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Mechanochemical synthesis and properties of thermoelectric material β-FeSi$_2$

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The mechano-chemical synthesis of thermoelectric material on the basis of β-FeSi$_2$ has been investigated. The mixture of FeSi and amorphous Si has been shown to be a optimum precursor to produce the thermoelectric ceramics. The ceramics properties (thermoelectric power α, μV/K, electrical conductivity σ 1/$\Omega * $cm) have been considerably improved by means of doping with superequilibrium quantity of 12% of aluminium (substitution of silicon) or 10% of cobalt (substitution of iron). The mechanical alloying in a high energy ball mill, under the acceleration of treating balls 800 m/sec^2 produced homogeneous powder with a superequilibrium quantity of dopant, which conversed into thermoelectric ceramics after short annealing in vacuum at low temperature (780°C). The samples of ceramics with the maximum content of doping elements have increased thermoelectromotive force-up to 800 μV/K. Mechanically alloyed ceramic is a promising material as a medium temperature thermoelectric with advanced properties for autonomous power supply units.

1. Introduction

Thermoelectric cells are used as autonomous sources of electricity and small power refrigerating sets [1, 2]. The thermoelectric generators are produced for cathode protection of oil-pipe line, domestic generator of electricity and thermoelectric generator for utilization of heat wastes [3]. The thermoelectric refrigerators are produced for infrared detectors and microprocessors cooling and medical devices for freezing biological objects [4]. The wide using of thermoelectrical devices is limited by the low efficiency of thermoelectric power transformers.

Undoped β-FeSi$_2$ has a low thermoelectic characteristics. However, after doping by cobalt (4%) or aluminium (6%) it becomes the semiconductor of p or n types, respectively, with good thermoelectic properties. The thermoelectric characteristics reach the best values at a maximum level of doping. The possible quantity of dopants is dictated by the equilibrium phase diagram. It is possible to introduce no more than 6% of cobalt and 8% of aluminium through the usual pyrometallurgical methods [5].

Mechanical alloying is convenient for the synthesis of silicides and production of supersaturated solid solution. The synthesis of β-FeSi$_2$ is known to proceed through the mechanochemical formation of product containing Fe and Si phases [6] or amorphous phase [7], followed by annealing. We found the formation of other mechanochemical products under the higher intensive mechanical treatment of initial elements, namely, FeSi and Si amorphous phases, and investigated the thermal transformation of these products into β-FeSi$_2$.

The aim of the research was to synthesize β-FeSi$_2$ with superequilibrium quantities of dopants using higher intensive mechanical alloying and to produce thermoelectric ceramics.

2. Experimental

Powders of Fe (99,95%), Al (99,9%), Co (99,9%), Si (99,99%) with the size of particles not bigger than 100 microns were used as initial substances.

For synthesis of FeSi$_2$ the powders of elements were mixed stoichiometrically and exposed to mechanical treatment. Mechanical treatment was carried out in a planetary ball type mill-activator AGO-2, in jars of volume 150 sm^3, in argon, acceleration of milling bodies (steel balls of 5 mm diameter) being 800 m/s^2. In certain intervals of time the powder was sampled for the analysis with XRD (DRON-4, Cu K$_\alpha$ irradiation) and DTA (Paulic system derivatograph).

To produce ceramics on the basis of iron disilicide the powders were mixed up in stoichiometric quantities Fe$_{1-x}$Co$_x$Si$_2$, $x = 0.02$–0.1 and FeSi$_{2-y}$Al$_y$, $y = 0.40$–0.12, and treated mechanically under the above conditions. Some of samples were prepared by mechanically treatment of FeSi$_2$ and precursors-FeAl$_2$ or CoSi$_2$. The powders were pressed into pellets with a diameter of 12 mm and a height of 1–2 mm at a pressure of $1.5 * 10^8$ Pa and annealed in a vacuum $1.3 * 10^{-3}$ Pa at 1163 K and 1208 K for 3 hours.

Seebeck coefficient and conductivity were measured in air at the temperatures from 550 K down to ambient temperature. Installation for measuring sample characteristics included two brass electrodes, each equipped with thermocouple, signal wire and heater. This electronic device allowed to heat sample with a definite temperature difference (either zero for conductivity measurements, or approximately ten degrees per minute for thermo-emf measurements). Temperature was controlled with a copper-constantan thermocouple, the cold junction was held at 273 K. Thermocouple emf was measured with photoelectric microvoltmeter R341 with an accuracy of 0.2 K. For samples thermo-emf measuring microvoltmeter V7-28 was used (accuracy 1 mV). The samples conductivity was measured with an AC bridge at a frequency of 1000 Hz.

Initially samples were heated up to high temperature and kept until the definite temperature was achieved. After data measuring the sample was cooled at a controlled rate of 10 K/min. Our experiments to check data reproducibility in thermocycling showed parameters stability in three to five cycles of heating-cooling.

3. Results and discussion

3.1. Synthesis of iron disilicide

In [8] it has been shown that synthesis of iron disilicide by the reaction of thin solid films of elements passes through formation of intermediate monosilicide FeSi. However, the low temperature β-FeSi$_2$ modification can be formed at interaction of monosilicide FeSi and the high temperature modification α-FeSi$_2$ by a peritectic reaction [9]. As a result of a volume reduction of the crystal lattice by 20% during transformation from the high temperature modification to the low one the ceramic samples are destroyed [10].

Fig. 1 shows how the phase structure of a mixture of elements changes during processing in a planetary ball mill. Monosilicide FeSi forms after 10 min treatment, α-FeSi$_2$-after 25 min, then β-FeSi$_2$ starts to form after treatment for 35 min. Obviously, only ten minutes long mechanical treatment is needed to produce the β-silicide instead of ten hours in the case of using a less intensive equipment [6, 7].

Fig. 2 shows DTA curves for samples selected at different moments during treatment. Each of the first three curves contains the wide peak at 140°C–340°C and the sharper peak at 490°C. For FeSi$_2$ synthesized by the annealing of specially prepared element films [11], the sharp peak at 490°C was shown to correspond to the evolving of the heat of the disilicide cristallization.

It has been found that the maximum yield of β-iron disilicide is reached at the annealing of the sample characterized by the most high heat evolution at 490°C (sample marked as ⟨⟨15 min⟩⟩ in Fig. 2). This sample contains the phases FeSi and Si (Fig. 1). Most probably, β-iron disilicide forms as a result of the thermal reaction of these components during annealing. Mechanical activation during times longer than 15 min produces α-iron disilicide and decreases the yield of β-FeSi$_2$ at subsequent annealing.

Previously, the synthesis of β-FeSi$_2$ was carried out using low intensive mechanical treatment and annealing of mechano-chemical product containing Fe and Si phases [6] or an amorphous phase [7]. We have found, that the product of intensive mechanical treatment of Fe and Si mixture containing FeSi and Si phases can be efficiently annealed into β-FeSi$_2$.

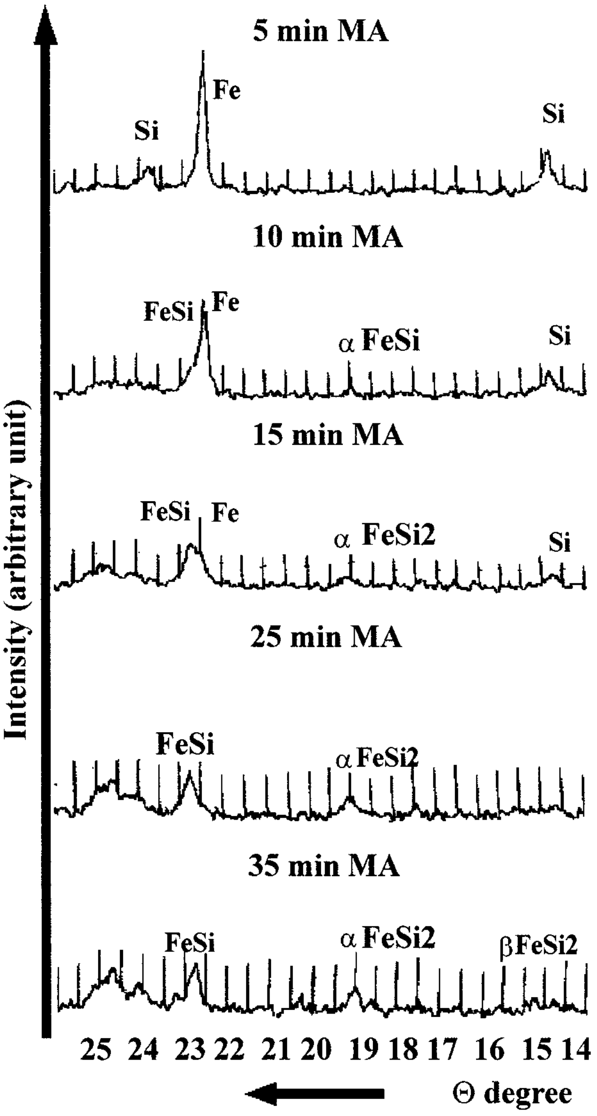

Figure 1 Phase composition changing during mechanical alloying of Fe and Si mixture (XRD).

Electron microscopic photos of particles of a sample after 15 min mechanical treatment are presented in Fig. 3 to demonstrate the degree of size uniformity and phase homogeneity.

3.2. Synthesis of superequilibrium doped iron disilicide

Fig. 4 presents the phase diagram from [5], showing the projections of the maximum contents of doping elements: 10% for cobalt (p-type conductivity) and 12% for aluminium (n-type). Clearly, these contents are in different regions of the phase diagram. So, the main impurities may differ, namely, FeSi for p- and α-FeSi$_2$ for n-ceramics.

XRD diffractograms of annealed ceramic samples with the various contents of doping elements are shown on Figs 5 and 6. We see the formation of FeSi phase. The electron microscopic photos of ceramics with the maximum quantities of doping elements are presented in Figs 7 and 8.

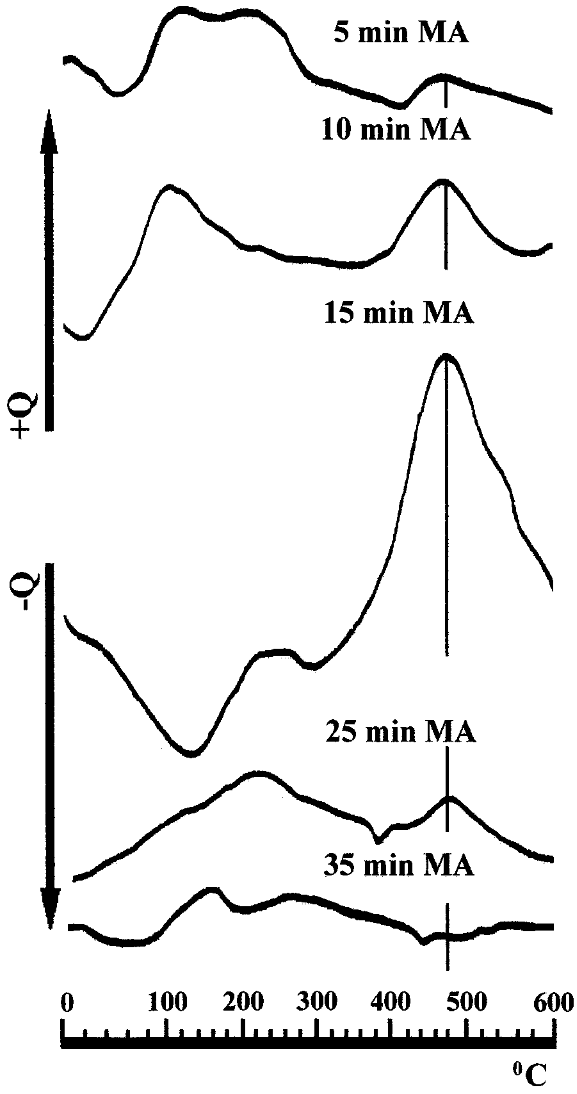

Figure 2 DTA curves of samples with a different time of mechanical alloying.

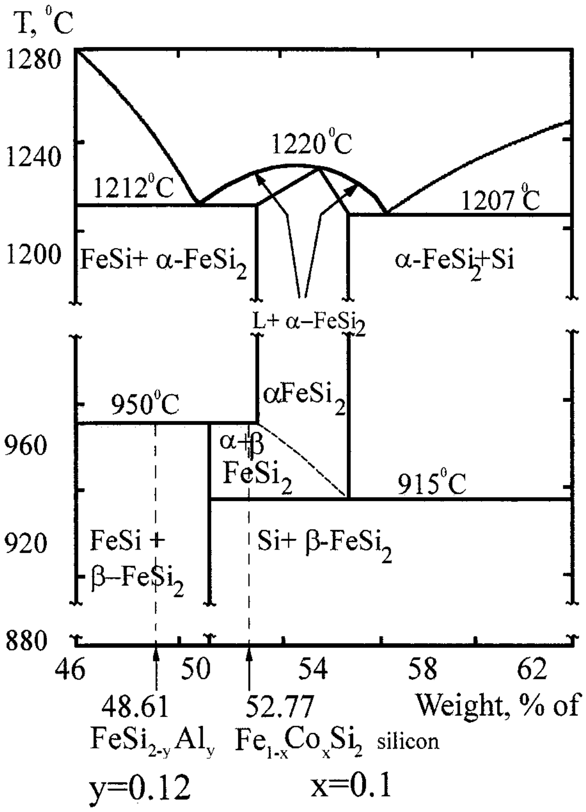

Figure 4 Phase diagram of Fe-Si system.

3.3. Data of electrical measurements

It's known, that the temperature dependence of $FeSi_2$ thermo-emf has several regions. At low temperatures thermo-emf increases, then it is constant, and at high temperatures thermo-emf decreases to zero. The width of the low temperature range depends on the sample composition and has a high limit of about 400 K, since the high temperature range is spread begins

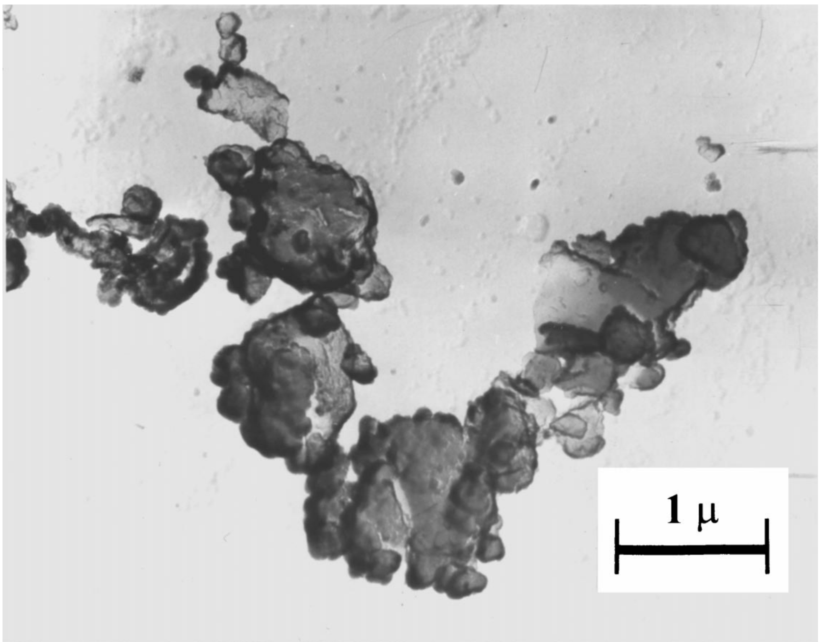

Figure 3 Electron microscope photo of sample after 15 min of mechanical alloying.

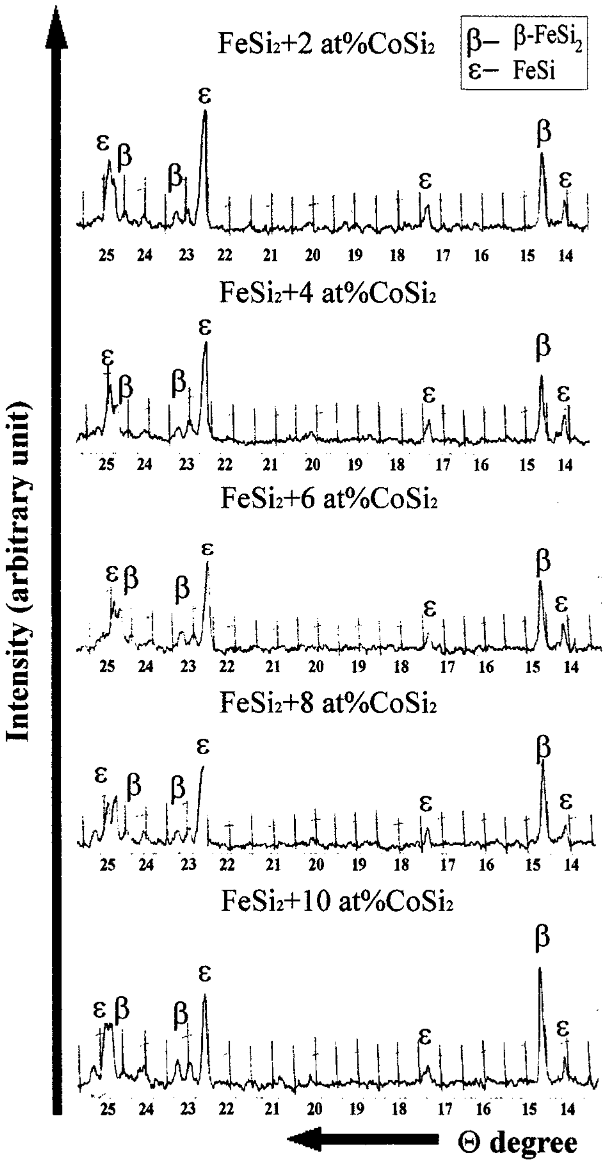

Figure 5 X-ray diffractograms of sintered ceramics of $FeSi_2$ with various content of Co dopant.

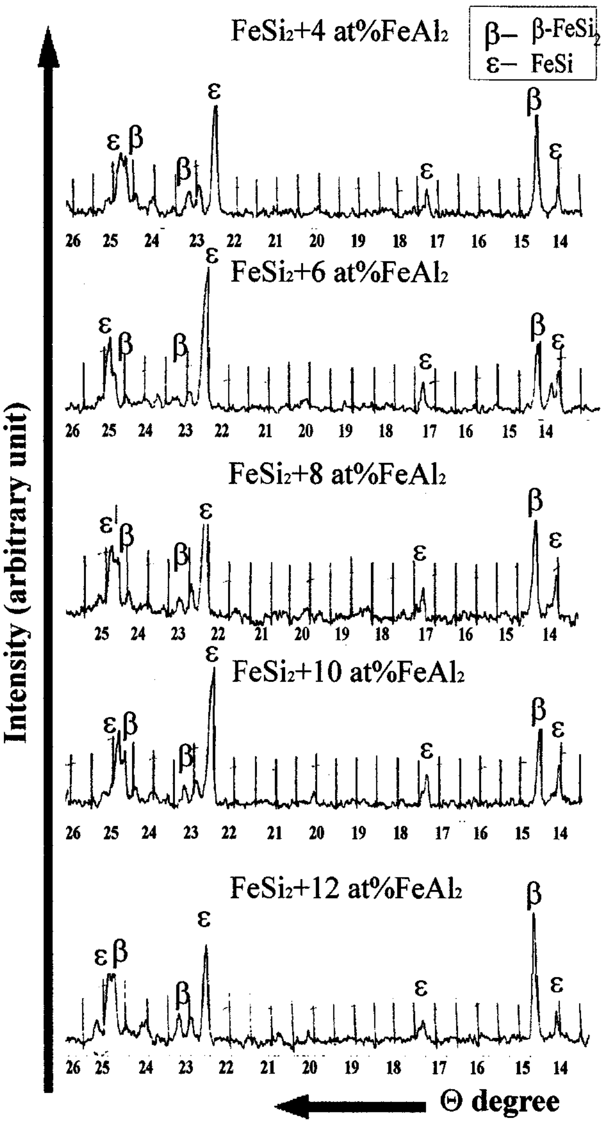

Figure 6 X-ray diffractograms of sintered ceramics of $FeSi_2$ with various content of Al dopant.

from 500–1200 K. At medium temperatures all samples demonstrate constant or slightly varying thermo-emf values.

Fig. 9 shows the temperature dependencies of thermo-emf of β-$FeSi_2$ annealed at 1163 K, Fig. 10—analogous dependence for annealing at 1208 K. Each diagram has two families of curves, corresponding to conductivities of p- and n-type. Since thermo-emf was constant at 400 K (⟨⟨α -T ⟩⟩ dependence) we have chosen exactly this temperature to measure the concentration dependence of emf (Fig. 11).

Analyzing the last figure, one can observe some peculiarities. First, all samples with maximum dopant equilibrium concentration (5–6 at.%) annealed at 1208 K show thermo-emf values $\alpha = 200$–250 μV/K, which are close to literature data [12, 13].

Mechano-chemical synthesis in high energy planetary mills allows to prepare strongly non-equilibrium alloys and compounds. According to [14, 15], one can observe the formation of amorphous and nanocrystalline alloys in similar metal systems. In our situation, the compositions with dopant concentration 8–10 at.% are nonequilibrium and correspond to region FeSi+β-$FeSi_2$ on the phase diagram. Evaluation of the grain size of mechanically treated undoped system ⟨⟨iron-silicon⟩⟩ gives values of 10–20 nm [16]. The grain size of our samples (see Figs 7 and 8) is about 200–400 nm. Annealing of samples at temperatures below 1208 K during times used in the present work does not allow to approach diffusional equilibrium and inhibits the grain growth. Probably, extremal thermo-emf values can be attributed to the above reasons. Further increase of dopant concentration, as usual, leads to semiconductor degeneration and large scale thermo-emf decreasing with the same value sign. Probably, thermo-emf changes at high dopant concentrations due to this phenomena.

The curves 1 and 3 in Fig. 11 corresponding to the samples annealed at 1163 K attract the major attention. One can see that the curves do not reach the limitation and demonstrate the higher value of thermo-emf in comparison with the literature data. Looking at the base curves 2 and 4 (annealing temperature 1208 K),

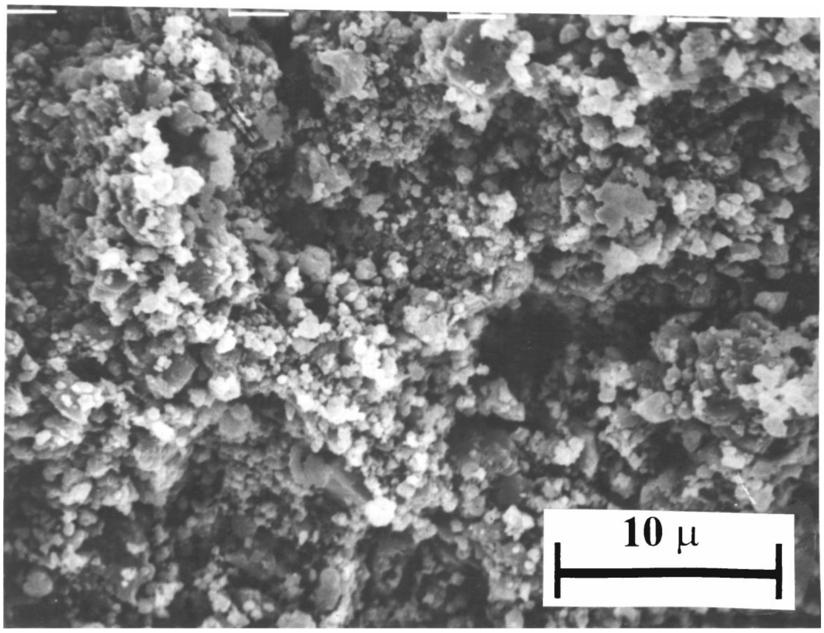

Figure 7 Electron microscope photo of ceramic $Fe_{0.9}Co_{0.1}Si_2$ stoichiometry-superequilibrium contents of n-type dopant.

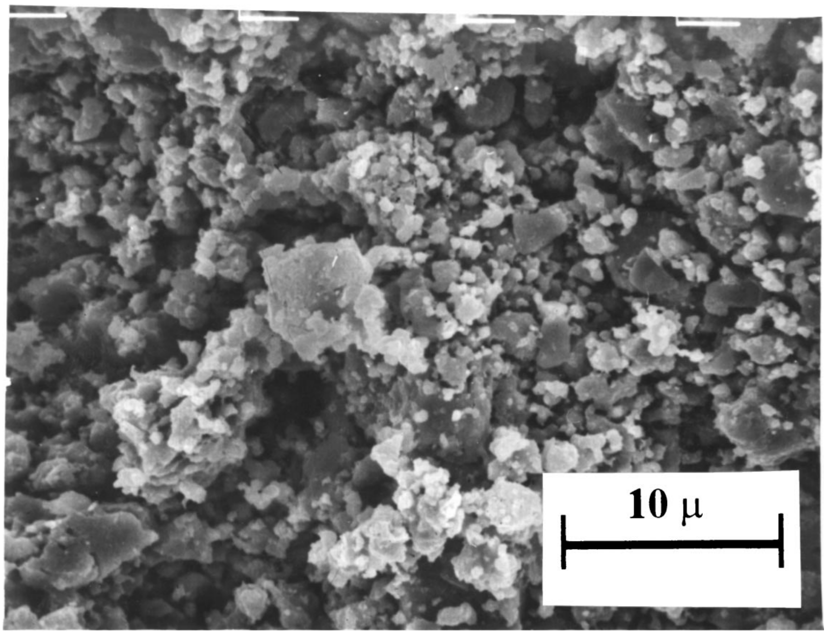

Figure 8 Electron microscope photo of ceramic $FeSi_{1.88}Al_{0.12}$ stoichiometry-superequilibrium contents of p-type dopant.

one can suppose, that minimum grain sizes, exist under formation conditions of samples 1 and 3. The density of surface states increases, preventing the semiconductor from degeneration. On the contrary, in samples made by secondary treatment (curves 5,6) probably, some difficulties to increase grain size exist. So the decreasing of the dopant diffusion into the iron disilicide grain and impossibility to reach the equilibrium concentration is observed.

On more peculiarity is the decrease of thermo-emf of samples 5, 6 compared with samples 1–4. It is interesting to note that samples prepared by mechanical pretreatment of $FeSi_2$ with $CoSi_2$ or $FeAl_2$ not only demonstrate degeneration region, but do not reach the saturation (curves 5 and 6 in Fig. 11).

The efficiency of thermoelectric units is the function of thermoelectric figure of merit. The thermoelectric figure of merit is used as a basis for evaluating the usefulness of a material as a thermoelectric generator or a cooler. It is a function of three specific characteristics of a material: electrical conductivity (σ, $1/\mathrm{Ohm} * \mathrm{cm}$), thermal conductivity (λ, $\mathrm{W/m} * \mathrm{K}$) and thermo-electromotive force (α, mV/K): $z = \alpha^2 * \sigma/\lambda$. Another parameter can be used to evaluate the thermoelectric properties, assuming thermal conductivity to be approximately constant—so called power factor $\alpha^2 * \sigma$. According to [17], this value is about 10^{-5}–10^{-4} $(\mathrm{mV})^2/\mathrm{K}^2 * \mathrm{Ohm} * \mathrm{m}$ for iron silicides.

In Fig. 12 the results of measurements of electrical conductivity of β-$FeSi_2$ samples are presented.

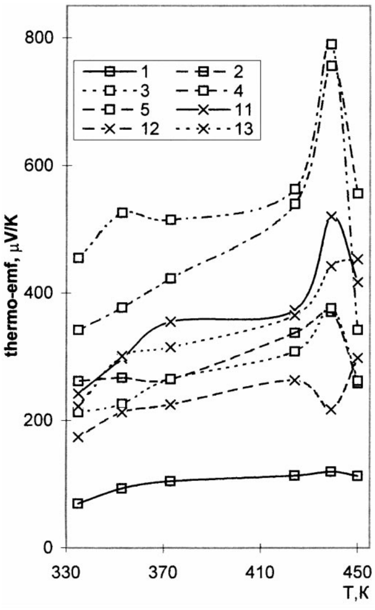

Figure 9 Temperature dependence of thermo-emf of β-FeSi$_2$ samples doped by Co (curves 1–5) and Al (11–13). Annealing temperature 1163 K. Dopant contents for curve numbers are, at.%: 1-2, 2-4, 3-6, 4-8, 5-10, 11-2, 12-4, 13-6.

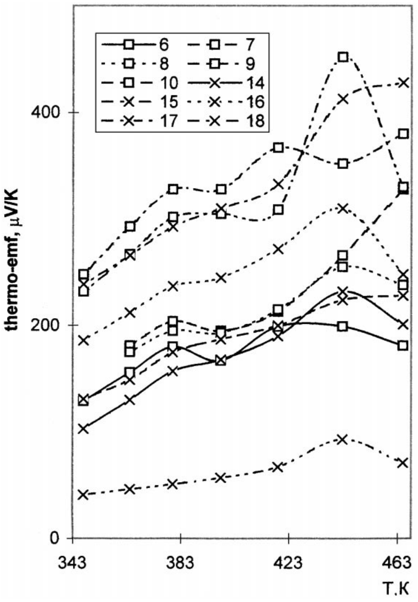

Figure 10 Analogous dependence for annealing temperature 1208 K. Dopant concentrations (Co-6 to 10, Al-14 to 18) for curve numbers are, at.% : 6-2, 7-4, 8-6, 9-8, 10-10, 14-2, 15-4, 16-6, 17-8, 18-10.

All curves are approximately parallel. The electrical conductivity of our samples varies from 10^{-3} to 10^{4} 1/Ohm $*$ m, depending on the dopant concentration, pressure and annealing conditions. Literature overviews show values of electrical conductivity in the similar range. Power factor $\alpha^2 * \sigma$ for our samples is 10^{-4} (mV)^2/K^2 $*$ Ohm $*$ m.

Thus, β-FeSi$_2$ can be efficiently synthesized using highly intesive mechanical alloying, the material properties can be improved by non-equilibrium doping. The new material is promising as the medium temperature thermoelectric for autonomous power supply units.

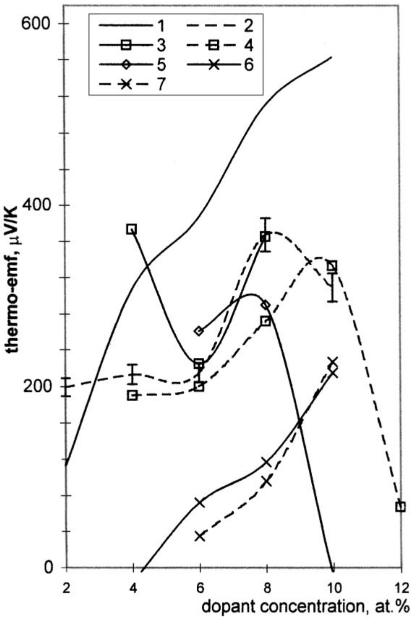

Figure 11 Concentration dependence of thermo-emf (number-type of dopant-annealing temperature, K): 1-Co, 1163; 2-Co, 1208; 3-Al, 1163; 4-Al, 1208; further samples with secondary mechanical treatment: 5-Co, 1208; 6-Al, 1208.

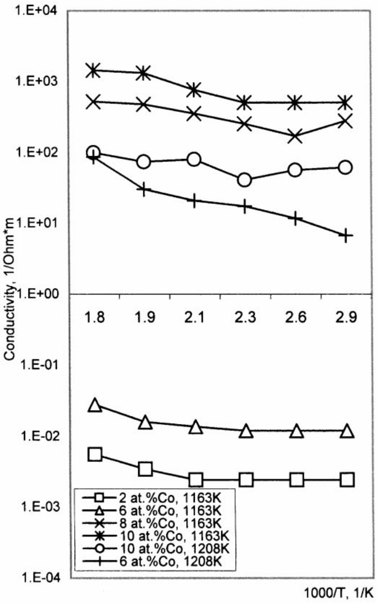

Figure 12 Temperature dependence of electrical conductivity of β-FeSi$_2$ cobalt doped samples: 2 at.% Co, 1163 K; 6 at.%, 1163 K; 8 at.% Co, 1163 K; 10 at.% Co, 1163 K; 10 at.% Co, 1208 K; 6 at.% Co, 1208 K.

4. Conclusions

The process of mechano-chemical synthesis of iron disilicide via intensive mechanical treatment with acceleration of milling bodies 800 m/sec^2 has been designed. The optimum conditions of β-FeSi$_2$ synthesis have been found. The method to produce β-FeSi$_2$ ceramics is developed using reactive sintering of mechanically produced powders containing FeSi and Si.

The β-FeSi$_2$-based ceramics with the superequilibrum contents of doping elements-aluminium up to 12% (p type) and cobalt up to 10% (n type) has been produced.

The thermo-emf of samples, prepared by mechanochemical method, depends on the concentration of dopant. The samples of ceramics with the maximum contents of doping elements have increased thermoelectromotive force attaining up to 800 μV/K. This exceeds respective values for materials produced pyrometallurgically.

The samples electrical conductivity can be regulated from 10^{-3} to 10^4 $1/\text{Ohm} * \text{m}$, power factor $\alpha^2 * \sigma$ attained $6 * 10^{-4}$ $(\text{mV})^2/\text{K}^2 * \text{Ohm} * \text{m}$.

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