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METAL-CERAMIC COMPOSITE Bi2Te3-Gd: THERMOELECTRIC PROPERTIES

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The purpose of this work was to investigate the possibility of improving the thermoelectric properties of the metal-ceramic composite $Bi_2Te_3 + 0.5$ at. % Gd. It was established that spark-plasma sintering of the initial Bi_2Te_3 and Gd powders does indeed form the microstructure of the composite, represented by Ni inclusions randomly distributed inside the polycrystalline matrix of Bi_2Te_3 . The resistivity of Bi_2Te_3 increases and the full thermal conductivity decreases on the addition of Ni filler. The composite's maximum thermoelectric Q (about 0.63) turns out to be somewhat higher than that of the matrix material (about 0.58).

Keywords: metal-ceramic composites [cermet], bismuth telluride, spark plasma sintering, thermoelectric properties.

INTRODUCTION

Metal-ceramic composites, or cermets, consisting of a ceramic matrix and a metal filler randomly or orderly distributed inside the matrix, are an important class of modern structural and functional materials [1-3].

Structural cermets, which have an entire range of improved performance characteristics, such as high strength, wear resistance, heat resistance, and corrosion resistance, are widely used in different application in the aircraft industry, shipbuilding, automotive industry, mechanical engineering, and so on. Functional cermets find fewer applications. An example of the use of functional cermets is in radio engineering, electrical engineering, and instrument engineering as metal-ceramic resistors with high temperature stability of electric resistance.

Functional cermets have are now being supplemented by thermoelectric composites with magnetoactive inclusions [4-9]. In such composites a conventional thermoelectric semiconductor material is used as a ceramic matrix and a ferromagnetic metal (as a rule, transition *d*-metal: Ni, Fe, Co) is used as a filler. The introduction of a ferromagnetic filler

makes it possible to implement specific physical mechanisms in such composites (the formation of a rectifying electrical contact at the metal/semiconductor interface, which effects an increase in the number of electrons, electron scattering on the magnetic moments of the filler atoms, which affects the electron mobility, magnon drag of phonons, which affects the lattice thermal conductivity and etc.), which can have a positive effect on the thermoelectric properties of composites. These specific mechanisms will act in addition to the conventional mechanisms for thermoelectric composites, such as scattering of electrons and phonons at the matrix/filler interfaces or energy filtering of electrons at these boundaries. So, in thermoelectric composites with magnetoactive inclusions, there are different physical prerequisites for improving their thermoelectric efficiency.

The purpose of the present work was to study the possibility of upgrading the thermoelectric properties of a cermet composite in which thermoelectric bismuth telluride Bi_2Te_3 is used as the matrix material and metallic gadolinium Gd as filler. Bismuth telluride is used to create the solid solutions $Bi_2Te_{3-x}Se_x$ and $Bi_{2-x}Sb_xTe_3$, which are the main thermoelectric materials in commercially used low-temperature thermoelectric generators and solid-state refrigerators [10]. In contrast to the fillers Ni, Fe, and Co, which are transition *d*-metals and are already used in the development of thermoelectric composites, ferromagnetic Gd is a transition *f*-metal. Until now, Gd has not been used as a filler to improve the thermoelectric properties of composites.

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Fig. 1. X-ray diffraction patterns of the initial Bi_2Te_3 (*a*) and Gd (*c*) powders and images of particles in these initial powders [*b*) TEM image of particles in the initial Bi_2Te_3 powder, *d*) SEM image of particles in the initial Gd powder].

OBTAINING SAMPLES AND METHODS OF STUDY

In the present work, the metal-ceramic composite material $Bi_2Te_3 + 0.5$ at.% Gd was obtained for the investigations. Bi_2Te_3 was used as a reference material, which is the matrix material of the composite $Bi_2Te_3 + 0.5$ at.% Gd and was obtained by the same technology as the composite itself. An analysis of the thermoelectric properties of the matrix material and the composite itself made it possible to determine the effect of the filler on the properties of the composite.

The initial Bi_2Te_3 and Gd powders were used in preparing the composite. Powders of chemically pure oxides Bi_2O_3 and TeO_2 oxides taken in stoichiometric ratio were used as precursors to obtain the initial powder of the matrix material. The mixture of powders was dissolved in ethylene glycol and the alkaline agent KOH was added to control the pH. Next, the solution was poured into a flask and heated to boiling. After the water evaporated, the flask was hermetically sealed with a reflux condenser and kept at 458 K for 4 h. The resulting suspension was cooled to room temperature. The synthesized Bi_2Te_3 powder was purified by filtration and washed three times with ethanol and acetone. The powder was finally dried in an argon atmosphere at 523 K for 2 h. A 99.9% pure commercial powder was used as the initial Gd powder.

To obtain a composite, mixtures of the initial Bi_2Te_3 and Gd powders, taken in the required ratio, were thoroughly mixed in a planetary mill for 60 min and then underwent spark plasma sintering (SPS-25/10 system) at 40 MPa and 623 K for 30 min. To obtain the reference material, only the Bi_2Te_3 powder was sintered under the same conditions as the composite. As a result of sintering, bulk materials of both the composite and the reference material were obtained in the form of cylinders, 20 mm in diameter and 15 mm high. To study the thermoelectric properties of materials, samples in the form of rectangular bars with dimensions $2 \times 2 \times 10$ mm

and in the form of disks with dimensions $\emptyset 10 \times 2$ mm were cut from cylinders.

The following methods were used as the main methods for studying the crystal structure and the phase and elemental compositions of the microstructure of the samples: x-ray phase analysis (XRD, Rigaku SmartLab x-ray powder diffractometer); scanning electron microscopy (SEM, scanning electron microscope Quanta 600F), including using backscattered electron diffraction (BSE); energy dispersive x-ray spectroscopy (EDS, same microscope); and, transmission electron microscopy (TEM, transmission electron microscope Jeol 2100). The resistivity ñ and the Seebeck coefficient S of the bar-shaped samples were measured by the four-probe method and the differential method (ZEM-3 setup), respectively, and the total thermal conductivity k of the disk-shaped samples was measured by the laser flash method (TC-1200H setup). Further, the values of ρ , S, and k were used to calculate the thermoelectric O-factor ZT according to the Ioffe formula

$$ZT = S^2 T/k\rho$$

where T is the absolute temperature.

EXPERIMENTAL RESULTS

According to XRD data, the initial Bi_2Te_3 powder was single-phase and corresponded to a rhombohedral crystal structure with symmetry space group 3 and unit cell parameters a = 0.4354 nm and c = 3.035 nm. The x-ray diffraction pattern of the Bi_2Te_3 powder is shown in Fig. 1*a*. The powder consisted mainly of particles in the form of thin hexagonal plates with average size equal to several hundred nanometers and thickness about 100 nm. A typical TEM image of several



Fig. 2. BSE image of the polished surface of the composite (*a*) $Bi_2Te_3 + 0.5$ at.% Gd, BSE image of a separate filler inclusion (*b*) and SEM image (*c*) of a cleavage of the composite surface oriented perpendicular to the direction of pressure application during spark plasma sintering.

Bi₂Te₃ particles is shown in Fig. 1*c*. The commercial Gd powder was also single-phase and corresponded to a hexagonal structure with symmetry space group $P6_3/mmc$ and unit cell parameters a = 0.3638 nm and c = 0.5785 nm. The diffraction pattern of the Gd powder is displayed in Fig. 1*b*. This powder consisted of irregularly shaped particles having pronounced crystalline faceting and sizes of the order of $40 - 50 \mu$ m. An SEM image of Gd particles is displayed in Fig. 1*d*.

An analysis of the BSE image of the polished composite surface (Fig. 2a) confirms that a matrix-filler microstructure, characteristic of any composite, is formed in the composite $Bi_2Te_3 + 0.5$ at.% Gd obtained by spark plasma sintering of the initial Bi2Te3 and Gd powders. This image clearly shows filler inclusions as dark gray irregularly shaped islands randomly distributed in a light gray matrix. As follows from EDS analysis (the results themselves are shown below), the inclusions indeed correspond to Gd and the matrix to Bi₂Te₃. The size of the inclusions corresponds to the size of individual particles in the initial Gd powder (see Fig. 1d). Figure 2b shows one of the individual filler inclusions, whose shape is close to a parallelepiped. It can be seen that the inclusion is not single-crystal and consists of many small particles (grains) of micron size. The composite matrix has a well-defined grain structure. The SEM image of a cleavage



Fig. 3. BSE image of a filler inclusion in $Bi_2Te_3 + 0.5$ at % Gd (*a*), scanning profiles of Bi, Te, and Gd (*b*) taken along the lines crossing the inclusion.

of the composite surface oriented perpendicular to the direction of pressure application during spark plasma sintering is shown in Fig. 2c. This image clearly shows the grain structure, represented by irregularly shaped grains several microns in size.

It should be noted that reflections from the Gd phase are not observed in the diffraction pattern of the composite $Bi_2Te_3 + 0.5$ at.% Gd; this could be due to both its small amount and the fact that the main reflection with the highest intensity from the (111) plane of gadolinium overlaps with the main reflection from the (015) plane of bismuth telluride, so that these reflections do not differ in the diffraction pattern.

To determine the exact elemental composition of both the inclusions themselves and the matrix material, the distribution of Bi, Te, and Gd along the line crossing one of the inclusions was studied using the EDS method. The BSE image of this inclusion is displayed in Fig. 3*a*. According to the analysis of the scan profiles of various elements it was found that the inclusion consists only of Gd and the matrix of Bi₂Te₃. The boundary between the matrix and filler materials is sharp and narrow, and no possible chemical interaction was found between these materials and the redistribution of material atoms in the contact area during high-temperature sintering.

Note that in the composite based on the Bi_2Te_3 matrix and with Ni filler, in the spark plasma sintering process, because of the high-temperature diffusion redistribution of the atoms of the matrix materials and filler materials and the



Fig. 4. Temperature dependences of the resistivity (*a*), Seebeck coefficient (*b*), total thermal conductivity (*c*), and thermoelectric Q(d) of the Bi₂Te₃ reference sample (curves *l*) and the composite Bi₂Te₃ + 0.5 at.% Gd (curves 2).

chemical interaction between Bi₂Te₃ and Ni, the initial Ni filler particles are transformed into almost spherical, local-gradient, inclusions of the core - shell type (Ni@NiTe₂) shape, larger in size than the initial Ni particles [7-9]. The different evolution of Gd and Ni particles in the same Bi₂Te₃ matrix during high-temperature sintering of the corresponding initial powders can be related to the difference in the atomic radii of these elements. The atomic radius of Ni (135 pm) is much smaller than the atomic radius of Gd (180 pm). Consequently, the high-temperature diffusion of Ni atoms in the Bi₂Te₃ structure, which is necessary in order for the chemical reaction Ni + Bi₂Te₃ \rightarrow NiTe₂ to occur, will be more intense than the diffusion of Gd atoms in the same structure. As a result, the initial Ni particles in the $Bi_2Te_3 + Ni$ composite will transform into core - shell inclusions, while in the composite $Bi_2Te_3 + Gd$, the Gd inclusions will correspond in terms of elemental composition, shape, and size to the initial Gd particles.

The temperature dependences of the basic thermoelectric properties — the resistivity, Seebeck coefficient, total thermal conductivity, and thermoelectric Q — of the composite Bi₂Te₃ + 0.5 at.% Gd and the reference sample Bi₂Te₃ taken in the heating regime in the temperature range 280 – 520 K are displayed in Fig. 4. Although there are no qualitative differences in the temperature behavior of these properties, the introduction of the Gd filler into the Bi₂Te₃ matrix significantly affects the absolute values of ρ , k, and ZT of the matrix material. The resistivity of both the composite and reference sample increases with increasing temperature (Fig. 4*a*). This behavior, which is characteristic of metals and degenerate semiconductors, is typical of compounds based on Bi_2Te_3 [11 – 14]. In this case the temperature increase in ρ is associated with the scattering of electrons by acoustic and optical phonons (i.e., reduction in the electron mobility with increasing temperature at temperature-independent electron concentration). It can be seen that the resistance of the composite is higher than that of the reference sample. Clearly, this is due to the fact that Gd inclusions in the composite act as scattering centers for electrons, additionally reducing their mobility and increasing the electrical resistance.

The temperature dependences of *S* for the composite and reference sample are bell-shaped with maximum at $T_{\text{max}} \approx 450$ K (Fig. 4*b*). The Seebeck coefficient has a negative sign, which corresponds to electronic type of conductivity in the studied materials. Similar dependences S(T) are also typical for compounds based on Bi₂Te₃ [11 – 14]. The appearance of a maximum is associated with the onset of intrinsic electrical conductivity. As shown by the dashed lines in Fig. 4*b*, below the maximum temperature the Seebeck coefficient of the samples increases linearly with increasing temperature in accordance with the expression [11]

$$S = \frac{2k_{\rm B}^2 T m^*}{3e\hbar} \left(\frac{\pi}{3n}\right)^{2/3},\tag{1}$$

where $k_{\rm B}$ is the Boltzmann constant; *e* is the electron charge; \hbar is Planck's constant; m^* is the effective mass of the density of state for the conduction band; *n* is the electron concentration.

The temperature T_{max} and the maximum value of the Seebeck coefficient for the composite as well as the reference sample are approximately the same. The dependences S(T) were used to estimate the band gap E_g in the samples under study using the Goldschmit–Sharpe expression [15]

$$E_g = 2e \left| S_{\max} \right| T_{\max}, \qquad (2)$$

where S_{max} is the maximum value of the Seebeck coefficient.

Using the experimental values $T_{\text{max}} \approx 450$ K and $|S_{\text{max}}| = 148 \,\mu\text{V}\cdot\text{K}^{-1}$, the expression (2) gives the estimate $E_g \approx 0.13$ eV. This value corresponds to the published value of the band gap in Bi₂Te₃ [2]. The temperature dependences of the total thermal conductivity of the composite and reference sample are shown in Fig. 4*c*. These dependences have a minimum at temperature $T_{\text{min}} \approx 380$ K. The appearance of this minimum, which is also characteristic of compounds based on Bi₂Te₃, is associated with a change in the thermal conductivity mechanism [11 – 14]. Below T_{min} the main contribution to the total thermal conductivity is made by lattice (phonon) thermal conductivity (only phonons transfer heat phonons), and above T_{min} only by bipolar thermal conductivity (heat transfer occurs as a result of joint diffusion of electrons and holes from the heated section of the sample to the

cold one, where electron-hole pairs recombine with phonon emission). The total thermal conductivity of the composite $Bi_2Te_3 + 0.5$ at.% Gd is lower than the thermal conductivity of the Bi_2Te_3 matrix. This indicates that the inclusions of the Gd filler are scattering centers not only for electrons (the resistivity increases) but also for phonons (the total thermal conductivity decreases).

The thermoelectric Q of the composite turned out to be somewhat higher than that of the matrix material (Fig. 4*d*). The maximum value of *ZT* for both samples is reached at about 420 K: about 0.63 for the composite and about 0.58 for the matrix. According to the Ioffe formula $ZT = S^2T/k\rho$, to increase the thermoelectric Q of a material it is necessary to simultaneously decrease the resistivity and total thermal conductivity and increase the Seebeck coefficient. In Bi₂Te₃ + 0.5 at.% Gd the introduction of Gd increases the resistivity (negative effect), but at the same time reduces the total thermal conductivity (positive effect). However, a reduction in thermal conductivity is the dominant contribution, which ultimately effects a slight increase in the thermoelectric Q of the composite.

CONCLUSIONS

In this work, for the first time, a composite consisting of a Bi_2Te_3 matrix (low-temperature thermoelectric material) and a Gd filler (*f*-transition metal) was obtained. It was shown that the introduction of the filler does indeed effect a slight increase in the thermoelectric Q of the composite. In the future it is necessary to study the influence of the concentration and size of the filler particles on the observed effect.

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