The possibility of replacing metal alloys with Si-SiC composites in certain technical applications

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Abstract: Present patent review is devoted to the analysis of some fields, important for mechanical engineering, where details made of silicon-carbon composites can be used successfully replacing traditional articles made of metal alloys. The advantages of the proposed materials are as follows: (i) almost threefold reduction of the thermal expansion coefficient, (ii) higher hardness, (iii) higher chemical stability to oxidation at high temperature, (iv) an increase of limiting operating temperature of approximately 200°C, (v) practical absence of marked deterioration of physical--mechanical characteristics at heating under loading. Among the disadvantages are the complexity of mechanical treatment and the laboriousness of producing details of complex geometry. That is why we have concentrated on the analysis of the capabilities to use the proposed materials only for production of relatively small, but important and vulnerable to heating articles, one of which is the element of a trunk brake of artillery shells. The review is based on recent patents received with the participation of the author.

Keywords: TEC (thermal expansion coefficient); Thermo-cycling; Chemical Stability under Heating; SiC (silicon carbide); CFM (carbon fibrous materials); High-temperature Properties; Composite Materials

1. Introduction

It is traditionally assumed that high-temperature metal alloys are dominating when producing articles to which increased requirements in part of mechanical and heat stability, as well as manufacturability under treatment, are imposed. Among their advantages are high values of tensile and flexural strength, sufficiently significant limiting operating temperatures, and certain stability to oxidation. Among the disadvantages are a significant time change of physical--mechanical properties at high temperature under loading, the large thermal expansion coefficient (TEC), hardship of welding of separate elements under assembling an article, and also low stability under chemical interaction with corrosive media.

A significant number of scientific and technical results which have currently been obtained permit to single out the fields where articles made of metal alloys can be replaced by analogous articles made of nonmetal composites. In present work we investigate only one of these composites: a polycrystalline silicon matrix reinforced with SiC fibres. Figuratively speaking, this material can be compared to an adobe brick made of clay reinforced with straw fibres. An adobe brick was used in building in ancient Mesopotamia[1] and is still being used. The use of pure silicon for achievement of the technical results is almost impossible, since it transits to a plastic range at temperature >6000 C. Furthermore, it is considerably inferior to the proposed composite in hardness. The physico-mechanical properties are provided only after reinforcement of the matrix with SiC fibres. Among the advantages of our material are the extremely low TEC, a low specific weight, high mechanical properties, including hardness, high stability.
in corrosive media, the absence of change of physico-mechanical properties under prolonged heating, and a relatively low cost. The disadvantages of the material are the necessity to use a diamond tool for finishing mechanical treatment and the laboriousness of producing details of complex geometry.

On the basis of the existing literature data and the data obtained by us, we can mark some fields where the mentioned composite can have advantages compared with metal alloys:

a) structural articles;

b) base plates for firing ceramic articles;

c) resistive heaters for the work in oxidizing media;

d) high-temperature filters for aggressive liquids and gases;

e) bushing keys for application under extreme conditions, including drilling rigs and wheel chokes of artillery shells;

f) portable units for pyrolysis of engine fuel.

g) It can be assumed that this list will be extended with time.

2. Articles and producing techniques

2.1. Structural articles

The use of directed impregnation of CFM-based primary profiled billets\(^2\text{-}^4\) with molten silicon enables to obtain various articles, some examples of which are shown in Figure 1. They can be used for production of crucibles, base plates, cassettes for placing treated details heated in the air at temperature up to 1300°C. The articles presented in Figure 1 possess high resistance to thermo-cycling and TEC at the level of \(4.6 \cdot 10^6\) K\(^{-1}\).

Figure 1. Article samples made of Si-SiC composites (from left to right) – profiled silicon plate in a gap between the layers of a siliconized graphite fabric, crucible, profiled cassette.

2.2. Base plates for firing ceramic articles

Base plates are used for installation of raw billets under firing ceramic articles (electrical insulators, ware etc.) in domical kilns with gas heating. The temperature can be more than 1300°C, the time of being in a kiln is measured in days, the weight of separate articles reaches 15 kg. These conditions cause strict requirements to flexural strength of the plates material and its heat stability. Furthermore, it is desirable to use plates with small thickness in order to reduce the consumption of energy carriers for heating of the plates.

The method\(^5\) of producing articles of a siliconized carbon composite with a variable content of SiC is known. This method includes production of a layer billet of a carbon composite based on a framework of carbon fibrous filler compacted with carbon, and its siliconizing.

The disadvantages of the method\(^5\) are the complexity of producing a layer billet of CFM with variable porosity and the impossibility to obtain plates of siliconized CFM with a significant area.

We have proposed the method\(^6\) providing obtainment of a composite material in the form of plates with a large area and a relatively small thickness fit for production of high-strength thin base plates being able to be used at high temperatures in oxidizing media.

For this to be done, an initial billet is produced in the form of a carbon felt layer on a ribbon made of a graphite fabric, whereupon drawing of the obtained billet with respect to the capillary feeder supplying silicon melt and crystallization of the melt according to the scheme provided in\(^7\) are carried out.

As a result of siliconizing, the fibres of initial CFM turn into SiC fibres reinforcing the silicon matrix. To achieve this result, the process of displacement of ribbons made of carbon felt and a carbon fabric, superimposed on one another, is carried out in a horizontal plane in the medium of vacuum or an inert gas. The use of the bottom layer of a carbon fabric is caused by the fact that it is impossible to draw felt by virtue of its low mechanical strength.

Phase composition of the material (mass.%) is: SiC – 8, Si – 90, C – 2. The total thickness of the obtained
plates was 5.2 mm, the width – 120 mm, the length – 450 mm.

The structure of a siliconized felt layer is demonstrated in Figure 2: a – cross-section, b – view of the outer surface. It is seen that the outer surface of the composite is characterized by the presence of projecting siliconized fibres that upsets the planeness of plates surface. However, the results of temperature tests have shown the absence of deformation of ceramic articles fired on plates surface.

![Figure 2](image)

**Figure 2.** Photomicrographs of the structure of a siliconized nonwoven carbon material

In view of the peculiarities of application of the developed materials, their ultimate bending strength in a range between 800 and 1250°C was defined. The results of the measurements are presented in Figure 3. Curve 1 relates to the composite including the layer of carbon felt on carbon fabric surface. The ultimate flexural strength is 420 MPa in a rather wide temperature range. It should be noted that this parameter changes little with an increase of temperature. Curve 2 corresponds to the data for a siliconized graphite fabric without addition of a felt layer.

![Figure 3](image)

**Figure 3.** Measurement results of bending strength of the plates obtained on the basis of the composite in a temperature range.

The values of ultimate flexural strength in the case of the fibre reach 200 MPa; however, the obtained material has a small thickness (not more than 1.1 mm) and cannot withstand a significant concentrated weight load, the value of which can reach 15 Kg in the centre of the plate.

### 2.3. Resistive heaters

The traditional process of producing silicon carbide heaters is described in US4336216 (Watanabe et al. 1982) and includes primary sintering of SiC mixture, carbon and boron powders, at 1600°C and secondary sintering at 2200°C. The known method requires preparation of initial powders and fairly high processing temperatures. Besides, it can hardly be adapted to production of hollow articles.

RU2286317 (Brantov et al. 2007) reported on the design and fabrication stages of the heater.

The heaters produced are 0.8 to 1 m long with an outer diameter 40 to 50 mm, inner diameter 32 to 47 mm, and the total resistance 0.18 to 0.25 W with respect to AC (alternative current), including the contribution of the external contacts at room temperature. The service life in the air at the above-mentioned temperatures is practically unlimited. The heaters are absolutely stable to thermos-cycling.

The method has one disadvantage being the necessity to calculate the mass of crushed silicon, poured into a billet pipe, precisely. At the lack of silicon there are unimpregnated regions on the pipe, at the excess of silicon there are silicon “overlaps” which are to be eliminated by mechanical treatment then.

In this regard, a novel variation of directed impregnation of a billet pipe using capillary feeding of molten silicon to its outer surface has been developed according to patent RU2620688 (Brantov 2017). The circuit diagram of the method is shown in Figure 4.

![Figure 4](image)

**Figure 4.** Schematic diagram of producing pipes of Si-SiC composite material.
Billet 1 made of several layers of a graphite fabric is displaced in a horizontal plane with respect to U-shaped graphite heater 2. For feeding of the melt to the outer surface of billet 1, capillary feeder 3 is used; it is made of dense graphite and is fixed to silicon melt 4 in graphite crucible 5. For heating of crucible 5, graphite heater 6 is used. To avoid congelation of a melt, in a forebody of feeder 3 free-standing graphite heater 7 is used. The process of billet 1 impregnation occurs in a relatively narrow area 8. After cooling, siliconized billet 9 is extracted from a pusher furnace.

2.4. High-temperature filters for aggressive liquids and gases

The field of usage of filter materials is extremely wide, that is why we shall attract attention to only those spheres where high temperatures and chemically aggressive liquids or gases are used.

For these purposes filters containing grid elements made of stainless steel or a nickel wire are applied. The filters can stand high temperatures, but they are vulnerable to chemically active substances. The attempts to replace them by more chemical-resistant elements are made.

The method to obtain a ceramic fibrous high-temperature gas filter is known according to patent RU2163833 (Hill 2012)[11]. A composite filter combining distribution of a continuous ceramic fibre and staple ceramic fibres over the thickness of its wall is used. A ceramic fibrous composite structure or a filter is obtained by the method in which a continuous ceramic fibre in the form of a filament is wound around a porous vacuum mount at simultaneous application of a diluted suspension of staple ceramic fibres on it.

The disadvantage of the method[11] is the high laboriousness of winding a brittle ceramic fibre around a porous vacuum mount at simultaneous application of a suspension of ceramic fibres on it.

We have proposed a novel filter material for aggressive liquids and gases representing a grid of SiC fibres according to patent RU2576439 (Brantov 2016)[12]. Under obtaining this material, directed impregnation of the displaced in a horizontal plane drawn ribbon made of a carbon grid fabric with molten silicon occurs. As a result of siliconizing, carbon of the initial grid fabric turns to SiC with conservation of the fabric structure.

Due to an unavoidable increase of the specific volume of carbon fibres at transition to SiC, the area of a gap of filter material plates reduces twice. The bundle of warp longitudinal filaments and weft transversal filaments is naturally provided under fabric siliconizing. A carbon grid fabric is an inexpensive material which is mastered in mass production in a number of countries. The obtained material (a grid made of silicon carbide) is acidic media-inert and can be used in the air at temperature up to 1300°C. After washing and drying, the material can be used as a filter one in the form of both separate plates and packs of them.

The structure of the initial carbon grid fabric is illustrated by photomicrographs in Figure 5. The specific area of its gap calculated by the method of histograms in Photoshop 6.0 is 19 %. The structure of the grid substrate after its siliconizing and chemical elimination of free carbon is presented in Figure 5 (B, D). At that the specific area of its gap decreases to 10%.

Figure 5. Photomicrographs of the structure of the filter material. A – the initial grid fabric, B – the same fabric after siliconizing and chemical elimination of free silicon, C and D – cross-sections of the composite along the line of fabric warp in the same sequence. Weft filaments are normal to the photomicrographs plane.

The method[12] permits to obtain a high-temperature and chemical-resistant filter material, but does not solve the problems of producing articles on its basis. It is known that fuel filters in the lines of feed of dimethylhydrazine and oxidizing agent to the combustion chambers of a liquid-fuel jet engine can be located near them in the coverage of high temperature. That is why the article should include a filter material.
resistive to thermal action and effectively connected to the body of a bush or a ring which is also resistive to thermal action and significant hydrodynamic pressure.

The article is produced by robust connection of SiC filaments in a textile fabric form to the end face of a bush or a ring made of siliconized graphite according to patent RU2617105 (Brantov et al. 2017) [13]. To produce this article, before impregnation with silicon, a layer (layers) of a graphite fabric is glued to the end face of a bush or a ring made of siliconized graphite with a layer of PVAC, ground silicon is poured onto the surface of a fabric layer (layers), and then heating in vacuum medium is carried out at temperature exceeding silicon melting point. Depending on the type of a carbon fabric and the number of its layers, the gap area varies in a range between 4 and 10%, and the prevailing pore size varies in a range between 200 and 1000 m. An appearance of such articles is shown in Figure 6.

2.5. Material of a bushing key for high-temperature applications

The invention relates to the field of mechanical engineering and can be used in units under the operating of which release of a big amount of heat is possible leading to thermal expansion of a bushing key and jamming of the unit. Among such units are, in particular, a core-drilling rig head and a muzzle brake of artillery shells (a howitzer). The current elements of alignment of mechanism (bushing key) parts are produced of metal alloys (usually of carbon steel) characterized by TEC at the level (10 - 15) × 10⁻⁶ K⁻¹.

The method to obtain a bushing fey is known to patent RU2663146 (Brantov, Borisenko 2018) [14].

Such a bushing key should provide the possibilities of both high-speed rotation and plane-parallel moving-in of a rig (in the case of a drilling rig). In the case of artillery shells a bushing key prevents rotation of a barrel in the direction opposite to the direction of projectile spin and provides alignment of a barrel and a cradle of brake under recoil. In this regard, the length of such bushing keys is significant, thermal and mechanical loads are large, and wear occurs rapidly enough. Under production of bushing keys for the mentioned purposes strict requirements are imposed to the accuracy of their geometrical dimensions which are significantly disturbed under scaling in the process of operation.

The use of bushing keys and/or rods made of a Si-based metal composite reinforced with carbon-silicon fibres enables to increase considerably reliability of the units, since the TEC of this material is 4.6 × 10⁻⁶ K⁻¹. In addition, temperature limit of using the parts made of special steels under load is maximum 800°C, whereas this parameter for the parts made of the proposed material reaches 1300°C.

There are the following disadvantages of metal alloys under usage at high temperatures and large dynamic loads:

a) Limiting operating temperature 800°C can be insufficient under extreme operating conditions and can lead to a change ("dulling") of the bushing key form.

b) The TEC of the material reaches the value of 15 × 10⁻⁶ K⁻¹ that can be reason for mechanism jamming at bushing key heating.

c) The coefficient of dry friction for metal alloys has a satisfactory value; however, its reduction would be desirable as applied to operation of bushing keys under plane-parallel moving-in of mechanism parts.

d) Scaling on the outer surfaces of details made of metal alloys is unavoidable under heating in the air.

To achieve the technical result, silicon is used instead of iron as a material basis, and the layers of a siliconized graphite fabric are applied instead of carbon and numerous dopants in the solid alloy solution.

The comparative functional characteristics of steel and the proposed material are presented in Table 1. Multifold increase of operating parameters as compared with metal alloys follows from the presented data. Short time tensile strength coincides for the compared materials for the most part, that is why it is not shown in Table 1.

Figure 6. Appearance of the articles with a filter element.
Table 1. Functional characteristics of steel and the proposed material

The structure of the proposed material is illustrated in Figure 7 (the photomicrographs were performed on the optical microscope). Billet thickness is determined by the number of layers of a graphite fabric before its impregnation with molten silicon. Figure 7A demonstrates a cross-section of the fabric layers impregnated with silicon at low magnification. Figure 7B shows a longitudinal section of the material at 100-fold magnification. Figure 7C, 7D demonstrates cross- and longitudinal sections at higher magnification. The data on a phase composition of the proposed composite are summarized in Table 2.

Table 2. Phase composition of the proposed material

Table: | Phase               | Content in mass% |
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Free silicon (Si)</td>
<td>85 - 65</td>
</tr>
<tr>
<td>Silicon carbide (SiC)</td>
<td>5 - 35</td>
</tr>
<tr>
<td>Free carbon (C)</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

Figure 7. Microstructure of the composite used for production of bushing keys

It is assumed that composites of the proposed type can be effectively used for replacement of metal alloys in a number of technical fields beside those mentioned in the review.

Directed impregnation of several layers of a predrawn highly active graphite fabric with molten silicon according to patent RU2617114 (Brantov 2017)[14], cutting of the obtained material into plates, and further treatment of the billets on a surface grinder up to the attainment of bushing keys with the required geometrical dimensions and quality of their surfaces are used to obtain the proposed composite.

2.6. A portable unit for pyrolysis of engine fuel

The invention refers to the field of chemical engineering and can be used for producing a portable unit for thermal pyrolysis of engine fuel in the line of fuel supply from a fuel tank to an engine carburetor. The unit is produced in the form of a hermetic cell, containing a heated element, and is located in the engine fuel supply line forward of an engine carburetor. The use of a filament made of Si-SiC composite as a heated element underlies development of the unit permitting to reduce the electric power, necessary to reach temperature, and the amount of current, obtained from an accumulator, by virtue of using the mentioned material instead of traditional materials based on metal resistance alloys. It should be noted that under the use of standard voltage 12V DC the heating element (the filament) reaches temperature 1200°C, and power consumption does not exceed 50W.
One knows the ways to increase operating medium energy for engines consisting in advancing electroexcitation pulse, for instance, a magnetic field, a laser beam, or an electric arc, through an operating medium. However, in the description of these ways only principle possibility to reduce a molecular weight of engine fuel components under external energy deposition is stated which is obvious. Moreover, some of the proposed ways are not safe.

The unit for treatment of fuel components with catalysts providing an increase of fuel combustion efficiency is known according to patent RU1799429 (Andreev, B.I. et al. 2004)[15]. The unit contains a hermetic cylinder with a granulated catalyst. Such units are used in practice, but their usage is limited by catalyst lifetime.

All the known approaches to reduction of a molecular weight of hydrocarbon fuel are based on the use of thermal or thermocatalytic cracking of the feed stock. At that temperatures from 300 and 450°C are applied.

It should be understood that there is a distinction between cracking and pyrolysis of engine fuel. Pyrolysis occurs at considerably higher temperatures and faster rate. A filament made of silicon-silicon carbide composite is used in the proposed unit; filament temperature reaches 1200°C at total power consumed from an accumulator not more than 50W.

The technical result of using the proposed unit is elimination of mutually displacing mechanical elements and constructs, a significant increase of temperature in the fuel pyrolysis cell and reduction of cell dimensions. To achieve this result in the unit containing a hermetic chamber with a heating element, placed in the fuel supply line between a fuel pump and a carburetor, the heating element is produced of Si-SiC composite in the form of a filament, and a car battery is used for heating of this element. Resistivity of the mentioned material is approximately 100 times higher than that of nickel-chrome alloys that enables to reach high temperature of the heating element in a small volume at voltage 12V available from the accumulator. Bench tests have demonstrated that the electric power consumed by the cell is not more than 50W. Under passage of fuel through the heating cell, its partial pyrolysis occurs accompanied by an increase of a fuel octane number, completeness of its combustion, and an increase of exhaust gases purity.

Design of the heating chamber is illustrated in Figure 8, patent RU167759 (Brantov, et. al. 2016)[16]. Body 1 made of stainless steel is airproof. Cover 3 also made of stainless steel is attached to it through teflon seal 2. To the lateral faces of body 1 two electrodes 4 and 5 isolated from the body with bushings of teflon are introduced hermetically. On the longitudinal faces of body 1 connecting pipes 6 and 7 are set for connection to the fuel line of a car. Inside body 1 filament 14 made of Si-SiC composite is fixed to electrodes 4 and 5 with screws 8 made of nickel. Teflon bushings 10 bucked with the threaded elements are used to seal electrodes 4 and 5. In conclusion, we shall notice that the cell has small dimensions, is easily set in the lines of fuel supply from a pump to a carburetor, and is safe in service.

![Figure 8. Schematic diagram of the heating chamber for pyrolysis of engine fuel.](image)

**2.7. Discussion**

Composite materials based on silicon matrix reinforced with SiC fibres are usually considered as substances with semiconductor properties. Not drawn attention to the possibility of their use in structural purposes. Conduct a detailed comparison of their characteristics with high-temperature metal alloys is difficult and somewhat pointless.

The proposed Si-SiC material is essentially single, and high-temperature alloys very much. The key factor is that these alloys contain several alloying elements and the heat flow of diffusion processes leading to changes in physico-mechanical parameters. These changes are studied mostly empirically and there is no general approach to their reliable prediction. Properties of the
proposed Si-SiC material can not significantly change during heating in oxidizing environments because it includes no dopants. A significant advantage is the low coefficient of thermal expansion. The maximum use temperature and the tensile strength and bending close to the same parameters of high-temperature alloys.

3. Conclusions

A steady trend of gradual exclusion of metals and alloys from traditional fields of their application and their replacement by composites which can both contain metal parts and be made without their usage has recently been observed. This trend is most evident in the fields of military and paramilitary technologies which are especially sensitive to novel engineering solutions. To produce heat-resistant steels, it is necessary to use a significant amount of alloying additions the reserves of which can be deficient. It is important to remember that one of the reasons for Germany’s defeat in the Second World War was weakening of its military industry after interception of supply chains of metals of VI-VIII groups of the Periodic Table. In Russia and the USA there are virtually little natural reserves of molybdenum and tungsten; their ore concentrates are supplied mainly from China. Any dependence on supply of scarce raw materials cannot be desirable.

At that the reserves of raw materials for production of silicon and carbon are limitless on the planet. To obtain the necessary articles, development of production basis for raw material processing is required. It is clear that a considerable time period is required for development and practical use of the ideas and proposals stated in present work; however, we believe that this process is unavoidable.

4. Current & future developments

Currently, we are conducting R&D in the field of improving the quality and reliability of the above-described materials, products and technologies. One of the main parameters is working resource/durability of the proposed options which requires conducting long-term and time-consuming bench tests.

Future development is possible only when establishing permanent business contacts with industry, to talk about premature.

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Conflict of interest

The review was performed by the author within the scope of his employment at the Institute of Solid State Physics RAS.

References


