

Characterization of Bulk Nanostructural Bi₂Te₃-based Material Prepared by Microwave-solvothermal Synthesis and Hot Isostatic Pressure

O.N. Ivanov, R.A. Lyubushkin, O.N. Soklakova

Belgorod State National Research University, 85, Pobedy Str., 308015 Belgorod, Russia

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The bulk nanostructural Bi₂Te₃-based material was prepared by microwave assisted solvothermal method and hot isostatic pressure. Optimal synthesis conditions of the Bi₂Te₃ nanopowder were found. It was established that hot isostatic pressing of the nanopowders at the temperature of 400 °C and the pressures of 2, 4, 6 and 8 GPa allowed us to prepare the homogeneous and dense Bi₂Te₃-based material with the mean grain size of ~ 50 nm. It is found that an electrical resistivity increases as the mean grain size of the material under study decreases.

Keywords: Microwave-solvothermal synthesis, Hot isostatic pressure, Bismuth telluride, Grain structurePACS numbers: 68.37.Hk, 68.37.Lp, 68.37.Yz,
68.47.De**1. INTRODUCTION**

Thermoelectric materials are of interest for applications in electrical power generation devices and solid-state cooling due to many attractive properties (long life, no emissions of toxic gases, no moving parts, low maintenance, etc) [1]. At present, bismuth telluride, Bi₂Te₃, based compounds are known to be the most excellent thermoelectric materials for around room temperature applications [2]. The semiconductor bismuth telluride materials are acceptable for some specialized applications, but they are far less so for commercial refrigeration on a large scale. A number of investigations have focused on optimizing the composition, tuning doping with other heavy metals, optimizing device design, etc in order to improve thermoelectric properties of the Bi₂Te₃-based materials [3-5]. However, the thermoelectric efficiency of these materials has not improved obviously and thermoelectric figure of merit (ZT) has been approximately 1 for many years. Figure of merit is defined as $(S^2\gamma/k)T$, where Z is the figure-of-merit, T is the absolute temperature, S is the Seebeck coefficient, γ is the electrical conductivity, and k is the total thermal conductivity with contributions from the lattice and the charge carriers [6].

According to theoretical and experimental investigations, the thermoelectric nanomaterials, such as quantum wells, superlattices, quantum wires, nanograined thin films, bulk nanostructural materials including nanocomposites can demonstrate much higher thermoelectric coefficients than their traditional alternatives [7-10].

The bulk nanostructural materials are now considered to be ones of perspective thermoelectric materials. It is assumed that high enough electrical conductivity, but low enough lattice thermal conductivity can be for the same time reached for these materials. The grain size is one of important characteristics optimizing both electrical conductivity and thermal conductivity of thermoelectric nanomaterials [11].

A specific technology should be developed to fabricate thermoelectric nanostructural materials with ad-

vanced properties and reproducible phase composition, crystal structure and grain arrangement.

One of technological approaches can be based on two principal stages as follows:

- The synthesis of a starting nanosized powder with desired structure, phase and element compositions, size and shapes of particles, etc.
- The consolidation of a synthesized nanopowder by using a pressuring and a high temperature treatment in order to preserve a nanostructure and fabricate a bulk dense material with the high enough mechanical strength and thermoelectric parameters.

In present work such a kind of technology based on the microwave-solvothermal synthesis and the hot isostatic pressure was applied to prepare the bulk nanostructural Bi₂Te₃-based material.

2. EXPERIMENTAL PROCEDURE

The nanosized bismuth telluride powders have been prepared via the microwave-solvothermal synthesis in closed reactor ERTEC (Model 02-02). As is known, compared with the conventional methods, the microwave-assisted heating technique has the advantages of very short time of synthesis, simplicity and energy efficiency, small particle size of the products, narrow particle size distribution and high purity [12].

The analytical grade Bi₂O₃, TeO₂ and ethylene glycol were used as starting components. A 110 ml teflon-lined stainless-steel autoclave was used and the temperature was regulated by a digital-type temperature-controlled oven. Microwave assisted reactions were conducted in a 300 W microwave oven with a 2450 kHz working frequency.

The ethylene glycol was used as both the solvent and the reducing agent in the reaction. A few routes of synthesis were applied to determine the optimal reaction conditions. After synthesis, the reaction product as a black precipitate was washed with alcohol and then centrifuged and dried.

The nanopowders after synthesis were hot isostatically pressed (HIP) at temperature of 400 °C during 5 min by using a toroidal press. The powder for compac-

tion was placed in a graphite matrix with hexagonal BN powder as a media to spread the isostatic pressure to the object under pressing. The HIP-pressure of 2, 4, 6 and 8 GPa were applied.

X-ray diffraction (XRD) analysis both the nanopowder and the sintered material was performed for phase and crystal structure determination using a Rigaku Ultima IV diffractometer with CuK α - radiation (a step width of 0.03° and a counting time of 1.6 s/step).

The particles size and morphology of the powders were observed using a model JEM – 2100 transmission electron microscope (TEM, for an accelerating voltage of 200 kV).

Electrical resistivity measurements were made by four-probed method at 1 mA dc current using the sintered samples with Au and In-Ga electrodes.

3. RESULTS AND DISCUSSION

In order to optimize the phase composition of the bismuth telluride powders, a few routes of the microwave-solvothermal synthesis, which differ the content of the starting reagents and the parameters of synthesis (the temperature, pressure and duration of reaction), were applied (Table 1). According to Table 1, the phase composition of the powders is drastically dependent on the synthesis conditions. Only one of synthesis routes allowed us to prepare a single-phase powder of the Bi₂Te₃ composition. The optimal synthesis conditions are as follows: the temperature is 250 °C, the pressure is 15 atm., the duration of synthesis is 50 min and the ratio of Bi₂O₃ and TeO₂ is 1 : 1.

The XRD pattern for the single-phase Bi₂Te₃ powder taken at room temperature is shown in Figure 1. The diffraction peaks can be exactly indexed with the standard diffraction planes of hexagonal Bi₂Te₃. This powder synthesized at the optimal conditions was used for further examination.

TEM images in Figures 2 and 3 show typical morphology of microwave-solvothermally synthesized powder. It is seen that the powder mainly consists of irregularly shaped nanoparticles of 20-50 nm in size (Fig. 2).

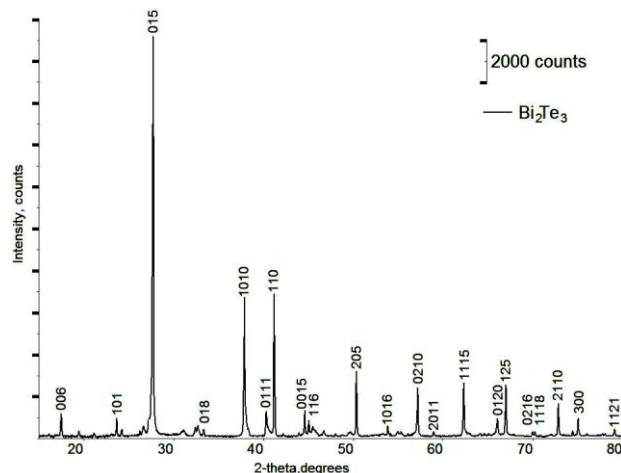


Fig. 1 – XRD pattern of the Bi₂Te₃ nanopowder

Besides, larger (~ 100 nm) hexagonal nanoplates are in the powder under study (Figure 3). The formation of the hexagonal Bi₂Te₃ nanoplates is due to their anisotropic structure. It is known [13] that the Bi₂Te₃ crystal consists of 15 layers stacked along the c-axis and presents a combination of three hexagonal layer stacks of the composition in which each set consists of five atoms (Te₁–Bi–Te₂–Bi–Te₁). The bonding within the Te₁–Bi–Te₂–Bi–Te₁ layer is assumed to be covalent, while the bonding between the Te₁–Te₁ layers is formed by van der Waals forces.

It is known that the growth of grains can occur during the long-time and high-temperature sintering of material consisting of a starting nanosized powder [14]. This phenomenon can destroy nanostructural state of material. In order to retain the nanostructure due to nanosized powder, the hot isostatic pressure method was applied to sinter the bulk nanostructural Bi₂Te₃-based samples. Both the high temperature and the high pressure simultaneously act on the material in this method. Therefore, the sintering duration is significantly reduced and growth of grains can be assumed to be negligible.

Table 1 – Parameters and results of microwave-solvothermal synthesis of the powders

Reagents	Parameters of synthesis	Phases
Ethylene glycol – 60 ml <i>m</i> (Bi ₂ O ₃) – 4.6 g <i>m</i> (TeO ₂) – 2.3 g	Temperature – 280 °C Pressure – 25 atm. Duration of reaction – 100 min.	Bi ₂ Te ₃ , Bi, BiTe
Ethylene glycol – 60 ml <i>m</i> (Bi ₂ O ₃) – 4.6 g <i>m</i> (TeO ₂) – 3 g	Temperature – 280 °C Pressure – 37 atm. Duration of reaction – 45 min.	Bi ₂ Te ₃ , Bi, Te
Ethylene glycol – 60 ml <i>m</i> (Bi ₂ O ₃) – 2.3 g <i>m</i> (TeO ₂) – 1.5 g	Temperature – 250 °C Pressure – 30 atm. Duration of reaction – 35 min.	Bi ₂ Te ₃ , Bi, Bi ₄ Te ₃
Ethylene glycol – 60 ml <i>m</i> (Bi ₂ O ₃) – 2.3 g <i>m</i> (TeO ₂) – 2.3 g	Temperature – 250 °C Pressure – 15 atm. Duration of reaction – 50 min.	Bi ₂ Te ₃
Ethylene glycol – 60 ml <i>m</i> (Bi ₂ O ₃) – 2.3 g <i>m</i> (TeO ₂) – 2.45 g	Temperature – 250 °C Pressure – 20 atm. Duration of reaction – 35 min.	Bi ₂ Te ₃ , Bi ₄ Te ₃

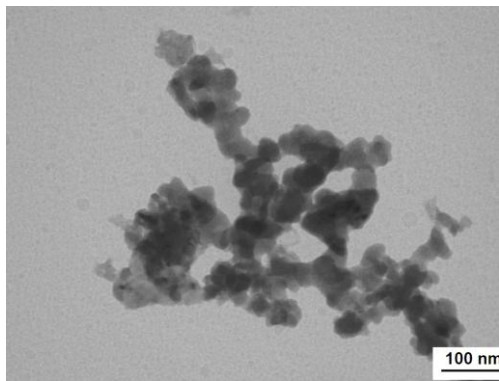


Fig. 2 – TEM image of the Bi_2Te_3 nanopowder

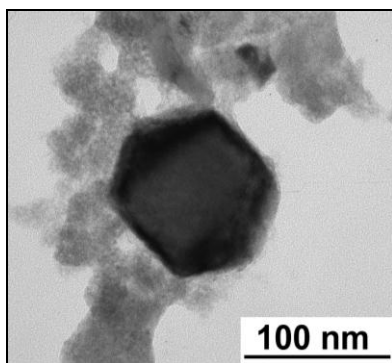


Fig. 3 – TEM image of the hexagonal Bi_2Te_3 nanoplate

In addition to the temperature, the HIP-pressure is one of the important parameters influencing the characteristics of the sample microstructure formed during the sintering.

Figure 4 shows the SEM images of the surfaces of the bulk Bi_2Te_3 -based material sintered at the HIP-pressures of 2, 4, 6 and 8 GPa and at the same temperature (at 400 °C) and the same sintering duration (for 5 min). The materials sintered by the HIP-method have dense, homogeneous and porousless, nanocrystalline structures. Spherical formations with diameters of 150-350 nm are observed for the sample with the HIP-pressure of 2 GPa (Figure 4A). Since the particles size of the microwave-solvothermally synthesized powder was less than 50 nm (Figure 2), the large spherical structures should be considered as agglomerates consisting of a lot of nanoparticles. Smaller spherical particles can be also seen for this sample. So, the grain structure of the bulk polycrystal material is not yet formed at 2 GPa. The large spherical agglomerates typical for the HIP-pressure of 2 GPa are practically absent for other HIP-pressures (Figure 4 B, C and D). Only smaller grains mainly with sizes less than 100 nm are now observed on the SEM images. The grains have a crystal faceting that can be taken as evidence of intense sintering of the nanopowder.

In order to characterize the HIP-pressure effect on the microstructure characteristics in detail, histogram of the grain size distributions in detail, histogram of the grain size distributions are plotted (Figure 5). Diameters of more than 200 grains were measured on the SEM images (Figure 4) to obtain reliable size distribution. The grain size distributions are discretized by dividing them into the 20 nm – width segments.

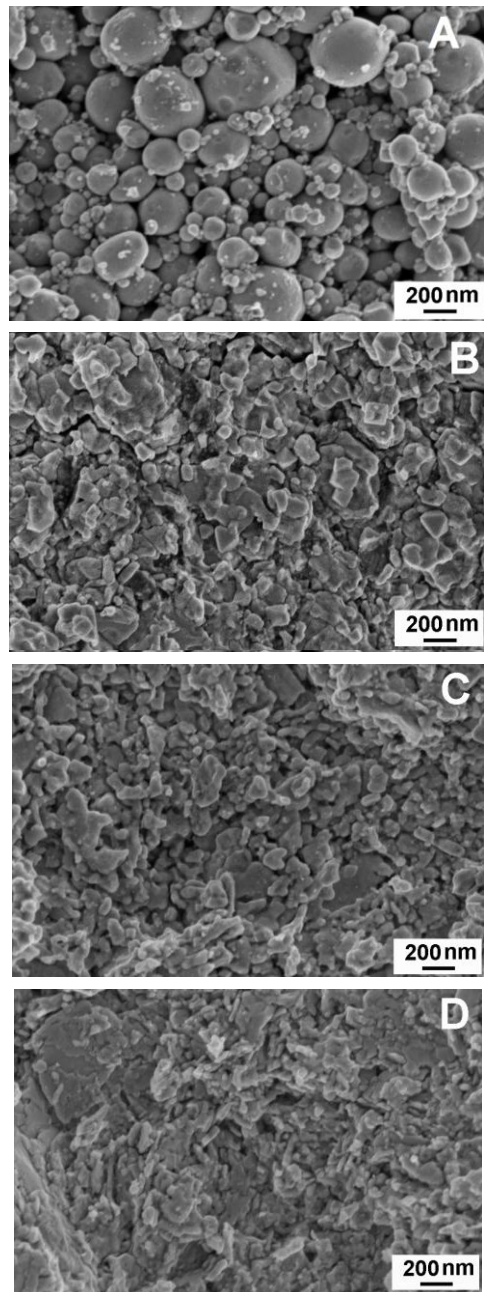


Fig. 4 – SEM images of the bulk nanostructural Bi_2Te_3 -based material sintered at the various HIP-pressures: 2 (A), 4 (B), 6 (C) and 8 GPa (D)

The study of the microstructure and elemental composition of the transverse sections of samples with composite coatings showed that were obtained uniform

The visible boundary of the coating-substrate interface has no defects. Figure 1 shows that in the contact area of coating and substrate is mixed structure consisting of islands covering the substrate a very different shapes and sizes. Part of the powder material penetrated deeply and firmly connected to the substrate material (see. Fig. 1). At impact a large powder particles, it corrects and deforms the surface layer of the substrate. There are "splashes" of the substrate material, which are located in surface (see. Table 2). Area of the coating thacaused by the shock effect of plasma-detonation wave.

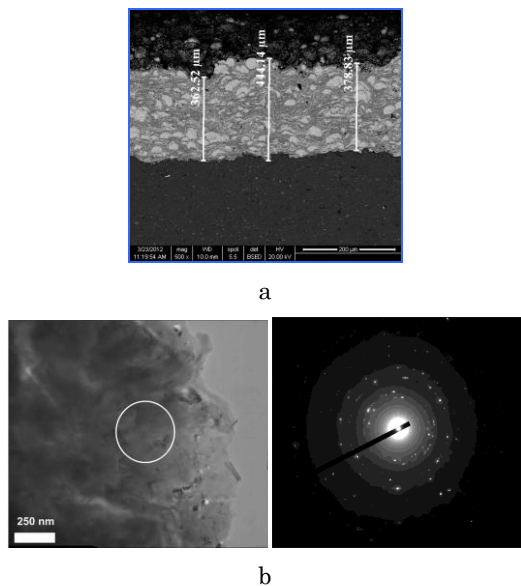


Fig. 1 – SEM image of cross section of the nanocomposite Ti/H coating layer and substrate (a), TEM image of the coating-substrate interface (b), diffraction TEM photographs of a transition layer of intermetallic TiAl

3.1 TEM Observation of the System «Nanocomposite Coatings - Substrate»

Local phase and structure analysis of the composite coatings based on Ti, O, C and H showed that lamellas in the coatings consisted of the mixture of titanium nanocrystalline grains with face-centered close-packed lattice and amorphous phases, and nanoamorphous oxide of titanium (see. Fig. 2). This is confirmed by results of diffraction analysis of the nanocomposite coatings (see. Fig. 3). This structure could be caused by a high-temperature cycle in formation of composite coatings [11, 12].

Therefore, it can be assumed that the values of hardness in fine lamellae of the nanocomposite coatings are attributable to the absence of dislocations inside the crystalline grains and ratio of the volume contents of nanocrystalline to amorphous phases of metallic and non-metallic titanium compounds.

Strength of intermediate and near-interface layers leads to increase of deformation resistance of nanocomposite coatings. The absence of dislocations inside the crystalline grains leads to increase in elasticity and, at the same time, in plasticity of nanocomposite coatings. It was detected for the first time ever [12], as far back as 20-25 years ago, that ceramic materials of titanium oxides acquire super plastic properties at room temperature at the characteristic sizes of crystals equal to several nanometers.

3.2 XRD Analysis of the Nanocomposite Coatings

Carried out phase analysis showed that the main phase of the coating layer, which is located at a distance of about 1-2 mm from the free surface was Ti with a face-centered close-packed lattice ($a = 2.965 \text{ \AA}$) (see. Fig. 3). The calculated interplanar distances reflections suggest the presence in the coatings and the following phases: TiO with a cubic lattice ($a = 4.197 \text{ \AA}$),

rutile TiO_2 with tetragonal lattice ($a = b = 4.585 \text{ \AA}$, $c = 2.972 \text{ \AA}$), anatase TiO_2 with tetragonal lattice ($a = b = 3.775 \text{ \AA}$, $c = 9.492 \text{ \AA}$), Ti_2O_3 with a hexagonal lattice ($a = b = 5.129 \text{ \AA}$, $c = 13.815 \text{ \AA}$). In the nanocomposite coatings formed from the hydrogenated powder, recorded the presence of $\delta\text{-TiH}$ phase with a cubic lattice ($a = 4.415 \text{ \AA}$) and TiH_2 with tetragonal lattice ($a = b = 3.148 \text{ \AA}$, $c = 4.140 \text{ \AA}$). The studies did not report the presence of boron in the coatings. Apparently this is due to the fact that micron particles of amorphous boron overheat and evaporate in the environment of the combustion products.

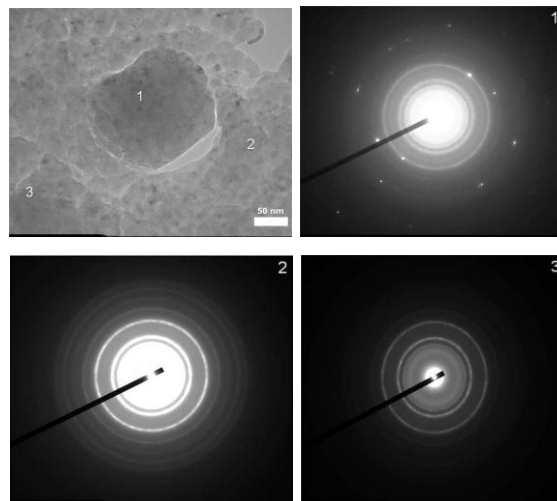


Fig. 2 – TEM image and diffraction photographs of material of nanocomposite coating of TiH powder: mixture of titanium nanocrystalline grains with face-centered close-packed lattice and amorphous phases (1), amorphous phases (C, Ti, Al, O) (2), nanoamorphous oxide of titanium (3)

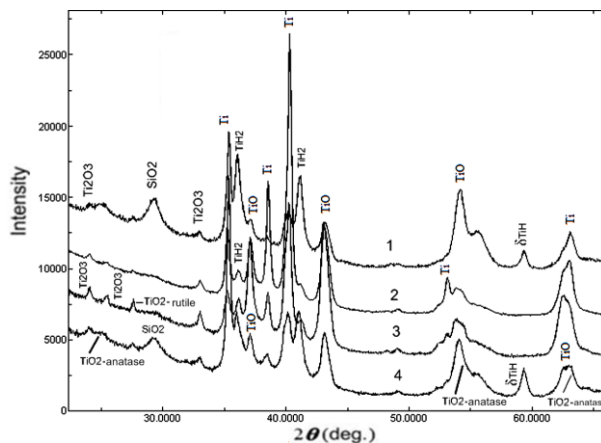


Fig. 3 – XRD analysis of the nanocomposite coatings: 1 – Ti/H, 2 – Ti, 3 – Ti/B, 4 – Ti/B/H

4. CONCLUSIONS

Cumulative-detonation technology provides formation of dense composite coatings based on Ti, O, C, H thickness of 100-400 microns. The porosity of coatings was $\sim 1-2 \%$, which correlates with the technological requirements of industrial coatings. The apparent limit of adhesion of the coating to the substrate is free of defects. It was found a transition region coating / substrate consisting of a nanocrystalline TiAl. The

main phases of the composite coatings are Ti, TiO, rutile, anatase, Ti₂O₃. In the composite coatings formed from the hydrogenated powder was recorded the presence of δ-TiH phase and TiH₂.

Based on the results of the study could be offered energy-saving technology for deposition of composite coatings based on Ti, O, C, H on substrates of aluminum alloy.

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