UDC 621.793.6:620.181.4

RESEARCH OF A VACUUM DIFFUSION BORON SILICIFICATION PROCESS FOR CONSTRUCTIONAL MATERIALS

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Received 21.01.2013

In this work process of vacuum diffusion boron silicification of materials in sodium chloride vapour were researched. Gaseous medium composition was found by using the thermodynamic calculations of chemical reactions between NaCl vapour and the components of saturating powder mixture in the process for the temperature $T = 1400 - 1600$ K and pressure $P = 1.33 - 1333$ Pa, when the content of boron is 1 weight percent and 10 weight percent in backfilling. Formation mechanism of diffusion layer on example of the vacuum activated boron silicification of graphite was determined.

Keywords: boron silicification, diffusion saturation, activator, vacuum, graphite.

ИССЛЕДОВАНИЕ ПРОЦЕССА ВАКУУМНОГО АКТИВИРОВАННОГО БОРОСИЛИЦИРОВАНИЯ КОНСТРУКЦИОННЫХ МАТЕРИАЛОВ

В.И. Змий, С.Г. Руденький

В работе были проведены исследования механизма процесса вакуумного диффузионного боросилицирования материалов в парах хлористого натрия. Используя термодинамический расчет химических реакций между парами активатора и компонентами насыщающей порошковой смеси был определен состав газовой среды в этом процессе для температур $T = 1400 - 1600$ К и давлений $P = 1.33 - 1333$ Па, при содержании бора 1 и 10 вес.% в засыпке. На примере вакуумного активированного боросилицирования графита установлен механизм образования диффузионного слоя.

Ключевые слова: боросилицирование, активатор, вакуум, графит, диффузионное насыщение

ДОСЛІДЖЕННЯ ПРОЦЕСУ ВАКУУМНОГО АКТИВОВАНОГО БОРОСИЛІЦІЮВАННЯ КОНСТРУКЦІЙНИХ МАТЕРІАЛІВ

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В роботі були проведені дослідження механізму процесу вакуумного дифузійного боросиліціювання матеріалів у парах хлористого натрію. Використовуючи термодинамічний розрахунок хімічних реакцій між парами активатора та компонентами насичуючої порошкової суміші був визначений склад газового середовища у цьому процесі для температур $T = 1400 - 1600$ К та тисків $P = 1.33 - 1333$ Па, при вмісті бору 1 та 10 ваг.% в засипці. На прикладі вакуумного активованого боросиліціювання графіту встановлено механізм утворення дифузійного шару.

Ключові слова: боросиліціювання, активатор, вакуум, графіт, дифузійне насичення.

INTRODUCTION

The performance characteristics of constructional materials must meet high requirements, if the machinery working in harsh environments. It is possible to apply a different coatings for the development and deriving of such materials. There are different methods of formation of such coatings. Structure and physical-chemical features of each of these coatings are formed by the composition, manner and mode of receipt of this protective layer. A team of specialists at the National Science Center “Kharkov Institute of Physics and Technology” (NSC KIPT) has developed a method of vacuum activated diffusion saturation [2, 3]. This method is environmentally friendly, provides a strong adhesion of the coating to the surface of the processed materials of construction and allows you to create effective integrated multipurpose protective layers. Such diffusion coatings protect the surface of construction materials from wear, i.e. they are durable. Also, these coatings are corrosion resistant. The coatings prevent the destruction of refractory metals and carbon materials from oxidising. Corrosion resistance of the coating is persistent in the temperature range from room temperature up to 2000 °C. Silicification or boron silicification of metals and carbon materials is one of the stages of a chemical-thermal treatment for creation of these protective coatings. Layer of silicide’s is formed on the surface of the material after the chemical-thermal treatment. Many of this silicide's are corrosion resistant. Coating of silicon carbide SiC is formed on the carbon materials after the chemical-thermal treatment. This coating has high hardness and heat resistance. Molybdenum silicide and tungsten silicide can be got by silicification method of these refractory metals. These silicide's are widely used to protect products from high-temperature oxidation. During the boron silicification process a boron is injected simultaneously with the silicon saturation of the surface. Boron atoms have a small size and prevent the degradation of the coating. This boron silicide coating is heat resistant at high temperatures. The process of vacuum diffusion silicification in vapour of sodium chloride was investigated in [4, 5]. However, the process of boron silicification is not yet sufficiently studied.

VACUUM DIFFUSION BORON SILIFICATION PROCESS AND COMPOSITION OF GASEOUS SATURATION MEDIUM

In this work we investigated the mechanism of vacuum diffusion boron silicification in the presence of a vapour of sodium chloride. We have established the dependence of a composition of the gaseous saturation medium from temperature and pressure during the process. And the influence of the composition of the gaseous saturation medium on the composition of the resulting diffusion layer.

Vacuum activated diffusion boron silicification of materials occurs by reaction of sodium chloride vapour with boron and silicon. This process takes place under reduced pressure. The result is a saturating gaseous medium. Gaseous activator interacts with saturating elements. This interaction is described by chemical reactions:

$$\mathrm{NaCl}(g) + \mathrm{B}(s) \rightleftharpoons \mathrm{BCl}(g) + \mathrm{Na}(g), \quad (1)$$

$$\mathrm{NaCl}(g) + (1/2)\mathrm{B}(s) \rightleftharpoons (1/2)\mathrm{BCl}_2(g) + \mathrm{Na}(g), \quad (2)$$

$$\mathrm{NaCl}(g) + (1/3)\mathrm{B}(s) \rightleftharpoons (1/3)\mathrm{BCl}_3(g) + \mathrm{Na}(g), \quad (3)$$

$$\mathrm{NaCl}(g) + \mathrm{Si}(s) \rightleftharpoons \mathrm{SiCl}(g) + \mathrm{Na}(g), \quad (4)$$

$$\mathrm{NaCl}(g) + (1/2)\mathrm{Si}(s) \rightleftharpoons (1/2)\mathrm{SiCl}_2(g) + \mathrm{Na}(g), \quad (5)$$

$$\mathrm{NaCl}(g) + (1/3)\mathrm{Si}(s) \rightleftharpoons 1/3)\mathrm{SiCl}_3(g) + \mathrm{Na}(g), \quad (6)$$

$$\mathrm{NaCl}(g) + (1/4)\mathrm{Si}(s) \rightleftharpoons (1/4)\mathrm{SiCl}_4(g) + \mathrm{Na}(g). \quad (7)$$

The formation of the gaseous saturation medium occurs in accordance with the chemical reactions (1) – (7). The degree of progress of chemical reactions determine the composition of the gaseous medium. In order to define the composition of the gaseous medium in the vacuum activated diffusion boron silicification we need to choose initial conditions: quantity of vapours of sodium chloride, silicon and boron. Also it is necessary to establish the degree of chemical reactions (1) – (7). It is possible by solving set of equations which are prepared in accordance with the law of mass action for these reactions. Set of equations is based on the fact that the initial amount of gaseous sodium chloride is 1 mole and saturating powder mixture is 1 mole. Saturating powder mixture is composed from boron and silicon. We established that the percentage of sodium chloride, which reacted by chemical reactions (1) – (7), respectively, will be x, y, z, k, l, m, n.

Using the law of mass action we can establish a connection between the equilibrium constants for reactions (1) – (7) and the equilibrium partial pressure of substances that are present in the system NaCl-B-Si.

$$K_1 = \exp\left(-\frac{\Delta G_1}{R \cdot T}\right)\Delta G_7 = \frac{x \cdot (x+y+z+k+l+m+n)}{\left(1+x+\frac{y}{2}+\frac{z}{3}+k+\frac{l}{2}+\frac{m}{3}+\frac{n}{4}\right)} \times$$

$$\times \frac{P}{\left[1-(x+y+z+k+k+m+n)\right] \cdot a_B}; \quad (8)$$

$$K_2 = \exp\left(-\frac{\Delta G_2}{R \cdot T}\right) = \frac{(y/2)^{1/2} \cdot (x+y+z+k+l+m+n)}{\left(1+x+\frac{y}{2}+\frac{z}{3}+k+\frac{l}{2}+\frac{m}{3}+\frac{n}{4}\right)^{1/2}} \times$$

$$\times \frac{P^{1/2}}{\left[1-(x+y+z+k+k+m+n)\right] \cdot a_B^{1/2}}; \quad (9)$$

$$K_3 = \exp\left(-\frac{\Delta G_3}{R \cdot T}\right) = \frac{(z/3)^{1/3} \cdot (x+y+z+k+l+m+n)}{\left(1+x+\frac{y}{2}+\frac{z}{3}+k+\frac{l}{2}+\frac{m}{3}+\frac{n}{4}\right)^{1/2}} \times$$

$$\times \frac{P^{1/3}}{\left[1-(x+y+z+k+l+m+n)\right] \cdot a_B^{1/3}}; \quad (10)$$

$$K_4 = \exp\left(-\frac{\Delta G_4}{R \cdot T}\right) = \frac{k \cdot (x+y+z+k+l+m+n)}{\left(1+x+\frac{y}{2}+\frac{z}{3}+k+\frac{l}{2}+\frac{m}{3}+\frac{n}{4}\right)} \times$$

$$\times \frac{P}{\left[1-(x+y+z+k+k+m+n)\right] \cdot a_{Si}}; \quad (11)$$

$$K_5 = \exp\left(-\frac{\Delta G_5}{R\cdot T}\right) = \frac{(l/2)^{1/2}\cdot(x+y+z+k+l+m+n)}{\left(1+x+\frac{y}{2}+\frac{z}{3}+k+\frac{l}{2}+\frac{m}{3}+\frac{n}{4}\right)^{1/2}}\times$$

$$\times\frac{P^{1/2}}{\left[1-(x+y+z+k+k+m+n)\right]\cdot a_{\mathrm{Si}}^{1/2}}; \quad (12)$$

$$K_6 = \exp\left(-\frac{\Delta G_6}{R\cdot T}\right) = \frac{(m/3)^{1/3}\cdot(x+y+z+k+l+m+n)}{\left(1+x+\frac{y}{2}+\frac{z}{3}+k+\frac{l}{2}+\frac{m}{3}+\frac{n}{4}\right)^{1/3}}\times$$

$$\times\frac{P^{1/3}}{\left[1-(x+y+z+k+l+m+n)\right]\cdot a_{\mathrm{Si}}^{1/3}}; \quad (13)$$

$$K_7 = \exp\left(-\frac{\Delta G_7}{R\cdot T}\right) = \frac{(n/4)^{1/4}\cdot(x+y+z+k+l+m+n)}{\left(1+x+\frac{y}{2}+\frac{z}{3}+k+\frac{l}{2}+\frac{m}{3}+\frac{n}{4}\right)^{1/4}}\times$$

$$\times\frac{P^{1/4}}{\left[1-(x+y+z+k+l+m+n)\right]\cdot a_{\mathrm{Si}}^{1/4}}; \quad (14)$$

Here K_1, K_2, K_3, K_4, K_5, K_6, K_7 and ΔG_1, ΔG_2, ΔG_3, ΔG_4, ΔG_5, ΔG_6, ΔG_7 – respectively, are the equilibrium constant and Gibbs energy for reactions (1 – 7); R – universal gaseous constant; a_B and a_{Si} – activity of boron and silicon.

Solution of this system was carried out for the temperature $T = 1400 \div 1600$ K and pressure $P = 1333 \div 1.33$ Pa and is presented in tabl. 1.

The values of the Gibbs energy was calculate using thermodynamic data from sources [6, 7].

Tabl. 1 shows the structure of the gaseous saturation medium in the system environment NaCl – B – Si during boron silicification process.

Table 1

Equilibrium composition of the gaseous mixture in the system NaCl-B-Si

Substance	$T = 1400$ K			
	Composition of powder mixture			
	10 atomic percent of B+90 atomic percent of Si		1 atomic percent of B+99 atomic percent of Si	
	Pressure P, Pa		Pressure P, Pa	
	1333	1.33	1333	1.33
BCl	$7.253\cdot10^{-8}$	$5.953\cdot10^{-6}$	$7.067\cdot10^{-9}$	$5.732\cdot10^{-7}$
BCl_2	$1.734\cdot10^{-7}$	$1.154\cdot10^{-6}$	$1.647\cdot10^{-8}$	$1.070\cdot10^{-7}$
BCl_3	$1.0211\cdot10^{-5}$	$5.511\cdot10^{-6}$	$9.456\cdot10^{-7}$	$4.912\cdot10^{-7}$
SiCl	$1.083\cdot10^{-4}$	$8.886\cdot10^{-3}$	$1.161\cdot10^{-4}$	$9.412\cdot10^{-3}$
$SiCl_2$	$6.502\cdot10^{-4}$	$4.328\cdot10^{-3}$	$6.792\cdot10^{-4}$	$4.412\cdot10^{-3}$
$SiCl_3$	$2.805\cdot10^{-6}$	$1.514\cdot10^{-6}$	$2.855\cdot10^{-6}$	$1.485\cdot10^{-6}$
$SiCl_4$	$1.703\cdot10^{-8}$	$7.453\cdot10^{-10}$	$1.689\cdot10^{-8}$	$7.039\cdot10^{-10}$
Na	$1.448\cdot10^{-3}$	$1.757\cdot10^{-2}$	$1.486\cdot10^{-3}$	$1.824\cdot10^{-2}$
NaCl	$9.986\cdot10^{-1}$	$9.824\cdot10^{-1}$	$9.985\cdot10^{-1}$	$9.818\cdot10^{-1}$
$T = 1500$ K				
BCl	$4.815\cdot10^{-7}$	$3.122\cdot10^{-5}$	$4.673\cdot10^{-8}$	$2.968\cdot10^{-6}$
BCl_2	$6.406\cdot10^{-7}$	$2.731\cdot10^{-6}$	$6.034\cdot10^{-6}$	$2.502\cdot10^{-7}$
BCl_3	$1.223\cdot10^{-5}$	$3.428\cdot10^{-6}$	$1.118\cdot10^{-6}$	$3.027\cdot10^{-7}$
SiCl	$5.622\cdot10^{-4}$	$3.645\cdot10^{-2}$	$6.002\cdot10^{-4}$	$3.812\cdot10^{-2}$
$SiCl_2$	$1.345\cdot10^{-3}$	$5.736\cdot10^{-3}$	$1.394\cdot10^{-3}$	$5.780\cdot10^{-3}$
$SiCl_3$	$3.515\cdot10^{-6}$	$9.853\cdot10^{-7}$	$3.534\cdot10^{-6}$	$9.570\cdot10^{-7}$
$SiCl_4$	$1.058\cdot10^{-8}$	$1.851\cdot10^{-10}$	$1.033\cdot10^{-8}$	$1.820\cdot10^{-10}$
Na	$3.302\cdot10^{-3}$	$4.797\cdot10^{-2}$	$3.402\cdot10^{-3}$	$4.968\cdot10^{-2}$
NaCl	$9.967\cdot10^{-1}$	$9.520\cdot10^{-1}$	$9.966\cdot10^{-1}$	$9.503\cdot10^{-1}$
$T = 1600$ K				
BCl	$2.428\cdot10^{-6}$	$1.102\cdot10^{-4}$	$2.347\cdot10^{-7}$	$1.030\cdot10^{-5}$
BCl_2	$1.864\cdot10^{-6}$	$4.600\cdot10^{-6}$	$1.742\cdot10^{-7}$	$4.184\cdot10^{-7}$
BCl_3	$1.266\cdot10^{-5}$	$1.700\cdot10^{-6}$	$1.145\cdot10^{-6}$	$1.505\cdot10^{-7}$
SiCl	$2.286\cdot10^{-3}$	$1.037\cdot10^{-1}$	$2.432\cdot10^{-3}$	$1.067\cdot10^{-1}$
$SiCl_2$	$2.356\cdot10^{-3}$	$5.816\cdot10^{-3}$	$2.423\cdot10^{-3}$	$5.819\cdot10^{-3}$
$SiCl_3$	$3.814\cdot10^{-6}$	$5.122\cdot10^{-7}$	$3.793\cdot10^{-6}$	$4.986\cdot10^{-7}$
$SiCl_4$	$2.035\cdot10^{-12}$	$4.362\cdot10^{-11}$	$5.741\cdot10^{-9}$	$4.130\cdot10^{-11}$
Na	$7.054\cdot10^{-3}$	$1.155\cdot10^{-1}$	$7.293\cdot10^{-3}$	$1.183\cdot10^{-1}$
NaCl	$9.928\cdot10^{-1}$	$8.845\cdot10^{-1}$	$9.927\cdot10^{-1}$	$8.816\cdot10^{-1}$

These data are expressed in moles, depending on the ratio of the components of powder filling, temperature and pressure. After analysis of these data we concluded that the main products involved in the formation of the diffusion layer through disproportionation reactions are those BCl, BCl_2, SiCl, $SiCl_2$. Gaseous mixture contains boron trichloride in large quantities. It may participate in the etching of the substrate material depending on a temperature and pressure in the reaction zone. For a more complete understanding of the mechanism of vacuum activated diffusion boron silicification we also investigated the interaction of the lower chlorides of boron and silicon with the treated material, for example, graphite. Boron and silicon with carbon forms B_4C and SiC. We conducted a thermodynamic calculation of possible chemical disproportionation reactions, which describe the interaction of the lower chlorides of boron and silicon with carbon. The results of these calculations are presented in tabl. 2.

The data presented in tabl. 2 shows that the conversion reactions rate of borides and silicides is close to one. Based on the composition of the saturating gaseous mixture we established that the preferred is the formation of silicon carbide compared with boron carbide. Also heat-resistant of boron carbide is lower than heat-resistant of silicon carbide. Because of this using of boron as a dopant is preferred than using it as a primary component of

Table 2

The conversion rate of α reactions of the lower chlorides of boron and silicon with carbon at a temperature $T = 1500$ K

Chemical reaction equation	Pressure P, Pa	
	1333	1.33
$BCl(g) + (1/6)C(s) \leftrightarrows (1/6)B_4C(s) + (1/3)BCl_3(g)$	0.995	0.388
$BCl_2(g) + (1/12)C(s) \leftrightarrows (1/12)B_4C(s) + (2/3)BCl_3(g)$	0.999	0.99
$SiCl(g) + (3/4)C(s) \leftrightarrows (3/4)SiC(s) + (1/4)SiCl_4(g)$	0.999	0.986
$SiCl_2(g) + (1/2)C(s) \leftrightarrows (1/2)SiC(s) + (1/2)SiCl_4(g)$	0.80	0.012

the protective coating. Therefore, the process of boron silicification of carbon must be carried out in appropriate conditions. Based on tabl. 1 we can see that the equilibrium partial pressure of the lower chlorides of boron is about three orders of magnitude lower than the corresponding value for the silicon chloride. And the concentration of boron in the resulting diffusion layer is much smaller than silicon. This should facilitate to boron carbide doping of heat-resistant diffusion coating based on silicon carbide. Below, on fig. 1, a microstructure of boron silicificated graphite is shown.

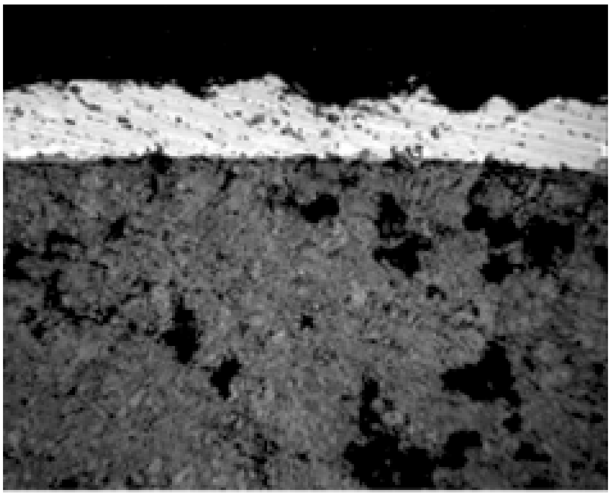

Fig. 1. The microstructure of graphite with coating after vacuum activated boron silicification at a temperature $T = 1280$ °C during 7 hours (×400).

CONCLUSIONS

1. We carried out calculation of gaseous medium for the process of vacuum diffusion boron silicification in vapours of sodium chloride for the temperature $T = 1500$ K and pressure of 1.33 Pa and 1333 Pa.
2. We found that the main components of the gaseous saturation medium in the process of vacuum boron silicification are lower chlorides of boron and silicon. These chlorides are a cause of the diffusion layer formation.
3. We defined the chemical reaction conversion degree of boron carbide and silicon carbide formation during diffusion boron silicification of graphite surface.

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