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Studies of Polytype Silicon Carbide Produced from Recycled Materials

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Base positions of crystallography of polytypic carbide of silicon are considered. Influence of different technological factors is shown such as: temperature, maintenance of admixtures and terms of forming of crystals on polytypic composition of material. X-ray structure studies of industrial and experience carbide of silicon are undertaken. The fundamental differences of polytypic composition of the investigated materials are shown.

Keywords: CARBIDE OF SILICON, POLYMORPHIC MODIFICATIONS, POLYTYPISM, INFLUENCE OF ADMIXTURES, X-RAY STRUCTURE ANALYSIS

Introduction

The increased interest to silicon carbide, observed in recent years, is characterized neither only to its high abrasive, not an unique combination of physical, chemical and electrical characteristics. Materials and products produced using the silicon carbide has rare qualities. They have a high mechanical strength and thermal conductivity, low coefficient of thermal expansion, resistant to chemically aggressive areas and abrasive wear in a wide range of temperatures. The unique properties of SiC determine the wide range of applications: from the production of high-frequency electronics to nuclear reactors and space technologies, and also metals and abrasive industry.

Special properties of silicon carbide can be explained by the electronic structure of its compound. Carbon and silicon, forming the compound SiC, are sp-elements of IV-th group of the Periodic Table. Electronic s → p – transitions in atoms Si and C lead to the formation of stable energy sp^3 configuration with predominantly covalent chemical bond.

Silicon carbide is the only existing in the condensed state of compounds in silicon - carbon system. Using the methods of differential thermal analysis, metallography and x-ray phase analysis R.V. Olesinski and G. J. Abbashian [1] specified the state diagram of the Si-C system and evaluated the stability of SiC depending on temperature and pressure (**Figure 1**). The eutectic at 1404±5 °C and the peritectic transformations at 2545±40 °C are shown on the graph. Found, that the alloy of eutectic composition at 1404±5 °C has 0,75±0,5% (mol) C. According to others, the calculated eutectic composition contains 0.026% (mol) C, and t_{eut} = = 1401±2 °C [2].

Silicon carbide exists in two versions, the cubic β-SiC with a structure of sphalerite (ZnS) and hexagonal α-SiC with the wurtzite structure. According to [1], at temperatures above 2273 K β-SiC transforms into α-SiC with a change of volume 0.06%. The authors suggest that the transition takes place with the gas phase, because the activation energy of a such transition is 660.44 kJ/mol and is close to the heat of vaporization 556 kJ/mol.

Besides two main polymorphic modifications α-SiC and β-SiC, silicon carbide forms a large number of polytypes based on hexagonal α-SiC (there are known more than 200 polytypes of α-SiC) with unit cell dimensions a = 0.3078 nm and c = 0,2518*n* nm, where n - number of layers in the unit cell. Polytypic structures are intermediate structures of pure cubic β-SiC to pure hexagonal 2H. Crystal lattice of β-SiC can be produced as consisting of two interpenetrating face-centered lattices, shifted relative to each other by a quarter of cube diagonal, and one of lattices composes of silicon atoms, the other – of carbon atoms. α-SiC polytypes vary by the rotation of double planes Si-C. In each of polytypes, atoms the same type are the center of the tetrahedron, in the center of which are atoms of the other type. Atomic models of silicon carbide polytypes are shown in **Figure 2**.

The difference between the size of the unit cell of silicon carbide polytypes, predefined energetically stable electron configurations for thepresent polytype, leads to a difference in its physical properties. Some properties of silicon carbide polytypes are shown in **Table 1**.

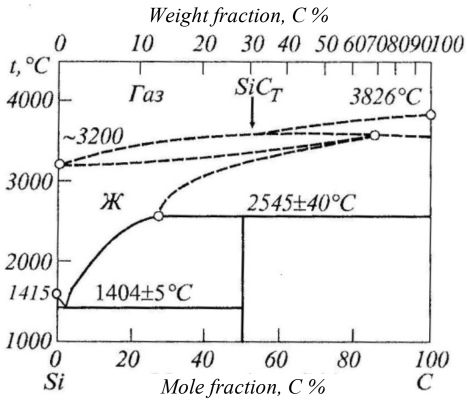

Figure 1. State diagram of Si-C system [3]

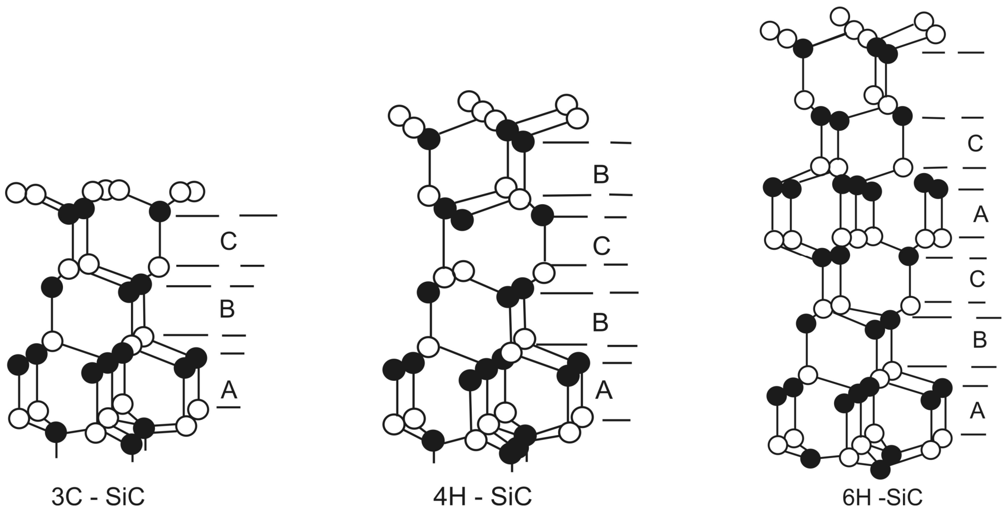

Figure 2. Atomic models of silicon carbide polytypes: 3C - cubic β-SiC; 4H, 6H - polytypes of hexagonal α-SiC

Table 1. Some properties of silicon carbide polytypes

Characteristic	Identificationof silicon carbide							
	β-SiC	α-SiC I	α-SiC II	α-SiC III	α-SiC IV	α-SiC V	α-SiC VI	α-SiC VII
	3C	15R	6H	4H	21R	51R	33R	87R
The number of tetra-hedralayers	3	15	6	4	21	51	33	87
The extent of the hex-agonal	0	0,4	0,33	0,5	0,29		0,36	
The lattice parameters, nm:								
a	0,435	0,308	0,308	0,308	0,307	0,307	0,307	0,307
c	–	3,781	1,509	1,008	5,289	12,84	8,310	21,91
The axis ratio c/a	–	12,28	4,90	3,27	17,18	41,71	27,00	71,16
The distance between the layers, nm	–	0,252	0,251	0,252	0,251	0,251	0,251	0,251
The bandgap width, h eV	2,2	2,9	2,86	3,1	2,77	–	–	–
Specific weight (calcu-lated), g/cm^3	3,210	3,217	3,218	3,217	3,217	–	3,217	–
Microhardness, MPa	278				254			

The formation of a polytype is determined by external factors, such as – the temperature, pressure and the availabilityof impurities. There is a diagram of Knipenberga in **Figure 3**, which shows the temperature areas of the existence of individual polytypes.

Research of the different zones of industrial resistor furnace showed, that during dollying out from the hot core to the periphery, the polytype composition changes to the following chain: 6H → 15R → 4H → 3C. The upper part of the black silicon carbide contains mainly 6H polytypes (up to 60%). The bottom of the unit contains 4H polytype (up to 50%), content of polytype 15R is evenly and ranges from 15-25%. During dollying out from the core, thesize of the crystals decreases, crown surface of the block crisp, disoriented crystals. Green silicon carbide contain mainly 6H polytype of level at 90% and 15R – at 10%. The block of green silicon carbide has a single-phase zone 6H crystals, that are at the bottom of the block of black furnaces, or very narrow or absent. Black silicon carbide is different from the presence of green polytype 4H.

During dollying out from the core in the Acheson furnace, is changed not only the temperature field [5], but also the composition of the gas phase, the gas permeability of the charge, the rate of crystallization of silicon carbide, content of impurities and other factors.

The presence of aluminum in silicon carbide directly affects on its polytype composition (**Figure 4**).

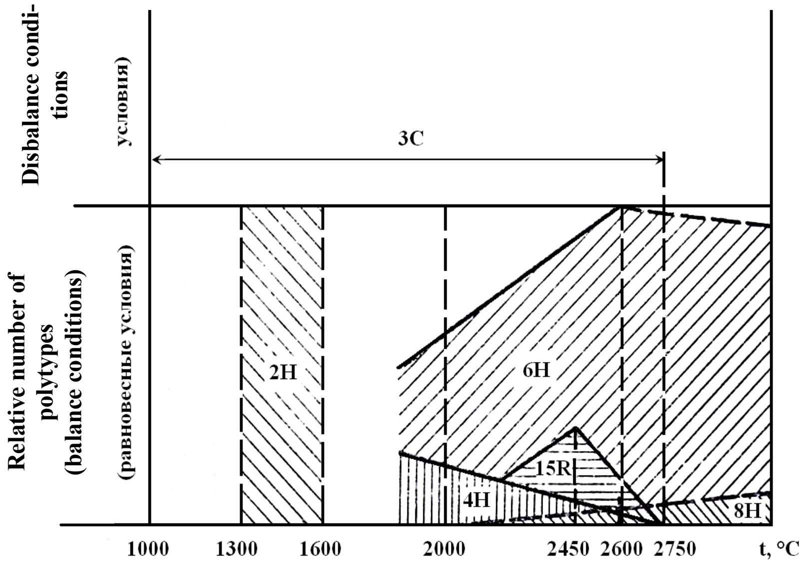

Figure 3. Dependence polytype SiC on temperature [4]

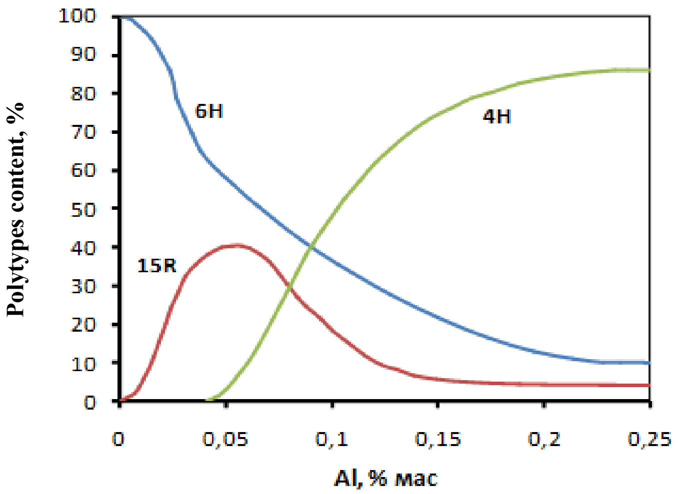

Figure 4. Dependenceα-SiC polytypes on the content of Al in silicon carbide

The saturation of the upper colder horizons of the charge by impurity oxides is implemented by chemical gas-transport reactions [6] to the technically accepted critical level Al2O3 + CaO + Fe_{bar} > 2%, above of the charge is depleted product and is derived from the production cycle.

The aim of this work – to study the composition of silicon carbide polytype with metallurgical quality, received from the recycled electrometallurgical materials [7]. X-ray analysis checked material, obtained with restoration moldboard charge of production of abrasive silicon carbide by graphite. The chemical composition of the product, except for free carbon is, % wt.: 76,36 SiC; 6,3 SiO_2; 5,6 Al_2O_3; 2,9 Fe_2O_3; rest – impurities.

Comparative studies of restoration and industrial metallurgical silicon carbide were carried out on a DRON-3 in the characteristic radiation Cu-Kα at U = 30 kV, I = 20 mA. The results of X-ray phase analysis are shown in **Figure 5** and **6.**

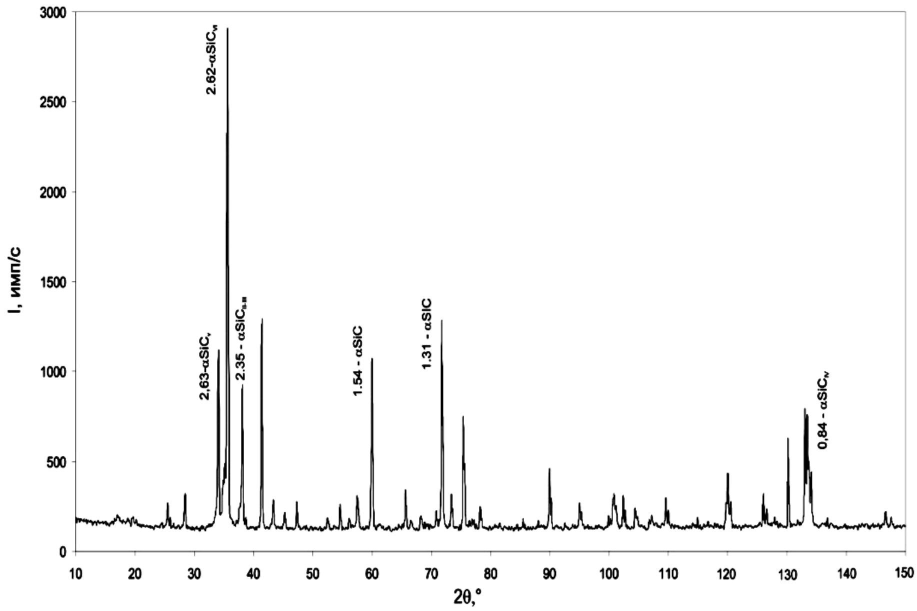

Figure 5. Radiograph of industrial metallurgical silicon carbide

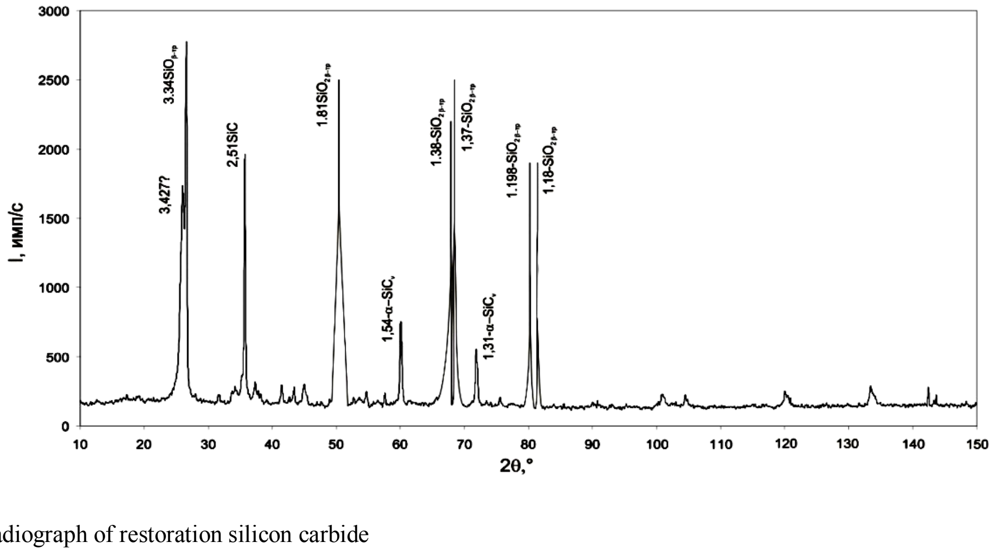

Figure 6. Radiograph of restoration silicon carbide

Radiographs show, that the industrial metallurgical silicon carbide have a pronounced crystalline structure and is represented mainly 6H and 4H polytypes of silicon carbide. Restoration product is characterized by lines unreacted SiO2 – β-tridymite, SiC is mainly represented by the cubic modification of β-SiC and α-SiC 4H. In the experimental product in a small number of polytypes were marked lines: 6H, 15R and 51 R. Smooth of some peaks indicates about presence in the sample of pseudomorphosis of silicon carbide on carbon.

The availability in restoration product 6H polytype can be explained by its presence in the source material, got out of industrial furnace by sorting block. Getting pseudomorphosis silicon carbide on carbon and cubic modification of β-SiC – the result of failure of temperature at the recovery of the material in the Tamman furnace.

Thus, studies have shown, that on the composition of silicon carbide polytype, influence various factors, such as temperature, the presence of impurities and gas dynamics of the process. It's impossible to get silicon carbide with abrasive quality by restoration of secondary electrometallurgy materials, but the material can be used in the metallurgical and refractory industries.

Conclusions

1. The analytical studies of polytype silicon carbide and influence on it various technological factors have been done.
2. Using X-ray structure analysis have been shown the difference between polytypic composition of industrial silicon carbide and produced in the laboratory from dumped materials.
3. It's shown that the sampled silicon carbide does not meet requirements for abrasive industry on polytype composition, but can be successfully used in metallurgy and refractory industries.

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Исследования политипного состава карбида кремния, полученного из вторичных материалов

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Рассмотрены базовые положения кристаллографии политипов карбида кремния. Показано влияние различных технологических факторов таких как: температура, содержание примесей и условий формирования кристаллов на политипный состав материала. Проведены рентгеноструктурные исследования промышленного и опытного карбида кремния. Показаны принципиальные отличия политипного состава исследуемых материалов.