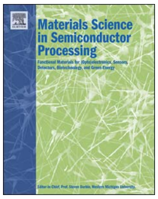
Materials Science in Semiconductor Processing xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Rapid production of Iron Disilicide thermoelectric material by Hot Press Sintering Route

V.S. Poddar[a,*], N.B. Dhokey[a], R.R. Garbade[a], S.P. Butee[a], Deep Prakash[b], R.D. Purohit[b]

[a] *Department of Metallurgy and Materials Science, College of Engineering Pune, 411005, India*
[b] *Powder Metallurgy Division, Bhabha Atomic Research Centre, Navi Mumbai 400705, India*

ARTICLE INFO

Keywords:
Iron Disilicide
Attritor milling
Thermal cycling
Thermoelectric
Hot press sintering

ABSTRACT

In present research work, a method has been established through powder metallurgical route to produce β-$FeSi_2$ thermoelectric material without giving long time mechanical alloying treatment to the elemental powders and long duration heat treatment cycle. The elemental powders of iron (98.9% purity, 200 mesh) and silicon (98.5% purity, 400 mesh) have been mechanically alloyed for 6 h using high-energy Attritor ball-mill and was subjected to Hot Press Sintering (HPS). Effect of HPS parameters on density of compacts was studied. The compacts with higher densities (82–92% relative density) were later on subjected to the thermal cycling treatment. The density as well as the amount of β-$FeSi_2$ phase formation got enhanced due to thermal cycling treatment.

1. Introduction

Waste heat energy can be converted to usable electrical energy through thermoelectric materials. Thermoelectric Material is utilized in various applications such as in power generators, coolers, and thermal sensors [1]. Iron Disilicide (β-$FeSi_2$) is one of the members of thermoelectric family which is having good thermoelectric conversion capability within $500-1200$ K [2]. β-$FeSi_2$ is also a promising material for photovoltaic (PV) applications with a theoretical energy conversion efficiency of 16–23% [3]. Iron disilicide (β-$FeSi_2$) exhibit d-band character in the valence and/or conduction band which makes it able to combine the Seebeck enhancement effect (as Seebeck values are much larger for d-band alloys than for related respective metals) characteristic of transition metal alloys, with the ability to achieve optimum doping levels [4]. It is an intermetallic phase in the iron-silicon system with 53.4–58.2 wt% Si [5]. The overall phase formation process for β-$FeSi_2$ is very slow [6] which curb difficulties during its preparation.

Mechanical alloying results in reduction in powder particle size and intense mixing effect which later on assist in phase homogenization and reduction in lattice thermal conductivity [7,8], resistance heating process result in densification, and thermal cycling cause nearly complete β-$FeSi_2$ phase formation. In this research work, a combination of mechanical alloying, resistance heating and thermal cycling with optimized process parameters has been tried to enhance the kinetics of β-$FeSi_2$ phase formation and to reduce the time period required to produce it. The process parameters in each of these processes were optimized to achieve maximum density.

2. Experimental procedure

In current research work, elemental powders of iron (98.9% purity, 200 mesh) and silicon (98.5% purity, 400 mesh) have been mechanically alloyed for 6 h using high-energy Attritor ball-mill (water cooled SS 304 vial, 400 rpm, 6 mm Φ SS 304 balls, BPR = 10:1, Ar atmosphere). The milled powder was then hot pressed in Hot Press Sintering Equipment (HPS) (Model: TSN – 25/8, Make: KEJETHERM, Capacity: 25 KVA, Tonnage: 8 t) using a square high – strength graphite die to produce pellets with the dimensions nearly 10 × 10 × 3 mm under vacuum atmosphere of around 2.7 mbar. Here the job (in this case pressed milled powder) to be heated was held in secondary circuit of voltage step down transformer. To heat the job to specified temperature a current of low voltage (usually 3–8 V) and high value (up to several Kilo-Amps) was passed through the job which was clamped across at the secondary of the transformer. In HPS, the phase homogenization advantage is carried one step ahead to the desired phase transformation by applying high temperature and high pressure simultaneously. It thus provides thermodynamic conditions (high temperature, high pressure) required for densification of compacts during hot compaction itself. In HPS, effect of temperature, pressure and time on densification of $FeSi_2$ was studied. The process variables were varied as: (1) Holding period was varied from 2 min to 6 min at the interval of 2 min, temperature and pressure was kept constant, (2) Pressure was varied from 25 to 35 MPa at the interval of 5 MPa keeping holding period and Temperature constant, (3) Temperature was varied from 900 °C to 1100 °C at the interval of 100 °C, pressure and holding period were kept

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[*] Corresponding author.
E-mail address: vaishu_ultimate@yahoo.com (V.S. Poddar).

http://dx.doi.org/10.1016/j.mssp.2017.06.027
Received 18 January 2017; Received in revised form 27 April 2017; Accepted 17 June 2017
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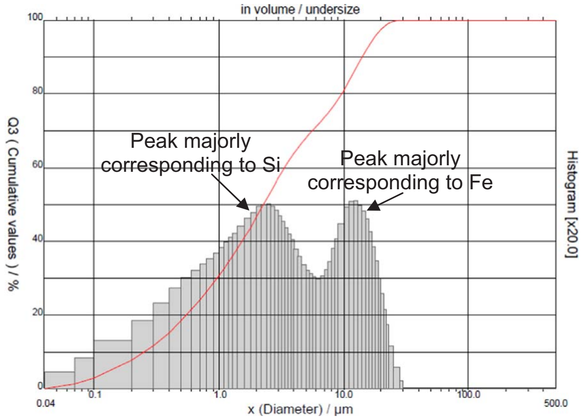

Fig. 1. Laser Particle Size Analysis for Fe-Si milled powder.

constant. The compacts were subsequently annealed at 800 °C for nearly 6 h in vacuum of 10^{-5} mbar and cooled to room temperature (HT1). They were again annealed at 800 °C for nearly 6 h in vacuum of 10^{-5} mbar and cooled to room temperature (HT2). Annealing or thermal cycling treatment was carried out in tubular furnace (maximum temperature: ~ 1100 °C, vacuum: 10^{-5} mbar).

The milled powder was analyzed for particle size using laser particle size analyzer (Make: Cilas, range 0.04–500.00 µm / 100 Classes). Also SEM-EDS (Make: Carl Zeiss, sigma model) and XRD (powder X-ray diffractometer with Cu Kα (λ = 1.5406 A°) radiation operating at 40 kV and 30 mA) analysis were carried out to study the powder distribution and phase formation after milling stage. The sintered and annealed compacts were characterized using XRD and SEM - EDS. The amount of β-$FeSi_2$ phase formation got enhanced due to the thermal cycling treatment.

3. Results and discussion

3.1. Particle size distribution after mechanical alloying

The effect of 6 h attritor milling on particle size is shown in Fig. 1. The plot shows that particle size reduction has taken place. The size range squeezes from around 0.04–74 µm to 0.04–30 µm. First peak corresponds to Si particles whereas the second peak corresponds to Fe particles [9]. The two peaks may be due to the difference in the initial particle sizes of the two as well as the difference in the response of the two types of material to milling. Silicon is brittle while iron is ductile. So Si is broken down into small particles and Fe agglomerates at some locations to combine small particles into a bigger one as shown in Fig. 2. Also as can be seen from the SEM-EDS analysis (Fig. 2a), ε-FeSi phase formation was confirmed during milling stage.

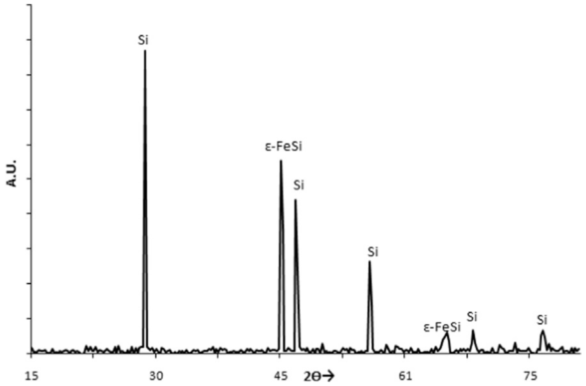

Fig. 3. XRD analysis of 6 h Attritor milled powder.

Fig. 3 shows the XRD analysis of the attritor milled powder and it also confirmed formation of ε-FeSi phase during milling. This led us to observation that the increase in surface energy and the particle to particle contact has assisted the phase formation and that the powder may be in metastable stage [8]. ε-FeSi phase formation is more feasible to be formed compared to other phases because of the sluggishness in reaction kinetics of other phase formations.

3.2. Expected behavioral pattern of Fe-Si interaction during heating

The powders of Fe and Si are mechanically alloyed stoichiometrically for β- $FeSi_2$ phase formation. Mechanical alloying results in uniform distribution of Fe and Si throughout the milled powder yield. This powder is then compacted to pellets. However, after compaction depending upon the particle to particle contact regions and hence density, either α-Fe_2Si_5 or ε-FeSi forms during heating the pellet. So if more Si particles are interacting with Fe particles then α-Fe_2Si_5 phase is expected and if few Si particles interact with Fe particles ε-FeSi forms. β-$FeSi_2$ phase formation is thermodynamically very sluggish [10], so its formation during initial heating is ruled out. The expected phase formation in reference to the Fe-Si binary phase diagram [5] is as shown in Fig. 4.

The peritectoid reaction of the solidified α- Fe_2Si_5 and ε-FeSi to the semiconducting β-$FeSi_2$ phase at 982 °C,

$$\alpha\text{ -}Fe_2Si_5 + \varepsilon\text{-FeSi} \rightarrow \beta\text{- }FeSi_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad \text{(i)}$$

On lowering the temperature of the system, the eutectoid decomposition of the remaining phase at 937 °C is expected as,

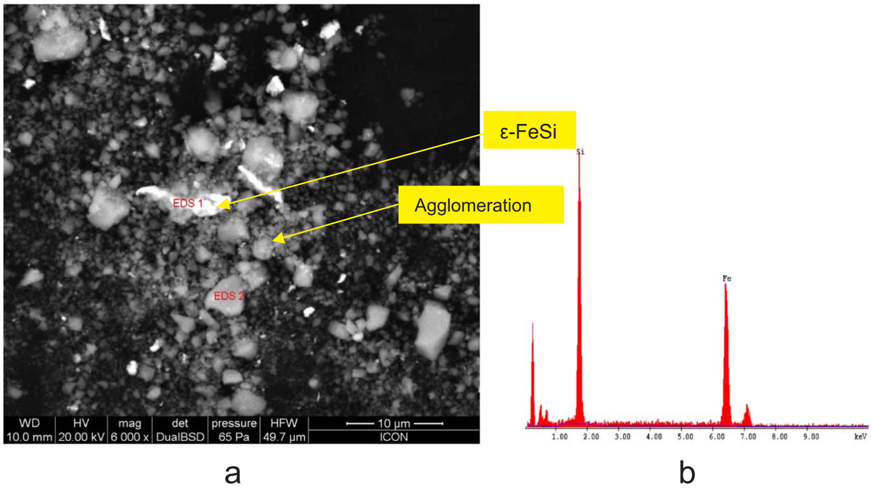

Fig. 2. (a) SEM-EDS image of AM 6 h powder showing initiation of ε-FeSi phase formation (b) EDS 1 spectrum of spot shown in (a), showing distribution of ε-FeSi (36.10% Si, 63.90% Fe) phase.

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