Self-propagating high-temperature synthesis of $\text{Fe}_2\text{TiSn}$ based Heusler alloys with following spark plasma sintering

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Abstract. The $\text{Fe}_2\text{TiSn}$ based Heusler alloys were synthesized and studied. The samples were fabricated by a combination of self-propagating high-temperature synthesis (SHS) followed by spark plasma sintering (SPS). An optimal mechanical activation (MA) regime, favoring for successful SHS process was experimentally defined for the stoichiometric mixture of elements powder. The phase evolution of the $\text{Fe}_2\text{TiSn}_{1-x}\text{Si}_x$ ($x = 0, 0.10, 0.15, 1$) compound and the morphology of a bulk specimens were studied. It was shown that with the presence of an impurity side phase Fe$_2$Ti the electrical resistivity of material decreased by an order of magnitude, while the Seebeck coefficient remains unchanged in the range from 3 to 8 μV K$^{-1}$.

1. Introduction
With the human population constantly increasing the issue of the energy efficiency becomes more and more important. Involving recycling process into the any technology is a necessary step and it also concerns recycling of the wasted heat. There is a class of materials which can convert the heat energy directly into electricity and vice versa, which is called thermoelectric materials. Thermoelectric (TE) devices can have variety of applications such as for solar heat conversion [1], waste heat recovery [2, 3], local cooling of electrical devices [4] and air conditioning [5]. However, relatively low conversion efficiency of the commercially available TE materials hinders their wider application.

Conversion efficiency mainly defined by the temperature difference between cold and hot side of thermoelectric module and the dimensionless figure of merit $zT = \alpha^2\sigma T/\kappa$, where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature and $\kappa$ the total thermal conductivity [6]. For high efficiency, high power factor ($\alpha^2\sigma$) coupled with low thermal conductivity ($\kappa$) is essential. Semiconducting intermetallic compounds with general formula $\text{Fe}_2\text{YZ}$ (so called full-Heusler alloys), where $Y$ is basically 3d- or 4d- transition metal, and $Z$ is a metalloid have attracted considerable attention as thermoelectric materials [7]. It has been reported that theoretically $\text{Fe}_2\text{TiSn}$ based compounds can achieve the Seebeck coefficient as high as $-300$ μV K$^{-1}$ [8]. It was proposed that substitution of titanium or tin may improve the TE characteristics of the alloy.

Voronin with others [9] investigated the $\text{Fe}_2\text{TiSn}_{1-x}\text{Si}_x$ Heusler alloys fabricated by the conventional melting procedure followed by annealing and reported that it is hard to obtain the single-phase material by the traditional approach, more over the impurity phases decrease expected thermoelectric performance. There are several ways to enhance the figure of merit, (a) carrier concentration optimization, (b) band structure engineering, (c) nanostructuring [10–12] and (d) defects engineering.
All of the listed parameters can be controlled in a fabrication process which leaves a lot of space for the better materials development.

There are few traditional synthesis approaches which include multi-step techniques with melting and annealing as a main step and some additional pre- and post-treatment procedures [15, 16]. Such methods are hard to adopt for large-scale production of TE materials especially of nanostructures ones. Among the relatively new techniques the self-propagating high-temperature synthesis (SHS) could be a most promising approach for the direct single-phase TE material fabrication at a minimal cost and on the timescale of seconds [17–24].

In the present work we adapt the spark plasma sintering method for the thermoelectric bulk material fabrication. Fe$_2$TiSn$_{1-x}$Si$_x$ ($x = 0, 0.10, 0.15, 1$) single-phase compound were synthesized by the SHS with the mechanical activation of the precursor powders. Product structural characteristics and thermoelectric properties was investigated.

2. Materials and Methods

The following reagents were used: commercially available powders of iron (99.7%, 50–200 μm) titanium (99.1%, 50 μm), tin (99.1%, 45–80 μm) and silicon (99.9% less than 5 μm) were used as starting materials.

The batch mechanical activation (MA) was conducted in an Activator-2S planetary ball mill from 5 to 20 min. The stoichiometric mixture of the pure element powders was ball milled under argon atmosphere using steel jars with steel grinding balls 6 mm in diameter at the powder-to-balls weight ratio of 20:1. MA was performed under centrifugal acceleration of 250 m/s$^2$ for different times. After mechanical activation the powder was pressed into the pellets with a diameter, $d$, of 10 mm, a height, $h$, of 15 mm, and a relative density of 40–50%. After compression the pellet were placed inside the SHS reactor and the sample was ignited by tungsten coil connected to the external current lead. Each time before the synthesis the reactor was evacuated (~ 300 Pa) and refilled with the argon (2 atm). The resultant specimens were grinded to powder and then were densified using the spark plasma sintering (SPS) machine (Labox 650, SinterLand, Japan) according to the scheme shown in Figure 1.

![Figure 1. Schematic of spark plasma sintering and direct hot pressing (without SPS puls) process.](image-url)
The powders were put into a cylindrical graphite die which was placed in the SPS chamber evacuated to 10 Pa. Uniaxial pressure was then applied through top and bottom plungers. The sintering temperature was ranged from 700–900°C with the heating rate of 50–100°C/min. Pressure of 50 MPa and a dwelling time of 10 min were kept constant for all the samples, respectively. The compacted disc specimens had a diameter of 12.7 mm and height of 2–3 mm. In case of Fe₂TiSi the direct hot-pressing DSP-515 SA (Dr. Fritsch, Sondermaschinen GmbH, Germany) were used. The sintering temperature was ranged from 800 to 1000°C while other parameters were the same as for the case of Fe₂TiSn₁₋ₓSiₓ (x = 0, 0.10, 0.15).

The phase analysis of the samples was performed at room temperature by X-ray diffraction (XRD) with a Difray 401 diffractometer (Scientific Instruments, Russia) using CrKα (λ = 2.2911 Å) radiation. Scanning electron microscopy in conjunction with energy-dispersive X-ray spectroscopy (SEM, EDX; Vega 3 SB, Tescan, Czech Republic) was employed to determine the chemical composition and to observe microstructure of as-synthesized specimens. Temperature dependencies of the electrical resistivity and the Seebeck coefficient were simultaneously measured in He atmosphere from 298 to 473 K by the four-probe and differential methods, respectively. The uncertainty of the Seebeck coefficient and the electrical conductivity measurements was within 8%.

3. Results and discussion

Preliminary thermodynamic calculations of the adiabatic combustion temperature (Tₜₐ) and other thermodynamic parameters were performed for all the compositions of Fe₂TiSn₁₋ₓSiₓ (x = 0, 0.10, 0.15, 1) Estimated values of the adiabatic combustion temperature depending on the composition are presented in table 1 (for Fe₂TiSn and Fe₂TiSn₀.₉Si₀.₁). The calculations revealed that values of the adiabatic temperature of combustion increase with respect to silicon doping level.

| Parameter (units) | Fe₂Ti (C) | Fe₂Si (C) | Fe₂Ti (C) | Fe₂Si (C) |
|------------------|-----------|----------|-----------|----------|
| Volume of gas products (l) | 0.0000 | 0.0000 |
| Pressure of gas products (atm) | 1.0000 | 1.0000 |
| Temperature (K) | 1002.1988 | 1068.1669 |
| Gas product amount (mol) | 4.28·10⁻¹⁵ | 8.69·10⁻¹⁴ |
| Products heat capacity (J/K) | 121.4135 | 122.8608 |
| Products entropy (J/K) | 275.6490 | 279.3739 |
| Products enthalpy (KJ) | 0.0736 | 0.0790 |

It is known that during the high energy mechanical treatment not only the material mixing occurs, but the morphology and inner energy of material can be changed as well. Chemical reaction between mixture components is also possible. Defect accumulation and powder grinding scientifically affect the following SHS process and the products which can be formed. Experimentally we have found an optimal regime for the mechanical activation (MA) of the initial powders which effectively promotes the SHS process. It appears that 10-min mechanical pretreatment of the pure element’s mixture leads to the easier ignition of the pallet. Carrying out the synthesis in an argon atmosphere leads to the formation of a phase Fe₂TiSn, but there are also minor peaks of titanium oxide (figure 2). Figure 3 shows phase change in a mixture of Fe/Ti/Sn powders. After MA of stoichiometric components ratio some intermediate phases such as Fe₃Sn, FeSn, FeTi and SHS, Heusler Fe₂Sn₃Ti were formed. However, during the following SHS process almost all secondary phases disappeared and two-phase sample Fe₂TiSn–FeSn were synthesized. Such phase evolution is an in good agreement with the Fe–Ti–Sn system phase equilibria [25].
The same phase evolution was observed for the samples with different amount of silicon: $x = 0.10, 0.15$, respectively. Additional TiSi$_2$ impurity phase were formed after MA for Si doped samples.

During the synthesis of the silicon containing material such as Fe$_2$TiSi another phase equilibrium of the Fe–Ti–Si system should be considered [26]. Under the same parameters of MA and SHS as for the composition without the silicon, only ~10% of the desirable Fe$_2$TiSi phase was obtained. Leading the SHS process in air atmosphere is one of the ways to increase the temperature of synthesis to the level where the Fe$_2$TiSi formation could be promoted. Indeed, only Fe$_2$Ti impurity phase was observed while the amount of the main Fe$_2$TiSi phase increased from 10% to 75% for SHS performed in air atmosphere (figure 3). It should be noted, that EDX revealed a small amount of TiO$_2$ at the grain boundaries for both of the samples. Formation of TiO$_2$ can be caused by an air atmosphere during SHS.

For the SPS process the initial material were hot pressed under the 800 and 1000°C. As it was expected, for the specimen compacted at higher temperature the amount of the main phase is higher (see figure 4a). The electrical resistivity of the Fe$_2$TiSi sample hot pressed at 1000°C was higher by an order of magnitude comparing to the Fe$_2$TiSi sample pressed at 800°C (figure 4b). The Seebeck coefficient was ranged from 3 to 11 $\mu$V K$^{-1}$ in the whole temperature range, which is in an good agreement with other experimental results for Fe$_2$TiZ (Z = Sn, Si, Sb) based systems.
Heating rate significantly affects the microstructure of the Fe$_2$TiSn$_{1-x}$Si$_x$ samples ($x = 0, 0.10, 0.15$). For the bulk samples compacted with heating rate of 100°C/min the microstructure looked like for non-reacted powder with the matrix of Fe$_2$TiSn containing grains of impurity phases (see figure 5). Completely another microstructure was observed for the samples SPSed at 50°C/min heating rate (see figure 6). It can be suggested, that for this Fe–Ti–Si–Sn system more time required for elements diffusion and formation of the targeting Fe$_2$TiSn (Si) phase. However, even for these specimens some TiO$_2$ was observed at the grain boundaries (figure 6).

![Figure 5](image1.png)

**Figure 5.** SEM images of the surface for Fe$_2$TiSn SPSed at the heating rate of 100°C/min in back-scatter electron mode and the corresponding mappings for the elements Fe, Ti, and Sn.

![Figure 6](image2.png)

**Figure 6.** SEM images of the surface for Fe$_2$TiSn SPSed at the heating rate of 50°C/min in back-scatter electron mode and the corresponding mappings for the elements Fe, Ti, and Sn.
4. Conclusion

The theoretical prediction of possible increase of thermoelectric figure of merit for the Fe$_2$TiSn was contradicted with experimental data. Partial substitution of Sn with Si did not improve the material thermoelectrical properties, because the formation of a multiphase states in Fe$_2$TiSn$_{1-x}$Si$_x$ ($x = 0; 0.1; 0.15$) alloys. In general, impurity phases lead to a decrease in the electrical resistance and Seebeck coefficient and an increase in the thermal conductivity. Based on data obtained in this study, it can be assumed that the Seebeck coefficient in Fe$_2$TiSi in the vicinity of room temperature is much lower than in Fe$_2$TiSn, while the electrical resistance and thermal conductivity of these compounds are close.

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