Journal of the European Ceramic Society 17 (1997) 415–419
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0955-2219/97/$17.00

PII: S0955-2219(95)00150-1

Development of Self-Hardening Slip Casting

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(Received 15 September 1995; accepted 23 July 1996)

Abstract

The self-hardening slip casting 'NK-Process' has been developed. It becomes possible to form near-net shapes and thick bodies of advanced ceramics, etc., with excellent properties when sintered. Y-PSZ slip containing a small quantity (3 wt%) of epoxy resin and hardener, was self-hardened at room temperature to 70°C. The increase of the slip viscosity depended on the curing temperature, and the time for hardening could be shortened to 10 min at 70°C. The three-point bending strength of sintered Y-PSZ increased up to 1300 MPa. This process can be applied to various advanced ceramics, such as Y-PSZ, alumina, and silicon nitride. In particular, we have succeeded in forming ceramics turbo rotor and gas turbine rotor made of silicon nitride. © 1996 Elsevier Science Limited.

1 Introduction

Conventional slip casting has been used in the Japanese ceramics industry because it can form near-net shapes more easily than any other forming method.[1,2] In conventional slip casting, the slip is cast into the plaster or synthetic resin molds containing continuous pores. The slip adheres to the mold by capillary forces to obtain the green body. A homogeneous green body can only be obtained for thin products by a pressureless cast. Generally, the green density of the body close to the mold formed in conventional slip casting is higher than that in the other forming methods, but the density of the body away from the mold surface becomes lower.

Furthermore, it is difficult to use an inner mold because the inner mold receives the compressive stress from the adhered product due to shrinkage, and it thus becomes difficult to extract the inner mold set in the outer mold. Therefore, it is difficult to form a large, thick, complicated green body using conventional slip casting. To solve these problems the slip should become hard rapidly by itself in the mold.

Recently, a new technique for the slip casting method, the 'NK-Process', has been developed to eliminate the problem of conventional slip casting.[3] This process utilizes a self-hardening slip containing thermosetting resin and hardener. The slip is cast into a metal or resin mold instead of a porous mold and it self-hardens in 10 min at 70°C. Homogeneous green bodies are obtained on removal from the mold. This paper only outlines self-hardening slip casting using Y-PSZ powder and some trials with alumina and silicon nitride powders.

2 Experimental Procedures

The flow chart for the self-hardening slip casting process is shown in Fig. 1. Table 1 shows an example of the mixing ratio for Y-PSZ. The mixing ratio was decided by a preliminary experiment. The characteristics of Y-PSZ powder are listed in Table 2. Y-PSZ powder was ball-milled with water and an epoxy resin dispersing agent (ammonium poly-carboxylate) for 12 h. The dispersed slip was then de-aired in vacuum for 30 min. The hardener was added into the dispersed slip at the theoretical proportion to epoxy resin, which was also de-aired and stirred for 10 min. The hardening slip was cast into a polypropylene mold measuring 80 mm × 50 mm × 20 mm at 70°C. The hardened bodies were then removed from the mold and dried at room temperature and at 80°C in an oven for 12 h. The green bodies were calcined in order to burn out organic materials at 600°C for 1 h (total schedule was 24 h), and sintered at 1500°C for 1 h (total schedule was 8 h) in air. The slip viscosity was measured by a rotational viscosity meter (type; VT-04, Rion Co., Ltd Japan). The three-point bending strength was measured based on the Japanese industrial standard (No. R-1601) and the density of the sintered body was measured by the Archimedean method. The linear shrinkage from the mold after sintering was also measured by a digital calliper. The microstructures of green and sintered bodies were observed by SEM (type; T-300, JEOL, Japan).

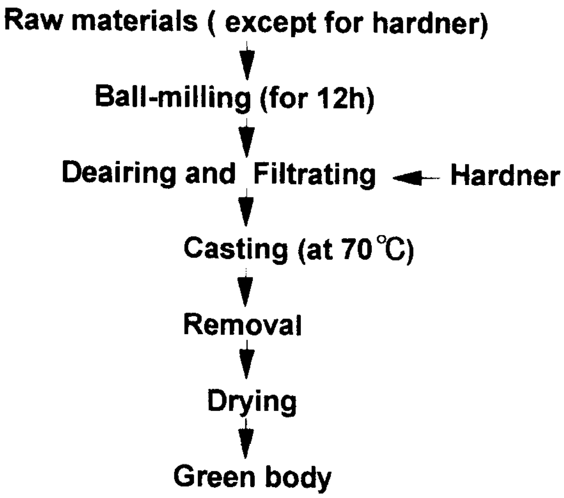


Fig. 1. Flow chart for self-hardening slip casting.

Table 1. The mixing ratio for Y-PSZ slip

Raw materials	*wt%*
Y-PSZ powder	100
Water	15
Hardening resin	3
Dispersing agent	0·5
Hardener	0·4

Table 2. Characteristics of Y-PSZ powder

Ave. particle size	0·5	μm
Surface area	7·5	m^2/g
Yttria	5·3	wt%
Alumina	0·15	wt%
Silica	0·05	wt%

In other experiments, some complicated shapes were formed by this process when using alumina and silicon nitride ceramics.

3 Results and Discussion

3.1 Curing temperature and time

Hardened bodies are removed from the mold easily after 10 min. The self-hardening time depends on the amount of epoxy resin in the slip and the curing temperature. The hardening time can be shortened by increasing the amount of the epoxy resin, but an excessive amount of epoxy resin over 5 wt% for the slip is not recommended for the calcination process and for the properties of sintered bodies. The effects of the curing temperature and time on the viscosity of the hardening slip are shown in Fig. 2. The slip viscosity just before casting was 0·8 Pa s. The slip viscosity is affected by the curing temperature. and the value increases with increase of the curing temperature. The viscosity of the hardening slip increases to over 20 Pa s rapidly at 70°C. The pot life of hardening slip depends on the slip temperature; it becomes long with a decrease in the curing temperature, and it takes about 90 min to harden at 25°C. Furthermore, the amount of hardener influences the hardening time and the properties of green bodies.

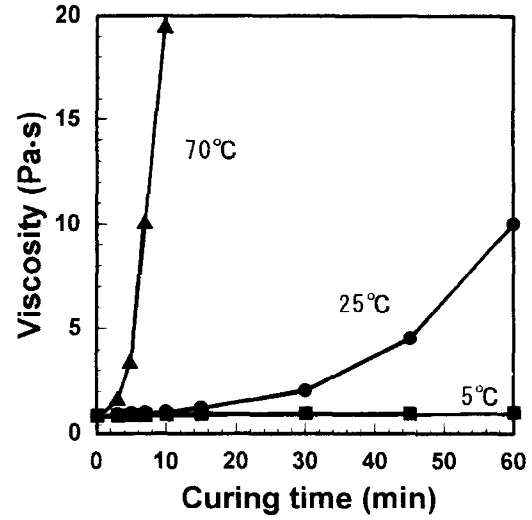


Fig. 2. Effect of hardening temperature and curing time on the viscosity of the slip.

3.2 Mechanism of self-hardening

The mechanism of self-hardening slip casting consists of three stages, as shown in Fig. 3. At the first stage, the slip viscosity increases by the reaction between epoxy and hardener. The Y-PSZ particles are suspended in the slip, and the water with dispersing agent and hardening materials restricts the motion of particles. The reaction equation between the epoxide group of the epoxy resin and the active hydrogen of amine is shown in Fig. 4. By selecting molecular weight, the structures, and the amount of epoxide or the active hydrogen of the amine, a three-dimensional network of

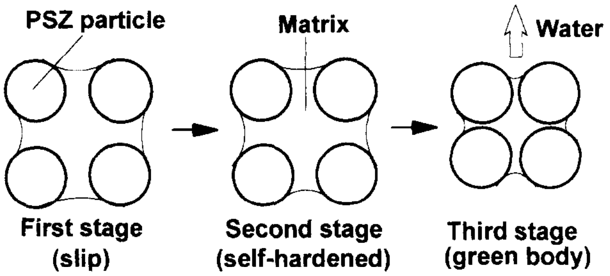
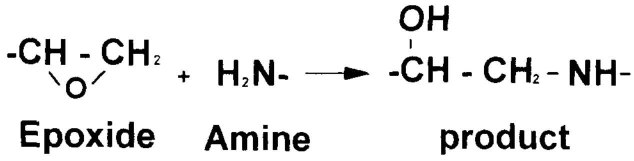


Fig. 3. Schematic model of forming mechanism in self-hardening slip casting.



$$\text{-CH-CH}_2\text{(-O-)} + \text{H}_2\text{N-} \rightarrow \text{-CH(OH)-CH}_2\text{-NH-}$$

Fig. 4. Reaction equation between epoxide of epoxy resin and amine in self-hardening slip casting.

epoxy resin can be formed in the slip. In this reaction, by-products are not produced because it is an addition reaction. The reaction continues until the slip becomes hard. At the next stage, the hardening slip loses its fluidity and becomes strong. At the last stage, the strength of the hardened body further increases due to self-dewatering and the drying process. It is considered that the driving force of self-dewatering is the formation of a three-dimensional network of epoxy resin in a hardened body. The removal of the green body should be performed before the last stage, if the inner mold is rigid or the shape of the outer mold is also very complicated. The hardening resin should have high mechanical strength and water solubility. Therefore, epoxy resin is appropriate for this process. The point of this process is to prepare high powder concentration in the slip and to select the self-hardening resin and hardener.

3.3 Drying and calcination

The volume fractions of raw materials in the self-hardening slip are shown in Fig. 5. The water content is very high. At the early period of drying, care should be taken to ensue no cracks or deformation in the green body occurs, because the water contained in the body is not absorbed into the mold. However, by using a homogeneous drying method, the drying time can be shortened to 12 h without cracks or deformation of the body in this experiment. The calcination schedule for the green body is shown in Fig. 6. The decomposition of epoxy resin starts around 300°C and finishes around 500°C in air. The total schedule for this calcination process is shorter than that for the injection molding method because of the low amount of organic materials in the green body in the 'NK-Process'.

3.4 Microstructures of green and sintered bodies

The microstructures of the green and sintered bodies are shown in Fig. 7. The three-dimensional network structures with hardened resin cannot be recognized on the fracture surface of the green body at this magnification level. The microstructure of the sintered body is similar to those in conventional slip casting, and large defects are not observed in either body.

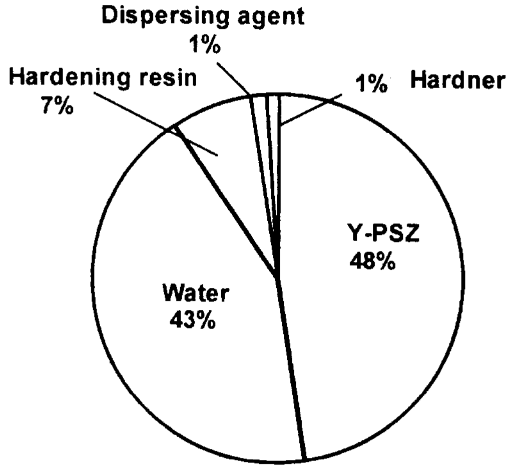


Fig. 5. Volume fractions of raw materials in the hardening Y-PSZ slip.

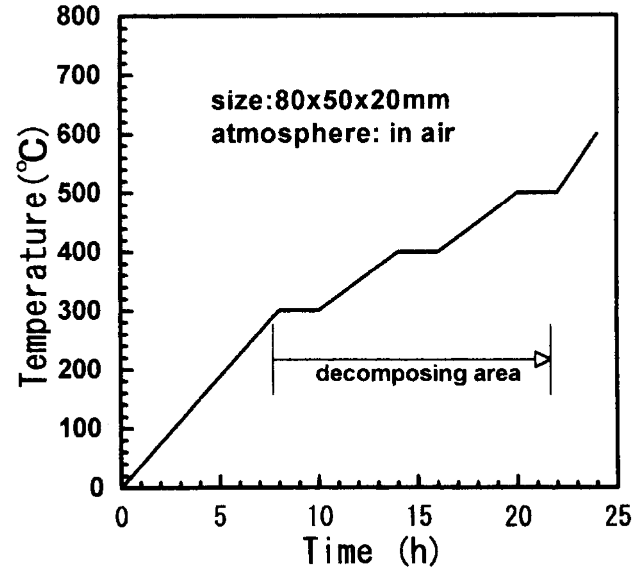


Fig. 6. The calcination schedule for Y-PSZ green body in air.

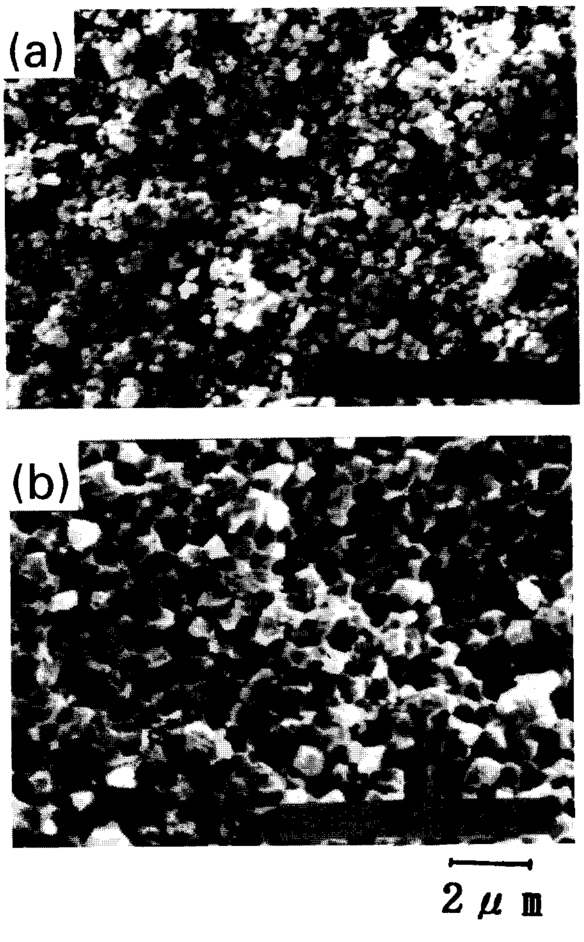


Fig. 7. Microstructures of green and sintered bodies on Y-PSZ. Fracture surface of (a) green body, and (b) sintered body.

3.5 Characteristics of sintered body

The types of Y-PSZ green bodies made by self-hardening slip casting and conventional slip casting (SSC and CSC, respectively) were sintered. The average bending strength of sintered Y-PSZ(SSC) is 1300 MPa which is superior to that of Y-PSZ (CSC) (1000 MPa). The density of sintered body and total linear shrinkage are 6·02 g/cm^3 and 22·0%, respectively. The linear shrinkage directly depends on the slip composition. The theoretical total shrinkage calculated with the slip composition in SSC is 21·7%, this value being nearly equal to the measured one. To decrease the linear shrinkage, it is necessary to increase powder concentration in the slip.

From this point of view, the appropriate control of the slip composition is essential. The selection of raw materials such as powder, a dispersing agent, hardening resin and hardener should be made carefully. In another test with sintered silicon nitride (SSC), it was recognized that the bending strength was also higher than that of silicon nitride (CSC). It is considered that the increase of the bending strength relates to the mechanism of self-hardening in this process.

3.6 Formability

SSC has superior formability to CSC because the self-hardening does not cause a volume change of the slip before removal from the mold. Therefore, the shapes of the molds used in SSC have no limitation. A thick body can also be obtained easily, but the calcination schedule may become longer in proportion to the thickness of the green bodies. In view of the accuracy of the shapes, it is recommended to use a metal or resin mold rather than a rubber mold. The samples, such as chemical valve parts made of high purity alumina, and a turbo rotor made of silicon nitride are shown in Fig. 8. In forming these samples, a metal mold or a resin mold can be used, but a plaster mold can also be used by coating the cavity with an organic film. Furthermore, the gas turbine rotor, which has a complicated shape from SSC can be formed.

4 Conclusion

The outline of the self-hardening slip casting 'NK-Process' has been described mainly for Y-PSZ. This process has an excellent formability for complicated shapes and gives high mechanical strength for sintered bodies. This process can be applied to various raw materials, such as Y-PSZ, alumina, silicon nitride, etc., in order to form near-net shapes. Slip casting is not a new technology but after considering the characteristics of powder, dispersing method and organic materials, it has become practically suitable for forming advanced ceramics.

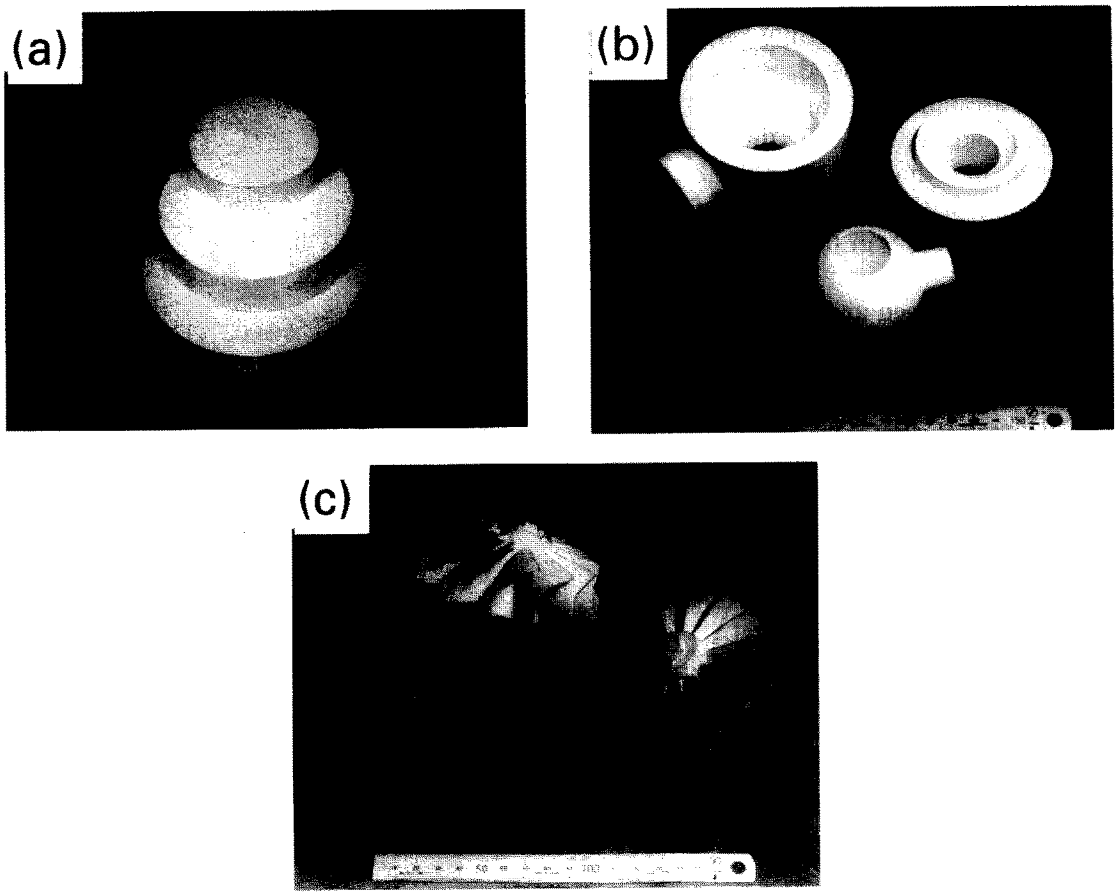


Fig. 8. Samples of some advanced ceramics formed by self-hardening slip casting. (a) Thick bodies of Y-PSZ, (b) valve parts made of alumina for the chemical industry, (c) turbo rotor made of silicon nitride.

Advantages of self-hardening slip casting are:

(1) Formability of near-net shapes and large thick bodies.
(2) Obtainment of sintered bodies with high mechanical strength.
(3) Utilization of metal and resin molds instead of porous molds.

Key points this process are:

(1) Preparation of high powder concentration in the slip.
(2) Selection of self-hardening resin with high strength and water solubility.
(3) Preparation of homogeneous and stable slip.

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