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OBTAINING COMPOSITE MATERIALS BY IMPREGNATION WITH A SUBSTANCE DEPOSITED FROM THE GAS PHASE

S.A. Krokhmal, V.V. Shcherbakova
National Science Center "Kharkiv Institute of Physics and Technology", Kharkiv, Ukraine
E-mail: krokhmal@kipt.kharkov.ua

The possibility of obtaining composite materials with a refractory matrix by deposition from the gas phase is investigated. A scheme for carrying out the impregnation process with high efficiency of using the precursor for obtaining dispersed fuel elements is proposed. The degree of impregnation can reach 95…96%.

INTRODUCTION

Obtaining composite materials with high strength and protective properties that can operate under high temperature conditions is of particular interest for the creation of new products that can be used in modern technology. One of the areas of use of such materials may be the creation of dispersed-type fuel elements for power supply of space technology. The matrix material must have adhesive strength to the fuel element material, appropriate nuclear-physical, mechanical and chemical properties, and have a high melting point. The filling of the volume with the matrix material should be as high as possible.

This is especially facilitated by the high penetrating ability of the coating material for hard-to-reach cavities and microcracks [1], which allows the volume around the frame to be filled as completely as possible.

There are many ways to obtain composite materials, but obtaining a composite with a refractory matrix presents certain difficulties of both a technical and economic nature. In addition, the frame material in some cases may have a lower melting point than the matrix material.

One of the methods for obtaining a refractory matrix may be impregnation with a substance deposited from the gas phase of organometallic compounds [2], which can significantly reduce the temperature of the process [3]. The material obtained during the pyrolysis of the industrially produced HOZ "Barkhos" (TU-6-01-1149-78) may be used as a precursor for obtaining a refractory carbide-chromium matrix. The minimum boiling and decomposition temperatures of the HOZ "Barkhos" are 145 and 300 °C, respectively. The physicochemical properties of such a precursor [1, 4] and the features of the gas-phase deposition method make it convenient for solving such a technical problem.

However, when implementing the impregnation process by passing the HOZh vapors through the frame of spheres, the channel was hermetically sealed, which led to the cessation of pumping out the decomposition products and the cessation of the impregnation process. To implement the impregnation process, it was proposed to supply the liquid precursor and pump out the gaseous decomposition products from the pyrolysis zone through the same channel, creating the necessary temperature regime in the zone above the impregnated product to separate the precursor vapors and the precursor decomposition products, which have a lower condensation temperature. This made it possible to maximize the utilization factor of the original precursor and eliminate the cessation of the impregnation process.

MATERIALS AND METHODS OF RESEARCH

To implement the proposed process, an installation was manufactured, the basic diagram of which is shown in Fig. 1.

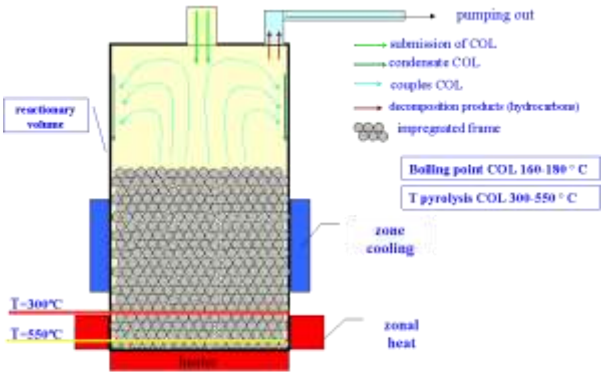


Fig. 1. Schematic diagram of the installation for obtaining composite materials by impregnation with a substance deposited from the gas phase

The framework used in the impregnation experiments was Ø1 m spheres made of ball-bearing steel, which were fixed inside a stainless steel tube with an internal diameter of 8 mm. The assembly of spheres was preliminarily compacted on a vibration stand under load. The degree of filling the volume with spheres after compaction reached 59.9…65.2% (±1%). The bulk density of the backfill of spheres without vibration compaction was 58.6…59.8% (±1%).

The degree of filling of the volume after impregnation was determined from transverse sections of the obtained composite material using a semi-automatic coordinate meter [5].

EXPERIMENTAL PART

The setup was first pumped down to a pressure of 1.3…6.7 Pa, since both the working joint and the frame material oxidize when heated in the atmosphere to the pyrolysis temperature. The section above the heating zone was cooled to a temperature of 80…90 °C. The product was heated to a temperature of 500…550 °C, and the reagent was supplied at a rate of 0.6 g/h. The zone drawing rate was 0.65 mm/h.

The process of impregnation of the framework was carried out as follows. The reagent from the container with the working connection through the dosing device was fed by gravity from top to bottom into the sealed pumped-out volume, in which the impregnated framework of spheres was located. A high vertical temperature gradient inside the impregnated framework was created by heating its bottom part with a zone heater while cooling the overlying section with a zone cooling system. Gaseous decomposition products formed in the pyrolysis zone with the help of the pumping system were removed from the reaction zone and frozen in a nitrogen trap. In this case, the vapors of the initial reagent that did not react in the reaction zone, pumped out together with the decomposition products, condensed on the cooled vertical walls and returned back to the reaction zone together with the liquid reagent fed there. The intensity of the pyrolysis process was controlled according to the pressure sensor readings. The required speed of movement of the reaction zone from the bottom up relative to the stationary heating and cooling zones was ensured with the help of the pulling mechanism.

To determine the required speed of drawing the deposition zone, it was necessary to know the pore sizes between the spheres, the dependence of the coating growth rate on temperature, and the temperature distribution profile and the coating growth rate in the deposition zone.

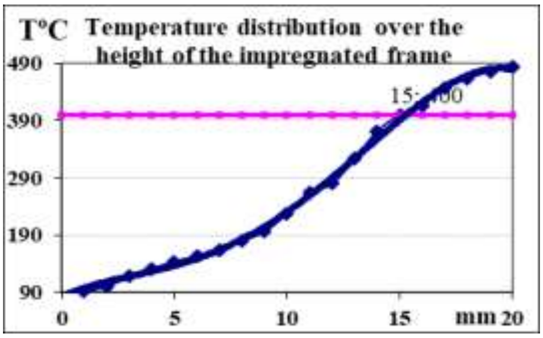


Fig. 2. Temperature distribution in the deposition zone without feeding the reagent into the deposition zone

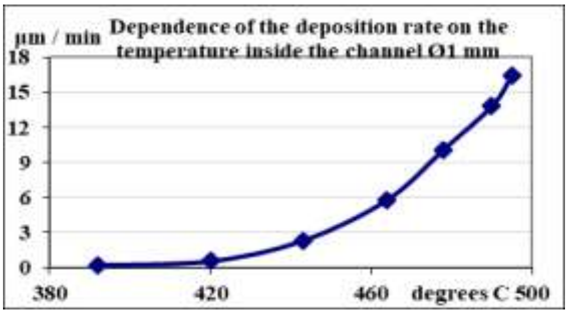


Fig. 3. Dependence of the growth rate of the coating inside a channel with a diameter of 1 mm on temperature

The temperature inside the frame was measured using a sheathed chromel-alumel thermocouple with an outer diameter of 1 mm, which was placed inside the spheres, drawing the heating zone along a column of spheres without feeding the precursor. The temperature distribution inside the frame is shown in Fig. 2.

To estimate the deposition rate, data on the growth rate of the chromium carbide coating inside a channel with a diameter of 1 mm after their processing were used (Fig. 3) [7].

Analysis of flat sections of the elementary FCC cell shown in Fig. 4 showed that the narrowest and widest sections of the pores for an ideal packing of spheres will have the types shown in Fig. 5. Estimates of the required coating thickness on the surface of the spheres when impregnating a framework of spheres, the growth of which occurs along the normal to the surface, showed that for complete overgrowth of the two types of these pores, these thicknesses are ≈77 and ≈207 μm, respectively, for a framework of spheres with a diameter of 1 mm.

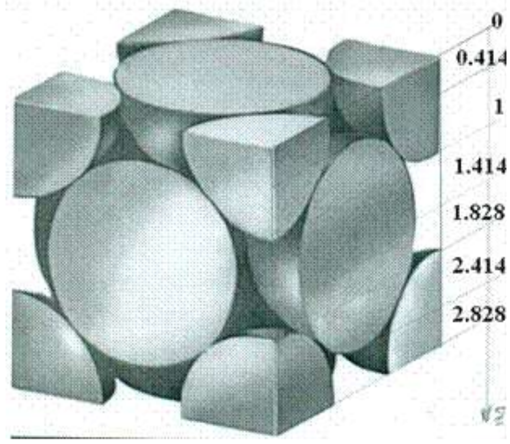


Fig. 4. Unit cell of the FCC lattice with a sphere diameter equal to 1 mm

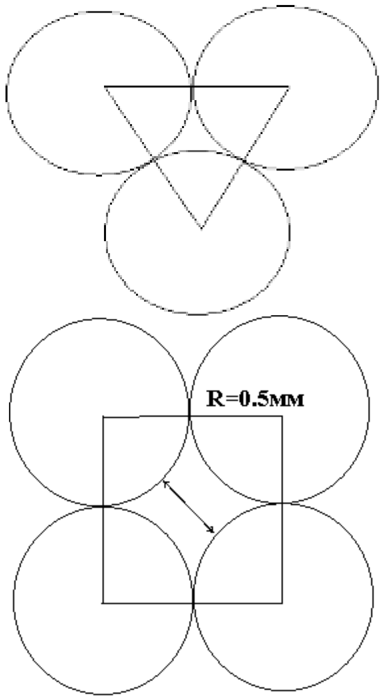
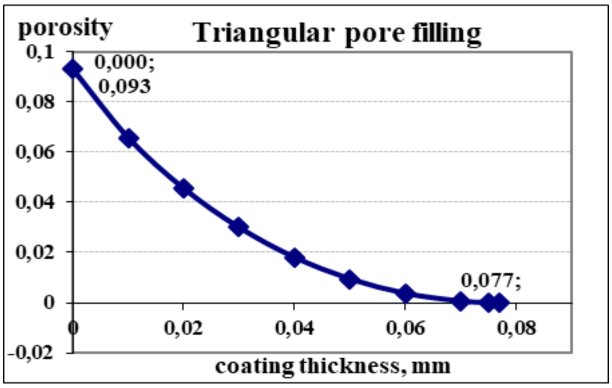


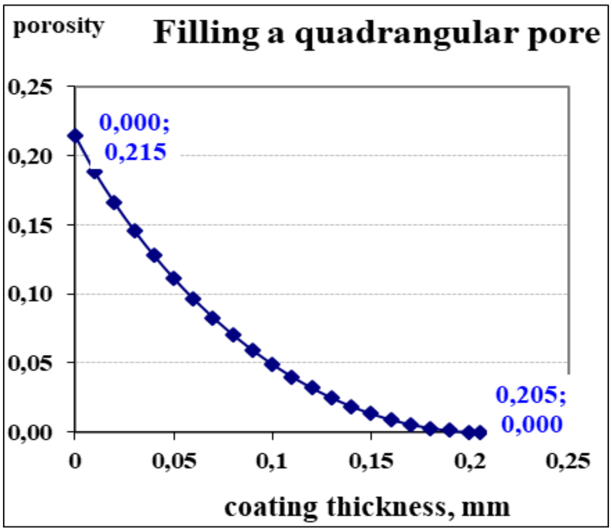
Fig. 5. Cross-sections of pores in a cell of the FCC lattice

In this case, each quadrangular pore is connected to four triangular pores from below and four from above. This allows us to estimate the required time of the impregnated frame section from spheres, knowing the range of coating growth rates. The change in the cross-section of two types of pores as the coating grows on the surface of the spheres is shown in Fig. 6. Fig. 7 shows a section of the section with the highest degree of impregnation after deposition according to the described process scheme, where both triangular and quadrangular pores are visible in the frame after deposition of the coating.

The actual filling [6, 7] of the pore volumes between the framework spheres may differ somewhat from the calculated curves of the dependencies shown in Fig. 6. The change in the angle between the surfaces of the spheres at the points of their contact, combined with the growth of the coating along the normal to the surface, will most likely lead to the effect shown in Fig. 8, i.e., faster growth at smaller angles at the initial stage of the impregnation process. Due to the small volumes of these areas, this does not significantly affect the rate of pore filling.



a



b

Fig. 6. Dependence of the pore cross-section on the coating thickness on a sphere:
a – triangular pore, b – quadrangular pore

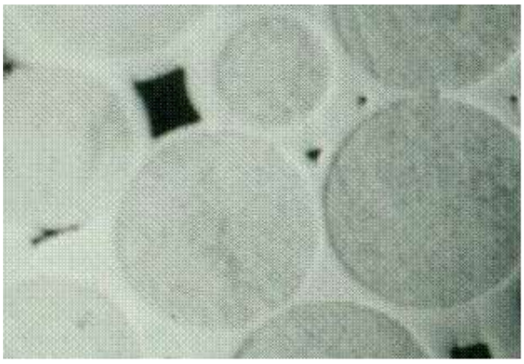


Fig. 7. Fragment of a section of a frame made of spheres with a deposited coating. Sphere diameter – 1 mm

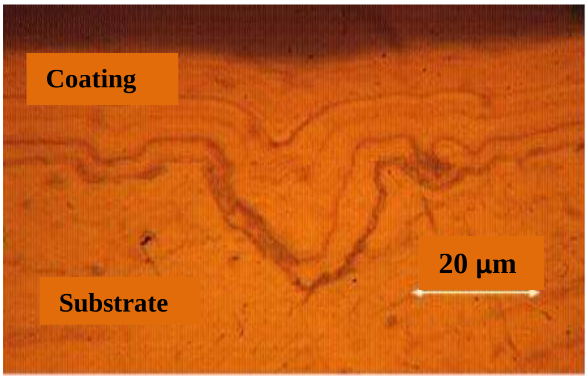


Fig. 8. Structure of a transverse section of a chromium carbide coating on the surface of a flat sample with defects formed during its processing.
Coating thickness is 20 µm

RESULTS AND DISCUSSION

As theory and practice show, it is impossible to achieve ideal packing of spheres. This is due to both the discrepancy between the volume of the form in which the spheres are placed during their compaction and the sizes of the spheres themselves, and the occurrence of voids in the volume similar to what happens in real crystal lattices. The sizes of such voids can significantly exceed the sizes of voids characteristic of ideal packing.

To achieve a high degree of impregnation of the framework, it is necessary to ensure the maximum possible temperature gradient in the reaction zone and, based on these data, estimate the zone movement rate. To estimate the zone drawing rate, we used the data on the dependence of the deposition rate of the carbide-chromium coating from the Barkhos HOZh on the temperature and the temperature distribution profile inside the impregnated framework, shown in Fig. 2 and Fig. 3. In this case, it is necessary to take into account the differences in the delivery of the precursor to the reaction zone for capillaries and a porous framework of spheres. Obviously, the efficiency of precursor delivery in the case of a capillary is significantly higher, and, consequently, the coating growth rate will also be higher. If we assume that the main coating will be deposited in the temperature range of 430…500 °C, then the length of the deposition zone will be 3 mm. Consequently, the average deposition rate along the length of the zone will be at the level of 10 µm/min.

The maximum coating thickness for complete impregnation of an ideal sphere package is 207 μm, and, therefore, the zone drawing speed should be at the level of 0.6…0.7 mm/h. The zone drawing was carried out at a speed of 0.65 mm/h, in accordance with these estimates and taking into account a significant decrease in the speed of precursor delivery to the deposition zone. As a result of the experiments, the above-mentioned degrees of impregnation were achieved with high efficiency of precursor use. The view of the transverse section of the impregnated framework of spheres is shown in Fig. 9.

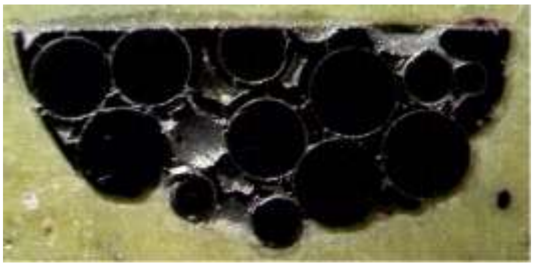


Fig. 9. Segment of a frame made of steel spheres impregnated with pyrolytic chromium by vapor deposition. The diameter of the spheres is 1 mm. The density of filling the volume with spheres before the process was 0.64

CONCLUSIONS

• A scheme of the method for obtaining composite materials with a high degree of impregnation with a substance deposited from the gas phase has been developed.

• It has been experimentally shown that the developed method for obtaining composite materials allows obtaining materials with a degree of volume impregnation reaching 95…96% with an efficiency of precursor use at the level of 75…80%.

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ОТРИМАННЯ КОМПОЗИЦІЙНИХ МАТЕРІАЛІВ ЗА ДОПОМОГОЮ ПРОСОЧЕННЯ РЕЧОВИНОЮ, ЩО ОСАДЖУЮТЬ ІЗ ГАЗОВОЇ ФАЗИ

С.О. Крохмаль, В.В. Щербакова

Досліджено можливість отримання композиційних матеріалів із тугоплавкою матрицею осадженням із газової фази. Запропоновано схему проведення процесу просочення з високою ефективністю використання прекурсора для отримання паливних елементів дисперсного типу. Ступінь просочення може досягати 95…96%.