NASA TECHNICAL MEMORANDUM NASA TM-77736

(NASA-TM-77736) INJECTION MOLDING OF SILICON CARBIDE CAPABLE OF BEING SINTERED WITHOUT PRESSURE (National Aeronautics and Space Administration) 16 p HC A02/MF A01 N85-10221
CSCL 13H G3/31 Unclas 24245

INJECTION MOLDING OF SILICON CARBIDE CAPABLE OF BEING SINTERED WITHOUT PRESSURE

A. Muller-Zell, R. Schwarzmeier

Translation of "Spritzgiessen von drucklos sinterbarem Siliciumcarbid", Keramische Zeitschrift, vol. 36, no. 10, 1983, pp. 524-527.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 SEPTEMBER 1984

STANDARD TITLE PAGE

1. Report No. NASA TM-77736	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle
INJECTION MOLDING OF SILICON CARBIDE CAPABLE OF BEING SINTERED WITHOUT PRESSURE

5. Report Date September, 1984

6. Performing Organization Code

7. Author(s)
A. Muller-Zell, R. Schwarzmeier

8. Performing Organization Report No.

10. Work Unit No.

9. Performing Organization Name and Address
SCITRAN
Box 5456
Santa Barbara, CA 93108

11. Contract or Grant No.
NASw- 3542

13. Type of Report and Period Covered
Translation

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes
Translation of "Spritzgiessen von drucklos sinterbarem silicium-carbid", Keramische Zeitschrift, vol. 36, no. 10, 1983, pp. 524-527.

16. Abstract

The most suitable SiC mass for injection molding of SiC articles (for subsequent pressureless sintering) consisted of β-SiC 84, a wax mixture 8, and polyethylene or polystyrene 8 parts. The most effective method for adding the binders was by dissolving them in a solvent and subsequent evaporation. The sequence of component addn. was significant, and all parameters had to be optimized together rather than singly.

ORIGINAL PAGE IS
OF POOR QUALITY

17. Key Words (Selected by Author(s))

18. Distribution Statement
Unclassified and Unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 16	22. Price

INJECTION MOLDING OF SILICON CARBIDE CAPABLE OF BEING SINTERED WITHOUT PRESSURE*

A. Muller-Zell, R. Schwarzmeier**

Various tests are described arising from the development of a β silicon carbide body, capable of being injection molded and sintered, waxes and/or organic polymers and/or oils being used as a means of plastifying, sliding and separating. Various methods of preparation are compared. The influence of machine parameters and of types of preparation is shown.

Introduction and Purpose

/524*

Silicon carbide is becoming more important as a construction material in machine technology and as a material to be used at high temperatures. Silicon carbide combines a number of exceptional properties, such as high form stability up to high temperatures, exceptional strength which does not decrease up to 1400°C and even more, good alternating temperature characteristics, extreme hardness, low thermal expansion and good resistance to oxidation and high chemical resistance.

The injection molding process is a process which has been used for a long time in plastic technology with success. [1] It offers the possibility of producing complicated parts in high volume and at a high rate at a low cost, either without or very little post-processing. Injection molding as a shaping process is also becoming more important for ceramic materials, as numerious publications have shown recently. [2-20] Therefore, ceramic materials and the injection molding process have to be developed. Therefore, we decided to develop a mass which could be injection molded based on silicon carbide which can be sintered without pressure.

---

*Communication from the Central Laboratory of Hutschenreuther AG, Selb.

**Selb. Excerpt from a diplomacy No. 142 in the area of material and technology of the Nurnberg Special School.

*Numbers in margin indicate foreign pagination

One can convert non-plastic powders for injection molding by adding organic plastification agents. These plastification agents also act as sliding agents and are very important for the wear of cylinders, worm gears and tools. The advanced development of the silicon carbide powders with large specific areas (10 to 20 m^2/g) and substantially improved sintering capacity requires an appropriate adjustment of the injection molding process. Waxes and/or plastics (thermoplasts, duroplasts, elastomers) can be used as plastification agents, binding agents and sliding agents for silicon carbide material. Also, oils with a low boiling point are added. The materials mentioned are also temporary binding agents during manipulation and the first processing of the injection molded part.

In the literature one finds only a small amount of data about the ceramic injection molding compositions. For example, one can use 20% mass fraction of organic binder [12] or 47% volume fractions of polymers [13] for producing reaction-bound silicon carbide cast parts. We should also mention the plastification of silicon carbide powders which can be sintered without pressure using thermoplastics and an oil or wax component [15]. The reports state that usually this is prepared by dry mixing in spherical mills or in heated band mixers.

The preparation methods mentioned do not seem to be optimum, however, especially when the fraction of plastifying materials has to be reduced further. If one considers the highest possible initial densities, it is then necessary to reduce the plastic component in masses which can be injection molded even further. The literature states very little about this. Most papers are concerned with the optimization of machine parameters, the influences of various initial materials as regards to grain size and grain distribution. Even the best plastification mixture leads to unsatisfactory results if it is not possible to mix the binders homogeneously in the ceramic raw material. Most of the work is concerned with the mixing problems, sometimes with the use of solvents. Even the order of introducing the individual components into the mixture being processed has been found to be important.

Test Description

Various organic polymers such as thermoplasts, duroplasts, copolymers and elastomers are used as plastification agents. Also, waxes are used as sliding and separation agents. Oils are used as sliding agents and removal aids.

Among the many available plastics and waxes, in preliminary tests we made a selection with consideration of their flow properties, plasticity, wetting behavior for silicon carbide, capacity to absorb solids, melting and volatility properties as well as separation and final molding behavior. For this purpose, we used a melting index device, a thermal balance and a heating microscope.

We used a β-SiC as the silicon carbide with a specific area of 15 m^2/g and an average corn size of <1 μm. Metalic sintering additives and carbon in various forms were added.

A commercial injection molding machine with 250 kN force capacity and a maximum injection pressure of180 MPa was used. The injection cylinder and the worm gears were of various designs. A multiple rod tool was used (rod dimensions 60 mm x 6 mm x 3 mm).

The first tests to compare materials were performed using mixtures of 80 parts of silicon carbide and 20 parts of wax or plastics, using a heated kneading mixer.

The machine adjustments which led to injection defects and processing difficulties are shown in Table 1. We also show the possible correction measures. The cylinder temperature, injection molding pressure and rate, post-compression pressure, dosing, cooling time, tool heating and their effects on the injected parts were investigated systematically. We evaluated this according to the defects which occurred on the injected parts, the dimensions, mass and density and the injection behavior and mold removal properties. The injected parts /525 were inspected visually for defects. This could be caused by unsuitable plastification agents, and also in the varying operating parameters of the injection molding machine.

A combination of the flow and diffusion processes in the sample [3] determined the important annealing process of the organic components. The heating rate can only be selected as high to allow the individual components to anneal one after another, since they had different softening and volatility points. However, the external shape of the part and the inner cohesion must not be disturbed. For heating rates between 1 K/h and 10 K/h depending on the size and binder fraction of the parts and by maintaining the corresponding holding times of several hours, such an annealing process can last over 100 hours. As can be seen from Figure 1, for temperature of 600°C almost all organic components have been annealed and this was determined using a thermal balance. The course of the mass loss-temperature curve depends on the type and composition of the plastification agent used. This also determines the number, time and duration of the individual heating times and holding times. Improper heating leads to the defects shown in Figure 2. The silicon carbide injected parts were sintered using a graphite oven in a protective gas-hydrogen atmosphere at temperatures between 2100°C to 2250°C.

Ceramographic investigations with light and raster electron microscopes in non-annealed samples, and also in those whose binding fraction had been annealed, and on sintered rods were also performed. The densities achieved were determined according to the mercury buoyancy method. The bending strength was determined in green and sintered samples using the three-point bending method, and a statistical evaluation according to Weibull was carried out.

Preparation

The purpose of the preparation of a mass which can be injection molded is to distribute the materials homogeneously. The preparation of the injection molded parts was done using five different preparation methods using wax mixtures and plastic mixtures. Figure 3 gives a summary of the preparation methods using waxes. We made tests with molten, dispersed and dissolved waxes. We tried to determine which of these preparations gave the optimum results.

Variation I shows the mixing and homogenization of all of the initial materials in a heated kneading mixer at temperatures above the wax melting points over the duration of several hours. Variation II is characterized by a dispersal of the waxes and powders in acetone which subsequent distillation in a rotation vaporizer, which prevents decomposition. Finally, in the /526 preparation method III the waxes are dissolved in benzene. All of the other components are added to the solution while mixing. The other working processes are just like in method II. Extensive tests have shown that mixtures of several wax components have to be used in order to insure that as the binders are slowly removed, no deformations occur nor will microcracks develop. The softening points must extend over a wide interval of at least 100 K.

In other tests we drop the wax fraction in steps from 20% to 10% mass fraction. For this we use the preparation method III in order to provide a homogeneous distribution as the wax fraction was decreased. As can be seen from Figures 4 to 6, the mass and the density of the non-annealed samples increase as the mass fraction is increased. The strength of the non-sintered rods on the other hand for a mass fraction of 14% wax has a maximum and then drops off again. There is similar behavior in the bending strength of sintered injection molded cast parts. A maximum occurs at 16% of mass fraction wax. Since the flow capacity decreases during preparation as the wax fraction is decreased, we can assume that macro defects and insufficient covering and binding occur, and that the samples will have a reduced strength in spite of the higher density.

The densities and strengths in the sintered state achieved are still not perfect. Therefore, the injection molding test was extended to using organic polymers (16% mass fraction) as the plastification agent, but this did not lead to any improvement.

Finally, we considered plastics (such as thermoplasts, polystyrene, polyethylene, polyproplylene, polyamide) and duroplasts (phenol resins) which were added. Figure 7 shows the preparation method IV and V for these mixtures. The best processing properties resulted using polyethylene and polystyrene.

A mixture using 8 parts of wax mixture and 8 parts of plastic gave the best results with regard to the strength in the sintered state $(\delta_R = 360\ \mathrm{N/mm^2})$. By optimizing tests with various polyethylene and polystyrene types, we were able to increase the strength of the sintered samples to an average of $(\delta_R = 390\ \mathrm{N/mm^2}$. Figure 8 shows the lattice of the sintered samples, for which we measured a bending strength of 360 $\mathrm{N/mm^2}$.

In additional tests, we determined the influences of the order of introducing waxes and plastics during the preparation. It was found that by surrounding the silicon carbide grain with a layer, we were able to bring about a further improvement. According to this kind of preparation, bending strengths of 450 N/mm^2 with a relative density of 92% of the theoretical densities and a Weibull modulus of $m = 15$ were attained.

Summary

/527

We have been successful in producing a mass based on β silicon carbide which can be sintered without pressure and which can be injection molded. Waxes and organic polymers and oils were used as plastification agents, sliding agents and separation agents. The best results were found with a ratio of 8 parts of wax mixture, 8 parts of a plastic and 84 parts powder. Polystyrene and polyethylene were found to be most suitable of the plastics used. Out of the preparation methods examined, the dissolution and precipitation of the plastification agents gave the best results. The order of introducing the individual components into the mixture was found to be important. Preparation temperature, injection pressure and injection rate clearly influence the injection results. The cooling time, holding time and tool temperature have an influence on the surface quality and mold removal capability of the injected part. We should emphasize that the optimization of a process step is not sufficient. Instead, all of the process parameters have to be tuned to one another in order to achieve a product of the required quality.

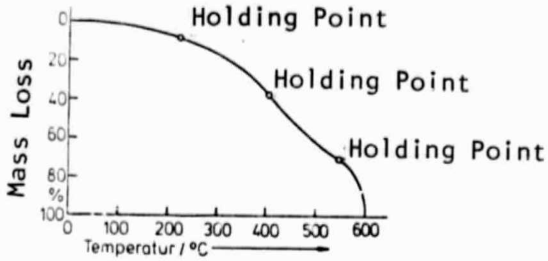

Figure 1. Annealing process.

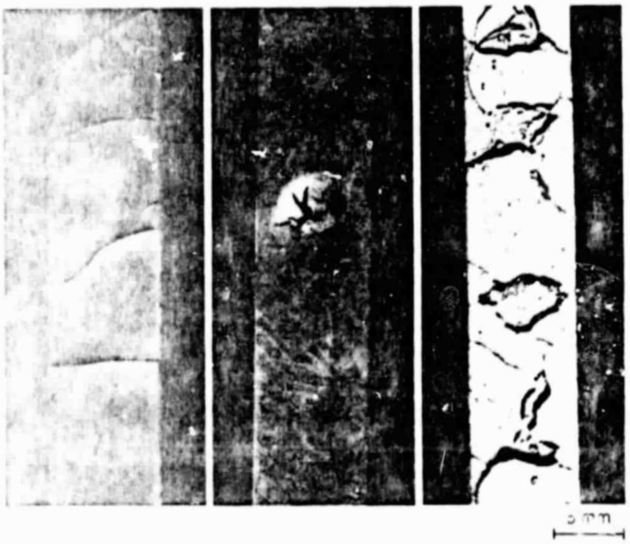

Figure 2. Errors occurring during improper annealing.

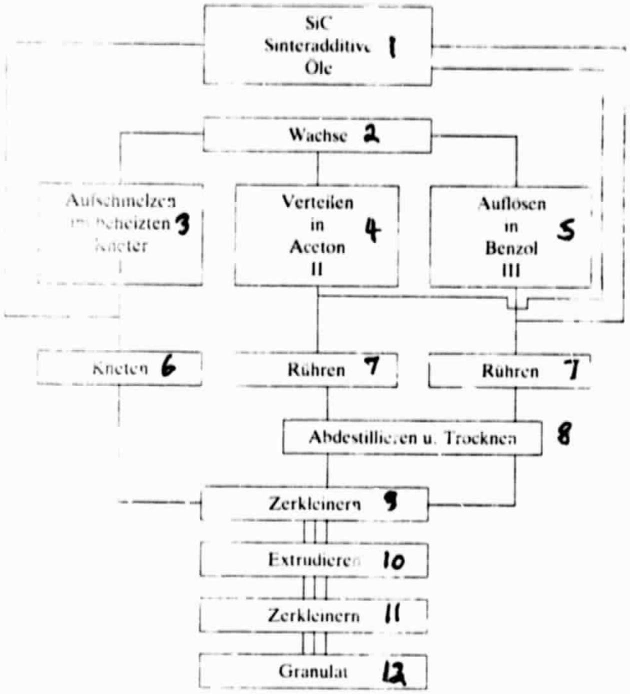

Figure 3. Preparation variations for wax mixtures.

Key: 1--SiC Sintering additives oils; 2--waxes; 3--melting for the heated kneader; 4--distribution of acetone; 5--dissolving in benzene; 6--kneading; 7--stirring; 8--distillation and drying; 9--size reduction; 10--extrusion; 11--size reduction; 12--granulate.

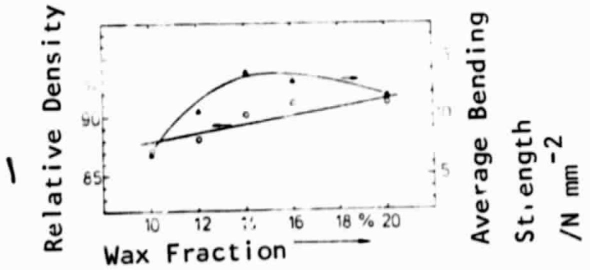

Figure 4. Relative density (refer to theoretical density) and fracture strength of non-annealed samples.

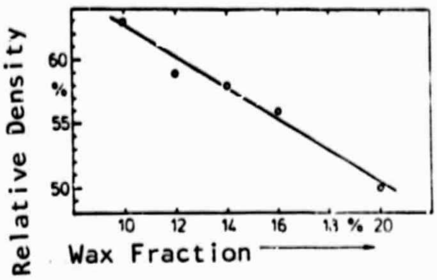

Figure 5. Relative density (refer to theoretical density) of samples, whose binding component was annealed.

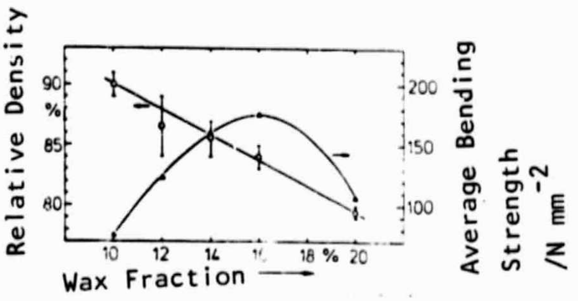

Figure 6. Relative density (refer to theoretical density) and fracture strength of sintered samples.

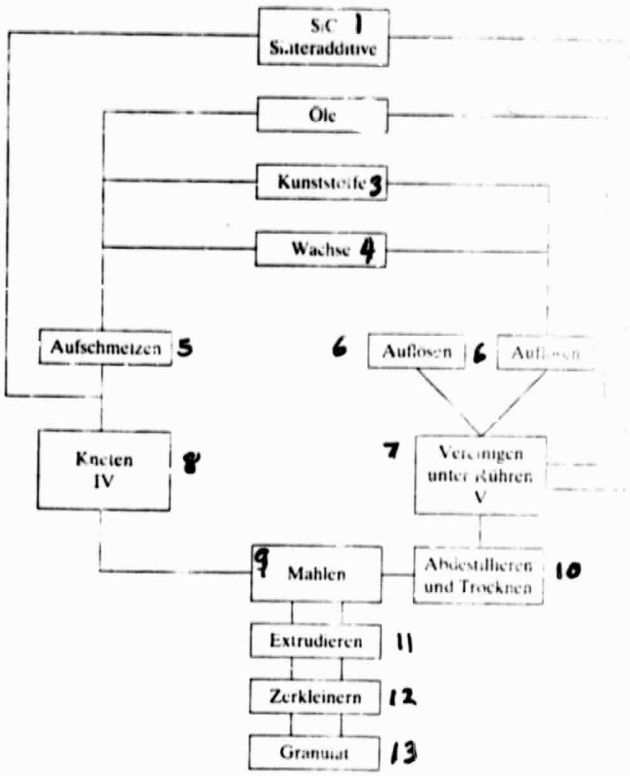

Figure 7. Preparation variations for wax-plastic mixtures.

Key: 1--Sinter additives; 2--oils; 3--plastics; 4--waxes; 5--melting; 6--dissolving; 7--combination with stirring; 8--kneading; 9--grinding; 10--distillation and drying; 11--extrusion; 12--reduction in size; 13--granulate.

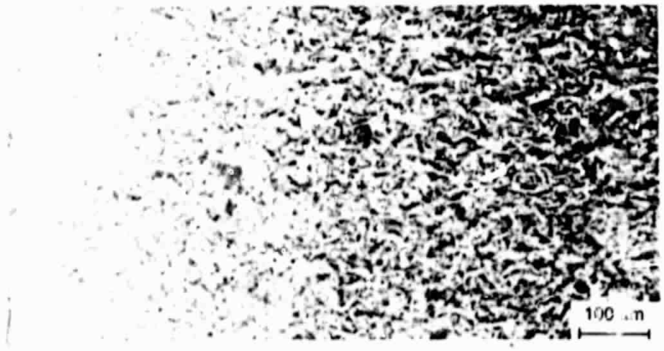

Figure 8. Fracture image of a sintered injection molded β-SiC sample

Table 1. Defects which occur, processing difficulties and corresponding elimination measures.

Insufficient Chilling	Pores and Holes	Ridge Formation	Schlieren, Oblique Features	Inhomogeneity	Mold Removal Difficulties	Bubble Formation	Defects and Difficulties Parameters
+	±	-	-	+	-	-	Cylinder Temperature
0	+	-	0	+	-	0	Post Compression Pressure
+	+	-	+	+	-	0	Injection Pressure
+	+	-	0	0	-	0	Dosing
+	0	-	±	+	-	0	Injection Rate
0	0	0	0	0	+	0	Cooling Time
+	+	0	+	+	+	-	Tool Temperature
0	0	+	0	0	0	0	Closure Pressure

Notation for redemption measures:

+ Increased Parameter
− Reduced Parameter
0 No Influence

REFERENCES

1. Beck, H.: Spritzgiessen, 2. Auflage. (Injection Molding, Second Edition). Carl Hanser Verlag, Munich, 1968.

2. Bahn, R., Blechschmidt, H.: Forming of Non-Plastic Ceramic Materials Using the Injection Molding Process. Silikattechnik 10 (1959) 442-445.

3. Hennicke, H. W., Neuenfeld, K.: Injection Molding Technique as a Molding Method in Ceramics. Ber. Dt. Keram. Ges. 45 (1968) 469-473.

4. Mostetzky, H., Hennicke, H. W.: Injection Molding of Ceramic Powders, With Quartz Sand as an Example. Ber. Dt. Keram. Ges. 52 (1975) 25-30.

5. Burke, J. J., Gorum, A. E., Katz, R. N.: First Edition: Ceramics for High Performance Application by Brook Hill Publishing Company, Chesternut Hill, Massachusetts, (1974).

6. Bunk, W., Bohmer, M.: Keramische Komponenten im Fahrzeng-turbinen (Ceramic Components for Vehicle Gas Turbines). Springer Verlag, Berlin, Heidelberg, New York, (1978).

7. Johnson, C. F., Mohr, T. G.: Injection Molding 2.7 g/cc Silicon Nitride Turbine Rotor Blade Rings Utilizing Automatic Control. In: Ceramics for High Performance Application II. Hrsg.: John J. Burke, Edward N. Lehnoe., R. Nathan Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts, (1978), S. 193-206.

8. Fischer, E. A., Baer, J. R., Johnson, C. F.: Molding of Stator Vanes for the Garret/Arpa/Navsea Ceramic Turbine Engine. Proceedings of the 1977 DARPA/NAVSEA Ceramics Gas Turbine Demonstration Engine. Program Review. MCIC Report (March 1978), S. 365-380, Editors: John W. Fairbanks, Roy W. Rice, Metals and Ceramics Information Center, Battelle, Columbus, Ohio.

9. Lange, E., Muller, N., Olapinski, H. Stannek, W.: Turbinenbauteile aus spritzgegossenem Si_3N_4 (Turbine Components Made of Injection Molded Si_3N_4). In: Ceramic Components for Vehicle Gas Turbines.

10. Mangels, J. A.: Development of Injection Molded Reaktion Bonded Si_3N_4. In: Ceramics for High Performance Application II. Hrsg.,: John J. Burke, Edward N. Leneo and R. Nathan Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts, (1978), S. 113-130.

11. Heinrich, J.: The Influence of Manufacturing Conditions on the Lattice and Mechanical Properties of Reaction-Sintered Silicon Nitride.

12. DAS 2256 326: Method for Producing and Injected Part from a Mixture of α-SiC, Graphit und einem Bindemittel.

13. Willermet, P. A., Pett, R. A., Whalen, T. J.: Development and Processing of Injection - Moldable Reaction - Sintered SiC Compositions. Ceramic Bulletin 57 (1978) 744-747.

14. Whalen, T. J., Noakes, J. E., Terner, L. L.: Progress of Injection-Molded-Reaction-Bonded SiC. In: Ceramics for High Performance Application II. Hrsg.: John J. Burke, Edward N. Lenoe, R. Nathan Katz, Brook Hill Publishign Company, Chestnut Hill, Massachusetts, (1978), S. 179-189.

15. DAS 2854612: Ceramic Masses Which Can Be Injection Molded and Methods for Producing Injected Parts From It.

16. Larson, C. C., Bortz, S. A., Ruh, R., Tallan, N. M.: Evaluation of Four Commercial Si_3N_4 and SiC Materials for Tubine Applications. In: Ceramics for High Performance Application II. Hrsg.: John J. Burke, Edward N. Lenoe, R. Nathan Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts, (1978), S. 651-687.

17. Dworak, U., Olapinski, H.: Gasturbinenbauteile aus spritzgegossenem RBSN-materialentwicklung (Gas Trubine Companents Made of Injection Molded RBSN Material Development). In: Ceramic Components for Vehicle Gas Turbines. II. Hrsg.: W. Bunk und M. Bohmer. Springer Verlag Berlin, Heidelberg, New York, (1981), S. 385-395.

18. Lange, E., Muller, N.: Gasturbinenbauteile aus spritzgegossenem RBSN-Material- und Bauteilentwicklung (Gas Turbine Components Made of Injection Molded RBSN Material and Component Development). In: Ceramic Components for Vehicle Gas Turbines. II. Springer Verlag, Berlin, Heidelberg, New York, (1981), S 397-410.

19. Wedemeyer, R.: Injection Molding of Non-Plastic Ceramic Materials. Sprechsaal 109 (1976) 347-351.

20. Mangels, J. A., Williams, R. M.: Injection molding ceramics to high green density. Amer. Ceram. Soc. Bull. 62 (1983) 601-606.