

SYNTHESIS OF CERAMICS TITANIUM COMPOUNDS BY MECHANICAL ALLOYING OF TiB₂-TiN SYSTEMS

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Abstract

In recent years, there has been an increased interest in technologies for the production of titanium ceramic materials with properties, the level of which in terms of price-quality ratio exceeds the level of similar materials based on other metals. The strength of the bond with the metal in modern titanium ceramic products corresponds to the level of cermet systems based on noble metals or alloys without them. This work describes a method of obtaining and some properties of ceramic compounds based on titanium, such as TiBN by mechanical alloying. Heat treatment and spark plasma sintering were also carried out. The hardness of the obtained samples was determined and an X-ray phase analysis was carried out, which confirmed the presence of such phases as and Ti₃B₂N.

Keywords: Mechano-synthesis, spark-plasma sintering, titanium-based compounds, wear-resistant coatings, corrosion-resistant coatings, ceramic materials

1. INTRODUCTION

Ceramic materials based on titanium - its carbide, nitride, and boride - themselves have a high complex of properties, but their derivatives - carbonitrides, carboborides, oxynitroborides, and others - often inherit not only all the valuable and often unique properties of their predecessors but also acquire a new the level of previous properties (for example, strength or electrical) or a surge of other properties that their predecessors did not possess. It is enough to give an example of titanium oxynitride, which has already been successfully tested as implants of the organs of the cardiovascular system, although its "components" - nitride and oxide - could not be used in this area.[1]

Among such compounds, a special place is occupied by oxygen-free refractory compounds, including titanium nitroborides, the use of which as welded or deposited materials is currently increasingly expanding. These materials have increased hardness and wear resistance, making them an ideal choice for creating coatings that can withstand high mechanical loads. They also have good heat resistance and low friction. These properties make them attractive for a wide range of applications, including the manufacture of tools, machine parts and equipment.[2-3]

An increase in the requirements for the operational properties of coatings requires the search for new types of solid phase as a wear-resistant component, which are not inferior in hardness and heat resistance to carbides, but have a higher melting point and plasticity. Among such compounds, a special place is occupied by oxygen-free refractory compounds, including titanium carbonitrides, the use of which in the creation of surfacing materials is now increasingly expanding.[4]

Interest in nitroboride coatings arises from the fact that they are usually multiphase. Such systems have much in common with composite materials and often exhibit higher hardness and toughness values than single-phase materials. The TiBN_{0.5} coatings demonstrated a combination of high hardness and ductility. Annealing at 400 ° C for 6 hours increased the hardness and ductility by 40-50%. The reaction of titanium with boron nitride can lead to the formation of titanium nitroborides. The heat of formation of products is higher than the heat of formation of the starting materials, and the process will be exothermic. The resulting compound can be applied to titanium alloys and steels to improve the surface properties of the structure, such as sealing the surface of a mold, which can improve machining efficiency and tool life. Ti₃B₂N can also be used for the manufacture of DHCM. Superhard (up to 55 GPa) coatings of the Ti-B-N system of variable composition were obtained by sputtering a target, which is a boron nitride plate coated with Ti powder. [5-6]

2. MATERIALS AND METHODS

Mechanosynthesis was carried out in high-energy mills – attritors. The following materials were chosen as the starting compounds - titanium boride and titanium nitride. The charge for TiBN production is shown in (Table 1).

Table 1 The chemical composition of the T₃B₂N compound

Powder sample	Composition, mass. %	
	TiB ₂	TiN
Ti ₃ B ₂ N	25	75

The titanium nitroboride compound with the stoichiometry indicated in (Table 1), according to the literature, has an increased Vickers hardness and is approximately from 28 GPa, which is higher than that of crystalline titanium carbide (TiC), zirconium carbide (ZrC), titanium nitride (TiN).

The experiment was carried out as follows: the mixture was subjected to stage-by-stage mechanical treatment in an attritor. After 2000 seconds, the mill was stopped to cool the reaction mixture and ball charge. The processing time of the material in the mill was 10 hours.

After mechanical synthesis, the resulting material was subjected to spark plasma sintering.

Heat treatment was carried out in the following mode: pressing the press powder without heating with a pressure of 5 kN, when heated to 1800°C, the pressure was raised to 15 kN and held at this value for 5 minutes. As a result, a sample of a pressed tablet with a diameter of 12 mm and a height of 6 mm was obtained. Then the resulting tablet was analyzed using and microhardness measurements (Table 2).

3. RESULTS AND DISCUSSION

3.1. Obtaining Ti₃B₂N – compound by mechanical alloying.

After mechanical treatment, the product was investigated using the X-ray photoelectron spectroscopy (XPS) method implemented in the SPECS equipment (Germany). The energy scale is calibrated against the Au4f_{7/2} gold line, which is equal to 84.00 eV, and using X-ray phase analysis (XPA) on a D8 Advance from Bruker (Germany) using monochromatic CuK α radiation ($\lambda = 1.54178 \text{ \AA}$), with a scanning step of 0.02 ° and an exposure of 11 using scanning electron microscopy. The ICDD powder database (PDF-2) was used for phase analysis. The structure of the resulting phases was refined by the Rietveld method in the programmed introduction of DIFFRACplus Topas using the data of the ICSD structural database.

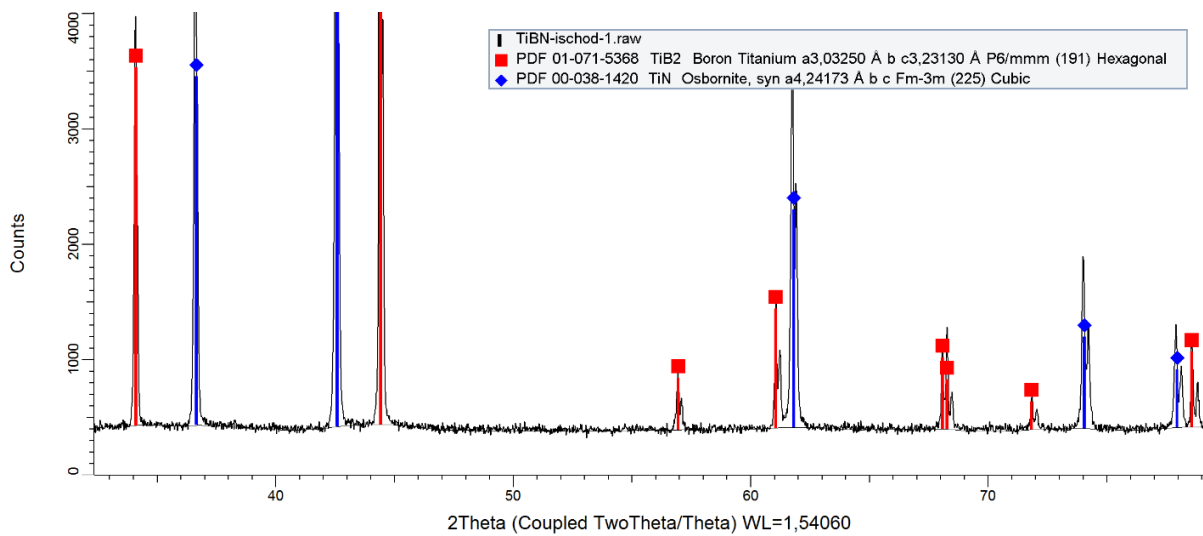


Figure 1 Diffraction pattern of the initial TiB-TiN mixture

In the presented diffraction pattern (**Figure 1**) of the mechanical mixture of the initial components before processing, one can see noticeable peaks of the initial components. It can be noted that the peaks of the initial components have a high intensity value and an unbroken shape of the peak itself, which indicates an unchanged crystal structure.

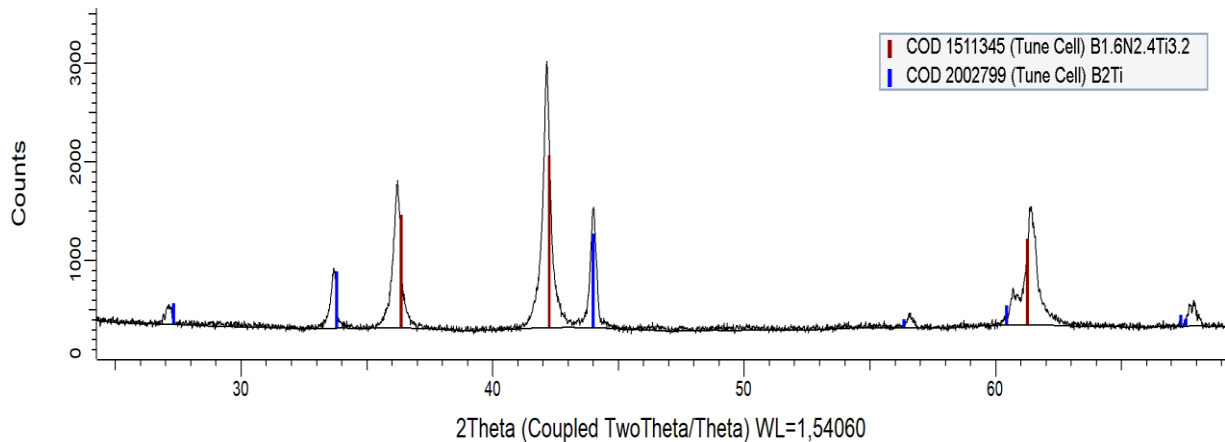


Figure 2 Diffraction pattern of the Ti_3B_2N mixture after 10 hours of mechanosynthesis

As can be seen from the diffraction pattern of the obtained sample, after 10 hours of mechanical synthesis (**Figure 2**), the compound $B_{1.6}N_{2.4}Ti_{3.2}$ is formed. Broadening of the peaks can be seen due to an increase in the number of microstrains and a change in the crystal lattice.

Subsequently, the material was subjected to heat treatment in an oven in an argon atmosphere at a temperature of 1600°C for 2 hours. After heat treatment, the sample was tested for strength by the Vickers method.

3.2. Heat treatment of the Ti_3B_2N compound by spark plasma sintering and determination of the hardness of the resulting material

Carrying out the reaction under adiabatic conditions makes it possible to obtain Ti-BbNc compounds under high-temperature sintering. The last method was used to obtain a new crystalline structure Ti_3B_2N , the

material of which has an increased Vickers hardness (≥ 28 GPa), which is higher than that of crystalline titanium carbide TiC, zirconium carbide ZrC, titanium nitride TiN.

Heat treatment was carried out in the following mode: pressing the press powder without heating with a pressure of 5 kN, when heated to 1800°C, the pressure was raised to 15 kN and held at this value for 5 minutes. As a result, a sample of a pressed tablet with a diameter of 12 mm and a height of 6 mm was obtained. Then the resulting tablet was analyzed using XRD (**Figure 3**) and microhardness measurements (**Table 2**).

The sample was split into several pieces of different sizes (**Figure 2**). The pieces were molded into acrylic resin. Before testing, the surfaces of the samples were prepared by grinding with abrasive SiC papers (400 to 1200 grit) followed by polishing with diamond suspension (9 to 3 μm).

The microhardness profiles of the sample were measured using a Buehler Micromet hardness test machine with a Vickers tip. Microhardness values for pieces (**Table 2**) was obtained using a load of 1000 g (HV1). The microhardness of the sample was measured in accordance to ISO 6507-1: 2018.

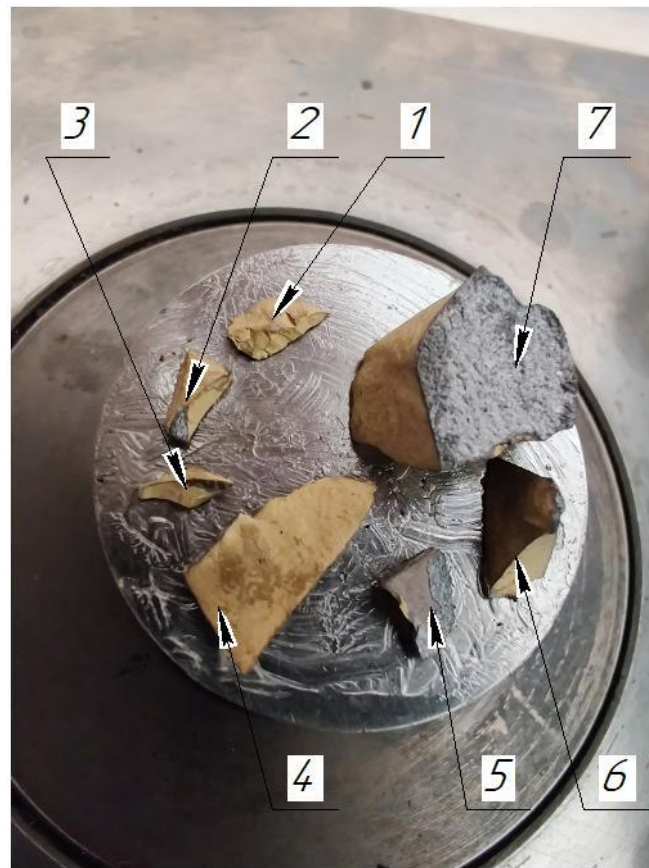


Figure 3 Image of samples pieces (1-7) after spark plasma sintering split into parts to determine the microhardness of the material.

Table 2 The microhardness profiles of the SPS sample, measured for different pieces

Samples piece	1	2	4	5	6	7
Microhardness value, MPa	1656	1622	2195	1775	2079	1512
	1514	1785	1776	1789	1641	1848
	1463	1632	1649	1906	1696	2165
Average, MPa	1544.3	1679.7	1873.3	1823.3	1805.3	1841.7

The measurement was performed 5 times for each part, after which the largest and smallest values were discarded. As we can see, the range of values is from 1463 MPa to 2195 MPa and on average is 1761 MPa.

4. CONCLUSION

Based on this work, it can be concluded that it is in principle possible to connect titanium nitroborides, namely, the $B_{1.6}N_{2.4}Ti_{3.2}$ compound, which is stoichiometrically similar to the Ti_3B_2N compound. The presence of such stoichiometry indicates that 10 hours of mechanical treatment is not enough for the synthesis of Ti_3B_2N . The hardness of the material after spark plasma sintering was also determined. The hardness range values from 1463 MPa to 2195 MPa and on average is 1761 MPa.

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