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CONSOLIDATION OF SLIP THIN-WALLED ELEMENTS BASED ON THIXOTROPIC DISPERSED SYSTEMS FOR PREPARING HIGHLY POROUS RSSN

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Features are considered for preparing highly porous workpieces of silica by warm molding of elements prepared by cutting castings from thermoplastic slip based on silica with addition of plasma chemical synthesis silicon nitride and appropriate highly porous silicon nitride materials, and also methods by means of which a molded workpiece or sintered object may be given additional channel porosity for improving permeability. Material is suggested for use in power generation installations as a porous barrier for feeding natural fuel through porous material and combustion, capable of withstanding extreme situations.

Keywords: reaction-sintered silicon nitride, RSSN, porosity, thermoplastic slip, thixotropy.

Materials based on reaction-sintered silicon nitride (RSSN) over a wide range of porosity exhibit good resistance to thermal shock and thermal cycling, to oxidation up to a minimum temperature of 700 – 800°C, and capacity to withstand extreme situations. These materials may be considered promising for use in power generation installations as porous barriers for supply of natural fuel though a porous medium and combustion.

The majority of materials based on silicon nitride, prepared by well-known technology, do not have adequate uniform porosity and permeability, required for this application, and therefore currently for this purpose highly porous cellular materials (HPCM) based on metallic heat-resistant materials of the chromal type are used. Traditional metal HPCM are made up from elements of the hollow thin-walled tube type, and therefore their life in an oxidizing atmosphere is limited. We have attempted to prepare ceramic highly porous material based on RSSN capable of competing in the future with chromal type HPCM.

In this work methods are considered for preparing highly porous workpieces made of silica and corresponding materials based on RSSN, and also methods by means of which workpieces or sintered objects are formed may be given additional channel porosity in order to increase permeability.

Much work has been devoted to technology for preparing porous ceramic materials [1 – 10]. Carbothermal reduction of silicon oxide and simultaneous nitriding [1, 2], sintering Si_3N_4 powder at reduced temperature, sintering with burning-off additions, partial hot pressing [3, 6, 8, 9], extrusion with organic binder [4], sol-gel methods [5], casting and freezing of aqueous suspensions (freeze casting) [7], and sintering of granules based on Si powder, prepared by spray drying [10], are used. In earlier work in order to achieve a highly porous condition suspension swelling methods or introduction of ceramic powders into a prepared organic foam, and application of a suspension to a cellular foam polyurethane substrate, followed by substrate destruction [11], have also been used.

We have proposed a method for controlling porosity of silicon nitride material by consolidation of slip thin-walled elements made of thermoplastic slip based on silicon with special additions [12 – 21], which is possible if the slip in a heated condition is a thixotropically dispersed system. The role of special additives includes increasing slip thixotropic properties. Different dispersed powders have been tried: silicon, silicon oxide, and plasma chemical synthesis silicon nitride (PCS). Only PCS Si_3N_4 powder gave a thermoplastic slip based on silicon powder with a paraffin binder with 15

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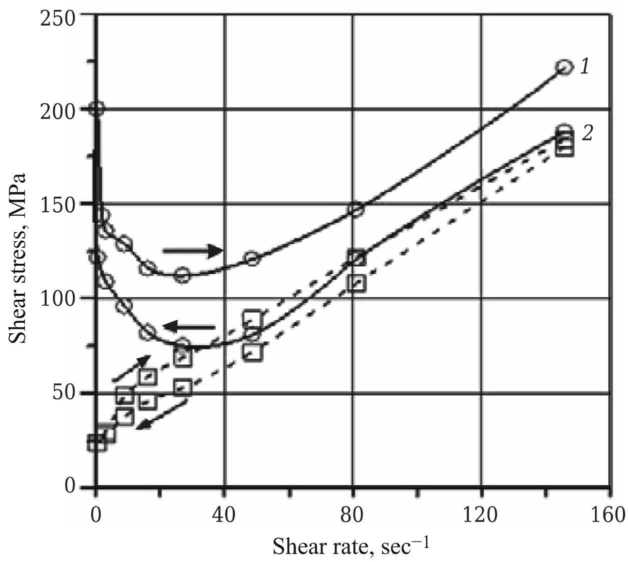

Fig. 1. Curves for flow of silica slip No. 4 at 70±5°C: *1*) (solid lines) in the first mixing stages; *2*) (broken lines) after prolonged mixing. Arrows indicate directions for change in shear rate for each curve.

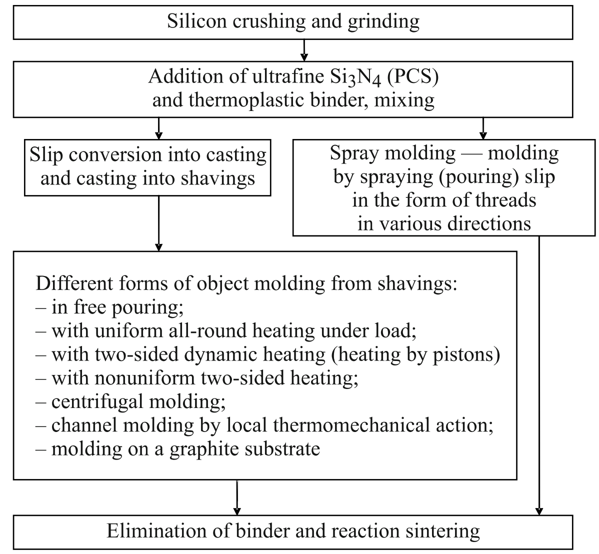

Fig. 3. Production scheme for preparing porous silicon nitride materials by molding thermoplastic slip elements.

Fig. 2. Thermoplastic slip shavings.

Fig. 4. Material structure obtained by heating shavings cut on a lathe from a casting prepared from slip based on silicon in a freely poured condition.

wt.% beeswax of clearly expressed thixotropic properties (Fig. 1) [13].

Rheological properties of slip were studied by rotation viscometry in a Reotest instrument with measurement of a cylinder measuring assembly. Details of the procedure are provided in [13]. Measurement was carried out in the range of shear rates (angular velocities of inner cylinder rotation) from 145.8 to 0.16 sec^{-1}, and then in reverse order. Curves obtained with a reduction in shear rate are placed lower.

The starting material used for consolidation of porous workpieces was shavings prepared by cutting a cooled casting from slip in a lathe (Fig. 2). The technology for forming highly porous materials from shavings makes it possible to vary porosity, pore size, and shape extensively. Apart from molding using elements of slip in the form of shavings, other ways are possible for object preparation. We have tried the possibility of molding porous objects by spraying (pouring) slip in the form of threads in varying directions (Fig. 3).

The simplest method for material preparation of this type is heating shavings in a free charge. The shape of shaving elements is retained most completely (Fig. 4).

First attempts to control molding porosity were made using a mold in the form of a cylinder of copper sheet and heated steel punches. The mold and punches were insulated from the pressed shavings by paper linings. The porosity of objects was not uniform (Fig. 5). Within the central part of moldings high porosity was maintained, and over the edges there was formation of a denser skin with a smooth transition between them.

Material with a uniform structure of slip shavings was obtained by two-sided dynamic heating using a cylindrical mold of heat insulating material and heated punches (Fig. 6). A mold of low thermal conductivity material, for example paper, and molding with metal punches heated to 100 – 150°C, were used. The punches used were a support and a load (see Fig. 6), which provided pressure in the course of the whole pressing cycle. Results depended markedly on heating conditions, which may be controlled by means of heating insulating linings of several layers of drawing paper on two sides of a pressed workpiece. The mold was glued from 20 – 30 layers of dense drawing paper with rubber glue, which provided the stiffness required and absence of distortion.

The slip used was based on silicon powder, prepared by grinding silicon grade Kr0 or Kr1 (specific surface S_{sp} = 4 m^2/g). The thermoplastic binder was a mixture of paraffin with 15 wt.% beeswax in an amount of 19 wt.% of the slip weight. A special addition was made to the slip in order to improve viscoelastic properties. Very fine silicon nitride powder grade PCS with S_{sp} = 60 m^2/g was sued as this additive.

With an increase in additive content slip viscosity and elasticity increase, as a result of which material porosity may be increased to 80 – 90%. In molding material elements 0.005 – 0.06 mm thick and 1.5 mm wide were used. The initial shape of an element 0.01 – 0.06 mm thick is twisted in the form of cylinders or cones 2 – 5 mm in diameter. Elements 0.005 mm thick as a result of electrification during preparation under action of Coulomb forces are straightened into rectilinear plates with a length of 10 – 15 mm.

The uniformity of material porosity distribution is provided with presence of a horizontal section in the shrinkage kinetics curve in the course of pressing shavings from slip (Fig. 7).

Processes occurring in the course of pressing shavings from thermoplastic slip may be described to a first approximation as follows. On contact with a heated punch sections of pressed body adjacent to it warm up. On reaching the binder melting temperature dispersed lamellar curved elements of the slip deform under action of pressing pressure and natural force of gravity, and stick together under the effect of capillary forces. The last effect is due an attempt of the system to reduce its own potential energy due to a reduction in area and elements surface energy. In addition, lamellar elements tend to adopt a circular shape under action of surface tension forces.

These processes are limited by slip viscoelastic properties. In the course of deformation of elements there is an increase in number and area of contacts between elements, whereas stresses acting on elements decrease. With stresses below the level of limiting shear stress for thermoplastic slip deformation (shrinkage) within a layer adjacent to a punch ceases. Then heating and deformation occurs within deeper layers. After passage of the thermal wave front through the whole compact the molding process almost ceases, and there is no subsequent marked shrinkage.

Molding technology of slip shavings is a developed method for casting thermoplastic slips [22, 23], and has a number of common features. In both cases there is the gen-

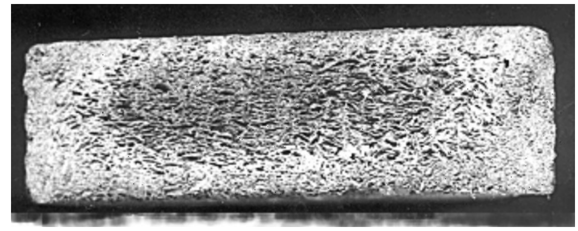

Fig. 5. Section of a porous silicon nitride object molded from slip shavings with uniform all-round heating under load.

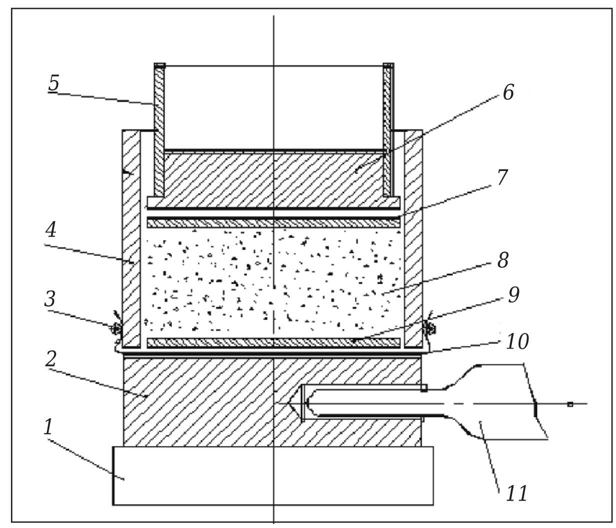

Fig. 6. Diagram of device for slip shaving consolidation by two-sided dynamic heating: *1*) electric plate; *2*) metal support; *3*) collar; *4*) low heat-conducting material (paper) mold wall; *5*) stabilizing cylinder; *6*) metal weight; *7*, *9*) heat-insulating lining; *8*) pressed mix; *10*) mold bottom; *11*) thermometer.

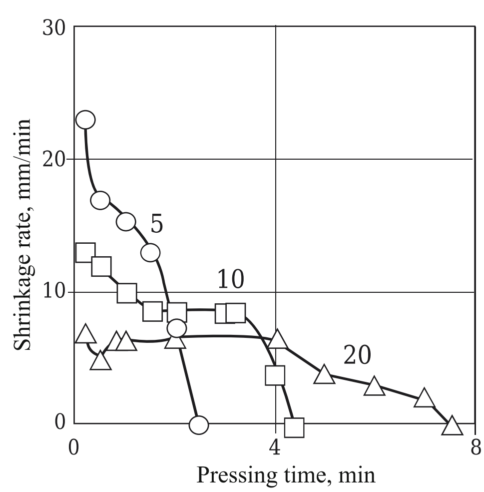

Fig. 7. Shrinkage kinetics over the height in the course of pressing thermoplastic slip shavings: pressing pressure 5 kPa, punch temperature 150 ± 3°C, numbers on curves are number of layers in heat insulation linings.

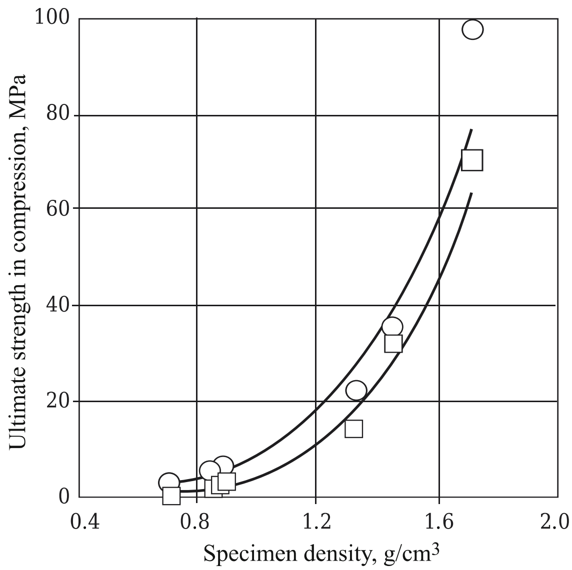

Fig. 8. Dependence of ultimate strength in compression at 20°C for silicon nitride materials from shavings on density: *1*) perpendicular to pressing axis; *2*) parallel to pressing axis.

eral problem of retaining a given slip shape on repeated heating, and therefore slip thixotropy, heating rate, and "structure formation by cooling" and "bond sweating" phenomena considered in [23], are important. Differences include the fact within a porous workpiece made of elements there are numerous internal cavities, serving as avenues for binder during sweating. This shortens the path of binder migration during sweating compared with that existing in castings at a minimum of one to two orders of magnitude. Another difference consists of the fact that in the technology in question slip element deformation, generally speaking, is desirable within any limits, since it provides regulation of porosity and pore structure, forming bonds between shaving elements.

Compaction pressure, heating conditions, and in fact the number of paper layers in heat insulating layer linings, charge weight per unit area, and shaving element thickness, affect the density of pressings prepared by this method. Slip composition and rheological properties, and also pressing pressure, have the main effect on compact density. However, the effect of element thickness and heating conditions in the course of pressing on workpiece density in magnitude is comparable with the effect of the main factors.

Materials prepared by two-sided dynamic heating (heating punches) have good mechanical properties and thermal shock resistance (Fig. 8). Strength increases with a reduction in shaving thickness.

Highly porous silicon nitride ceramic from slip shavings machine quite readily by normal hard alloy cutting tools: drilling, machining in a lathe, cutting with abrasive disks. The material removed during cutting is in the form of flakes or fine dust.

It is possible to increase the permeability of molded workpieces by mean of creating channel pores by local heating with a tool of the knitting needle type or in a sintered condition by laser drilling.

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