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Influence of carbon nanotubes on thermoelectric properties of *p*- and *n*-type Heusler alloys

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This paper presents the results of studying the effect of carbon nanotubes on thermoelectric properties of *p*-type $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ and *n*-type $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ half Heusler alloys. The experimental data obtained indicate a strong effect of the carbon nanotubes on electrical conductivity and Seebeck coefficient of the *n*-type compound, while the changes in these properties in the *p*-type compound were significantly less. It is suggested that a possible reason for this difference is the formation of a conducting cluster of carbon nanotubes in the sample of the *n*-type Heusler alloy.

Keywords: carbon nanotubes, thermoelectric properties, Heusler alloys, electrical conductivity, Seebeck coefficient.

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1. Introduction

One of the approaches to increasing the thermoelectric Q-factor ZT of materials is the composites formation based on a thermoelectric matrix and a nanodispersed filler. This approach makes it possible to significantly reduce the lattice thermal conductivity by enhancing the scattering of medium- and long-wavelength phonons at the interfaces between the matrix and the filler. Besides, the density increasing of electron states at the Fermi level and the effects of carriers filtering can lead to the Seebeck coefficient increasing [1].

Carbon nanotubes (CNTs) are widely used as additives to many structural and functional materials to improve their properties [2]. Despite the fact that CNTs have weak thermoelectric properties, which is mainly due to their high thermal conductivity and low Seebeck coefficient [3], they have been widely used as additives to a number of thermoelectric materials. The effect of CNTs on the thermoelectric properties of materials based on Bi_2Te_3 was actively studied [4–8]. CNTs shown significant improvement of ZT *n*-type bismuth tellurides [4,5], while no significant improvement of ZT was observed in *p*-type materials [6,7]. Along with this, the literature reported on the study of CNTs effect on the thermoelectric properties of $MnSi_{1.75}$ [9], $Yb_{0.3}Co_4Sb_{12}$ [10], α-MgAgSb [11], Bi_2S_3 [12], SnTe [13,14], ZnO [15] and a number of polymers [16–18].

As it is known, the CNTs effect on the thermoelectric properties of Heusler alloys was not yet studied. The large family of these alloys includes full-Heusler alloys, which are characterized by the general formula X_2YZ and a $L2_1$ type crystal structure, and half-Heusler XYZ alloys with a $C1_b$ type structure. In both cases X, Y are 3*d* or 4*d* transition elements, or rare-earth metals, while Z is metalloid. The highest values of thermoelectric Q-factor were obtained for half-Heusler alloys, where it was possible to achieve $ZT > 1$ both in *n*-type and in *p*-type compounds [19]. Considering the growing interest in studying the CNTs effect on the thermoelectric properties of materials [7–18], for such studies we selected materials based on half-Heusler alloys Ni(Ti, Zr, Hf)Sn of *n*-type and Fe(Nb, Ta, Ti)Sb of *p*-type.

2. Samples and study methods

Ingots of nominal chemical composition $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ (NFS) of *p*-type and $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ (TNS) of *n*- type were synthesized from initial chemical elements by arc and induction melting in argon atmosphere. To ensure homogeneity the alloy ingots were remelted three times in the arc furnace. An excess of Sb was added to the charge to compensate for its losses due to evaporation during induction melting. The fabricated alloys were annealed in evacuated quartz tubes for 72 h at different temperatures (923 K for $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ and 1073 K for $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$), then both alloys were quenched in cold water. The annealed ingots were crushed to a fine powder, divided into two parts, and carbon nanotubes were added to one of the parts in an amount of 1% by weight. The powder and CNTs were mixed in a ball mill in argon atmosphere for 2 h with a rotation speed of 450 rpm at a ratio of balls to powder mixture of 10 : 1. The powders were consolidated in a vacuum on a spark plasma sintering (SPS) unit Labox 650, Sinter Land at a pressure of 50 MPa and temperatures of 1023 K (NFS) and 1173 K (TNS) (the process of samples consolidation on the SPS unit is described in detail in [20]). Consolidated samples in the form of disks were annealed at 923 K (NFS) and 1073 K (TNS) for 3 days.

The phase composition of the studied samples was analyzed on a Difrey 401 diffractometer using CrK_α ($\lambda = 2.2909$ Å) radiation. For qualitative elemental analysis, a Tescan Vega 3SB scanning electron microscope (SEM) with an attachment for energy dispersive analysis was used. The thermal conductivity of the samples was determined from the temperature dependences of the thermal diffusivity measured on a Netzsch LFA 447 unit by the laser flash method in the temperature range 300−873 K. The temperature dependences of electrical conductivity and thermoelectric EMF coefficient were determined in the temperature range 300−873 K by four-probe and differential methods, respectively.

3. Research results

X-ray patterns taken at room temperature on powders of alloys $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ (NFS) and $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ (TNS) are presented in Fig. 1. The positions of the main peaks correspond to the cubic structure with the lattice parameter $a = 5.9950$ Å for NFS and $a = 6.0269$ Å for TNS, respectively, which is in good agreement with the literature data [19,21,22]. The results of X-ray and electron microscopic analyzes do not indicate the existence of impurity phases in the samples under study. According to the results of energy-dispersive analysis, it was found that the actual chemical composition of the ingots is (in at%) $Nb_{17.2}Ta_{7.8}Ti_{5.9}Fe_{34.3}Sb_{34.7}$ and $Ti_{17.3}Zr_9Hf_{8.1}Ni_{33}Sn_{32.6}$, which is close to nominal compositions.

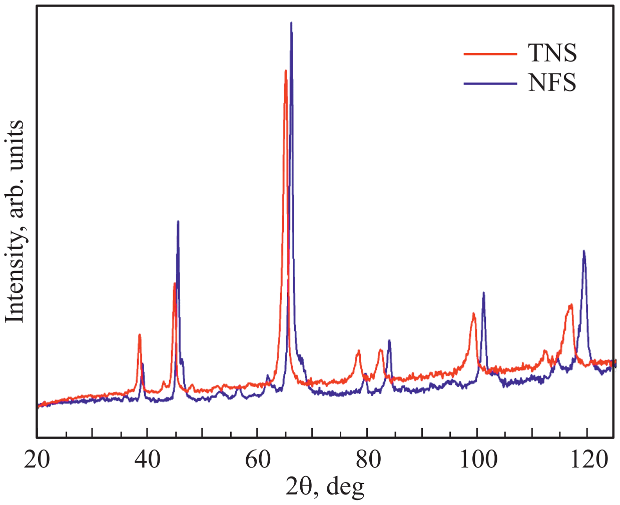

Figure 1. Diffraction patterns of samples $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ (NFS) and $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ (TNS) taken at room temperature.

Electrical conductivity σ and Seebeck coefficient S vs. temperature for samples $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ and $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ without additives (TNS and NFS) and with additives of carbon nanotubes (TNS + CNT and NFS + CNT respectively) are shown in Fig. 2. The obtained data show that the degree of CNTs effect on the thermoelectric properties of Heusler alloys strongly depends on the type of conductivity of these alloys. Whereas adding CNTs to the $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ compound of *p*-type leads to approximately two times increasing of the electrical conductivity and decreasing of the Seebeck coefficient, adding CNTs to $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ compound of *n*-type is accompanied by a change in the values of σ and S by almost an order of magnitude (Fig. 2, *a, b*). The power factor, which is defined as $PF = S^2\sigma$, is also more affected by CNTs in *n*-type alloy (Fig. 2, *c*). Note that a strong dependence of the degree of CNTs effect on the type of conductivity of materials was also observed for bismuth tellurides [4–7].

In our opinion, a significant difference in the degree of CNTs effect on the thermoelectric properties of *p*- and *n*-type Heusler alloys (Fig. 2) can be qualitatively explained taking into account the type of conductivity of the carbon nanotubes themselves. Considering that CNTs are conductors of *p*-type with the Seebeck coefficient at room temperature $\sim 20{-}40\,\mu V \cdot K^{-1}$ [3], their addition to the Heusler alloy $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ of *p*-type, that has a relatively small value $S \approx 50\,\mu V \cdot K^{-1}$ at room temperature and a relatively large electrical conductivity $\sigma \approx 2000\,Ohm^{-1} \cdot cm^{-1}$, leads to a relatively small change in both S and σ (Fig. 2). On the other hand, additions of *p*-type CNTs to the Heusler alloy $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ of *n*-type as expected lead to a large decreasing of the absolute value of the Seebeck coefficient from $S \approx -125$

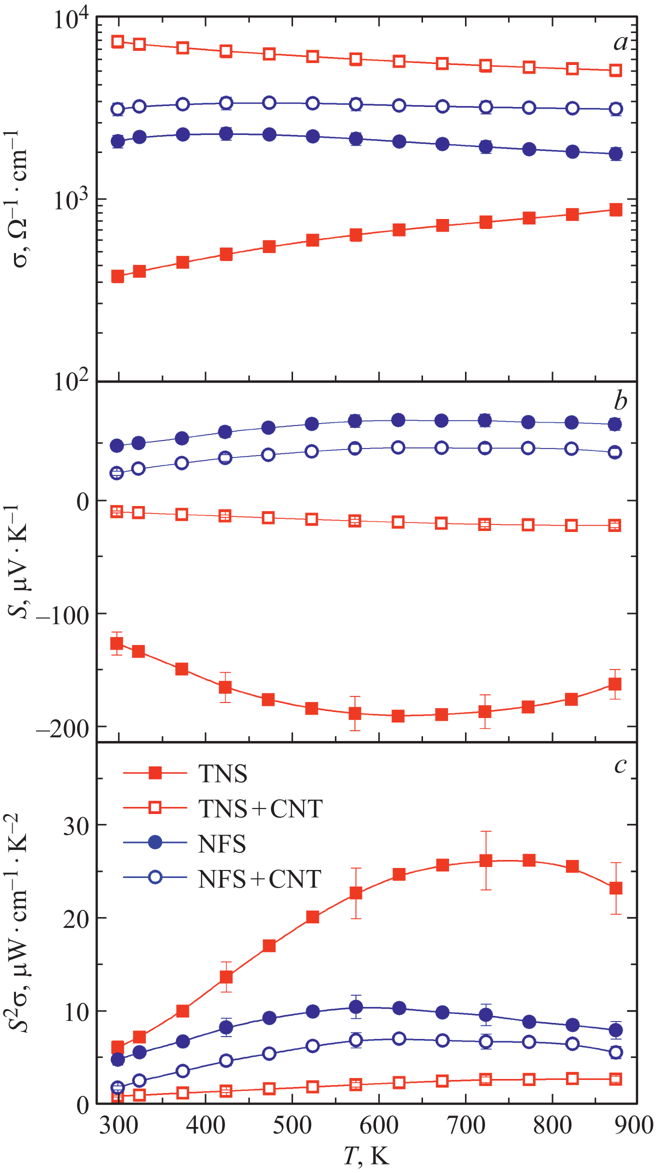

Figure 2. Electrical conductivity (*a*), Seebeck coefficient (*b*) and power factor (*c*) vs. temperature of samples $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ and $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ without additives (TNS, NFS) and with additives of carbon nanotubes (TNS + CNT, NFS + CNT).

to $-15\,\mu V \cdot K^{-1}$. The electrical conductivity increasing from $\sigma \approx 400\,Ohm^{-1} \cdot cm^{-1}$ in TNS sample without nanotubes to $\sigma \approx 8000\,Ohm^{-1} \cdot cm^{-1}$ in the TNS + CNT sample can be explained taking into account that the transport properties of the TNS + CNT sample are due to both electrons and holes.

Note that change by almost order of magnitude of the electrical conductivity and Seebeck coefficient upon the CNTs addition to $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ may indicate that the transport properties and thermoelectric EMF of the TNS + CNT sample were determined by the properties of CNTs that formed the conducting cluster in the $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ matrix. This assumption is supported by data on the thermal conductivity κ of the studied samples without and with the addition of carbon nanotubes. It can be seen from Fig. 3, *a* that the thermal conductivity of $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ slightly decreases upon CNTs addition, which, in all likelihood, is caused by the growth of phonon scattering processes at the interfaces between the matrix and nanotubes. On the other hand, the thermal conductivity of $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ at room temperature sharply increases from $\kappa \approx 2.8\,W \cdot m^{-1} \cdot K^{-1}$ in the sample without CNTs to $\kappa \approx 6\,W \cdot m^{-1} \cdot K^{-1}$ in a sample with CNTs, the phonon scattering processes at the interfaces between the matrix and nanotubes are overlapped by heat transfer processes along the conducting CNT cluster in the $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ matrix.

Summing up the data relating CNTs effect on the thermoelectric properties of Heusler alloys $(Nb_{0.6}Ta_{0.4})_{0.8}Ti_{0.2}FeSb$ and $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ (Fig. 3, *b*), it is necessary to note a strong drop of the thermoelectric Q-factor ZT of $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ alloy by adding carbon nanotubes to it. ZT decreasing by almost 10 times in this compound upon the nanotubes addition is primarily due to a very large decreasing of the absolute value of the Seebeck coefficient S (Fig. 2, *b*), and significant increasing of thermal conductivity κ (Fig. 3, *a*).

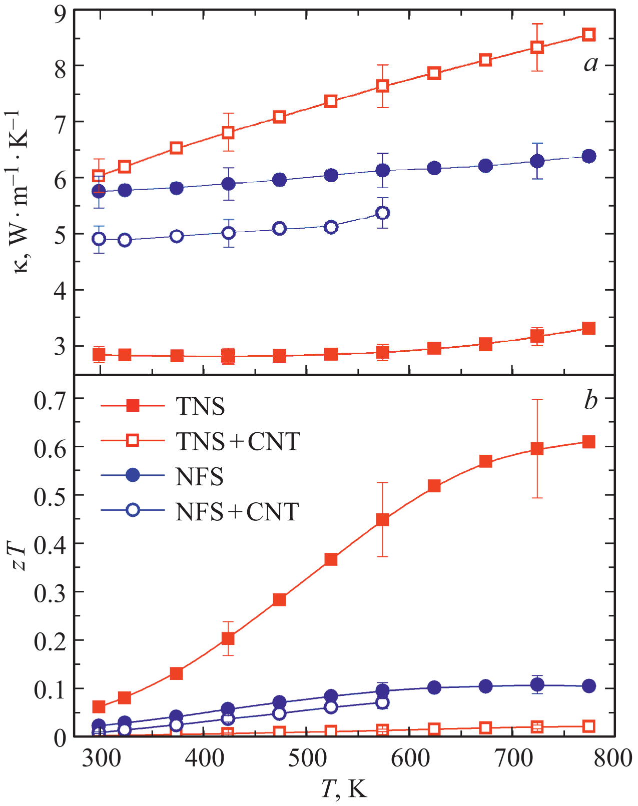

Figure 3. Thermal conductivity (*a*) and thermoelectric Q-factor (*b*) vs. temperature of samples $(Nb_{0.6}Ta_{0.4})_{0.8}$ $Ti_{0.2}FeSb$ and $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ without additives (TNS, NFS) and with additives of carbon nanotubes (TNS + CNT, NFS + CNT).

4. Conclusion

The effect of carbon nanotubes on the thermoelectric properties of *p*- and *n*-type Heusler alloys was studied for the first time in the paper. It was shown that additions of CNTs lead to the electrical conductivity and thermoelectric power change by 10 times in the *n*-type Heusler alloy, while the changes in these properties in the *p*-type alloy are much smaller. As a development of these studies in the future, it seems interesting to study the thermoelectric properties of materials with different CNTs content, which will make it possible to determine the percolation threshold and trends in the change in the thermoelectric properties of compounds of *n*- and *p*-type conductivity with the content increasing of carbon nanotubes.

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Conflict of interest

The authors declare that they have no conflict of interest.

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