Preparation of the Composite Powder Al – B4C by Ball Milling for Cold Spray

A E Chesnokov *, A V Smirnov, S V Klinkov, V F Kosarev

Khristianovich Institute of Theoretical and Applied Mechanics, SB RAS, Institutskaya str. 4/1, Novosibirsk, 630090, Russia

E-mail: * chae@itam.nsc.ru

Abstract. In the work, when ball milling of mixture of aluminum powder (ASD – 1) and boron carbide (F 500) powder in a high-energy planetary mill, composite particles sized from 10 to 100 microns were produced, in the volume of which ultrafine boron carbide particles were distributed in the size range from 0.1 to 20 microns. It is assumed that the use of such particles in the production of coatings by cold gas-dynamic spraying will increase the deposition efficiency and the weight fraction of boron carbide in the coating. An increase in the concentration of carbide particles in the processed powder mixture, under all other conditions being equal, leads to a decrease in the average volume size of the particles. It is noted that in this case, the boron carbide particles behave as a surfactant. The X-ray phase analysis has shown diffraction peaks corresponding only to aluminum and boron carbide, therefore, under the selected milling conditions, the phase composition remain the same as in the original powders.

Introduction

Currently, numerous works of russian and foreign authors are devoted to the method of gas – dynamic deposition of coatings made of composite materials (a mixture of metal powder and hard particles of intermetallics, oxides, carbides, etc.), which confirms the relevance of these studies [1 – 16]. At high-speed (~500 m/s) collision of the sprayed particle with the surface layer of the coating, its deformation occurs with the formation of a new surface of the particle and a large amount of heat is released (up to 95% of the kinetic energy of the particle). In the thin layer of the contact zone, a short-time pressure pulse can reach a value of $10^9 - 10^{10}$ Pa with an increase in temperature to $10^7$ K [17] of duration $10^{-8} - 10^{-9}$ s. The impacts of the sprayed particles during the formation of the coating create stresses in the already formed coating. As shown in papers [18, 19], changes in the shape, structure and increase in the microhardness of the particle material during ball milling in a high-energy planetary mill lead to the fact that coatings obtained from mechanically processed particles have a higher microhardness and porosity.

Reinforcement of metal particles with ultrafine hard inclusions, such as carbides, significantly increases the hardness of the material and reduces its ductility. An attempt to obtain coatings by the cold spray method from metal-ceramic particles of the composition WC – 12 wt.% Co, Cr,C2 – 25 wt.% Co, TiC – NiCr (usually used to obtain wear-resistant coatings by thermal spraying) will lead to erosion of the substrate without coating formation. In this regard, for cold spraying metal-ceramic coatings, powder mixtures consisting of a metal base material and hard ceramic particles are used.

Using the physical basis of mechanical processing and alloying of materials in high-energy planetary mills, it is possible to obtain agglomerated composite particles consisting of metal matrix, within which inclusions of hard ceramic materials are distributed. To obtain such particles, one can use the original powders of any shape and composition, but there are restrictions on their minimum size. According to [20], ultrafine powders of non-metallic materials partially behave as a surfactant, the role of which is associated with changes in the mechanical properties of the processed metal material, which can eventually lead to a decrease in the average volume size of the resulting particles.
The aim of the present work is to determine the treatment mode of mixture of aluminum powder and boron carbide powder in a high-energy planetary ball mill, at which carbides sized from 1 to 15 microns will be embedded in a metal matrix of agglomerated particles sized from 40 to 90 microns.

**Experimental methods**

Aluminum powder (ASD – 1) and boron carbide (F 500) were used in the work. The initial aluminum powder particles have a shape close to spherical, of average size 25 microns. Boron carbide particles are characterized by irregular shape of average size 18 microns. The histograms of the volume particle size distribution (Figure 1) were determined using laser diffraction analyzer LS 13 320 ( Beckman Coulter, USA).

![Histogram of particle size distribution](image)

**Fig. 1.** Volume particle size distribution. Aluminum powder – $d_{\text{mean}} = 25.16$ μm, $d_{10} = 7.55$ μm, $d_{50} = 22.10$ μm, $d_{90} = 47.45$ μm, boron carbide powder – $d_{\text{mean}} = 18.33$ μm, $d_{10} = 2.52$ μm, $d_{50} = 14.05$ μm, $d_{90} = 41.99$ μm.

Figure 2 shows micrographs of overall view of the initial powder particles obtained with aid of Evo MA15 electron microscope (Carl Zeiss, Germany) using a backscattered electron detector.

![Micrographs of powder particles](image)

**Fig. 2.** Overall view of aluminum powder particles (a) and boron carbide powder particles (b).

Ball milling of powder mixture of aluminum with 25 and 40 wt. % of boron carbide powder particles was carried out in high-energy planetary mill "Activator – 2SL" in air atmosphere with processing parameters: the mass of the loaded balls – 160 g for each vial; the acceleration of the grinding bodies -117 g; the loading mass of the processed material – 30 g. Steel balls of diameter 5 mm were used as grinding bodies. Mechanical processing of mixture of aluminum powder and boron carbide was carried out for 30, 60, 90 and 120 seconds.

Note that when ball milling aluminum particles (without the addition of boron carbide powder) for more than 90 seconds with the acceleration of the grinding bodies 117 g, the particle material reached a temperature close to the melting point; particles were observed to adhere to the surface of the grinding
bodies and the walls of the mill [21]. X-ray images of mechanically treated particles were obtained with aid of D8 ADVANCE diffractometer (Bruker Corporation, USA) using monochromated CuKα radiation.

Results and discussion

Figure 3 shows the experimental dependences that characterize the change in the volume particle size of a powder mixture of aluminum and boron carbide depending on the time of its mechanical processing. It is known from the reference literature that boron carbide is characterized by high hardness and brittleness, so that its mechanical treatment should be accompanied by permanent grinding. Aluminum particles, when heated due to the deformation of the material in the collision with grinding bodies, become more plastic, interact with each other and form large agglomerates.

When the ductile metal particles and hard ceramic powder particles (i.e., boron carbide in our case) are treated together, there are both processes simultaneously: the growth of agglomerated, already composite, particles and the crush of boron carbide particles. From the data presented in Figure 3a, it can be seen that an increase in the concentration of boron carbide particles in the treated powder mixture leads to a decrease in the average volume particle size. In this case, the boron carbide particles behave similar to the surfactant at mechanical treatment of materials [20].

Figure 3b shows the changes in the specific surface area of mechanically treated powder mixtures. An increase in the specific surface area indicates that ball milling is accompanied by breakage of boron carbide, as well as by increasing surface of composite particles (Fig. 4, 5).

![Graphs showing volume size distribution and specific surface area over time for ball milled particles mixture.](image.png)

Fig. 3. Characteristics of ball milled particles vs processing time: a – volume size distribution, b – specific surface area. Mixture between aluminum and boron carbides powders 1 – 25 wt.% B₄C; 2 – 40 wt.% B₄C.

Figure 4 shows overall views of two ball milled powder mixtures for 120 seconds. It can be seen that ball milling of aluminum powder together with 25 wt.% of boron carbide powder (Figure 4a) results, under all other conditions being equal, in the formation of a larger number of large composite particles compared to the ball milling of powder mixture containing 40 wt.% of boron carbide (Figure 4b). The letter powder contains a large number of individual crushed boron carbide particles sized less than 5 microns.
Fig. 4. Overall view of ball milled particles vs processing time 120 s. a – Al – 25 wt.% B₄C; b – Al – 40 wt.% B₄C.

Mechanical agglomerates, whose morphology is shown in Figure 5, are characterized by a developed surface and particle sizes from 10 to 100 microns. In its volume, the composite material contains distributed particles of boron carbide.

Fig. 5. Typical view of composite particles. a, b, c – Al – 25 wt.% B₄C; d – Al – 40 wt.% B₄C.

Figure 6 shows X-ray patterns of ball milled powder mixtures. X-ray patterns are quite correctly identified – the diffraction peaks almost perfectly coincide with the tabular values of aluminum and boron carbide. There is no noticeable broadening and blurring of the peaks for any time of ball milling, therefore, only mixing of the powders with the formation of composite particles without chemical transformations occurs.
Figure 6. X-ray patterns of ball milled powder mixtures between aluminum and boron carbide.  
a – Al – 25 wt.% B₄C; b – Al – 40 wt.% B₄C. Treatment time: 1 – 30 s; 2 – 60 s; 3 – 90 s; 4 – 120 s.

Figure 7 shows the dependence of the relative intensity of the main peaks corresponding to aluminum and boron carbide upon the time of mechanical processing of two mixtures: 1 – Al – 25 wt.% B₄C and 2 – Al – 40 wt.% B₄C. The relative intensity of the peaks was calculated using the formula

\[ \frac{I_{B_4C}}{I_{Al} + I_{B_4C}} = \frac{I_{B_4C}}{I_{Al}} \]

It can be seen that the obtained values of the relative intensity of the analyzed samples decrease with increasing ball milling time, regardless of the ratio of the weight percentages of B₄C to Al. As is known, the X-ray radiation of the diffractometer has a finite depth of penetration into the material under study. Therefore, the decrease in relative intensity can be explained by the fact that during the mechanical processing of mixtures in planetary mill, boron carbide particles are introduced into aluminum (see Figure 4, 5). An increase in the ball milling time results in increasing the number of embedded boron carbide particles. This leads to a decrease in the intensity of the reflexes corresponding to boron carbide.

**Conclusion**

The obtained results allow concluding that the increase in the content of boron carbide in the powder mixture from 25 to 40 wt.% leads to a decrease in the average volume size of the ball milled particles. Moreover, with an increase in the processing time (from 30 to 120 s), the average particle size decreases, in contrast to the mixture with 25 wt.% content, when an increase in the average particle size
is observed. Mechanical agglomerates (composite particles) are characterized by a developed surface and particle sizes from 10 to 100 microns; in their volume they contain ultrafine boron carbide particles sized from 0.1 to 20 microns. X-ray phase analysis has shown diffraction peaks corresponding only to aluminum and boron carbide, which indicates the absence of phase transformations under the conditions of ball milling adapted in this work.

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