

In this study, a new method for preparing homogeneous feedstocks for injection moulding of ZrO_2 ceramics was developed and explained in detail. Mixture homogeneity on a large scale was assessed by measuring green density after moulding and weight loss after partial debinding for several tube samples from different batches. The grain structure of a sintered specimen was examined using SEM for the packing of ceramic particles.

Key Words: Feedstock, Mixing, Injection Moulding, Zirconia

Zirkonya Esaslı Seramiklerin Enjeksiyon Kalıplama Yöntemiyle Üretimi için Homojen Besleme Stoklarının Hazırlanması

Özet

Bu çalışmada, ZrO_2 esaslı seramiklerin enjeksiyon kalıplama yöntemiyle üretiminde kullanılan besleme stoğunun homojen olarak hazırlanabilmesi için geliştirilen bir yöntem açıklanmıştır. Bu yöntemle hazırlanan ve enjeksiyon kalıplamayla üretilen ZrO_2 tüpler üzerinde yoğunluk ve kısmi bağlayıcı giderme işlemi sonrası ağırlık kaybı değerleri ölçülerek, hazırlanan besleme stoklarının homojenliği tesbit edilmiştir. Bu besleme stoklarından üretilen ve 1750 °C'de sinterlenen bir numune mikroyapısı SEM ile incelenerek, seramik partiküllerin homojen paketlenme davranışı gösterip göstermediği araştırılmıştır.

Anahtar Sözcükler: Besleme Stoğu, Karıştırma, Enjeksiyon Kalıplama, Zirkon

Introduction

Ceramic injection moulding (CIM) has emerged in the last 20 years as a manufacturing process for forming complex and near-net shape components. In this process, a high concentration of ceramic powder is mixed with a binder to form a moderate-viscosity feedstock. This feedstock is moulded in equipment that is very similar to that used for polymer injection moulding. After moulding, the binder is extracted from the component. The debinded piece is then heated to the sintering temperature to attain a high final product density. The process is applicable to a wide range of established and emerging materials, and can be used to obtain competitive final properties (Evans, 1996).

The CIM processing steps have been well documented (Mutsuddy, 1995). However, there is little information about the details of feedstock preparation. 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 moulding and subsequent processing (German, 1991). A

homogeneous feedstock having a 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 (Dow, 1988).

Two methods of mixing the binder with the ceramic powder have been developed (Waugh, 1970 and German, 1990). In one, the ceramic powder plus the organic binder are kneaded in a hot mixer to a homogeneous consistency at an elevated temperature. In the second mixing method, the organic binder is dissolved in a suitable solvent and the resulting solution is mixed with the ceramic powder in a ball mill or a blade-type mixer. The solvent then is removed by heating the mix for a sufficient time above the boiling point of the solvent.

The aim of the present study was to prepare homogeneous feedstocks for fine-grained ZrO_2 ceramics using the first method.

Experimental

Materials

In the present study, the ZrO_2-MgO (8 mole %) system was selected. The powders used for the present study were high grade ZrO_2, and natural hydromagnesite (Mg-HC) as the MgO source. The particle shapes of the powders were determined using a Jeol JSM 6400 scanning electron microscope (SEM). A Coulter LS 130 Particle Size Analyser was used to measure the particle size distributions of the powders.

The binder system consisted of a mixture of paraffin wax as primary binder and oleic acid as surfactant. This binder system was selected due to its low melting temperature, low viscosity, and easy debinding process. The paraffin wax: oleic acid ratio was maintained at a value close to 95:5 by weight. The role and properties of each component are summarised in Table 1.

Feedstock preparation

After a number of ways of preparing the feedstocks were investigated, the mixing procedure shown in Figure 1 was adopted. Firstly, ZrO_2 and Mg-HC powders were mechanically blended at room temperature for 30 min and then the powder blend was dried to remove humidity in an electrical furnace at 200°C for 30 min. At the same time, paraffin wax was melted in a sigma blender (Santos Inc., Spain) at 80°C and oleic acid was added. The powder mixture was gradually added to the polymer melt and mixed for 60 min to form a homogeneous mix. After de-airing with a vacuum, the powder plus polymer mixture was solidified and finally granulated into small pieces, as shown in Figure 2.

Table 1. Roles and the properties of the powders and the organic materials

Material	Role	Source	Melting Point, °C
ZrO_2	Ceramic powder	Sepr, France	-
Mg-HC	Stabiliser	Merck, Germany	-
Paraffin wax	Binder	Merck, Germany	56-59
Oleic acid	Surfactant	Merck, Germany	10

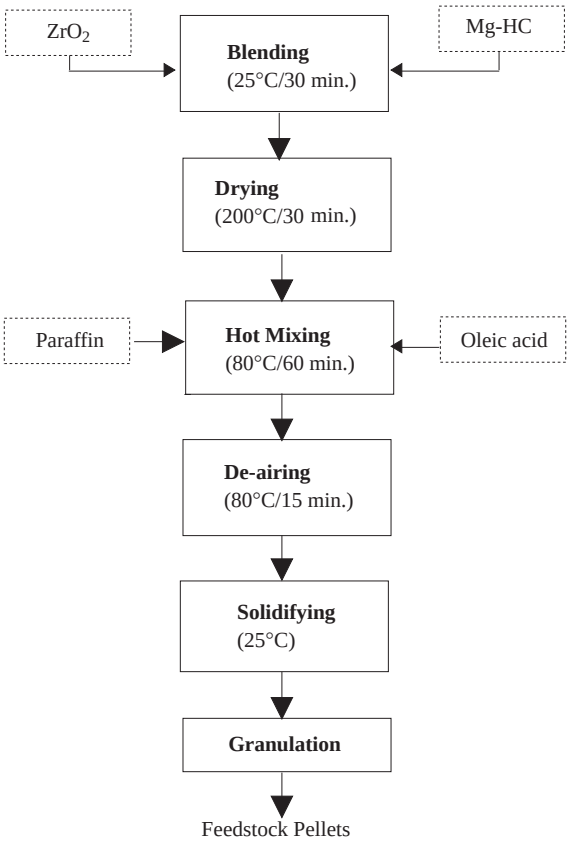

Figure 1. Flow diagram for preparing the feedstock

Moulding

Typical feedstocks contained 40 vol. % ceramic powder and 60 vol. % binder phase. These feedstocks were injection moulded using a 50 ton plunger-type plastic injection moulding machine (Florin Inc.,

England) to form them in the shape of ZrO_2 tubes with one closed end. Tubes were 6 mm in outer diameter, 4 mm in inner diameter and 50 mm in length.

Figure 2. Feedstock pellets of the powder plus polymer mixture

Density and weight loss measurements

In general, indices that can be used to quantify the extent of mixing are based on the standard deviation or the variance of the compositions of spot samples taken in intervals from the mixture. For this purpose, densities and weight losses of the samples were measured.

An Hg-displacement method based on Archimedes' Principle was used for density measurements and the results were compared with the calculated values. The consistency in the density was used to measure the homogeneity of the feedstock. The feedstock homogeneity on a macroscopic scale was also assessed from the sample weight loss measurements after partial debinding. For this test, the samples were embedded into ZrO_2 powder in a copper box and were put into a furnace at 130°C for 5 hours. In this process, partial debinding occurred with a wicking mechanism by capillary action. At the end of this test, the samples were re-weighed to determine the amount of binder that had been present in each. The deviation from the original amount of the binder in the feedstock mixture was calculated to determine the level of homogeneity.

Results and Discussion

With SEM studies, it was found that ZrO_2 particles were spherical in shape and Mg-HC particles were flake-type, as shown in Figure 3. The results of the particle size distributions are shown in Figure 4. ZrO_2 had a mean particle size of 1.3 m and did not contain any agglomerates. Mg-HC contained weak agglomerates (10-17 m) and its mean particle size was around 1.5 m. According to the results, these powders are suitable for injection moulding process.

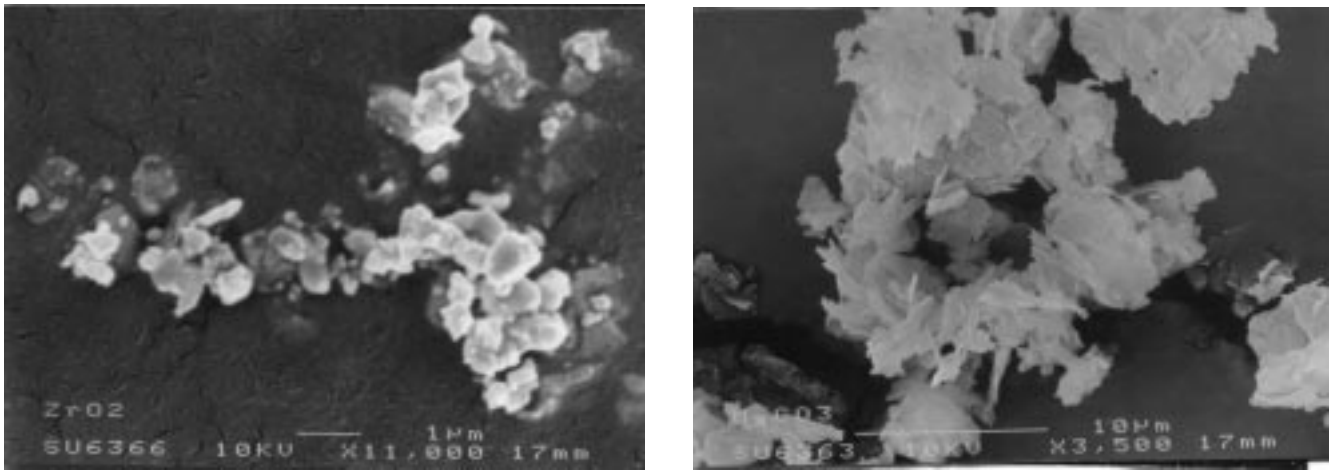

Figure 3. Scanning electron micrographs of the powders, a) ZrO_2 and b) Mg-HC

Green density results

The feedstock prepared with this method was injected easily at around 120°C using a cold mold. The viscosity of the feedstock was sufficient at moulding temperature. A setting time of 20 seconds was sufficient for the ejecting of the tubes from the mould without distortion and sticking. The green densities obtained from different batches are shown in Table 2. The values were very similar in all batches as a result of the well-mixed feedstock. The maximum differ-

ence between theoretical and measured sample densities was less than 3%. This shows that the binder and the ceramic particles were essentially uniformly mixed.

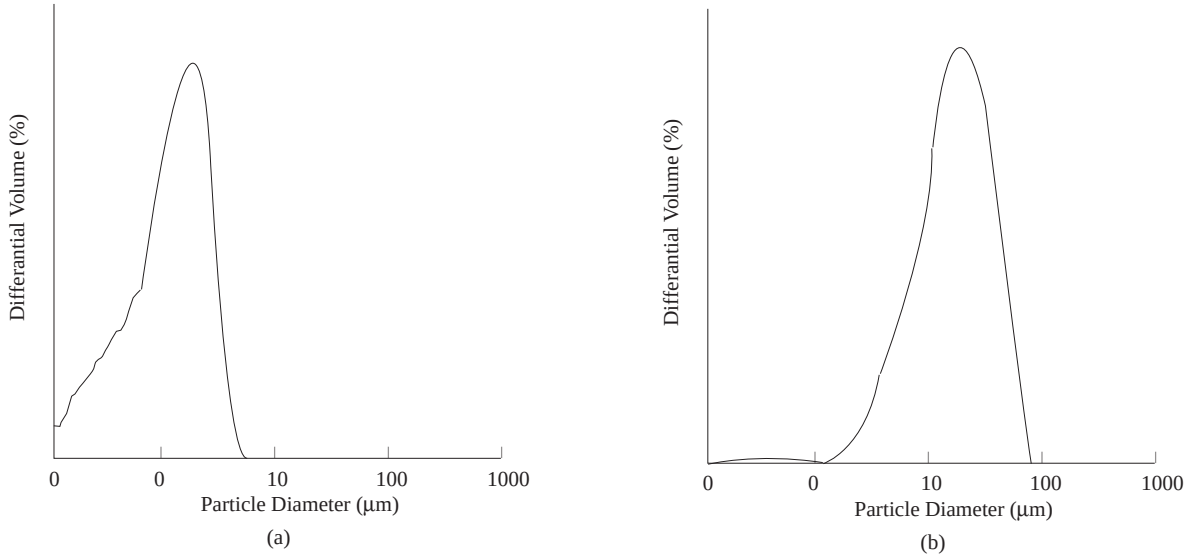

Figure 4. The particle size distributions of the powders, a) ZrO_2 and b) Mg-HC

Table 2. Results of the density measurements for feedstocks made by mixing 40 v/o ceramic powder

Batch No.	Sample No.	Green Density (g/cm^3)	Theoretical Density (g/cm^3)	Density Difference (%)
1	1	2.78	2.78	0
	2	2.75		1.08
	3	2.75		1.08
	4	2.76		0.72
	5	2.70		2.88
2	1	2.75	2.78	1.08
	2	2.74		1.44
	3	2.78		0
	4	2.77		0.36
	5	2.71		2.52
3	1	2.73	2.78	1.80
	2	2.77		0.36
	3	2.70		2.88
	4	2.75		1.08
	5	2.76		0.72

Weight loss results

The results of partial debinding are given in Table 3. The values for all the batches showed a uniform binder distribution on the scale of size examined, i.e., tubes of 2 grams. The debinding rate as weight loss divided by the initial binder content of sample changed in a limited range for three batches. The maximum difference in the debinding rates for all the batches was less than 1% and the values obtained from different samples for batches were close to each other. This is a result of mixture homogeneity.

Microstructure evaluation

A scanning electron micrograph of a specimen from which the binder had been removed completely and which was sintered at 1750°C for 5 hours is shown in Figure 5. This micrograph reveals uniform packing of the ceramic particles in terms of grain structure and grain size.

Table 3. The results of partial debinding for ZrO_2 tube samples made by feedstocks containing 40 v/o ceramic powder

Batch No.	Sample No.	Debinding Rate, %	Mean Debinding Rate, %	Difference, %
1	1	31.1	31.5	−0.4
	2	32.1		+0.6
	3	32.0		+0.5
	4	30.5		−1.0
	5	31.8		+0.3
2	1	31.3	31.7	−0.4
	2	31.9		+0.2
	3	32.7		+1.0
	4	32.1		+0.4
	5	30.8		−0.9
3	1	30.9	31.4	−0.5
	2	32.3		+0.9
	3	31.5		+0.1
	4	30.8		−0.6
	5	31.6		+0.2

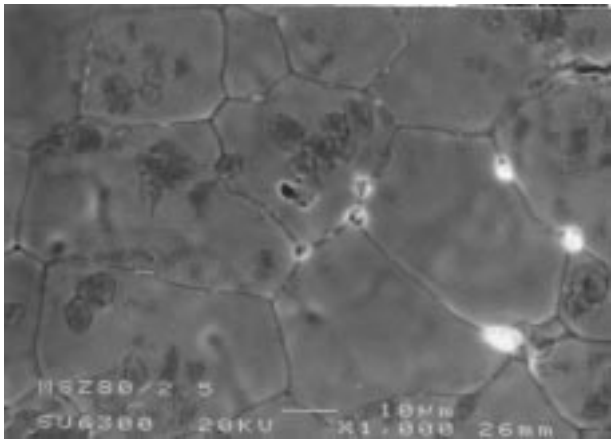

Figure 5. Scanning electron micrograph of a specimen, showing uniform grain size due to homogeneous packing of the ceramic particles

Conclusions

This study was carried out on products in the shape of small tubes. The results of this study indicate that the proposed feedstock preparation can be used for large-scale industrial applications. The use of vacuum in the feedstock during preparation eliminated air from the final mixture. This makes the moulding step very easy. Using this method, feedstocks without any segregation of the binder can be prepared and injected.

Acknowledgement

The authors gratefully acknowledge the TUBITAK-Munir Birsel Foundation for financial support.

References

Dow, J.H., Sacks, M.D., Shenoy, A.V., "Dispersion of Ceramic Particles in Polymer Melts", Ceramic Transactions, Vol. 1A, Ceramic Powder Science, The Ame. Cer. Soc., Ohio, 380-388, 1988.

Evans, J.R.G, "Injection Moulding", Materials Science and Technology: A Comprehensive Treatment, Vol. 17A, Processing of Ceramics, VCH, Weinheim, 267-311, 1996.

German, R.M., "Powder Injection Moulding", MPIF, New Jersey, 1990.

German, R.M., Hens, K.F., Lin, S.T.P., "Key Issues in Powder Injection Moulding", Cer. Bull., 70, 8, 1294-1302, 1991.

Mutsuddy, B.C., Ford, R.G., "Ceramic Injection Mgoulding", Chapman & Hall, London, 1995.

Waugh, A., "Process for Forming Sintered Leachable Objects for Various Shapes", U.S Patent 3.549.736, 1970.