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Air oxidation of titanium nanodiboride

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Abstract. The oxidation and thermal-oxidative stability of titanium diboride are studied during its storage and heating in the air. It was established that during the first 24 hours titanium diboride actively adsorbs oxygen and moisture: the oxidation of TiB_2 (1) reaches $11.06 \cdot 10^{-7}$, TiB_2 (2) $-8.15 \cdot 10^{-7}$, TiB_2 (3) $-31.5 \cdot 10^{-7}$ kg O_2/m^2 . Analytical dependencies were obtained for the calculation of oxidation. When heated in the air, titanium diboride nanocrystals are oxidized in the temperature range $(623 - 673) \pm 15$ K, microcrystals at a temperature of 688 ± 5 K and higher.

1. Introduction

Nanomaterials, as a rule, have high chemical activity due to the following features of their crystal structure and energy state [1-4]:

1) The small size of the grains determines the greater development and the length of grain boundaries: at a grain size from 100 to 10 nm, the boundaries contain from 10 to 50% of atoms of nanocrystalline solid.

2) Grains in the nanostate have various atomic defects: vacancies, their complexes, dislocations, the quantity and distribution of which are qualitatively different than in the large grains of 5-10 μm and of greater sizes.

3) Exceptionally high diffusion mobility of atoms along the grain boundaries of a nanocrystalline solid, 105 to 106 times higher than in the ordinary polycrystals.

4) The excited state in the nanograins of atomic layers near their surfaces, which makes the crystals shrink and the atoms in them deviate from the position corresponding to the equilibrium state.

5) The constant propensity of nanosystems to the excess energy relaxation.

Taken together, this leads to the manifestation of nanoscale effects in such properties as propensity to aggregate, active interaction with atmospheric and process gases, increased solubility in liquid media, diffusion mobility in matrices of composite materials, ability to solid-state coalescence and sintering, etc. The specific physical and chemical properties of nanomaterials make it necessary to carry out their comprehensive study with mandatory determination of characteristics that are practically significant for their further application, determination of competitive advantages and real cost. During the last 15 years a significant number of works were published, containing the results of study on the properties of nanopowders of metals, carbides, borides, and their compositions, in particular [5-8]. Their analysis in general confirms the specifics of the properties of nanocrystalline substances and the need to take them into account in the subsequent technological processes with their participation. However, for each substance in the nano-state its temperature-time conditions for the appearance of size effects and specific level values are characteristic, which allows the results in each case to be viewed as new information of scientific and applied importance.



Taking into account the properties of nanocrystalline materials offered to consumers, since 2000 the range of certification characteristics of powdered nanoproducts has been expanded. Alongside with the traditional characteristics (the phase and chemical compositions, the specific surface) the oxidation and the temperature of the beginning of oxidation are added.

2. Purpose and research methodology

The purpose of this work is to study the oxidation and thermal-oxidative stability of titanium diboride of nano- and microscale level of dispersity in the air environment and comparative analysis of the results.

Oxidation is determined by the amount of oxygen (kg) per 1 m² of powder surface. Determination of the specific surface area of titanium diboride was carried out on the TRISTAR 3020 analyzer and is based on the method of low-temperature nitrogen adsorption.

The temperature of the beginning of oxidation corresponds to the change in the mass of nanopowder by 1% when heated in the air. As the characteristic of thermal-oxidative stability, the most probable temperature interval in which the oxidation of the nanopowder begins when heated in the air can also be taken into account. Oxidation of titanium diboride powders in the air was studied by thermogravimetric analysis and high-temperature X-ray diffraction using the Setaram LabSys Evo thermal gravimetric analyzer and DRON-3 X-ray diffraction meter with the GPVT-1500 add-on unit.

Titanium diboride nanotubes not contacted with the air and obtained by plasmasynthesis from the charge Ti+B (TiB₂ (1)) TiO₂+B (TiB₂ (2)) as well as its micropowder produced by magnesium thermal method (TiB₂ (3)), were used as objects of research. Phase and chemical compositions, specific surface area, initial oxidation of the samples are given in table 1.

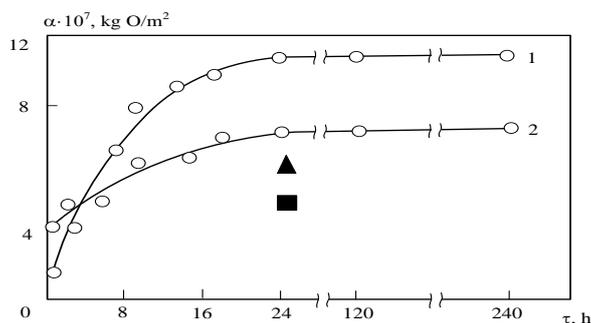
Table 1. Characteristics of test samples of titanium diboride

Characteristics	TiB ₂ (1)	TiB ₂ (2)	TiB ₂ (3)
Phase composition	TiB ₂	TiB ₂	TiB ₂
Chemical composition, %			
TiB ₂	96.32	93.61	97.24
free boron	1.00	0.42	0.42
titanium free	1.15	-	-
titanium dioxide	-	3.84	-
carbon	-	1.12	-
magnesium	-	-	0.41
oxygen	0.61	1.54	0.82
nitrogen	0.92	1.01	0.41
Specific surface, m ² /kg	43000	38000	2600
The particle size range, μm	0.01-0.06	0.02-0.08	<5
Oxidation x10 ⁷ , kg O ₂ /m ²	1.42	4.05	31.5

3. Results and discussion

3.1. Determination of oxidation

The oxidation of titanium diboride samples contacting with air during 240 hours is shown in figure 1. During the first 2 days, the oxygen content in the samples was monitored every 4 hours, on the following day – every 12 hours.



(1): $(1.42 \div 11.06) \pm (0.02 \div 0.18)$; (2): $(4.05 \div 8.0) \pm (0.06 \div 0.016)$

Figure 1. Change in oxidation (α) of titanium diboride samples when contacting with air (▲, ■ – oxidation of samples 1 and 2, thermally desorbed in vacuum after storage in the air for 24 hours).

The analysis of the obtained results makes it possible to single out the following four scientific aspects for discussion:

1) The significant increase in oxidation occurs during the first 20-24 hours. In the subsequent period of time the oxidation practically does not change. At the same time the increase in oxidation is observed for TiB_2 (1) approximately in 8 times (from $1.42 \cdot 10^{-7}$ to $11.06 \cdot 10^{-7}$ kg O_2/m^2), for TiB_2 (2) – ~ in 2 times (from $4.05 \cdot 10^{-7}$ to $8.15 \cdot 10^{-7}$ kg O_2/m^2). The oxides of titanium and boron are not detected in the X-ray patterns of the samples. The increase in oxidation is most likely due to the adsorption of oxygen and water vapor. This fact is confirmed in a number of works devoted to the study of high-temperature nanosized compounds [9-12]. However, the mechanism of sorption – physical adsorption or chemical adsorption – has not yet been studied.

The obtained data made it possible to determine the dependence of the titanium diboride oxidation on the duration of its contact with the air, which is described for TiB_2 (1) by the equation of the form

$$a = [-0.0134\tau^2 + 0.7065\tau + 1.5175] \cdot 10^{-7} \quad (1)$$

for TiB_2 (2) –

$$a = [-0.0044\tau^2 + 0.2672\tau + 4.1023] \cdot 10^{-7} \quad (2)$$

where a – the oxidation, kg of oxygen $\cdot \text{m}^{-2}$;

τ – duration of contact of TiB_2 with air, h.

These dependencies are graphically represented in figure 2.

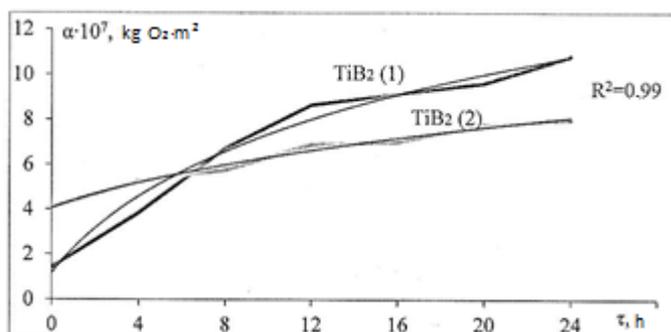


Figure 2. Graphical dependence of oxidation (α) of samples of titanium diboride TiB_2 (1) and TiB_2 (2) when they are in contact with the air (τ – the contact duration of TiB_2 with air ($\tau = 0 \div 24$ h), h, R^2 – the determination coefficient).

2) The sample of TiB_2 (2) is more resistant to the influence of atmospheric oxygen, which is due to its adsorption in the stage of carbon monoxide production having a high passivating power with respect to high-dispersed powders of transition metal and their compounds with carbon, boron and nitrogen. Indeed, the concentration of CO in the gas phase for option 2 is 3.2 – 5%, option 1 – 0.8 – 1.0%.

3) Vacuum annealing of samples (1) and (2) contacted with the air at a temperature of 973 K for desorption of gases ensures removal of only 40 % of oxygen (points ▲ and ■ in figure 1). The remaining amount of oxygen under these temperature conditions apparently participates in the surface oxidation of nanoparticles, with the formation of amorphous oxide films, which is confirmed by the results of determining the temperature of the beginning of samples oxidation described below.

4) The comparison of the oxidation of samples 1, 2, held in the air for 24 hours, and 3 ($11.06 \cdot 10^{-7}$, $8 \cdot 10^{-7}$ and $31.5 \cdot 10^{-7}$ kg O_2/m_2 surface, respectively) confirms that according to this characteristics nanopowders are not only inferior to micropowders, but also exceed them.

3.2. Determination of thermal and oxidative stability.

The oxidation process during heating in the air is usually investigated by two methods: high-temperature X-ray imaging and thermogravimetric analysis. In the first case, the temperature dependence of the intensity of one of the characteristic peaks of the studied material is considered, and therefore no special requirements concerning the content of the main phase and impurities are not imposed on the object of research. However, the method allows only the temperature interval to be stated in which the oxidation process begins. The temperature of the onset of oxidation can be determined much more accurately by thermogravimetric analysis, but with the condition that there is no or minimal content of impurities oxidized in the same temperature range as the main phase. Titanium diboride obtained according to options 1 and 2 is in fact a number of compositions, % $92.55\text{TiB}_2 + 1.05\text{Ti}_{\text{free}} + 1.05\text{B}_{\text{free}}$ (1) and $91.25\text{TiB}_2 + 0.83\text{B}_{\text{free}} + 1.21\text{C}$ (2). In this case, pyrolytic boron and carbon are oxidized in the temperature ranges 550-870 K and 671-790 K, respectively, which creates insurmountable difficulties for the correct thermogravimetric analysis of nanocrystalline TiB_2 (see figure 3).

It should be expected that the oxidation temperature of nanocrystalline TiB_2 can be 30-50° lower than TiB_2 micropowder [13], which oxidation begins at a temperature of 688 ± 5 K. The X-ray thermal characteristics of TiB_2 (1) and TiB_2 (2) nanopowders and TiB_2 micropowder is shown in figure 4. When the samples are heated in the temperature range $(273 - 623) \pm 15$ K, the change in the intensity of peaks is not observed. With further heating of samples TiB_2 (1) and (2) in the temperature range $(623 - 673) \pm 15$ K and heating of TiB_2 micropowder sample of the in the temperature range $(673 - 723) \pm 15$ K there is a significant decrease in the intensity of peaks, observed in the higher temperature range, which indicates the beginning and development of oxidation processes. In the temperature range under study, there are no peaks corresponding to titanium and boron oxides in the X-ray patterns, which suggests their formation in the amorphous state.

4. Conclusion

The oxidation and thermal-oxidative stability of titanium diboride nano- and micropowders in the air were studied. Titanium diboride, when stored in the air, actively adsorbs oxygen and moisture during the first 24 hours: the oxidation of TiB_2 (1) synthesized according to the option (Ti + B) varies within the range $(1.42 - 11.06) \cdot 10^{-7}$ kg O_2/m^2 , TiB_2 (2) synthesized by the variant (TiO₂ + B) – $(4.05 - 8.15) \cdot 10^{-7}$ kg O_2/m^2 and is described by the equations $a(1) = [-0.0134\tau^2 + 0.7065\tau + 1.5175] \cdot 10^7$, $a(2) = [-0.0044\tau^2 + 0.2672\tau + 4.1023] \cdot 10^7$. Comparison of samples oxidation 1, 2, held in the air for 24 hours, and 3 ($11.06 \cdot 10^{-7}$, $8 \cdot 10^{-7}$ and $31.5 \cdot 10^{-7}$ kg O_2/m^2 of the surface, respectively) confirms that in this characteristics the nanocrystalline diboride exceeds the larger microcrystalline diboride.

Titanium diboride thermally desorbs in vacuum at a temperature of 973 K not more than 40% of the oxygen absorbed during its storage, which confirms the adsorption-diffusion mechanism of its interaction with atmospheric gases and the possibility of oxidizing of nanoparticles with the formation

of amorphous oxide layers upon heating. Titanium diboride nanocrystals with heated in the air are oxidized in the temperature range $(623 - 673) \pm 15$ K, which is 66 degrees below the temperature of the beginning of oxidation of its microcrystals 688 ± 5 K. Pyrolytic boron and carbon accompanying diboride are oxidized in the temperature ranges $(550 - 870) \pm 12$ K and $(671 - 790) \pm 17$ K, respectively.

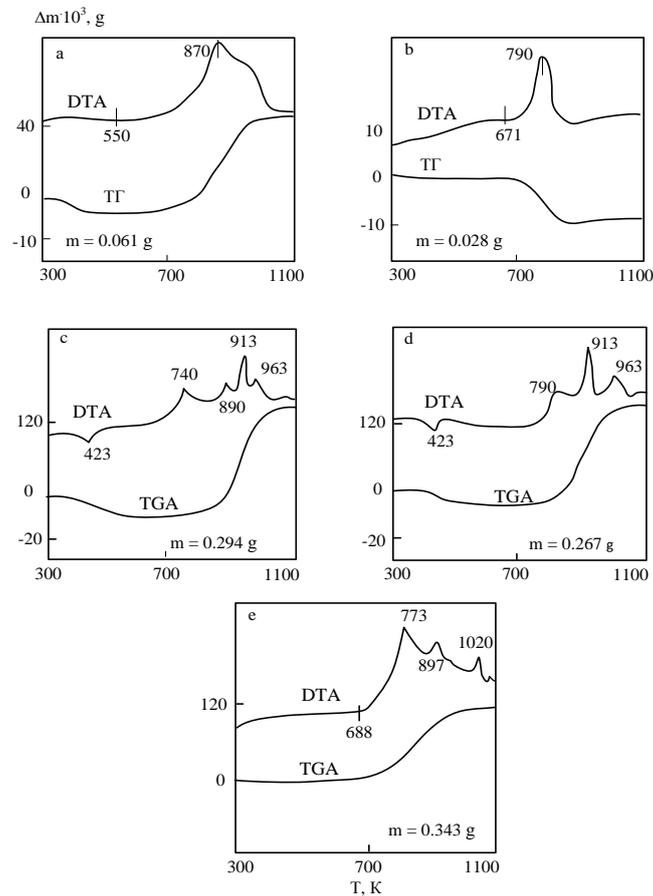


Figure 3. Thermograms of nanopowders with boron (a), carbon (b), titanium diboride (1) (c), (2) (d) and titanium diboride micropowder (e).

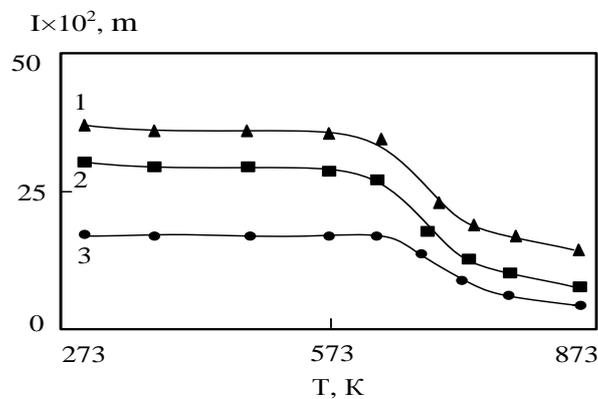


Figure 4. X-ray thermal characteristics of titanium diboride (1 – TiB_2 (1), 2 – TiB_2 (2), 3 – TiB_2 micropowder).

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