Experimental and First-principle study of TmNiSb half-Heusler Alloy

Zlata Rykavets[1], Diana Ryzhak[1], Lyubov Romaka[2], Sergiy Shvachko[1], Vitaliy Romaka[1]

1. Department of Materials Science and Engineering, Lviv Polytechnic National University, UKRAINE, Lviv, Ustiyanovycha 5, contact e-mail: zlata.rykavets.mmz.2017@lpnu.ua

2. Department of Inorganic Chemistry, Ivan Franko National University of Lviv, UKRAINE, Lviv, Kyryla & Mephodiya street 6

Abstract – The studied TmNiSb alloy crystallizes in the MgAgAs structure type (half-Heusler phases) and according to the results of DFT+U calculations revealed the presence of bandgap (Eg = 359 meV). Spin magnetic moment of Tm atoms equals 2.16 μB confirming its Tm^{3+} state. Calculated elastic properties as well as Vickers hardness of TmNiSb alloy was defined semi-empirically and equals 15.98 GPa. Experimentally determined microhardness is within the range of 2.90 – 4.06 GPa with the exception of TmNiSb phase.

Keywords – thermoelectric material, DFT+*U* modeling, half-Heusler phases, spin magnetic moment, mechanical properties

I. Introduction

One of the most significant current discussions in the energy sector is power generation from renewable sources. In this regard, the number of scientific papers (devoted to research more efficient thermoelectric materials) experienced steady growth. The research to date has tended to focus on highly effective thermoelectric materials to which belong half-Heusler alloys containing rare-earth metal. *R*NiSb compounds aren't completely investigated, so the profitable TmNiSb alloy which crystallizes in MgAgAs structure type [1] was chosen. The Curie-Weiss behavior for TmNiSb alloy is revealed [2]. From the point of electrical properties, the majority of *R*NiSb compounds are narrow-gap semiconductors. It should be pointed out that good mechanical performance is quite essential for the practical application of thermoelectric materials. In order to investigate structure peculiarities of TmNiSb alloy the X-ray diffraction, metallographic analyses and theoretical modeling of energetic, mechanical, and magnetic characteristics of Tm—Ni—Sb alloys were performed.

II. Computational Details

Crystal structure optimization was conducted using Elk [3] and Exciting [4] software packages. Modeling of the electronic structure for pure equiatomic TmNiSb was carried out in the framework of the theory of functional density by the DFT + *U** method, which is a combination of an exchange-correlation functional in local spin density approximation (LSDA) and the Hubbard parameter (*U*). The the *k*-point mesh size was equal to 10×10×10 for a single unit cell. Visualization of bulk data was undertaken under the program VESTA [5]. For the basic mechanical properties definition the program ElaStic [6] was applied. Maximum values of η_{max} (0.04) and the number of defective structures (31) were elected as input parameters for calculation each components which for TmNiSb alloy are: C_{11} = 156,1 GPa, C_{12} = 51,3 GPa, C_{44} = 86,4 GPa. For each option of deformed structure the calculation of the total energy of the system was carried out and used for further defining basic parameters of mechanical properties. Experimental determination was performed with a microhardness tester PMT-3, applying a stress of 0.196 N with a loading time of 10 sec. For each value a number of 5 measurements were performed and the average value was calculated.

III. Results and Discussion

The X-ray diffraction analysis showed that the majority alloys of Tm—Ni—Sb system are mostly two-phase and are composed of binary and ternary phases (Table 1). In samples of the following composition $Tm_{30}Ni_{40}Sb_{30}$ and $Tm_{34}Ni_{33}Sb_{33}$, except binary phase TmSb (*ST* NaCl), ternary phase – TmNiSb (*ST* MgAgAs) is also presented. Increasing of Tm content causes the appearance of another ternary phase Tm_5Ni_2Sb (*ST* Mo_5SiB_2). Among all samples there was only one single-phase – $Tm_{50}Ni_5Sb_{45}$, the basic phase is TmSb (*ST* NaCl). Ternary phases was not observed in the samples with Sb contain more than 50 at.% Sb. All attempts to get single-phase $Tm_{34}Ni_{33}Sb_{33}$alloy which corresponds to the structure of intermetallic TmNiSb (*ST* MgAgAs) were failed. This is due to the presence of impurity binary phase – TmSb which formation temperature (2293 K) is higher compared to the formation temperature of a TmNiSb ternary phase. Thus, for alloy TmNiSb with the least amount of impurity phase TmSb, the furnace should contain more Ni content.

Metallographic analysis showed that low-containing Tm alloys (e.g. $Tm_{25}Ni_{20}Sb_{55}$) are characterized by a three-phase area: dendrites, matrix and grains that form agglomerates, but increasing of Tm content causes porosity augmentation and its irregular distribution (e.g. $Tm_{65}Ni_{20}Sb_{15}$).

Realization of the DFT+*U* method required to find the optimal setting of Hubbard parameter. Defined value of Hubbard parameter is *U* = 0.4 Ha and following conditions are satisfied: 1) minimum total energy value → 5.71452 eV (E_0 = -586 972 eV); 2) adequacy of theoretical spin magnetic moments of Tm atoms ~ 2 μB (term $_3H^6$) → 1.93 μB.

Crystal structure optimization was conducted using software packages Elk, Exciting and optimization parameter of unit cell are 0.6191 nm and 0.6075 nm, respectively, which is close to the experimentally determined (0.6240 nm). The calculated value of the spin magnetic moment of atoms Tm is 2.16 μB which is close to the theoretical Tm^{3+} ion (2 μB) and is in comparison with experimental studies of TmNiSb magnetic characteristics in literature data [2].

TABLE 1

CRYSTALLOGRAPHIC CHARACTERISTICS OF ALLOYS OF TERNARY TM—NI—SB SYSTEM

Alloy	Phase	Structure type	Space group	Lattice parameters, *nm*		
				a	*b*	*c*
$Tm_{65}Ni_{20}Sb_{15}$	Tm_5Ni_2Sb	Mo_5SiB_2	*I*4/*mcm*	0.7472(7)	-	1.324(1)
	Tm_3Ni	Fe_3C	*Pnma*	0.684(2)	0.926(3)	0.596(1)
$Tm_{50}Ni_{20}Sb_{30}$	TmSb	NaCl	*Fm*-3*m*	0.6086(8)	-	-
	TmNi	FeB-b	*Pnma*	0.690(2)	0.4090(7)	0.5370(9)
$Tm_{30}Ni_{40}Sb_{30}$	TmNiSb	MgAgAs	*F*-43*m*	0.6240(1)	-	-
	TmSb	NaCl	*Fm*-3*m*	0.6112(9)	-	-
$Tm_{50}Ni_5Sb_{45}$	TmSb	NaCl	*Fm*-3*m*	0.6086(5)	-	-
$Tm_{25}Ni_{20}Sb_{55}$	TmSb	NaCl	*Fm*-3*m*	0.6092(1)	-	-
	NiSb	NiAs	$P6_3/mmc$	0.3914(1)	-	0.5138(4)
$Tm_5Ni_{45}Sb_{50}$	NiSb	NiAs	$P6_3/mmc$	0.3908(1)	-	0.5120(3)
	$Ni_{0.15}Sb_{0.85}$	Po	*Pm*-3*m*	0.3040(2)	-	-

The analysis of the distribution of DOS (Figure 1) showed that the TmNiSb alloy is characterized by the presence of a band gap (*Eg* = 359 meV), which has a Fermi level and should have semiconductor properties.

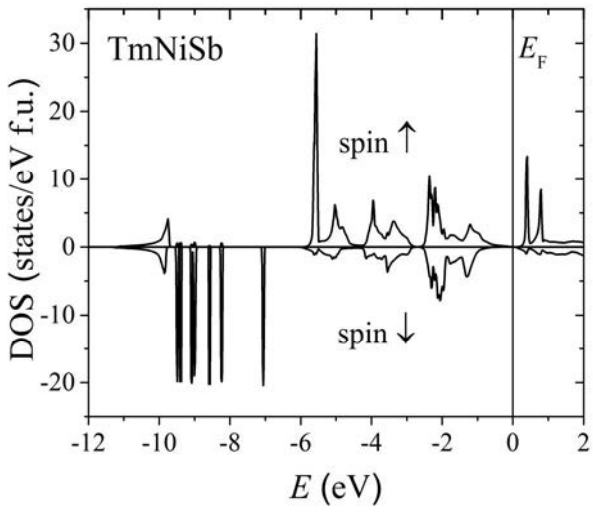

Fig.1. Distribution of the total and partial electron density of states (DOS) in the TmNiSb alloy.

Distribution of electron localization function (*elf*) revealed its localization between the atoms of Ni and Sb (Figure 2), indicating a significant contribution of the covalency into the Ni-Sb bonds. Spherical electron localized distribution around atoms Tm as polar intermetallic compound with positively charged ion Tm^{3+} and negatively charged sublattice $[NiSb]^{n-}$.

The 3*d*-shell of Ni atoms is completely filled, so atoms of the rare earth elements are in a R^{3+} state and are the source of TmNiSb magnetism.

Mechanical properties of alloys of Tm—Ni—Sb system has been investigated for the first time, so it was important to determine the order of hardness value.

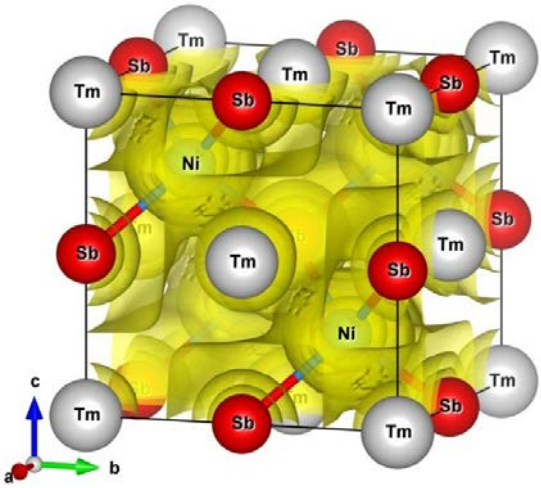

Fig.2. Distribution of the electron localization function in the TmNiSb alloy.

The experimental data showed that the value of microhardness is in the range 2.90 – 4.06 GPa. Samples inherent brittleness increases with Sb amount rising. Table 2 shows the fundamental parameters of mechanical properties of TmNiSb alloy computed by ElaStic and experimental data for $Ti_{0,50}Zr_{0,48}Nb_{0,02}NiSn_{0,98}Sb_{0,02}$ thermoelectric alloy, both intermetallic compounds are characterized by MgAgAs structure.

TmNiSb alloy is characterized by the low values of shear modulus, indicating a low resistance to deformation shift and the ratio 1/*B* together with Poisson's ratio *v* define poor fracture resistance, thus the material is brittle.

TABLE 2

MECHANICAL CHARACTERISTICS OF THERMOELECTRIC ALLOYS WITH MGAGAS-STRUCTURE TYPE: BULK MODULUS, ***B*** (GPA), SHEAR MODULUS, ***G*** (GPA), YOUNG'S MODULUS, ***E*** (GPA), POISSON'S RATIO, ***N***, ***B/G*** RATIO, AND VICKERS HARDNESS, H_V (GPA)

Mechanical parameter	TmNiSb	$Ti_{0.50}Zr_{0.48}Nb_{0.02}NiSn_{0.98}Sb_{0.02}$ [7]*
B	86.3	146,9
G	70.7	70,1
E	166.6	181,5
v	0.18	0,294
B/G	1.220	2,095
H_V	**15.98**	10,78

*Experimental.

According to the Pugh rule [8], the critical value of B/G ratio which separates ductile and brittle materials has been evaluated to be equal to 1.75. The *B/G* ratio equals 1.22, (*B /G* <1.75) and defines a brittle behavior of structure which is consistent with experimental results.

Based on the calculated values of bulk modulus and shear modulus for TmNiSb Vickers hardness value was defined semi-empirically and equals 15.98 GPa. This result close to hardness value in the highly effective thermoelectric material [7].

Conclusions

The X-ray diffraction analysis showed that alloys with the composition close to equiatomic contain except the TmNiSb main phase an impurity one – TmSb. In order to reduce its amount in alloy a higher Ni content in the sample is required. Metallographic analysis revealed that alloys of Tm-Ni-Sb system are characterized by dendrite structure. The disorder of structure is defined by the number and distribution of pores. The electronic structure modeling of TmNiSb alloy showed that spin magnetic moment of Tm atoms equals 2.16 μB and confirms Tm^{3+} state. The distribution of the density of electronic states predicts semiconducting properties of TmNiSb.

The microhardness of alloys with the exception of TmNiSb phase is within the 2.90-4.06 GPa range.

The modeling of mechanical properties showed that Vickers hardness of TmNiSb alloy equals 15.98 GPa that is close to the value of another $Ti_{0.50}Zr_{0.48}Nb_{0.02}NiSn_{0.98}Sb_{0.02}$ Half-Heusler alloy with high *ZT*. Brittle behavior from *B/G* ratio indicates a significant impact of covalency in the chemical bonds between Ni and Sb in TmNiSb.

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References

[1] Pecharskyj V., Pankevich Y., Bodak O. Crystal structures of the compounds RNiSb with various rare earth elements // Sov. Phys. Crystallogr. (Engl. Transl.), Vol. 28 (1983) P.97-98

[2] Hartjes K., Jeitschko W. Crystal structures and magnetic properties of the lanthanoid nickel antimonides LnNiSb Ln = LaNd, Sm, Gd, Tm, Lu. // J. Alloys Compd., Vol. 226 (1995) P. 81-86.

[3] All–electron full–potential linearised augmented–plane wave (FP–LAPW) code – http://elk.sourceforge.net.

[4] Golesorkhtabar R., Pavone P., Spitaler J., Puschnig P., Draxl C. *ElaStic: A tool for calculating second-order elastic constants from first principles* // Comp. Phys. Commun., Vol. 184 (2013) P.1861

[5] Momma K., Izumi F. VESTA: a three–dimensional visualization system for electronic and structural analysis – J. Appl. Crystallogr., Vol.41 (2008) P. 653 – 658

[6] Gulans A., Kontur S., Meisenbichler C., Nabok D., Pavone P., Rigamonti S., Sagmeister S., Werner U., Draxl C. E1983 Pecharskyj – *a full-potential all-electron package implementing density-functional theory and many-body perturbation theory //* J. Phys.: Condens. Matter., Vol. 26 (2014)— № 363202

[7] Rogl G., Sauerschnig P., Rykavets Z., Romaka V.V., Heinrich P., Hinterleitner B., Grytsiv A., Bauer E., Rogl P. (V,Nb)-doped half Heusler alloys based on {Ti,Zr,Hf}NiSn with high ZT // Acta Materialia, Vol.131 (2017) P.336-348

[8] Pugh S. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals // Philos. Mag. A, Vol.45 (1954) P.823.