

Thermoelectric properties of Fe-V-Al Heusler alloy with excess of Al and deficiency of Fe

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The results of the experimental studies of the thermoelectric properties of a $\text{Fe}_{1.68}\text{VAl}_{1.32}$ p -type Heusler alloy are presented. A comparison of the electrical resistivity ρ and the Seebeck coefficient S measured in a temperature range 300–475 K with data, published for other Fe-V-Al p -type with different chemical compositions, showed that $\text{Fe}_{1.68}\text{VAl}_{1.32}$ has the lowest ρ and one of the highest values of S . This leads to one of the record values of the power factor value $PF \approx 1.7 \text{ mW}/(\text{m}^{-1} \cdot \text{K}^{-2})$ (at $T = 384 \text{ K}$) in $\text{Fe}_{1.68}\text{VAl}_{1.32}$, which is an order of magnitude higher than that in the stoichiometric PF . The results of thermal conductivity measurements showed high values of κ ($\approx 1111 \text{ W}/(\text{m}^{-1} \cdot \text{K}^{-1})$) in the studied compound, which is comparable to thermal conductivity of the stoichiometric Fe_2VAl .

Keywords: Heusler alloys, arc melting, transport properties, power factor.

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1. Introduction

Heusler alloys are triple intermetallic compounds and are generally divided in two classes. The first type compounds, the so-called Full-Heusler alloys, are featuring X_2YZ stoichiometry and L2_1 structural type of a cubic lattice. The second type compounds include the so-called Half-Heusler alloys with XYZ stoichiometry and C1_b type of a cubic lattice. In both cases X, Y elements — are transition metals of 4–11 groups, and Z — are the elements of the main group (Al, Ga, In, Si, Ge, Sn, Sb) [1].

Stability of Heusler alloys is mostly defined by the valence electron rule. So, for XYZ alloys is equal to 18, and for X_2YZ alloys — 24. Deviations from these values in most cases lead to instability of the compound. However, recently it was suggested [2], that due to the introduction of some defects it is possible to obtain Half-Heusler alloys with 18 valence electrons from the unstable compounds with 19 valence electrons. By using this approach the paper [3] describes the study of an alloy with a composition close to $\text{Fe}_{1.25}\text{VAl}$ — a non-stoichiometric Full-Heusler alloy with 18 valence electrons the number of which was corrected by introducing new vacancies.

Compared to Half-Heusler alloys, the thermoelectric Q -factor zT of Full-Heusler alloys is much lower [4]. Yet, Full-Heusler alloys, Fe_2VAl in particular, attract a lot of interest from researchers because of the non-toxic nature and low cost of chemical elements in these alloys. Recent studies have demonstrated that a complex substitution of vanadium and aluminum positions in the stoichiometric Fe_2VAl enables to increase zT up to ~ 0.34 and obtain large values of the power factor $PF \approx 10 \text{ mW}/(\text{m}^{-1} \cdot \text{K}^{-2})$ in alloys of n -type of conductivity [5]. In addition, it was found that aluminum has high solubility in Fe_2VAl [6]

compounds, that, by varying the component contents, may impact the thermoelectric properties of the initial compound and obtain larger power factor values for alloys of p -type of conductivity. The purpose of this paper — study the influence of iron deficiency on the thermoelectric properties of Fe_2VAl alloy with excess aluminum.

2. Samples and measurement procedures

Nominal composition alloy $\text{Fe}_{42}\text{V}_{25}\text{Al}_{33}$ (at%) was obtained in the electric-arc furnace using pure (Fe — 99.99%, V — 99.93%, Al — 99.99%) chemical elements. Weight loss in melting didn't exceed 0.2%. The fabricated ingot was placed in a quartz tube and annealed in the tubular furnace at a temperature of 1073 K during 120 h, after that the ingot was quenched in cold water. The annealed ingot was mechanically grinded in a mortar bowl. Later, by means of spark-plasma sintering (SPS), samples were fabricated from the powder to measure the thermoelectric properties. SPS was carried out in vacuum at 1273 K, compaction pressure of 65 MPa, and heating and cooling rates of 30 and 50°C/min, respectively.

X-ray diffraction analysis was carried out at a room temperature on Difrey 401 diffractometer with CrK_α -emission ($\lambda = 2.2909 \text{ \AA}$). The microstructure and chemical composition were analyzed using scanning electron microscope (SEM) Tescan Vega 3SB, with an integrated energy-dispersive X-ray spectrometry (EDS) unit. Thermal conductivity κ was calculated from the measured temperature dependence of the temperature diffusivity factor χ , obtained by laser flashing on laser unit Netzsch LFA 447, and using formula $\kappa = C_p d \chi$, where C_p — specific heat capacity

calculated theoretically according to Debye model, d — density defined by hydrostatic weighing method. Electrical resistivity ρ and Seebeck coefficient S were measured on Cryotel unit by four-probe and differential methods, respectively.

3. Results and discussion

The results of X-ray diffraction analysis are given in Figure 1. As seen from the observed reflections it may be concluded that the sample has a cubic lattice peculiar to these compounds with a parameter of $a = 0.5815$ nm, which is slightly higher than for stoichiometric Fe_2VAl ($a = 0.5762$ nm) [7,8]. The absence of superstructure reflections (e.g., (111)) indicates that the studied alloy $\text{Fe}_{1.68}\text{VAl}_{1.32}$ doesn't have a structure ordering of $L2_1$ type which is peculiar to the fully ordered Heusler alloys X_2YZ , but is crystallized into a partially disordered structure of B2 type, where V/Al sub-lattice is disordered [1]. The reflections from secondary phases on the diffraction pattern are not observed, which, given the device sensitivity, indicates that if they are present their volume fraction will be $< 5\%$.

The analysis of microstructure images obtained using SEM method indicates that, apart from the ground phase, there's also a small amount of secondary phase present in the sample in the form of dendrite inclusions. Real chemical composition of a sample defined by ED in several points of the sample's grinded surface was found to be equal $\text{Fe}_{42.1}\text{V}_{24.2}\text{Al}_{33.7}$ (at%), which is close to the chemical composition ($\text{Fe}_{42}\text{V}_{25}\text{Al}_{33}$). It is not possible to determine the chemical composition by the same method because of very small (several μm) sizes of inclusions of this phase.

Temperature dependences of electrical resistivity ρ and Seebeck coefficient S are given in Figure 2. From Figure 2, a we may see that in the measured temperature range the

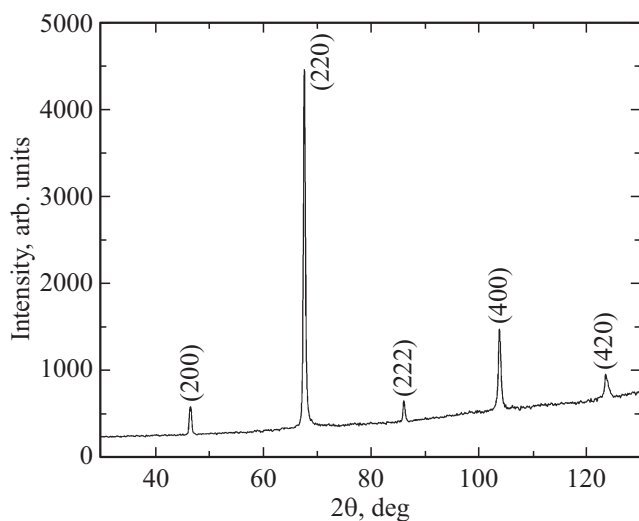


Figure 1. Diffraction pattern of $\text{Fe}_{1.68}\text{VAl}_{1.32}$.

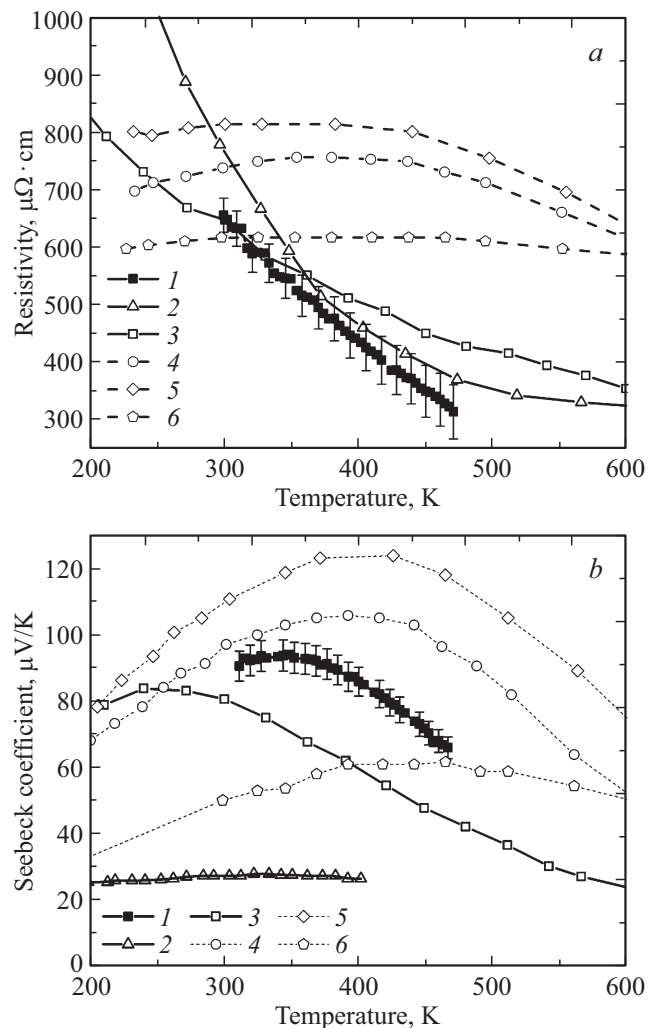


Figure 2. Temperature dependence of electric resistivity (a) and Seebeck coefficient (b) at $\text{Fe}_{1.68}\text{VAl}_{1.32}$ (1). Data from literature for Fe_2VAl (2) [7], $\text{Fe}_{2.08}\text{V}_{0.92}\text{Al}$ (3) [8], $\text{Fe}_2\text{VAl}_{1.2}$, $\text{Fe}_2\text{VAl}_{1.6}$ and Fe_2VAl_2 (4–6), respectively, are given for comparison [6].

dependence $\rho(T)$ in $\text{Fe}_{1.68}\text{VAl}_{1.32}$ is featuring a semiconducting nature going down from $\rho \approx 650 \mu\text{Ohm} \cdot \text{cm}$ at room temperature to $\rho \approx 320 \mu\text{Ohm} \cdot \text{cm}$ at $T = 475$ K. It should be noted that semiconducting nature of electrical resistivity is typical at $T > 300$ K both, in non-doped [3–5], and doped alloys [9,10] of Fe-V-Al system. By comparing the values ρ in the studied alloy with the values measured for the stoichiometric Fe_2VAl (curve 2), Fe-V-Al with excessive Fe (curve 3) and with excessive Al (curves 4–6), we may see that $\text{Fe}_{1.68}\text{VAl}_{1.32}$ has the lowest electrical resistivity among all presented materials at temperatures of > 310 K. At lower temperatures the values ρ in our sample exceed the values ρ in Fe_2VAl_2 , the electrical resistivity of which demonstrates behavior typical for metals up to $T = 4$ K [6]. Small values of electrical resistivity in $\text{Fe}_{1.68}\text{VAl}_{1.32}$ may be due to the increase of the charge carriers concentration (holes in our case, as shown below) when Fe is substituted by Al.

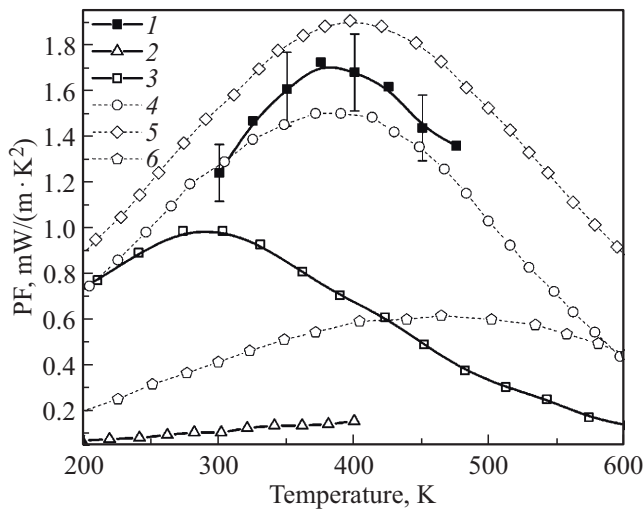


Figure 3. Temperature dependence of power factor in $\text{Fe}_{1.68}\text{VA}_{1.32}$. For comparison literature data for other semiconductors of p -type are given: Fe_2VAI (2) [7], $\text{Fe}_{2.08}\text{V}_{0.92}\text{Al}$ (3) [8], $\text{Fe}_2\text{VAI}_{1.2}$, $\text{Fe}_2\text{VAI}_{1.6}$ and Fe_2VAI_2 (4–6) respectively [6].

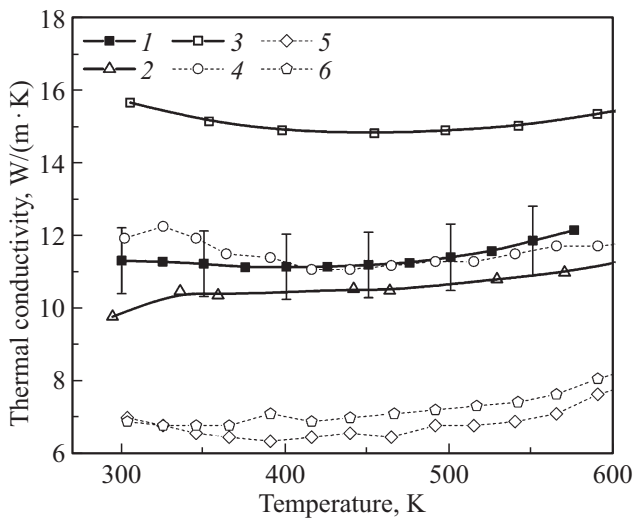


Figure 4. Temperature dependence of thermal conductivity in $\text{Fe}_{1.68}\text{VA}_{1.32}$. Data from literature for Fe_2VAI (2) [7], $\text{Fe}_{2.08}\text{V}_{0.92}\text{Al}$ (3) [8], $\text{Fe}_2\text{VAI}_{1.2}$, $\text{Fe}_2\text{VAI}_{1.6}$ and Fe_2VAI_2 (4–6), respectively, are given for comparison [6].

The results of measuring the Seebeck coefficient S demonstrate that $\text{Fe}_{1.68}\text{VA}_{1.32}$ is itself a semiconductor of p -type (Figure 2, *b*). The temperature dependence S in $\text{Fe}_{1.68}\text{VA}_{1.32}$ is typical for the degenerated semiconductors. I.e. from Figure 2, *b* we may see that during heating at room temperature S is slightly growing in the beginning, reaching its maximal value $S \approx 94 \mu\text{V/K}$ at $T = 350 \text{ K}$, and further it is going down with the following temperature growth. Fe_2VAI semiconductor alloys generally demonstrate peak values on $S(T)$ dependence [3,5], which is a consequence of a bipolar conductance representation. S values of the studied alloy are several times higher compared to the stoichiometric

Fe_2VAI and to the alloy with excess of Fe, but lower than in some compounds with excess of Al (Figure 2, *b*).

Low values of electrical resistivity along with relatively high Seebeck coefficient result in large values of power factor PF (Figure 3). It should be noted that thermoelectric materials based on Fe_2VAI of n -type demonstrate gigantic values of PF amounting to $\sim 10 \text{ mW}/(\text{m}^{-1} \cdot \text{K}^{-2})$ [5], whereas in materials of p -type the power factor is much lower. For materials with this type of conductivity the record value $PF = 1.9 \text{ mW}/(\text{m}^{-1} \cdot \text{K}^{-2})$ was achieved in alloy $\text{Fe}_2\text{VAI}_{1.6}$ [6]. Comparison of power factors in materials based on Fe_2VAI of p -type of conductivity shows (Figure 3) that power factor for $\text{Fe}_{1.68}\text{VA}_{1.32}$ studied in this paper is one of the largest ones reaching $PF \approx 1.7 \text{ mW}/(\text{m}^{-1} \cdot \text{K}^{-2})$ at $T = 384 \text{ K}$.

Temperature dependence of thermal conductivity κ in $\text{Fe}_{1.68}\text{VA}_{1.32}$ is shown in Figure 4. We may see that this alloy is characterized by high thermal conductivity which exceeds κ in stoichiometric Fe_2VAI . Thermal conductivity $\text{Fe}_{1.68}\text{VA}_{1.32}$ is practically independent from temperature, and rises only from values of $\kappa \approx 11.3 \text{ W}/(\text{m} \cdot \text{K})$ at room temperature of up to $\kappa \approx 12.2 \text{ W}/(\text{m} \cdot \text{K})$ at $T = 550 \text{ K}$. Alloy $\text{Fe}_2\text{VAI}_{1.2}$ studied in paper [6] with a slight excess of aluminum has similar values of thermal conductivity, while compounds with higher aluminum content demonstrate much lower values of κ .

4. Conclusion

This paper outlines the study of thermoelectric properties of Heusler alloy $\text{Fe}_{1.68}\text{VA}_{1.32}$ which is featuring excess of aluminum and deficiency of iron as compared to the stoichiometric compound. Comparing the properties of this alloy with Fe_2VAI alloys of other chemical compounds but of the same type of conductivity demonstrated that in the measured temperature interval $\text{Fe}_{1.68}\text{VA}_{1.32}$ has lowest values of electrical resistivity. This, apparently, is due to the rise of charge carriers concentration when Fe is substituted by Al. Along with this, $\text{Fe}_{1.68}\text{VA}_{1.32}$ demonstrates one of the largest Seebeck coefficient values allowing to reach the unprecedented power factor values. In spite of this, large values of thermal conductivity in $\text{Fe}_{1.68}\text{VA}_{1.32}$ didn't provide sufficient growth of thermoelectric Q factor zT for this material. However, given that sample of $\text{Fe}_{1.68}\text{VA}_{1.32}$ studied in this paper represented itself a coarse crystalline sintered powder, we may suggest that if crystallites are shrunk to sub-micron sizes the thermal conductivity of this sample can be significantly reduced and thus, zT can be increased.

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Conflict of interest

The authors declare that they have no conflict of interest.

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