Influence of the binder composition on the properties of the silicon carbide green compacts and sintered parts prepared from the powders produced by SHS

K S Torosyan$^{1,2}$ and V G Pak$^1$

$^1$Penza State University, Krasnya 40, Penza, Russia
$^2$National University of Science and Technology “MISIS”, Leninskii 4, Moscow, Russia

Abstract. In this work, the possibility of the application of binders based on the polyvinyl alcohol and paraffin instead of environmentally-dangerous phenol-formaldehyde resin-based binders in the production of silicon carbide ceramics are investigated. Introduction of citric acid and carbamide in the binder based on water solution of polyvinyl alcohol ensures the high wettability of the powders of non-oxide ceramics by the binder. The addition of castor oil and oleic acid in the solution of paraffine in petroleum leads to a decrease in the inter-particles frictions and an increase in the density of green compacts. The developed binders allow to reduce compaction pressure by 12–15%.

1. Introduction
In this work, SiC powders produced by self-propagating high-temperature synthesis (SHS) were used. SHS powders are peculiar due to the fine particles size ($\leq 1 \mu$m), which allows to produce parts with fine and uniform microstructure and increased mechanical, physical and electromagnetic properties. However, the application of fine powders leads to problems in the pressing of green compacts due to the higher friction between the particles and the agglomeration.

In the production of silicon carbide ceramics, phenol-formaldehyde resin-based binders and complex plasticizers are conventionally used to increase the powders pressability and decrease the sintering temperature. [1]. However, this binder does not provide a decrease in the inter-particular friction. Therefore, the development of surfactants which will allow to decrease the friction and to increase the wettability of powders by the binder is of current interest. Replacement of phenolformaldehyde resin-based binders by environmentally-friendly water soluble binders is another important task addressed in this study [2].

2. Materials and Methods
SiC specimens were produced by conventional powder metallurgy route, which includes the following operations: mixing of silicon and graphite powders, introduction of 20 wt % binder, granulation by rubbing through the mesh with 0.5 mm cells, pressing of $20 \times 12 \times 15$ rings under a pressure of 150–200 MPa, vacuum sintering in the furnace shown in figure 1. SiC powders produced by SHS were characterized by median particles size of 0.7 $\mu$m, whereas the powders synthesized by conventional Acheson process had an average size of 63 $\mu$m. To produce the specimens with various grains size the sintering temperature was varied from 1700 to 1800$^\circ$C.
To produce the paraffin-based binders, the calculated amount of molten paraffine (grade P-1, GOST 23683-89) and petroleum were mixed until the full dissolution of paraffine; afterwards, oleic acid (GOST 3652 - 69 “Ch”) and castor oil (GOST 6691-77 “Ch”) were added during the mixing. The produced binder was introduced into the mixture of powders of SiC (particles size of 0.5–0.8 µm) and carbon black. Binder ratio was equal to 20 wt %. The mixtures were then additionally mixed in the pan mixer with subsequent rubbing through the 0.5 mm mesh. The mixtures were dried until the residual petroleum content was 0.5–2.7 %.

Water-soluble binder for granulation was produced by the dissolution of polyvinyl alcohol (grade 16/1 GOST 10779-79), citric acid (“Ch” grade, GOST 3652-69) and urea (“Ch” grade, GOST 6691-77). 0.1% zinc stearate was introduced into the granulated powder before the pressing as the “surface binder” to decrease the pressure loss due to the friction of granulated powder against the die wall and therefore to decrease the wear of the dies and increase the density uniformity of the compacts. For comparison, press-powder was prepared using the phenol-formaldehyde resin. Influence of the binder on the rate of wear of dies was estimated as the decrease of the mass of the pressing insert after the pressing of 20 × 10 × 16 ring-shaped compacts at 100 MPa.

3. Results and Discussion

Characteristics of powder compacts and wear rate of the die pressing inserts are given in tables 1 and 2. Data are averaged from 10 measurements. Compositions of complex binders are also given in the tables 1, 2. Binder based on the solution of paraffine in petroleum and containing the castor oil and oleic acid allows to increase the density of compacts and decrease the wear of dies in the silicon carbide production. Addition of castor oil and oleic acid in a particular proportion ensure the simultaneous increase in the powder wettability, decrease in the pressure loss due to friction against the die walls, retention of high mechanical properties of the compacts. Paraffin glues the powder particles, providing the necessary compacts strength.

Binder based on the water solution of polyvinyl alcohol and containing the citric acid and urea also allows the increase on the compacts density and decrease the die wear in the production of silicon carbide ceramics. Addition of citric acid and urea in a particular proportion ensure the simultaneous increase in the powder wettability, decrease in the pressure loss due to friction against the die walls, retention of high mechanical properties of the compacts. Polyvinyl alcohol glues the powder particles, providing the necessary compact strength.

Application of the binder based on the solution of paraffin in petroleum led to the residual petroleum content of 1–2 wt %. Application of the binder based on the solution of polyvinyl alcohol in water leads to the residual water content of 0.5–2 wt %. Comparison of the data given in table 1 demonstrates that the application of binders based on the solution of paraffine in petroleum and containing castor oil and oleic acid leads to an increase in the relative density of the compacts up to 2.05–2.22 g/cm³ and reduction of the wear of the die inserts to 19.1–20.2 µm/cycle.
Table 1. Influence of the composition of binder based on a solution of paraffine in petroleum on the density of compacts and wear resistance of the dies.

| Technological properties of the press-powders and compacts | Residual petroleum content in the press-powder, wt % | Binder components ratio, wt % |
|----------------------------------------------------------|---------------------------------|-------------------------------|
| Compacts density, g/cm³                                  | 1.1                             | Paraffin 7.0                   |
|                                                          | 2.0                             | Oleic acid 0.2                 |
|                                                          | 1.1                             | Castor oil 2.0                 |
|                                                          | 2.0                             | Petroleum 90.8                 |
| Die insert wear rate, µm/cycle                           | 1.1                             |                              |
|                                                          | 2.0                             |                              |

As the tables 2 and 3 demonstrate, the binder based on water solution of polyvinyl alcohol without the addition of urea and citric acid does not provide the required quality of press-powders and compacts. Addition of urea and citric acid increases the wettability of the particles by the binder during the granulation, decreases the dust content and increases the density and strength of compacts.

Table 2. Influence of the composition of binder based on water solution of polyvinyl alcohol and phenol-formaldehyde resin on the density of compacts and wear resistance of the dies.

| Technological properties of the press-powders and compacts | The residual water content in the press-powder, wt % | Binder components ratio, wt % |
|----------------------------------------------------------|---------------------------------|-------------------------------|
| Compacts density, g/cm³                                  | 0.0                             | Polyvinyl alcohol 5.0         |
|                                                          | 1.1                             | Water 95.0                    |
|                                                          | 2.0                             | Citric acid 0.5               |
|                                                          | 0.0                             | Urea 4.0                      |
|                                                          | 1.1                             | Phenol-formaldehyde resin 100.0 |
|                                                          | 2.0                             |                              |

Table 3. Influence of the binder composition on the technological properties of press-powders and compacts

| Technological properties of press-powders and compacts | The water content in the press-powder, wt % | Binder components ratio, wt % |
|-------------------------------------------------------|---------------------------------|-------------------------------|
| The density of the compacts at pressure P = 100 MPa, kg/m³ | 0                              | PVA - 5.0 Water - 95.0        |
| The tensile strength of the ring specimens, kPa        | 2.7                             | PVA - 5.0, Citric acid - 0.5, Water - 90.5 |
| Dust content in the press-powder, wt %                 | 2.7                             | Phenolformaldehyde resin - 100 |
| Wetting angle, o                                      | 0                              |                               |
| The density of the sintered specimens, kg/m³          | 2.7                             |                               |
The developed binders with the addition of urea and citric acid allow to decrease the binder consumption by 10–15%, increase the density of compacts by 10–12% and increase the density of sintered parts by 5–7% as compared to the parts prepared on the base of polyvinyl alcohol without the additions. Results suggest that the used water-soluble binder can replace the phenol-formaldehyde resin-based binders.

Mechanical tests revealed that the structural ceramic produced using the powders synthesized by SHS surpass the analogs produced from conventional Acheson process (table 4).

Table 4. Influence of the composition of binder on the strength and density of silicon carbide ceramics produced from powders synthesized by SHS and Acheson process.

| Synthesis route | Paraffin – 8.5 | Castor oil – 0.6 | Oleic acid – 5.0 | Petroleum – 85.9 | PVA – 5.0 | Citric acid – 0.5 | Urea – 4.0 | Water – 90.5 | Phenolformaldehyde resin – 100 |
|---------------|---------------|-----------------|-----------------|-----------------|----------|------------------|-----------|------------|-----------------------------|
| The tensile strength of the sintered rings, MPa | SHS           | 135             | 132             | 123             | Acheson  | 108              | 104       | 97         |                              |
| The density of the sintered rings, kg/m³ | SHS           | 3184            | 3180            | 3085            | Acheson  | 3118             | 3107      | 3004       |                              |

Application of the developed binder compositions for the production of parts from non-plastic powders allows to reduce the production cost due to an increase in the wear resistance of the press-forms and due to an increase in the prime yield.

4. Conclusions
Based on the results of the research, the following conclusions could be made:

1. Binders based on the solution of the paraffin in petroleum and of PVA in water were used for powders produced by the SHS and Acheson process. Developed binders are advantageous as compared to phenol-formaldehyde resin due to being non-toxic. Water-soluble binders are non-flammable, providing the possibility to the increase in the working conditions during the production of silicon carbide ceramics.

2. Introduction of the solution of paraffine in petroleum allows to increase the density and strength of ceramics and increase the wear resistance of the dies. The inclusion of the citric acid and urea increases the wettability of the silicon carbide powder by the binder and increase the density and strength of the ceramics.

References
[1] Henit G and Rol R 1972 Silicon Carbide (M.: Mir) 349 p
[2] Belyaev A E and Konakova R V 2010 Silicon Carbide: technology, properties, application (Kharkov, «ISMA») 532 p