RESEARCH OF HIGH – ENERGY MILLING OF THE TiH_2-BN POWDERS IN NITROGEN

Khobta I.V., Petukhov A.S., Isaeva L.P., Lobunets T.F., Timofeeva I.I.
Frantsevich Institute for Problems of Materials Science of NASU
3 Krzhizhanovsky st., Kyiv, 03680, Ukraine
e-mail: hobta_igor@ipms.kiev.ua

The system TiN+TiB_2 is considered promising for creation of cutting tools with superior mechanical properties, such as hardness, fracture toughness, bend strength and wear resistance [1, 2].

Present study aimed at optimization of high-energy milling process of TiH_2+BN mixtures in nitrogen for reaction-driven consolidation of dense ceramic composite based on TiN and TiB_2.

Two types of titanium hydride TiH_2 and TiH_x were used, which have been reduced by magnesium and obtained by affinage technique, respectivly. They differs by quantity of impurities and crystallography [3]. TiH_2 has face-centered cubic lattice (CaF_2 – type structure), TiH_x - face-centered tetragonal lattice, which indicates that the last one has higher capacity of hydrogen [3].

Table.1 Properties of starting and milled of the powders and the mixtures.

Powder	XRD* results	S, m^2/g	d_m, nm	O, wt. %	Fe, wt.%
TiH_x	TiH_2 tetr.	0,233	8310	0,13	0,038
TiH_2	TiH_2 cub.	0,225	7050	0,12	0,25
BN	BN+B_2O_{3s}	2,82	930	5,40	0,034
TiH_x+ BN (1')	TiH_2+BN_w	3,63	580	1,55	0,48
TiH_x+ BN (5')	TiH_2+BN_w +$TiB_{2\,vw}$	10,81	190	1,6	1,03
TiH_x+ BN(20')	TiH_2+$BN_{v\,w.}$+$TiB_{2\,w}$	15,00	140	3,6	2,25
TiH_2+ BN (1')	TiH_2+ BN_w	3,44	540	1,86	0,4
TiH_2+ BN (5')	TiH_2+$BN_{v\,w.}$+TiB_{2vw}	10,54	173	2,11	0,76
TiH_2+ BN(20')	TiH_2+$TiB_{2\,w}$	12,34	150	4,57	1,37

*s – strong; w – weak peaks; vw – very weak peaks.

Properties of starting and milled powders and the mixtures are shown in Table 1. X-ray diffraction analysis (XRD) of boron nitride showed strong peaks of B_2O_3 (Table.1). The proportion between TiH_2 (TiH_x) and BN is 74,9:25,1, corresponds to stochiometric composition of the reagents in the reaction:

$$TiH_2 + BN = 2/3TiN + 1/3TiB_2 \quad (1)$$

Filling of the ball-mills with nitrogen was carried out under pressure of P=0,2 kPa for t=10min. The milling was made in planetary ball mill for 1, 5, and 20 min. Determination of the specific surface area was implemented by method low-temperature adsorption of nitrogen (BET). The average size of particles was calculated from the specific surface area suggesting spherical shape of particles [4], by formula:

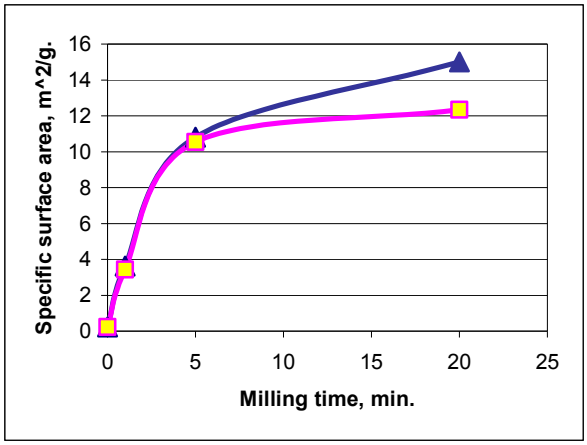
$$d_{m.}=6/(S\cdot\gamma), \quad (2)$$

where: $d_{m.}$- average size particles, μm; S- specific surface area of powder, m^2/g; γ−density of material, g/cm^3.

After milling for 1 min. the phase composition corresponded to initial one in fact. X-ray diffraction analysis (XRD) shows, that the phase composition changes after milling during 5-20 min. Thus, intensity of peaks for boron nitride decreases as a result of amorphization [5]. After 5-20 min. of milling, the mechano-chemical synthesis of TiB_2 was revealed. Table 1 shows, that as a result of milling for 5-20 min. significant oxidizing and pollution with iron occurs.

Results of the investigations of the specific area surface dependence on milling time are shown on Fig.1. The intensive increase of the specific surface area was observed for 1- 5 min. of milling. But growth of specific surface area is not so significant, as the last one, under increasing of milling time up to 20 min (Fig.1).

Investigations of the particle-size distribution were implemented by sedimentation analysis in terms of laser light scattering on device Zetasizer 1000HS. The 0,1% hexametaphosphate natrium solution in distilled water was chosen as a dispersion medium.



▲ - mixture TiH_x+BN.
□ - mixture TiH_2+BN.

Fig.1. Dependence of specific surface area on milling time.

Table.2 Results of the particle-size distribution investigations of initial and milled powders.

Powder	$d_{mean.log.}$ nm.	by intensity.		by volume	
		numb. peaks	scattering, nm.	numb. peaks	scattering, nm.
BN	455	2	40,5-5107	3	32,2-6430
TiH_x+BN (1')	272	1	38-3056	3	31-3848
TiH_x+BN (5')	226	1	20,1-801	3	16-801
TiH_x+BN(20')	192	1	22- 541	3	17-681
TiH_2+BN (1')	291	2	26-3264	4	21-4110
TiH_2+BN (5')	233	2	107-494	2	90-585
TiH_2+BN(20')	181	2	79- 279	2	69-321

Tabl.2 shows results of these investigations, which reveal, that the dispersion of powder BN takes place even after milling for 1 min. Increasing of milling time leads to narrowing of particle-size distribution. Magnitude of $d_{mean.\ log.}$ is average value of log-normal particle-sizes distribution.

Using the particle-size distribution in volume was caused by necessity of refinement of data on particle-size distribution in intensity according to Mie theory [6]. Therefore, as Table 2 shows, particle-size distribution in volume, as a rule, has higher modality and wider region of particle-size distribution. Sizes of starting powders particles, and also after milling for 1 min., have different magnitudes after specific surface definition and sedimentation analysis, that is bounded up with complex shape of particles surface of these powders. Increase of milling time leads to spheroidizing of particles shape.

Thus, high-energy milling for 1 min. is optimal at these conditions, as a consequence of that powder mixture with specific surface 3,44-3,63 m^2/g, oxygen contents 1,55-1,86 %wt., iron contents 0,40-0,48 %wt. is obtained.

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