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INCREASE OF HEAT-RESISTANCE OF TUNGSTEN BY SILICONIZING AND BORATING

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For the increase of fire resistance of tungsten at high temperatures three types of coverage's are investigated: boron, silicon as well as «boron-silicon». Kinetics of borating and siliconizing of tungsten in salt environments is studied; it is shown possibility of receipt of two-component coverage's on tungsten by the successive causing of boron and sili-con. The got coverages are tested on heat resistance at a temperature 1373, 1473 and 1773 K.

Keywords: siliconising, boriding, tungsten, heat resistance, melts

Introduction. For a modern technique large interest presents the increase of heat-resistence of refractory metals and expansion due to it their application. Most in detail in literature the galvanic, diffusive and mechanical (evaporation, cladding) methods of overcoating on a molybdenum and niobium are described, quite small works are sacred to defense of tungsten. The analysis of literary data showed perspective of no-current method of diffusive satiation of tungsten by silicon, boron and boron-silicon in molten salt environments [1-3].

The mechanism of receipt of diffusive coverages in ionic fusions is conditioned by the presence of natural difference of potentials: an electronegative metal will be discharge on an electropositive metal with formation of superficial alloy, if it is possible in the set conditions on the diagram of the state [2].

Analysis of publications. The phenomenon of transfer of boron in ionic fusions (liquid-phase borating) was initially applied for different steels, and then was widespread and on other metals and alloys. The row of monographs and publications is sacred to this process [4-10]. Also there are a number of variants of fusions compositions and boron containing powders and working temperatures of electrolytes for passing of the liquid-phase borating. In basis of transfer of boron on metals in ionic fusions lie the same electrochemical reactions [2]:

- generation in fusion of ions of more subzero degree for oxidization in obedience to a reaction

$$B + 2B(\mathrm{III}) \Leftrightarrow 3B(\mathrm{III})\ ; \qquad (1)$$

- their subsequent disproportionation on the surface of metal with the increase of energy due to formation of borides:

$$3yB(II)+xMe \Leftrightarrow 2eB(III)+Me_xB_y\ . \tag{2}$$

In work [2] there is reported about establishment of isothermal process of transfer of boron in ion-electronic fusion *Li-LiCl*, in which solute lithium dissociates on cations and delocalized electrons:

$$Li_{\text{расп.}} \Leftrightarrow Li^{b^+} + be\ . \tag{3}$$

In opinion of authors, the borides of lithium can have a covalently arctic type of chemical connection which is close to ion, and in fusion of *LiCl*, which contents several quantity delocalized electrons, can dissociate on cations of lithium and anions of boron of hypothetical connection B_m^-. Last anions can serve as mediators from the clean boron or higher borides of lithium to the particles of metal with generation thermodynamics of more resistant borides of refractory metals by a diffusive way. Chart of process of synthesis for borides of titan, zirconium, niobium and tantalum with the use of ion-electronic fusion presented on a fig. 1.

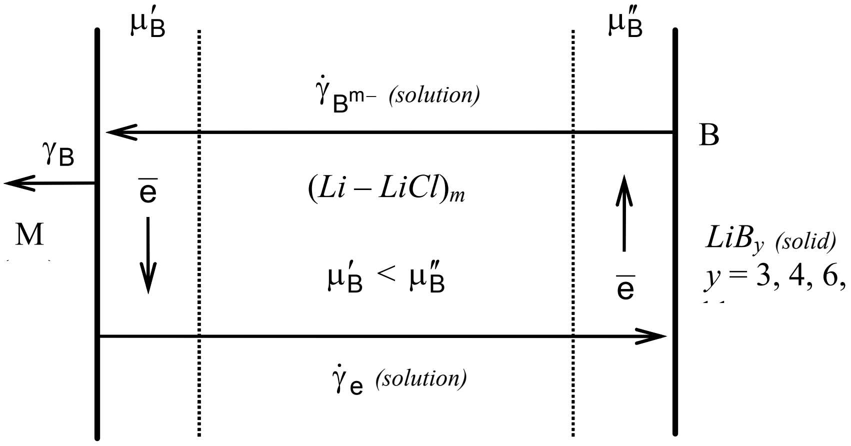


Figure 1 - Hypothetical chart of transfer of boron through ion-electronic fusion

Reactions on the border of hard and liquid phases can be written as follows:

- on a right side

$$2\ B\ ({}_{from}\ LiB_{y(solid)}) + 2\ me \rightarrow 2B^-_{(melt)}; \tag{4}$$

- on the left side

$$2B^{m-}_{(melt)} + Me_{solid} \rightarrow MeB_2 + 2me; \tag{5}$$

- a total reaction

$$Me_{solid} + 2B({}_{from}\ LiB_{y(solid)}) \rightarrow MeB_{2\ (solid)}. \tag{6}$$

The reaction of synthesis flows until all boron will not pass to the refractory boride. X-rayphasic analysis of products of synthesis of borides at a temperature 1173 K and durations of process of 10.0 hour are shown by the presence of phases TiB_2, ZrB_2, NbB_2 i TaB_2. For the receipt of monophase powders it is necessary to use more thin powders of metals.

The results of researches of no-electrolys siliconizing of steels in ionic fusions are generalized in a work [10]. Transfer of silicon on steel, that observed in fusions *KCl-NaCl-NaF*, *KCl-NaCl-Na*$_2$*SiF*$_6$ and *KCl-NaCl-NaF-Na*$_2$*SiF*$_6$ at a temperature

1173-1273 K in the atmosphere of air, conditioned by bringing in fusions of oxide of silicon (on the surface of powder-like ferrosilicon). As a result of partial solubility last oxychloride-oins appear and possibility of transfer appears on the mechanism of short-circuited element. Confirmation serves it dependence of thickness layer of coverage on the concentration of powder in fusion and stopping of process of transfer in default of contact steel and ferrosilicon.

In works [9,11] there are brought results over of siliconizing of steels in fusions of $NaCl\text{-}BaCl_2$ with addition 1520 % (mass) powder of ferrosilicon. The analysis of their processes in works such bath possibility to offer next gives possible chemical and electrochemical reactions in the system $Fe_{solid} \,|\, MCl_{melt} \,|\, Si_{solid}$. Iron in cleanly chloride fusions is more electronegative, than silicon, and in accordance with the theory of no-current transfer it must be carried on silicon.

The results of researches on the transfer of silicon on metals in ionic fusions are generalized in work [2]. Based on the worked out factorization of no-current transfer of metals in ionic fusions, authors investigated the transfer of silicon on the niobium alloy of BH-2 in fusions KCl - $NaCl$, KCl - $NaCl$ - NaF, KCl - $NaCl$ - Na_2SiF_6 and KCl - $NaCl$ - NaF - Na_2SiF_6 in the atmosphere of argon. In cleanly chloride fusion Cl - $NaCl$, in default of air, siliconising of alloy does not take place. Authors explain by insignificant corrosion of silicon at absence of another oxidants, possibly by the sublimation of product of corrosion as a tetrachloride of silicon and its insignificant solubility in fusion. Addition of fluoride of sodium in fusion KCl - $NaCl$ assists binding of silicon in got in fusion fluoride complexes. This is creating conditions for formation of silicon ions of more subzero degree for oxidization in obedience to a reaction:

$$Si_{solid} + Si^{4+}_{melt} \Leftrightarrow 2Si^{2+}_{melt} \;. \tag{7}$$

Accordingly there is appears possibility of disproportionation of silicon ions on metals with formation of sillicides:

$$2Si^{2+} + Me \Rightarrow MeSi + Si^{4+} \;. \tag{8}$$

According to results metallography and X-ray structute analyses, diffusive sillicide coverages fully consist of disillicides niobium, molybdenum and tungsten.

On the effect of solubility of SiO_2 in fusions of the alkaline-landed metals the method of siliconizing of such electronegative metals, as titan and zirconium, is founded. Peoducts of reaction of the mutual expulsing are coverages from disillicides metals.

Authors of work [11] are researched different fusions lead for no-current siliconizing of steels: fusions on the basis of silicates had composition of Na_2SiO_3-$NaCl(BaCl_2)$ and contained powders of carbide of silicon or silicocalcium, fusions on the basis of fluorides of alkaline metals with additions of SiC and SiO_2 and fusions on the basis of chlorides and carbonates of alkaline metals with addition of silicocontaining matter. In all indicated fusions a transfer of silicon on iron, cobalt, nickel, copper, molybdenum, tungsten, niobium, tantalum and platinoids executed on the chart of no-current transfer.

The method of siliconizing of such electronegative metals, as titan and zirconium, is offered in work [11]. In powdery mixture of Al - SiO_2 enter fluoride of sodium. In fact the aluminothermic process of siliconizing takes place without formation of liquid phase. In the same work there are also executed siliconizing of titanic alloys of BT-1 and BT-4 in fusion $NaCl$-$BaCl_2$-$CaSi$.

Problem formulation. Coming from perspective of no-current method of diffusive coverage of tungsten by silicon, boron and boron-silicon the problem of improvement of electrolytes and conditions of realization of corresponding processes was set. Therefore, the purpose of work was a study of kinetics of siliconizing and borating of tungsten in molte*n* environments and implementation of tests of the got coverages on heat-resistance.

Methods of experiment. For research there are used the hot-pressed sintered tungsten of cleanness 99.9 %. Samples of tungsten are borated in the electrolyte of composition (mass, %): $Na_2B_4O_7$ - 75, $NaCl$ - 15, B (amorphous) - 10. Them sampes siliconized in an electrolyte (masc, %): equmole mixture of KCl and $NaCl$ - 60, NaF and Na_2SiF_6 - on 17.7, silicon – 16.6.

Kinetics of coating of coverages was studied on overweight of sampleds and on change of depth layer. Phase composition of coverages was investigated by metallography [12] and x-ray-structure [13] methods, and also by partial layerwise chemical and spectral analysis. The microhardness of coverages was measured on the device ПМТ-3 [14] at loading 100. The structures of borating and boron-silliconizing tungsten stainsed in mixture 40 % HF + 40 % alcohol + 20 % H_2O, structure of silliconizing tungsten - in mixture of HNO_3 and HF (in correlation 1: 1).

Results and their discussion.

Borating of tungsten. Kinetics of borating of tungsten was studied at a temperature 1223, 1273 and 1323 K during 0.5-7.0 hours. Satiation was executed in the atmosphere of air. Parabolic dependence of height of coverage layer for all investigated temperatures is set inn time that testifies to existence of the limiting stage of diffusion in a hard phase. The constant of speed of borating in molten salt environments is related to the temperature by equation:

$$K = 9{,}16 \cdot 10^{-6} \cdot \exp\left(-\frac{41500}{R \cdot T}\right). \tag{9}$$

The offered composition of electrolyte kinetically is more advantageous, than compositions with the carbide of boron or powdery amorphous boron, described in literature [15,16].

At duration of self-control no more than 1.0 hours holeyer coverage of composition (appears on the surface of tungsten α-WB in thick 25-30.0 mcm with a microhardness 32-34.0 GPa. A microhardness of tungsten was 4.6-4.8 GPa. With the increase of duration of borating to 6.0 hours at a temperature 1323 K the duplex coating appears in thick 120.0 mcm and at a temperature 1273 K is coverage in thick 90.0 mcm, consisting of external boride of W_2B_5 with a microhardness 23-25.0 GPa and internal boride α-WB with a microhardness 31-33.0 GPa. The thickness of both layers increases with the increase of duration of self-control, thus internal layer α-WB grows quicker, than external lay. The phases of similar composition, at analogical temperatures, discovered in coverages and at the electrolytic synthesis of borides of tungsten [17].

Coverage of composition α-WB was tested on heat-resistant at a temperature 1373 and 1473 K. Destruction of protective layer was looked after through 1.5 hours.

Siliconising of tungsten. Kinetics of siliconizing of tungsten in molten salts was studied at a temperature 1073, 1123 and 1223 K at 2-12 hours in the atmosphere of argon. It is set that the height of coverage also submits to the parabolic law. Temperature dependence for speed of process is expressed by equation:

$$K = 1{,}10 \cdot 10^{-6} \cdot \exp\left(-\frac{6141500}{R \cdot T}\right). \tag{10}$$

Speeds of siliconizing of tungsten in molten salts and in powders are near on a size. One-layer coverage, consisting of disilicide tungsten (WSi_2) with a microhardness 13-15.0 GPa, appears on the surface of tungsten.

At a temperature 1223 K and durations of silicification of 12.,0 hours a layer was got in thick 35.0 mcm. Test of this coverage at a temperature 1373 K showed the increase of heat-resistant to 60-140.0 hours, at a temperature 1723 K - to 2.0 hours. Phases of similar composition, at analogical temperatures, are discovered in coverages and at the electrolytic synthesis of sillicides of tungsten [18]. Protective properties of WSi_2 are related to formation of glassy tape from α-SiO_2 on its surface, that marked by us and previously [19].

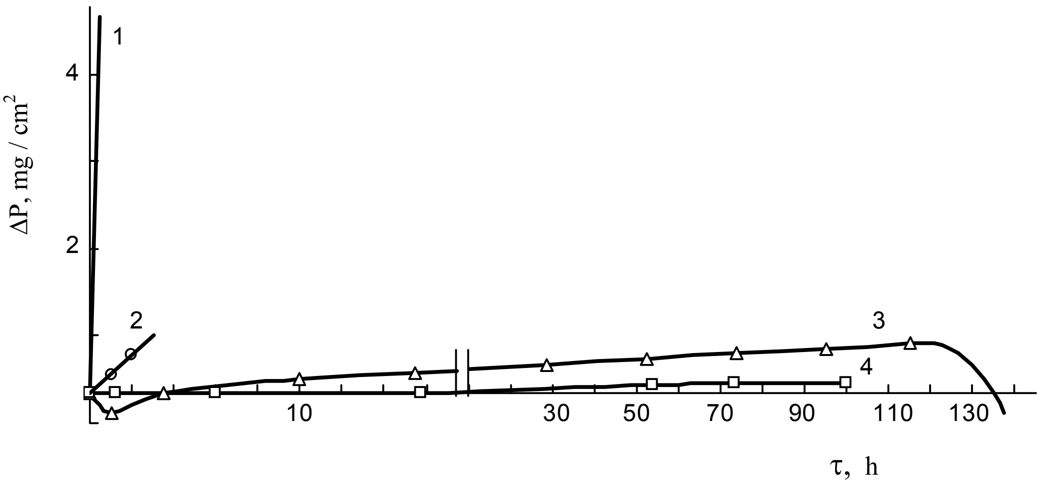
Boron-silicinizing of tungsten. With the purpose of increase of superficial hardness and erosive firmness of heat-resistant phase of WSi_2 the successive diffusive satiation of tungsten by boron and silicon was tested.

Two variants are studied. In first case samples of tungsten are siliconized at a temperature 1223 K during 12.0 hours (thickness of coverage – 35.0 mcm), and then there are borated at a temperature 1323 K during 1.0 hours. Tungsten disilicide practically fully disappears on the surface of samples, the boride of tungsten appears in thick to 65.0 mcm. Heat-resistance of such coverage did not exceed 4-6.0 hours at a temperature 1323 K.

In second case the samples of tungsten are borated during 1.0 housr at a temperature 1273 K (thickness of coverage – 45.0 mcm) or during 2-3 hours at a temperature 1323 K (thickness of coverage – 70-90.0 mcm), and then siliconizing 10,0 hours at a temperature 1223 K. Got coverage consisted of two layers: external - WSi_2 with content of 1.5-1.7 mass % boron and tracks of phase of $W_5(SiB)_3$, and internal - borides α-WB and W_2B.

Phase composition of the got boron-siliconizing coverage showed primary diffusion of the boron to basis. Heat-resistance of its at a temperature 1473 K 35-1170.,0 hours made, and at a temperature 1773 K - to 2.0-2.5 hours. After oxidization on the surface of coverage found out the glassy oxide of tridymite α-SiO_2 with tracks of WO_3 and B_2O_3. Coverage consists of WSi_2 and tracks of $W_5(SiB)_3$ and W_2B.

At the study of kinetics of oxidization (fig. 2) of boron-siliconizing tungsten in the first hours of test at a temperature 1473 K there is a decrease of mass of samples, and then through 3.0-4.0 hours is over weight of its mass. Probably, it can be explained by high speed of evaporation of appearing oxides WO_3 and, partly B_2O_3 to stabilizing of protective tape from SiO_2 at the investigated temperatures.



1 - *B*, 1373 K; 2 - *B+Si*, 1773 K; 3 - *B+Si*, 1473 K; 4 - *Si*, 1375 K

Figure 2 - Kinetics of oxidization for tungsten with coverages:

Decrease of mass for samples at a test on heat-resistance for sillicide coverages at a temperature 1373 K and boron-silliconizing coverages at a temperature 1773 K did not look after.

Conclusions.

1. The constants of speed of borating and siliconizing in molten salt environments are certain depending on the temperature of fusion.
2. The conditions of receipt of one- and double-base boride and sillicide coverages are studied.
3. Possibility of receipt of double-base coverages on a tungsten by the successive borating and siliconizing is shown.

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