

LOW-TEMPERATURE SYNTHESIS OF TITANIUM, NIOBIUM, AND CHROMIUM DIBORIDES

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Titanium, niobium, and chromium diborides have a number of physicochemical and mechanical properties, which enable one to use them both independently and in the composition of hard, wear-resistant, and refractory composite materials.

The aim of the work is to prepare highly disperse TiB_2 , NbB_2 , and CrB_2 powders by the method of mechanochemical synthesis and explain differences in processes of their formation.

As starting materials, we used commercial powders of metals and amorphous B with a purity of 99.8%. Mechanical treatment (MT) was carried out in an AIR-type planetary mill with a centrifugal acceleration of 25g in steel drums and an argon atmosphere. The total treatment time was 5, 10, 15, 30, and 60 min.

The X-ray diffraction analysis data are presented in the table, from which it follows that TiB_2 forms fairly rapidly under mechanosynthesis, namely, within 10 min. For the preparation of monophase NbB_2 powder, a longer time of 15 min is required. A monophase CrB_2 powder was not obtained even after MT for 1 h, and, according to the X-ray diffraction analysis data, the main phase of the MT product is Cr.

A practically monophase CrB_2 powder was obtained only after additional low-temperature heat treatment of the (Cr + B) mixture preliminary mechanoactivated at 1000 °C for 1 h in vacuum, which is lower than the temperature of traditional synthesis by 500 °C. This provided the high dispersity of the synthesized CrB_2 powder, which, according to the electron microscopy data, has a particle size $\geq 1 \mu m$.

The indicated differences in the processes of formation of diborides can be explained from the viewpoint of the donor-acceptor capability of atoms of the metals and B. Boron, having a p^1 unpaired electron on the external electron shell, tends to the formation of stable sp configurations, using for this purpose its own electrons and

electrons of the partner. In diborides, boron forms graphite-like network with a rigid covalent bond between atoms and, in formation of diborides, it is an acceptor of electrons.

The transition metals Ti, Nb, and Cr transfer their valence electrons to form Me–B bond and enhance the B–B bond. The donor capability of the metals decreases in passing from group IV to group VI with increase in the energy stability of d -orbitals as a result of the increase in the number of electron and their main quantum number.

Table

Initial mixture of powders	Time of MT, min	Specific surface area, m^2/g	Phase composition
Ti + 2B	5	4.8	α -Ti
	10	2.7	TiB_2
Ni + 2B	10	2.7	Nb
	15	2.2	NbB_2
Cr + 2B	60	3.1	Cr, CrB_2 (traces)
Cr + 2B*	30	2.2	CrB_2 , Cr_3B_4 (traces)

*specimen after additional vacuum heat treatment at a temperature of 1000 °C for 1 h.

Thus, having 2 electrons on the d shell and tending to the formation of a stable d^0 configuration, Ti transfers them easily to boron, which manifests itself in the high degree of interaction between titanium and boron atoms in the process of mechanochemical synthesis. The preparation of monophase NbB_2 powder requires a longer time of mechanosynthesis for the accumulation of the sufficient mechanical energy of activation, and CrB_2 (chromium has a stable d^5 configuration and, hence, a low donor capability) forms only after additional heat treatment of the preliminarily mechanoactivated initial mixture.