OBTAINING SILICON CARBIDE VIA CHEMICAL VAPOR, PLASMA-CHEMICAL AND SUBLIMATION METHODS

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In the present paper the results of studies on obtaining silicon carbide via chemical gas phase, plasma-chemical and sublimation methods are described. The thermodynamic analysis of chemical reactions of silicon carbide in the presence of hydrogen and without was provided. Was found that, without free hydrogen reaction of silicon carbide formation can't proceed. Established depending on ratio between the various active components of the gas phase $SiCl_4$:C_7H_8, entering the reactor, morphology of SiC layer. Was shown that, with increasing temperature of the substrate deposition rate increases, reaching a maximum temperature about ~ 1800 K with a steep decreasing at higher temperatures ranges, which is typical of a homogeneous reaction. From source (NbTa)SiC, received via chemical CVD, obtained films of SiC with sublimation method.

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INTRODUCTION

Ceramics, based on silicon carbide, have next properties: considerable mechanical strength at high temperatures, wear resistance, low coefficient of thermal expansion, a substantial resistance to oxidation at temperatures up to 1700 K; chemical inertness, corrosion resistance, resistance to radiation, high hardness and thermal conductivity [1].

With its unique combination of physical and chemical properties of SiC-ceramics has a great application in the nuclear industry, the defense enterprises, metallurgical industries, as well as in the design of the first wall and blanket of fusion reactors. Questions in obtaining and studying of the SiC-ceramics are in the focus of researchers and engineers, both in Ukraine and abroad [2].

Low volatility of the components or high desorption energy is the main problem in the obtaining of SiC-condensates, both C and Si [3]. Method of vapor deposition is considered as more promising from the existing methods for producing silicon carbide such as hot pressing, molecular beam epitaxy, magnetron sputtering.

Compaction is achieved mainly by moving particles and low plastic deformation in hot pressing. It is known that at pressures up to 60 MPa and temperatures below 2500 K pure silicon carbide ceramics can be obtained with a density above 2700 kg / m^3 and a porosity of at least 16 %, which does not satisfy the requirements for structural ceramics [4].

The method of molecular-beam epitaxy is carried out from two independent sources of silicon and carbon, and produces a crystalline thin film of the high purity. The deposition rate of the substance on the substrate is generally one monatomic layer per second [5], which limits its mass production.

Fused polycrystalline Si and C is commonly used on direct current in magnetron sputtering as sputtering-target. In general, literature data indicate that at temperatures below 800 K, the structure of SiC films is amorphous. Annealing in an inert or chemically reactive medium is suggested to enhance its crystallinity and improve electrical properties [6].

The selection of precursors plays a big role in gas-phase methods. Thus, silane SiH_4, SiH_2, methane CH_4, propane C_3H_8 and hydrogen H_2 are used in scientific works [7, 8]. The disadvantage of the use of silane is its pyrophoricity (the possibility of spontaneous combustion in the air and blast). This leads to the need to dilute the silane by argon to safe concentrations in the vessel. Furthermore, if the gas phase decomposition of silane is occurred, the reactor having no water cooling "overgrows" and tend to form defects in the growing layers [9].

EXPERIMENTAL PART

In this paper, the research on obtaining of silicon carbide by chemical gas phase plasma-chemical methods were carried out in the facility of the flow-type, scheme is shown in Fig. 1. The source of silicon was selected silicon tetrachloride $SiCl_4$, carbon – toluene C_7H_8, the activating gas – is hydrogen H_2, the substrates – were Mo, Zr1%Nb, NbTa.

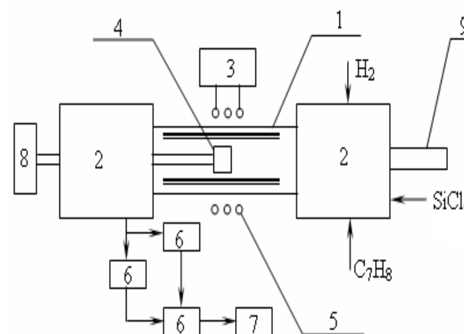
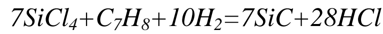


Fig. 1. The gas-phase-assembly scheme: 1 – reaction chamber; 2 – prechamber; 3 – generator; 4 – substrate; 5 – inductor; 6 – nitrogen trap; 7 – prepump; 8 – power supply for heater; 9 – viewing window

Calculations of thermodynamic reactions:

$$7SiCl_4+C_7H_8=7SiC+8HCl+10Cl_2$$



$$7SiCl_4+C_7H_8+10H_2=7SiC+28HCl$$

$$7SiCl_4+C_7H_8+20H=7SiC+28HCl$$

showed that without the formation of free hydrogen, silicon carbide reaction is carried out at temperatures above 2000 K. The gas-phase deposition reaction takes place at temperatures below 1500 K in the presence of free hydrogen. In the presence of atomic hydrogen in the plasma-chemical deposition, the reaction proceeds at relatively low temperatures, Fig. 2.

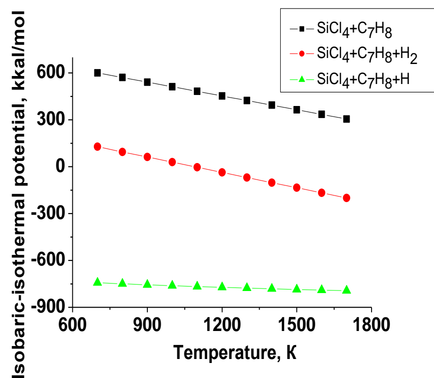


Fig. 2. The dependence of the isobaric-isothermal potential reaction on temperature

The ratio between the active components of the gas phase $SiCl_4$:C_7H_8, which feeds the reactor, is one of the main parameters that have a significant effect on the crystalline structure and morphology of the growing layer for any of the gas-phase systems with independent sources. Studies have shown that the ratio of $SiCl_4$:C_7H_8=3.5 irrelevant of the temperature obtaining almost all of the samples were low-strength precipitate with gray to black and flake-structured. Condensates consisting of silicon carbide and pyrolytic graphite are formed with the ratio of $SiCl_4$:C_7H_8=7.4. Concentration of silicon carbide particles in pyrocarbon increases with the temperature increasing from 1600 to 1800 K. Coatings obtained with the ratio of $SiCl_4$:C_7H_8=11 temperatures in the range of 1600 to 1800 K are dense, solid metal-like deposits having a smooth surface with bright luster and fine-grained structure, Fig. 3.

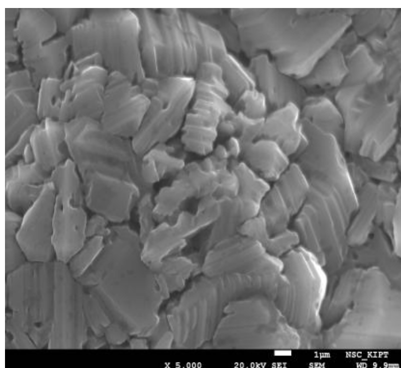


Fig. 3. Surface off silicon carbide

Studying of the kinetics of SiC deposition process showed that with the increase of substrate temperature from 1600 to 1800 K, a rapid increasing of the deposition rate. Subsequent reduction of the deposition rate caused due to mutual diffusion of gaseous reactants and products. In the range of the higher temperatures with high-level of supersaturation and reacting gases are superheated, nucleation occurs homogeneously with precipitation of solid reaction product, thereby reducing the deposition rate and thus the thickness of the coating on the substrate. Temperature dependence of deposition rate on the silicon carbide substrate is presented in Fig. 4.

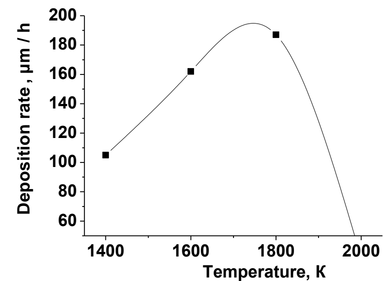


Fig. 4. The dependence of the deposition rate of silicon carbide on the temperature

Discharge excitation in the gas mixture $SiCl_4$:C_7H_8:H_2 was carried out by means of inductor of the high-frequency generator VCHI-63/0.44 at frequency of 440 kHz, power 63 kW. Electronic components of the plasma parameters were determined from the current-voltage characteristics of the dual probe. Electron temperature T_e was determined by the method of equivalent resistance by means of the current-voltage characteristics of the dual-probe. Next, electron density was estimated on the resulting T_e and the saturation current i_e of the dual-probe. It can be seen that the average values of the electron-parameters are equals to T_e = 4.5 eV, $N_e = 10^{12}\ldots10^{13}$ cm^{-3}.

Obtaining SiC by plasma method reduces the substrate temperature to 500 K and an increase SiC deposition rate, due to the stimulation of the process by means of excited and charged particles of the plasma.

Micro-X-ray-structural analysis showed that the obtained SiC condensates characterized by uniform distribution of silicon over depth of the samples, Fig. 5.

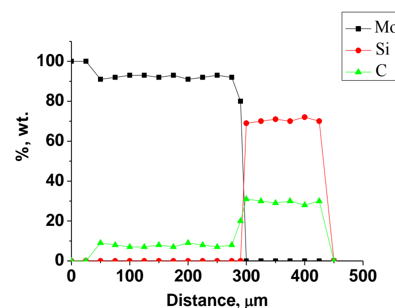


Fig. 5. The distribution of elements over the sample depth

XRD analysis indicated the presence of condensate SiC cubic structure FCC with the period a = 4.361 Å (known structure with a = 4.358 Å), a polycrystalline state having a particle size of ≥ 1 µm and microdistortions 0.1 %; a combination of textures (111) and (220).

The elemental composition of SiC coating was determined by nuclear-physical methods. As used analytical characteristic X-ray lines K-series: $K_{\alpha1}$=9885 eV, $K_{\alpha2}$=9885, $K_{\beta1}$=10980 eV, $K_{\beta2}$=11099 eV: Si – 67.20 and C – 30.97 wt. %, which corresponds to stoichiometry Si/C=1.

Resistance to the obtained coating microshock loading determined at the stand, in which cavitation zone is created in the water ultrasonic emitte. Stand options presented in the paper [10]. The magnitude of erosion measured sample weight loss after a certain time of exposure cavitation, Fig. 6.

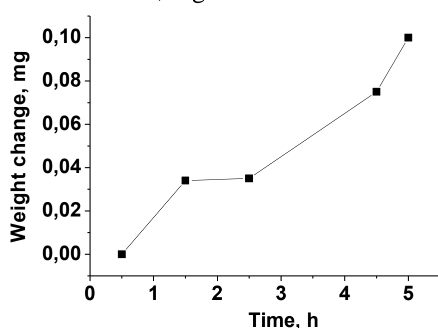


Fig. 6. Losing weight coating of SiC was caused by cavitation

Sublimation source, which is a SiC coating of about 100 microns thickness on a substrate NbTa size of 60×10×0.3 was obtained by chemical vapor. From the obtained source (NbTa)SiC the thin SiC films were precipitated by sublimation method with resistive heating of the (NbTa)SiC at high vacuum assembly. Source temperature (NbTa)SiC was 2400 K, the substrate temperature was varied in the range of 500…700 K, the pressure in the chamber $2\cdot10^{-6}$ mmHg. Surface morphology has no defects, Fig. 7.

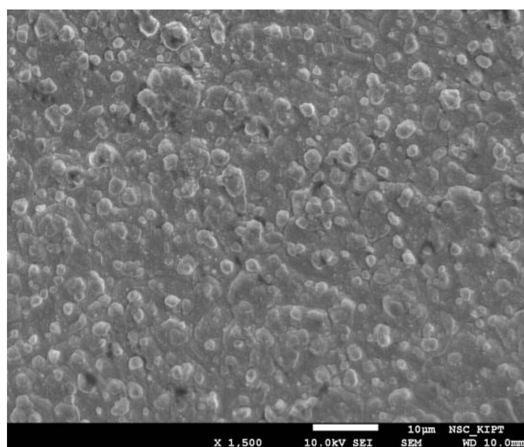


Fig. 7. Surface off silicon carbide

CONCLUSIONS

Coating of silicon carbide on substrates of Mo, Zr1%Nb, NbTa obtained with a cubic structure, regardless of the substrate and at the same temperatures.

With chemical gas phase and plasma-chemical methods, sources of silicon carbide on substrates of Mo and NbTa, were obtained. Morphology of SiC surface was studied, depending on the ratio of the starting reactants $SiCl_4$:C_7H_8 and substrate temperature.

Determined the composition and distribution of elements on the depth of the coating. On the high-vacuum facility obtained SiC film via sublimation method.

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ПОЛУЧЕНИЕ КАРБИДА КРЕМНИЯ ХИМИЧЕСКИМ ГАЗОФАЗНЫМ, ПЛАЗМОХИМИЧЕСКИМ И СУБЛИМАЦИОННЫМ МЕТОДАМИ

А.Ю. Журавлёв, Н.А. Хованский, Д.А. Хижняк, Б.М. Широков, Н.А. Семёнов, А.В. Шиян, С.В. Стригуновский, А.И. Евсюков, А.Б. Шевцов, Е.А. Назаренко, Н.Н. Пилипенко

Представлены результаты исследований по получению карбида кремния химическим газофазным, плазмохимическим и сублимационным методами. Проведен термодинамический анализ химических реакций получения карбида кремния в присутствии водорода и без него. Установлено, что без свободного водорода реакция образования карбида кремния протекать не может. В зависимости от различного соотношения между активными компонентами газовой фазы $SiCl_4$:C_7H_8, поступающими в реактор, изучена морфология SiC-слоя. Исследована кинетика процесса осаждения SiC. Показано, что с увеличением температуры подложки скорость осаждения возрастает, достигая максимума при температуре ~ 1800 K с резким снижением в области более высоких температур, что характерно для гомогенной реакции. Из полученного химическим газофазным методом источника (NbTa)SiC сублимационным методом получены плёнки SiC.

ОТРИМАННЯ КАРБІДУ КРЕМНІЮ ХІМІЧНИМ ГАЗОФАЗНИМ, ПЛАЗМОХІМІЧНИМ І СУБЛІМАЦІЙНИМ МЕТОДАМИ

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Представлено результати досліджень по отриманню карбіду кремнію хімічним газофазним, плазмохімічним і сублімаційним методами. Проведено термодинамічний аналіз хімічних реакцій отримання карбіду кремнію в присутності водню і без нього. Встановлено, що без вільного водню реакція утворення карбіду кремнію протікати не може. Залежно від різного співвідношення між активними компонентами газової фази $SiCl_4$:C_7H_8, які надходять в реактор, вивчена морфологія SiC-шару. Досліджено кінетику процесу осадження SiC. Показано, що зі збільшенням температури підкладки швидкість осадження зростає, досягаючи максимуму при температурі ~ 1800 K з різким зниженням в області більш високих температур, що характерно для гомогенної реакції. З отриманого хімічним газофазним методом джерела (NbTa)SiC сублімаційним методом отримано плівки SiC.