Study of the Influence of the Time of Mechanical Processing of Powder Mixture of Composition Ti – 25 wt. % TiN in a Planetary Mill on the Characteristics of Composite Particles

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Abstract. In this work, by the method of mechanical processing in a high-energy planetary mill of titanium powder (PTS – 1) and ceramic powder of titanium nitride, composite particles with a size of 10 to 100 μm were obtained, in the volume of which ultrafine particles of titanium nitride are distributed. It is assumed that the use of such particles in powder spraying by cold or thermal spray will increase the homogeneity of the distribution of refractory elements in the coating volume. Depending on the time of mechanical treatment of the powder mixture containing three weight fractions of ultrafine particles of titanium nitride, agglomerated composite particles were obtained. Their granulometric composition and surface morphology were studied; a map of the distribution of elements over the surface and volume of the particle material is obtained. It is noted that during mechanical processing of materials in a planetary mill, the behavior of titanium nitride particles is similar to the role of a surfactant. It is shown that the time of mechanical processing of the powder mixture for three minutes is optimal: composite particles have an average size of 38 microns; mass fraction of particles of fraction 20 – 90 μm more than 60 %.

Introduction

At present, in the practice of many areas of science and technology (metallurgy, chemistry, spraying of coatings, biomedicine, etc.), studies of the effect on the structural, physical, mechanical, electrical and other properties of the final product of additions to the initial material of ultrafine particles [1 – 10]. For example, in the modern foundry and welding industry, from 0.01 to 0.5 weight fraction of ultrafine particles based on titanium nitride, titanium carbonitride, silicon carbide, aluminum oxide and many others are used as modifying additives. During cooling, nanoparticles serve as additional crystallization centers that form a finely dispersed globular alloy structure. Such a change in the structure leads to an increase in hardness and an increase in the mechanical properties of the material [3]. It is noted in the works that the initial ultrafine particles of refractory compounds have low melt wettability; as a result, they cannot serve as effective centers of crystallization. In medicine, nanoparticles (for example, iron oxide) have been used as contrast agents for magnetic resonance imaging for many years. Work [7] reports on a new approach to obtaining particles with a magnetic core and a polymer shell, which have an average size of about 40 – 50 nm; noted that the particles are non-toxic and can be useful in biomedicine for drug delivery. Thus, at present, the problem of obtaining composite particles of various sizes and compositions, consisting of a base material and ultradispersed particles of another component distributed over the volume or surface, is urgent. The main methods for obtaining composite particles are mechanical processing of powders in high-energy planetary-type mills; obtaining composite compacts by high-temperature sintering from a mechanically mixed powder mixture; using spray drying; synthesis of chemical compounds in the mode of self-propagating high-temperature synthesis; vacuum arc coating of particles with metal films (Ti, Al, Cu, etc.). Separately, it is necessary to note the method of processing specially prepared composite powder granules in a plasma jet [11, 12].
The result of plasma treatment is spherical, including hollow, composite particles of decamicron size, in the volume of which ultradispersed solid inclusions of carbides and nitrides are uniformly distributed. The disadvantages of this method include high labor intensity and low productivity of obtaining granular powder.

Thus, taking into account the fundamentals of mechanical processing of materials in a high-energy planetary ball mill, the purpose of the work is to determine the processing mode of titanium powder and titanium nitride, in which ultrafine particles of titanium nitride will be embedded in the metal matrix of an agglomerated particle with a main fraction size from 20 to 90 μm.

**Experimental technique**

In this work used titanium powder (PTS – 1) and ceramic titanium nitride powder. The initial particles of titanium powder are in the form of dendrites, with an average size of 101 μm. Particles of titanium nitride are characterized by a fragmentation shape with an average size of 1.24 μm.

Determination of histograms of the volumetric particle size distribution (Figure 1) was carried out on a laser diffraction analyzer LS 13 320 (Beckman Coulter).

![Figure 1. Volume distribution of initial particles by size: (a) – titanium powder, (b) – titanium nitride powder.](image)

Figure 2 shows photomicrographs of a general view of the initial powder particles, obtained with an Evo MA 15 electron microscope (Carl Zeiss) using a backscattered electron detector equipped with an X-ray microanalysis attachment (Oxford Instruments X-Max 80 mm², UK).

![Figure 2. General view of the initial particles of titanium (a) and titanium nitride (b) powders.](image)

Mechanical treatment of titanium powder mixture with addition of 25 wt. % titanium nitride powder particles were carried out in a high-energy planetary mill "Activator – 2SL" in an air atmosphere with processing parameters: the weight of the loaded balls – 160 g for each vial; acceleration of grinding bodies – 117 g; loading weight of the processed material – 20 g. Steel balls 5 mm in diameter were used as grinding bodies. Ball milling of the powder mixture was carried out for 1, 3, 6 and 9 minutes. X-ray diffraction patterns of control samples of mechanically treated particles were obtained on a D8 ADVANCE diffractometer (Bruker Corporation, USA) using monochromatic CuKα radiation.
Results and Discussions

Figure 3 shows the experimental dependences characterizing the change in the volumetric size of particles of a powder mixture of titanium and titanium nitride, depending on the time of its mechanical processing. Particles of titanium heat up due to material deformation upon impact with grinding bodies, become more plastic, interact with each other and form agglomerates of larger sizes. During joint mechanical processing of ductile metal particles and ultradispersed titanium nitride particles, at the initial moment of time, they are mixed, then the growth of agglomerated particles is observed (fig. 3, a). Further mechanical treatment of the powder mixture is accompanied by a decrease in the volumetric particle size. In this case, the behavior of titanium nitride particles is similar to the role of a surfactant in the machining of materials [13]. Figure 3, b shows the dynamics of changes in the dependence of the specific surface area of mechanically processed particles of a powder mixture on their sizes, which reflects both individual processes of grinding and agglomeration of particles, and their simultaneous effect on particles (9 and 12 minutes). It should be noted that the mathematical model for processing the specific surface of particles built into the software package of the laser diffraction analyzer does not take into account their open macroporosity. Figure 3, b shows that mechanically processed mixtures contain particles smaller than 10 µm, the volumetric content of which is shown in Figure 3, c. Composite particles less than 10 µm in size are in demand as modifiers, for example, in laser welding.

![Figure 3](image)

Figure 3. Granulometric characteristics of mechanically processed powder mixtures. Dispersed composition of particles: (a) – volumetric distribution; (b) – specific surface area; (c) – the content of particles in the processed powder mixture with a size less than 10 µm. Ball milling time: 1 – 1 min, 2 – 3 min, 3 – 6 min, 4 – 9 min, 5 – 12 min.

Figure 4 shows a sequential change in the general appearance of a mechanically processed powder mixture for 1, 3, 6 and 9 minutes. The figure shows which of the processes (grinding or agglomeration of particles) prevails at a given time of mechanical processing. It should be noted that with a machining time of 9 minutes or more, a thin surface layer of the agglomerated particle reaches the melting point of titanium, as in [14], the particles stick to the surfaces of the grinding bodies and the walls of the glasses,
due to which the loss of the processed powder significantly increases from $5 \sim 10\%$ at $1 \sim 6$ minutes to $40\%$ at $9$ minutes.

![Figure 4. General view of the mechanically processed powder mixture for 1 minute (a) and 3 minutes (b), 6 minutes (c) and 9 minutes (d)](image)

**Figure 4.** General view of the mechanically processed powder mixture for 1 minute (a) and 3 minutes (b), 6 minutes (c) and 9 minutes (d)

![Figure 5. Diffraction patterns of mechanically processed powder mixtures (a), values of the region of coherent scattering of titanium (b) depending on the time of mechanical treatment: 1 – 1 min, 2 – 3 min, 3 – 6 min, 4 – 9 min, 5 – 12 min.](image)

**Figure 5.** Diffraction patterns of mechanically processed powder mixtures (a), values of the region of coherent scattering of titanium (b) depending on the time of mechanical treatment: 1 – 1 min, 2 – 3 min, 3 – 6 min, 4 – 9 min, 5 – 12 min.

Figure 5. a presents X-ray diffraction patterns, which shows the dynamics of changes in the shape and position of the main peak of titanium and titanium nitride, depending on the time of mechanical treatment of powder mixtures. The X-ray diffraction patterns are quite correctly identified - the
Diffraction peaks practically coincide with the tabulated values of titanium and titanium nitride. Mechanical processing of the powder is accompanied by constant volumetric deformation of the particles, which forms the structure and shape of the surface. In the volume of agglomerated composite particles, uneven defects and stresses of the crystal lattice are formed. In this case, a shift and broadening of the main peak occurs to the region of smaller angles, which is explained by the compression of the unit cell and, accordingly, a change in the grain size (Fig. 5b).

As is known from the theory of scanning electron microscopy [15], the construction of a map of chemical elements using an electron microscope equipped with an attachment for micro X-ray spectral analysis is carried out to a depth of 5 μm, depending on the material of the sample under study. Figure 6 shows the uniform distribution of elements corresponding to the titanium and nitrogen phases over the surface and the registered volume of machined particles.

Figure 6. Elemental analysis of a powder mixture mechanically processed for 3 minutes, obtained using scanning electron microscopy: a) – analyzed area, b) – titanium phase distribution and c) – nitrogen phase over the surface and volume of particles.

**Conclusion**

In this work, the influence of the time of mechanical processing on the characteristics of the resulting particles of a mixture of titanium powder with 25 weight percent of ceramic powder of titanium nitride was investigated. It is shown that the particles obtained after 3 minutes of treatment have a more globular shape and are most suitable for use in cold or thermal spray. The uniform distribution of nitrogen throughout the volume of particles allows us to speak of the effect of cladding, which makes it possible to use this composition as a modifier in casting. The particles obtained with a processing time of 9 minutes have a significantly smaller size, which allows them to be used for modifying welded seams and deposited layers.

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**References**

[1] Li Mei, Shi Zhenxue, Liu Zhaogang, Hu Yanhong, Wang Mitang, Li Hangquan, Effect of Surface Modification on Behaviors of Cerium Oxide Nanopowders // Journal of Rare Earths, Volume 25, Issue 3, 2007, Pages 368-372.

[2] S. P. Bardakhanov, V. N. Goverdovskiy, C.-M. Lee, O. C. Lee, V. T. Lygdenov, “Analysis and Alternate Selection of Nanopowder Modifiers to Improve a Special Protective Coating System”, Advances in Materials Science and Engineering, vol. 2017, Article ID 2397238, 11 pages, 2017.

[3] Kuzmanov, P. M. and Popov, S. I. and Yovkov, L. V. and Dimitrova, R. N. and Cherepanov, A. N. and Manolov, V. K. Investigation the effect of modification with nanopowders on crystallization process and microstructure of some alloys // AIP Conference Proceedings 2017 volume 1893, P. 030104
[4] Olga Riedel, Anke Düttmann, Simon Dühnen, Joanna Kolny-Olesiak, Christian Gutsche, Jürgen Parisi, Martin Winter, Martin Knipper, and Tobias Placke, Surface-Modified Tin Nanoparticles and Their Electrochemical Performance in Lithium Ion Battery Cells // ACS Applied Nano Materials 2019 2 (6), 3577-3589.

[5] Ahmed F. Halbus, Tommy S. Horozov, and Vesselin N. Paunov Surface-Modified Zinc Oxide Nanoparticles for Antialgal and Antiyeast Applications // ACS Applied Nano Materials 2020 3 (1), 440-451.

[6] Siva Kumar Natarajan and Stalin Selvaraj Mesoporous silica nanoparticles: importance of surface modifications and its role in drug delivery // RSC Adv., 2014,4, 14328-14334.

[7] A. K. Gupta and S. Wells, "Surface-modified superparamagnetic nanoparticles for drug delivery: preparation, characterization, and cytotoxicity studies," in IEEE Transactions on NanoBioscience, vol. 3, no. 1, pp. 66-73, March 2004.

[8] Esteban Florez, F.L., Trofimov, A.A., Ievlev, A. et al. Advanced characterization of surface-modified nanoparticles and nanofilled antibacterial dental adhesive resins. Sci Rep 10, 9811 (2020).

[9] Yong Chen, Zhongxing Su & Hui Xu (2007) The Preparation and Characterization of Surface-Modified VO2 Nanopowders, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 37:4, 275-277.

[10] Marharyta Lakusta Igor Danilenko Galina Volkova Larisa Loladze Valeriy Burkhovetskiy Oleksandr Doroshkevich Irina Brykhanova Inna Popova Tetyana Konstantinova. Sintering kinetics of ZrO2 nanopowders modified by group IV elements // Applied ceramic technology Volume16, Issue4 2019 Pages 1481-1492.

[11] Chesnokov A.E., Smirnov A.V. Peculiarities of the formation of the internal structure of cermet particles during plasma processing // Inorganic Materials. –2019. –Vol. 55 No. 4. –P. 395-400.

[12] Drozdov V.O., Chesnokov A.E., Cherepanov A.N., Smirnov A.V. Study of the formation of nanostructured composite powders in a plasma jet // Thermophysics and Aeromechanics. –2019. –Vol. 26 No. 5. –P. 739-744.

[13] Chesnokov A.E., Smirnov A.V., Vidyuk T.M. Influence of surface active agent on the size of metal powder particles during their ball milling in a planetary mill // Journal of Physics: Conference Series XVI All-Russian Seminar with international participation "Dynamics of Multiphase Media" (Novosibirsk, 30 Sept. - 5 Oct. 2019). –S.l.: IOP Publishing, 2019. –Vol. 1404. –P. 012011(4).

[14] Klinkov S.V., Kosarev V.F., Chesnokov A.E., Smirnov A.V., Vidyuk T.M. Investigation of influence of Input energy during ball milling of aluminum powder // Solid State Phenomena. –2021. –Vol. 313. –P. 143-151.

[15] Joseph I. Goldstein Dale E. Newbury Patrick Echlin David C. Joy Charles E. Lyman Eric Lifshin Linda Sawyer Joseph R. Michael Scanning Electron Microscopy and X-ray Microanalysis Publisher Name Springer, Boston, MA P.689, 2003.