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Fabrication and thermoelectric properties of β-$FeSi_2$ prepared by mechanical alloying

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Abstract: Thermoelectric β-$FeSi_2$ was successfully fabricated by mechanical alloying followed by sintering process. The influence of milling time and sintering conditions on alloying progress was studied by X-ray diffraction. The electrical and thermoelectric properties of undoped β-$FeSi_2$ and Mn-doped β-$FeSi_2$ were both measured for comparison. The results show that the powder, which is mechanically alloyed by milling for 50 h, is completely changed into β-$FeSi_2$ phase after sintering at 890 ℃ for 15 h in Ar atmosphere. The maximum value of power factor of $Fe_{0.92}Mn_{0.08}Si_2$ is 28.5 $\mu W \cdot m^{-1} \cdot K^{-2}$ at 600 ℃, while that of $FeSi_2$ is only 6.6 $\mu W \cdot m^{-1} \cdot K^{-2}$.

Key words: β-$FeSi_2$; mechanical alloying; thermoelectric properties

1 Introduction

Nowadays, thermoelectric materials are receiving extensive attention for various practical applications in power generators, coolers, and thermal sensors, due to their special temperature gradient-electricity conversion features[1]. β-$FeSi_2$ is one of the potential candidates for practical use in the high temperature range (up to 1 200 K) because of its abundance in raw material, its good resistance to oxidation and erosion and its non-toxicity[2−5]. However, the performance of β-$FeSi_2$ is now still not good for practical use compared with other thermoelectric materials, for example, Bi_2Te_3. Hence, its thermoelectric properties need to be improved[6]. In general, the thermoelectric efficiency is evaluated by its figure of merit (Z), $Z=\alpha^2/(\rho\lambda)$, where α is the Seebeck coefficient, ρ is the electrical resistivity, λ is the thermal conductivity. High ZT leads to high efficiency. In order to improve the electrical properties of the β-$FeSi_2$, the doping of various elements has been attempted during sample preparation[7−9]. Mechanical alloying is convenient for synthesis of silicides and production of supersaturated solid solution. The synthesis of β-$FeSi_2$ can be realized through milling followed by sintering[10−11].

In this study, mechanical alloying was employed to fabricate undoped and Mn-doped β-$FeSi_2$. The best preparation process of thermoelectric β-$FeSi_2$ was studied and designed. Besides, the electrical and thermoelectric properties of the samples were measured and analyzed. Comparison between undoped and Mn-doped β-$FeSi_2$ was also performed.

2 Experimental

Powders of Fe(99.5%), Si(99.9%), Mn(99.9%) with particle size not larger than 100 μm were used as initial substances and mixed in the composition of $FeSi_2$ and $Fe_{0.92}Mn_{0.08}Si_2$. Mechanical alloying was carried out in a high-energy planetary ball type mill-activator QM-1SP4. Three different milling times of 20 h, 38 h and 50 h were adopted. During the following sintering, 890 ℃ and 930 ℃ were selected as the sintering temperatures. The sintering time was fixed to be 10 h and 15 h. The sintering was carried out in GSL−1300X tubular furnace in Ar atmosphere.

The phase formation of the samples was characterized by X-ray diffraction (XRD) in a BRUKER D8-ADVANCE diffractometer using Cu K_α radiation. The Seebeck coefficient and the electrical resistivity of

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the prepared samples were measured in Ar atmosphere at 323−873 K using a self-developed testing system.

3 Results and discussion

3.1 Synthesis of iron disilicide

The milling rotation speed and ball-to-powder ratio are both important to the alloying progress. They were studied systematically and the optimum values were obtained first in our experiment. The milling rotation speed and the ball-to-powder ratio were then fixed to 365 r/min and 15:1, respectively. In this study, the influence of milling time and following sintering on the alloying progress was mainly investigated. Fe-Si milling system belongs to ductile-brittle components system. During high-energy milling, the powder particles are repeatedly flattened, cold welded and fractured rewelded. The fragmented brittle Si particles tend to become occluded by the ductile constituents and trapped in the ductile Fe particles. With further milling, the ductile powder particles get hardened and finally ruptured. Consequently, true alloying happens amongst constituent elements and fine-crystal composite structure can be obtained. Mechanical alloying is then achieved. So the time of milling is the most important alloying parameter. But it should be realized that the level of contamination increases with increasing the milling time[12].

The XRD patterns obtained from as-milled undoped samples with different milling times are compared as shown in Fig.1. Fe and Si related patterns even exist after milling for 20 h (sample c), containing a small Fe_3O_4 peak, which is resulted from oxidation of Fe in the low energy milling period. With the increase of milling time to 38 h (sample b) and 50 h (sample a), the diffraction peaks of Si gradually disappear and the peak-intensity of Fe decreases. Besides, the peak-position of Fe moves rightwards. This indicates that after milling of 50 h, Si atoms have been dispersed into the Fe lattices and the supersaturated solid solution has been formed. At this stage, the alloying progress has been largely advanced.

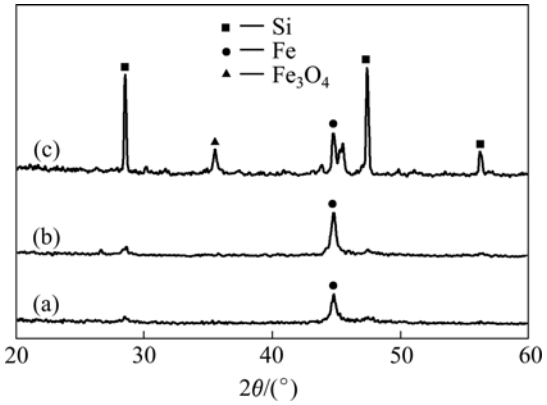

Fig.1 Influence of milling time on phase structure: (a) 50 h; (b) 38 h; (c) 20 h

Fig.2 shows the XRD results of 50 h milled undoped samples with different sintering processes. The patterns of 930 ℃−annealed samples a and b reveal the influence of annealing time on phase structure. Obvious β-$FeSi_2$ diffraction peaks appear in the pattern of sample a after sintering for 10 h, but small Fe diffraction peak still exists. When annealing time augments to 15 h (sample b), the Fe diffraction peak fully disappears and the intensity of β-$FeSi_2$ diffraction peaks largely increases compared with that of sample a. Besides, tiny ε-FeSi peak forms. The patterns of samples b and c display the influence of sintering temperature on phase structure. The sintering time was 15 h and the sintering temperatures were 890 ℃ for sample c and 930 ℃ for sample b, respectively. It can be seen from the two curves that the effects of phase transformation are similar when the sintering temperature is near the eutectoid temperature (937 ℃). Considering the cost of fabrication, the sintering temperature of 890 ℃ seems to be more suitable. The results in Fig.2 demonstrate the importance of sintering time and temperature to the phase transformation. Mechanical alloying can indeed induce the formation of β-$FeSi_2$, but it takes a lot of time and resource. While according to the milling conditions in this work, the energy of milling is not enough to entirely realize the alloying progress. The sintering process can make up the deficiency of milling and save time and resource. Based on the mechanical alloying process, solid state reaction can fully happen between Fe and Si to form β-$FeSi_2$ during sintering. Mn doped β-$FeSi_2$ was also prepared using the same preparation process as undoped samples.

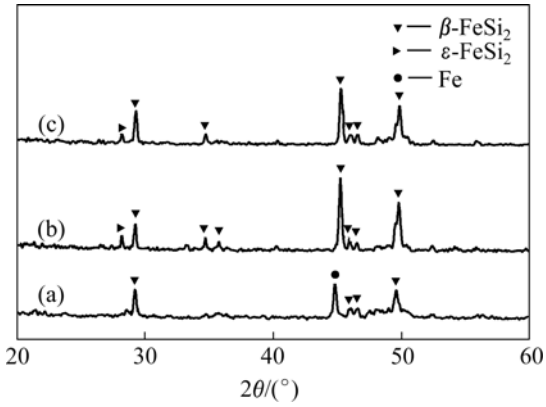

Fig.2 Influence of sintering conditions on phase structure: (a) 930 ℃, 10 h; (b) 930 ℃, 15 h; (c) 890 ℃, 15 h

3.2 Electrical and thermoelectric properties

Fig.3 shows the temperature dependence of Seebeck coefficient and electrical resistivity for $FeSi_2$ and $Fe_{0.92}Mn_{0.08}Si_2$. The preparation conditions for both samples are as follows: 365 r/min (rotation speed), 15:1 (ball-to-powder ratio), 50 h (milling time), 890 ℃

(sintering temperature) and 15 h (sintering time). It can be seen that the parameters of $Fe_{0.92}Mn_{0.08}Si_2$, especially the electrical resistivity excel those of $FeSi_2$. This indicates that doping is an effective method to improve the thermoelectric properties of β-$FeSi_2$. However, the trends of the parameters for the two samples are similar. Fig.3 (a) shows that the values of Seebeck coefficient of both samples increase with the temperature to a maximum and then decrease with a further increase of the temperature. The transition temperatures and the maximal values for $FeSi_2$ and $Fe_{0.92}Mn_{0.08}Si_2$ are 673 K and 128 μV·K^{-1}, and 623 K and 178 μV·K^{-1}, respectively. Generally, Seebeck coefficient is reversely proportional to the carrier concentration. The preceding increase of Seebeck coefficient could be attributed to a stronger scattering of carriers with increasing the temperature, and the subsequent decrease of Seebeck coefficient could be due to a rapid increase in carrier concentration with the increase in temperature[13].

Both undoped *β*-$FeSi_2$ and Mn-doped *β*-$FeSi_2$ were verified to be p-type conduction by hot probe. The smaller electrical resistivity in $Fe_{0.92}Mn_{0.08}Si_2$ is due to the higher hole concentration from Mn acceptors, as shown Fig.3(b). It can also be seen that the values of electrical resistivity for both samples decrease with the temperature until 573 K, then they increase with further increasing temperature. Finally, a decrease starts at 673 K for $FeSi_2$ and 723 K for $Fe_{0.92}Mn_{0.08}Si_2$. Based on the trend, it is considered that the preceding decrease of the values could be attributed to the carrier concentration increase resulted from impurity ionization. The subsequent increase of electrical resistivity is due to the carrier scattering from the enhanced lattice vibration. The final decrease of values in the even high temperature region may be induced by the intrinsic carrier excitation. In addition, the difference of hole concentrations in the two kinds of samples leads to the dissimilarity of transition temperatures of electrical resistivity in the higher temperature region[14].

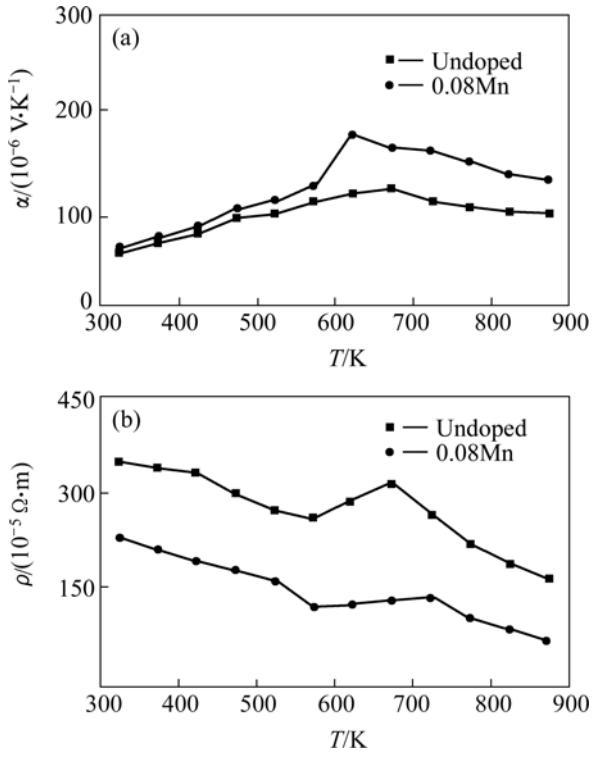

Fig.3 Temperature dependence of thermoelectric and electrical parameters of $FeSi_2$ and $Fe_{0.92}Mn_{0.08}Si_2$: (a) Seebeck coefficient; (b) Electrical resistivity

The power factor refers to α^2/ρ, which is a very important representation parameter for the thermoelectric properties of the materials. Fig.4 shows the temperature dependence of power factor of $FeSi_2$ and $Fe_{0.92}Mn_{0.08}Si_2$. It can be seen that the trend of the power factor is consistent with that of electrical conductivity ($1/\rho$) for each sample. The power factor values of $FeSi_2$ and $Fe_{0.92}Mn_{0.08}Si_2$ both increase monotonously with the temperature in high temperature region (after 723 K), which indicates β-$FeSi_2$ is a high temperature-used thermoelectric material. However, the difference of the power factor between the two samples is large. The maximum value of $Fe_{0.92}Mn_{0.08}Si_2$ is almost as eight times large as that of $FeSi_2$. The maximum value of power factor for $Fe_{0.92}Mn_{0.08}Si_2$ is 28.5 μW·m^{-1}·K^{-2} at 873 K, while that of $FeSi_2$ is only 6.6 μW·m^{-1}·K^{-2}. The value of $Fe_{0.92}Mn_{0.08}Si_2$ is similar to the reported data [15].

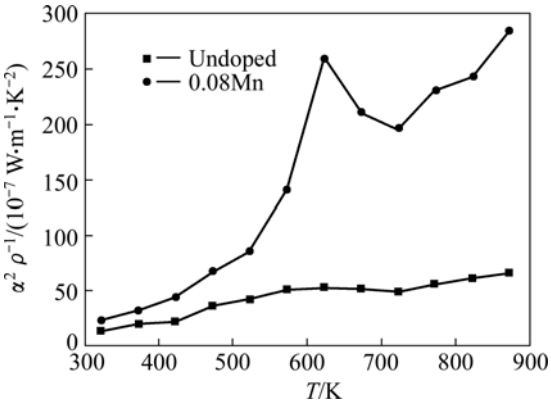

Fig.4 Temperature dependence of power factor of $FeSi_2$ and $Fe_{0.92}Mn_{0.08}Si_2$

4 Conclusions

1) *β*-$FeSi_2$ is prepared by mechanical alloying and sintering process. The optimized condition for β-$FeSi_2$ synthesis is achieved.

2) The trends of thermoelectric parameters of $FeSi_2$ and $Fe_{0.92}Mn_{0.08}Si_2$ with increasing the temperature are similar, but the values of Mn-doped sample are far larger than those of undoped sample.

3) By milling for 50 h with the ball-to-powder ratio being 15:1 and rotation speed being 365 r/min, mixed powder can be completely alloyed after sintering at 890 ℃ for 15 h in argon atmosphere. The maximum values of power factor for $FeSi_2$ and $Fe_{0.92}Mn_{0.08}Si_2$ are 6.6 $\mu W \cdot m^{-1} \cdot K^{-2}$ and 28.5 $\mu W \cdot m^{-1} \cdot K^{-2}$ at 600 ℃(873 K), respectively.

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