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About the mechanism of titanium diboride formation in the conditions of plasma flow

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Abstract. The analysis of technological results of titanium diboride production is provided, that indicates the uniqueness of the mechanism of boride formation for all methods of production depending on the composition and size of the charge materials, reaction conditions, etc. To formulate the ideas about the mechanism of boride formation processes, occurring during plasma treatment of titanium-boron-containing raw materials, the temperature dependence on the composition of gaseous and solid products, the composition of gaseous compounds thermally desorbed from the titanium diboride surface and the nanoparticles morphology were studied. Analysis of the results suggests a possible mechanism for the titanium diboride formation according to “vapour – melt – crystal” scheme, which includes the condensation of titanium vapour as aerosol, boronizing the nano-drops of the melt with borohydrides and crystallization of the titanium-boron melt. A generalized hypothetical scheme of boride formation containing 2 zones is developed: a high temperature zone (5400-3500 K) with formation of the reaction mixture in which processes of evaporation of a powdered titanium-boron-containing charge and “gasification” of boron into borohydrides occur, and a lower-temperature zone (3500-2000 K), in which the condensation of titanium vapour, a significant decrease in the concentration of borohydrides and the formation of titanium diboride take place.

1. Introduction

Modern metallurgy provides the world economic system with a variety of metal products for both mass and special purposes. According to the World Steel Association, in the structure of consumption of metal products 94% – ferroalloys, 5% – non-ferrous alloys, 1% is a diverse group of metal-containing materials with a specific set of properties.

This group includes titanium diboride TiB_2 studied and commercialized by the scientific school of the famous Russian material scientist Samsonov G.V. more than 50 years ago, and which is still in demand in the technology of various materials: ceramic-metal material tool and structural, refractory and abrasive, sprayed and fused materials, for modification and wetted by metal coatings [1-6]. At the same time, interest to application of titanium diboride is constantly growing: over the last 10 years, more than 115 papers have been published in the journals indexed in Scopus and Web of Science databases. They contain technological information on its production and use reflecting the transition trend from the application of coarse-grained titanium diboride to micro- and nanocrystalline one, which is due to the desire of scientists and technologists-practitioners to achieve a qualitatively new level of operational properties of materials and coatings on its basis.

The basis of modern production of titanium diboride is carbothermic, magnesium-thermal and gas-phase methods. Russian producers offer titanium diborides by the magnesium-thermal method of



production. The strategically important nanocrystalline segment of the market is completely covered by foreign suppliers, including such companies as American Elements, Nanostructured & Amorphous Materials, Inc., PlasmaChem GmbH, NEOMAT Co. This necessitates the development of Russian nanotechnology of titanium diboride.

In connection with this, research and technological realization of boride formation processes in plasmametallurgical processing of titanium-boron-containing raw materials is an important scientific and practical task, which is of great importance for the development of domestic metallurgy of titanium and its multifunctional alloys, as well as the effective solution of innovative problems in applied materials science.

2. Purpose, hypotheses, methodology

The purpose of this work is to study the processes of boride formation in the treatment of titanium-boron-containing raw materials in the conditions of plasma flow, to describe the probable mechanism of their flow and to determine the possibility of technological control over the impurities content accompanying titanium diboride, including free boron.

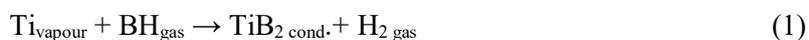
A three-jet plasma-metallurgical reactor was used to experimentally study the processes of boride formation. Thermotechnical, resource and technological characteristics of the reactor are described in [7-9]. The plasma flow is generated using three EDP-104AM DC electric arc heaters (plasmatrons) with a power up to 50 kW each, installed in the mixing chamber at angle of 30° to the reactor axis. To supply the reactor with highly disperse raw materials and gaseous hydrocarbon, a water-cooled tuyere is used. To reduce the radial gradient temperature in the near-wall zone, the reactor channel is lined from the inside by a high-temperature thermal insulation material – cylindrical inserts of zirconium dioxide with an internal diameter of 0.054 m.

Titanium powders of PTN-8 grade (option 1), titanium dioxide of R-1 (option 2), boron of grade B-99 were used as titanium and boron-containing components of the charge. The powders have a size range and are characterized by the following distribution by fractions: titanium 0.5 – 4 μm and + 0.5 – 2 μm - 48.2%, +2 – 4 μm - 51.8%, dioxide 0.2 – 1.0 μm and + 0.2 – 0.5 μm, – 48.7%, + 0.5 – 1.0 μm, - 51.3%, boron 0.05 – 0.25 μm and + 0.05 – 0.125 μm – 53.2%, + 0.125 – 0.25 μm - 46.8%. Technical nitrogen was used as a plasma-forming and transporting gas (GOST 9293-84, rev.), natural gas with a methane content of up to 93.6% vol. – as a reducing agent, hydrogen – as a technological additive (GOST 3022-80, rev.).

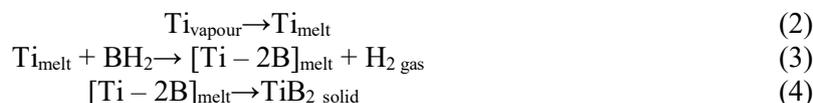
During the production of TiB₂ in the conditions of plasma flows, the possibilities of studying the process of boride formation are even more limited which is due to the following reasons: 1) extremely high temperatures: the average mass temperature is 2800÷5400 K; 2) high movement speeds of turbulent reaction chemically active mixture – (40÷60 m/s); 3) short-term process, estimated at 15 ms; 4) extremely limited volume of the reaction zone, 0.0001 m³; 5) the practical inaccessibility of the reaction zone for probe diagnostics due to the significant disturbing effect of a water-cooled probe technically designed with an external diameter not less than 0.6·10⁻² m; 6) complex composition of the gas phase, to be determined only after quenching, and possibly changing at the same time; 7) insuperable task with determining the content of unstable borohydrides in the gas phase. At the same time, the study of the mechanism of boride formation, alongside with the theoretical problem, is of great practical importance, since it makes possible to establish the possibility for controlling the impurities content, including the content of free boron.

The results of thermodynamic modeling of the processes of boride formation, described in [10-12], make it possible to put forward two scientific hypotheses concerning the TiB₂ formation in the conditions of charge plasma treatment:

- during interaction in the gas phase according to the “vapour – crystal” scheme



- during interaction of titanium-containing metallic aerosol with gaseous borohydrides according to the “vapour – melt – crystal” scheme



To confirm hypothetical representations, accumulate and analyse the necessary scientific information, the following studies were carried out:

1) The temperature dependence of the composition of gaseous and solid products of charge treatment was studied. For this purpose the process was carried out in the reactor of various lengths – from 6 to 24 calibers, which made it possible to change the quenching temperature of products from 4000 to 2000 K and to carry it out during the gas outflow from the reactor to the precipitation chamber at a rate 104-105 degrees/s. The nanoproducs deposited on the water-cooled surface of the precipitation chamber were analyzed to determine the phase and chemical compositions. At each tempering temperature, samples of the gas-powder mixture were also sampled using a probe. For these purposes a steel intensively cooled probe was used (water flow 0.050 kg/s), made in the form of a tube with an internal diameter 0.003 m and a length 0.5 m, sequentially connected to a filter, a glass container with an absorber (ethyl alcohol), a pipette, a flowmeter and vacuum pump KVN-8, creating vacuum up to 20 kPa. The probe was installed at a distance 1 caliber from the gas flow inlet into the precipitation chamber orthogonally to the flow in such a way that its gas inlet hole coincided with the axis of the reactor. The filter was made of two cones with their bases in contact, separated by filtering baffle from twill-woven gauze made of steel grade C-120 and ensured the separation of powders from the sample, protecting them from contact with the air atmosphere. The container with an absorber made it possible to capture boron-containing compounds. The sample of the dust-free gas stream was collected into a pipette. The composition of the gas phase was determined chromatographically (see figure 1). The curves H_2^* and BH_2^* correspond to a 1.5-fold excess of boron.

2) The composition of thermal desorption products of samples sampled during probing (see table 1) was studied by mass spectrometric analysis.

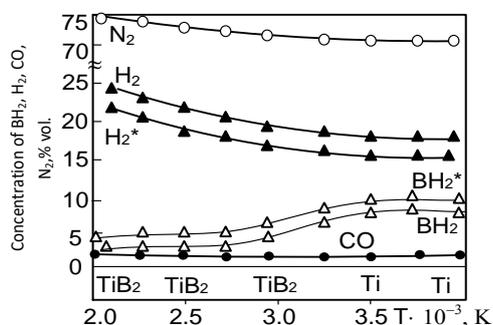
3) The morphology of TiB_2 nanoparticles was studied by scanning electron microscopy (see figure 2).

3. Results and discussion

The analysis of the obtained results confirms the presence of gaseous boron-containing compounds in the nitrogen-hydrogen flow. In the mass spectra of products of vacuum thermal desorption, there are components with molecular weights of 12,13, presumably corresponding to BH and BH_2 . Comparison of the temperature dependence of the concentrations of BH and BH_2^* calculated from the experimental content in the gaseous boron phase and the change in the phase composition of the trapped powder products confirm the unconditional participation of gaseous boron compounds in boride formation. At the same time, the study of the shape and size of TiB_2 particles, obtained in the form of a nanopowder with spherical particles, unambiguously indicates their formation by the “vapour – melt – crystal” mechanism.

Zone 1 corresponds to the temperature range of 5400-3500 K. Processes of heat- and mass transfer and the formation of a reaction mixture of the given composition take place there. Zone 2 corresponds to the temperature interval of 3500-2000 K. A characteristic feature of the zone is a significant decrease in the concentration of boron hydrogen BH_2 in the gas flow, corresponding to the appearance of TiB_2 in products. Thus, we can conclude that the formation of TiB_2 is possible during the crystallization of the melt titanium – boron – product of the boronizing by borohydrides of a metallic aerosol formed in the flow with volumetric condensation of titanium vapour. The nature of the change in the concentration of BH_2 alongside with the temperature at 1.5 times excess boron in the charge confirms its stability within the temperature range and indicates a real possibility of limiting the free

boron content in titanium diboride. The boride nanoparticles formed in the zone under consideration actively adsorb process gases and gaseous products of boride formation.



$\bar{a} \pm \Delta a$	Temperature, K			
	2000	3000	3500	4000
H ₂	23.12±0.94	19.31±0.82	18.72±0.71	18.11±0.73
BH ₂	0.82±0.06	3.62±0.10	7.00±0.39	7.31±0.42
H ₂ *	21.05±	17.62±0.53	16.05±0.50	18.25±0.44
BH ₂ *	3.37±0.10	6.54±0.28	9.12±0.49	10.21±0.63
N ₂	74.35±1.23	74.00±1.36	73.65±1.21	73.51±1.44
CO	0.98±0.04	1.00±0.05	1.14±0.04	1.11±0.05

Figure 1. Temperature dependence of the composition of gaseous products and phase composition of solid products of titanium-boron interaction in the nitrogen plasma flow ($\bar{a} \pm \Delta a$ – average arithmetic values and confidence intervals of concentrations).

Table 1. Composition and quantities of vacuum thermal desorption products of TiB₂ samples, non-contacting with the atmosphere.

Characteristic	TiB ₂ (1)	TiB ₂ (2)
Chemical composition, %		
TiB ₂	96.26	93.27
B _{free}	1.05	0.45
Ti _{free}	1.13	-
C	-	1.22
O	0.44	-
N	1.12	1.24
TiO ₂	-	3.82
Specific surface, m ² /kg	45000	37000
Particle ^a size, nm	37	45
Molecular masses of desorption products	2.12-13, 26-28, 32-36	2.12-12, 14- 16, 26-28, 32-36
The expected composition of the desorption products	H ₂ , BH, BH ₂ , N ₂ , CO, O ₂	H ₂ , BH, BH ₂ , CH ₃ , CH ₂ , N ₂ , CO, O ₂
Number of desorbed gaseous products	1.24	1.36

^aThe size was calculated from the specific surface area

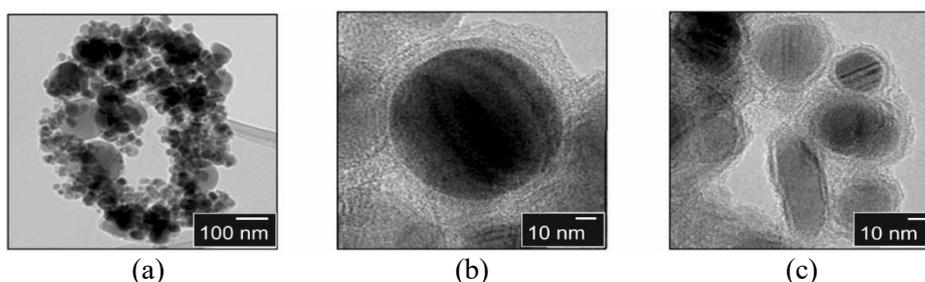


Figure 2. Micrographs of nanocrystalline titanium diboride TiB₂ (1) (a – particles and aggregates; b – morphological pattern of the aggregate, c – single particles).

The obtained results and their discussion make it possible to describe the process of boride formation in the form of the following scheme, which includes the two main temperature-space zones, presented in figure 3.

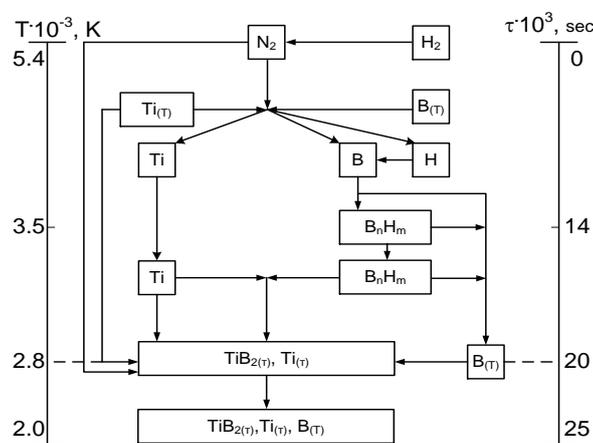


Figure 3. The proposed scheme for the interaction of titanium with boron in a flow of nitrogen-hydrogen plasma.

4. Conclusion

The process of boride formation with TiB_2 production in the conditions of plasma treatment of charge is characterized by features that substantially distinguish it from traditional technological options. The formation of TiB_2 is possible during crystallization of the melt titanium – boron – product of boronizing by the borohydrides of a metallic aerosol formed in the flow during volumetric condensation of titanium vapour. Alongside with the mechanism under discussion other reaction systems, that have not been identified by available means of diagnostics yet, are possible but typical for high-temperature non-ideal chemical-metallurgical reactors.

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