The Fabrication of Composite Materials Between Higher Manganese Silicide (HMS) and Silicon (Si) by Ball Milling and Hot-Pressing

การสังเคราะห์วัสดุเชิงประกอบระหว่างวัสดุซิลิไซด์ที่มีแมงกานีสสูงและซิลิกอนด้วยวิธีบอลมิลและอัดด้วยความร้อน

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ABSTRACT

The thermoelectric properties of bulk silicon materials could be enhanced by an addition of higher manganese silicide (HMS) for decreasing thermal conductivity. However, the preparation of powders between silicon and manganese were difficult, because manganese could not completely bond with all silicon and caused the remaining manganese or created a MnSi phase which possessed poor thermoelectric properties. In this work, the powders of silicon and manganese were prepared via ball milling and hot-pressing respectively. The conditions of ball milling with time and speed were adjusted and analysis by x – ray diffraction pattern (XRD). From XRD, the ball milling with 6 hr and the speed 400 rpm were appropriate and was used to prepare $Si_{100-x}(Mn_4Si_7)_x$ composite where x is 10, 20, …, 50. The peak of silicon and HMS were obtained without other phases. The images from scanning electron microscope showed that the HMS was well dispersed in silicon matrix.

บทคัดย่อ

ในการพัฒนาวัสดุเทอร์โมอิเล็กทริกของซิลิกอนสามารถทำได้โดยการการเติมวัสดุซิลิไซด์ที่มีแมงกานีส สูงเข้าไปเพื่อลดค่าสภาพนำความร้อนของวัสดุลง แต่การสังเคราะห์เป็นเรื่องที่ยาก เนื่องจากมีโอกาสที่ แมกกานีส จะทำพันธะกับซิลิกอนได้ไม่หมด ทำให้เหลือ แมงกานีส และเกิดเฟส MnSi ที่มีสมบัติทางเทอร์โมอิเล็กทริกที่ไม่ดี โดยในงานนี้แสดงการเตรียมผงซิลิกอนและแมกกานีสด้วยวิธีบอลมิลและนำไปเผาพร้อมอัด ซึ่งทำการเปลี่ยนเงื่อนไขบอลมิลที่ความเร็วรอบ กับเวลา หลังจากนั้นนำไปเผาพร้อมอัดที่ 1273 K และความดัน 70 MPa ตามลำดับ จากผลการเลี้ยวเบนของรังสีเอ็กซ์ ที่ความเร็วรอบ 400 รอบต่อนาทีและเวลา 6 ชั่วโมง เป็นเงื่อนไขที่เหมาะสม หลังจากนั้นใช้เงื่อนไขดังกล่าวทดลองเตรียมสารประกอบ $Si_{100-x}(Mn_4Si_7)_x$ เมื่อ x = 10 20 ... 50 จากผลการเลี้ยวเบนของรังสีเอ็กซ์แสดงให้เห็นว่าสามารถเตรียม $Si_{100-x}(Mn_4Si_7)_x$ ได้โดยไม่เกิดเฟสอื่น และจากภาพถ่ายจากกล้องจุลทัศน์อิเล็กทรอนแบบส่องกราดแสดงการกระจายตัวของวัสดุซิลิไซด์ในซิลิกอน

Keywords: Thermoelectric material, ball milling, Silicide material

คำสำคัญ: วัสดุเทอร์โมอิเล็กทริก วิธีบอลมิล วัสดุซิลิไซด์

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Introduction

Nowadays, a demand for energy is increasing. Most energy is produced from fossil fuels which produce pollution and has a limit on the earth. Alternative energy such as wild, water flow, solar and radiation become interesting because it can generate renewable energy. Thermoelectric is the one of the alternative energies. It can convert waste heat to electricity via thermoelectric materials, without any moving part. Thermoelectric devices, as shown in Figure 1, can converting heat from a lot of sources such as automobile exhaust, industrial processes and human body skin to electrical energy. On the other hand, it can be used as refrigerators or coolers. When thermoelectric materials have temperature difference along the length of materials, the charge carrier in materials moves from the heater to the heat sink. After that the voltage difference between hot side and cold side is generated and hence electrical driving force. The thermoelectric conversion performance of materials is directly determined by the dimensionless figure of merit, ZT, followed the equation, $ZT = (S^2\sigma/\kappa)T$, where S, σ, κ and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity (the summation between lattice κ_l and carrier κ_e thermal conductivity) and absolute temperature, respectively (Snyder and Toberer 2008) (Tritt and Subramanian 2006). Most of research groups who study in the field of thermoelectric are finding the way to improve ZT by enhancing each parameter in the ZT equation. The increase of ZT by raising the numerator term is very difficult because S and σ are oppositely dependent on carrier concentration. Moreover, changing the carrier concentration influences the carrier thermal conductivity as well. Thus, decreasing lattice thermal conductivity is an easier way to improve thermoelectric properties (Sootsman, Chung and Kanatzidis 2009).

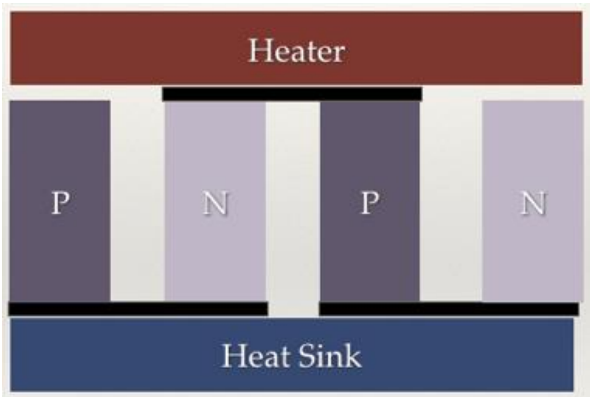

Figure 1 thermoelectric devices with p-type (p) and n-type (n) thermoelectric materials.

Silicon is a promising candidate for appropriate thermoelectric materials due to its advantages such as inexpensive and non-toxic. Generally, bulk silicon has good electrical properties with high charge carrier mobility. Unfortunately, bulk silicon exhibits a high thermal conductivity (>140 $Wm^{-1}K^{-1}$ at room temperature) and has ZT of ~0.02 at room temperature (Shanks, et al. 1963). The increase of the ZT of bulk silicon can be done by reducing lattice thermal conductivity, by doping or substituting heavy elements in bulk silicon for an obstacle of heat transfer in materials.

A lot of research groups are studying silicide materials by trying to reduce lattice thermal conductivity. Mingo et al calculated the thermal conductivity of bulk SiGe doped with silicide materials. The thermal conductivity of bulk SiGe can be significantly decreased (Mingo, et al. 2009). Yusufu et al improved thermoelectric properties of the bulk silicon by dispersing VSi_2 nanoparticle on silicon matrix. The thermal conductivity and the ZT of about 0.4 at 1073 K were observed (Yusufu, et al. 2016). Kurosaki et al studied chromium silicide fabricatied via arc melting and melt spinning. They could reduce the thermal conductivity to 12 $Wm^{-1}K^{-1}$ at room temperature (Kurosaki, et al. 2016). Petermann et al was interested in tungsten silicide. Tungsten was added to silicon film to form WSi_2 and the thermal conductivity was dropped to 8.5 $Wm^{-1}K^{-1}$ (Petermann, et al. 2015). Alternatively, higher manganese silicide (HMS), as a general form $MnSi_{1.72\text{-}1.75}$, is attracted for developing thermoelectric properties. From Bienert's work, the thermoelectric properties of HMS were improved via induction and hot-pressing method. They obtained the ZT of 0.38 at 675 K (Bienert and Gillen 1968). Thus, the addition of HMS to bulk silicon is promised to reduce lattice thermal conductivity and increasing the ZT of composite.

The preparation of composite powder between silicon and HMS is difficult because the two base materials are not uniformly distributed and the MnSi phase were observed. The MnSi phase showed poor thermoelectric properties, with low seebeck coefficient and low the ZT of 0.039 at 450K (Sakurai, Yamamoto and Komura 1998). On the other hand, Shin et al studied in thermoelectric properties of HMS via ball milling method and subsequent hot pressing. They could synthesis pure phase of HMS and obtained the ZT 0.28 at 823 K (Shin, et al. 2013). It could be done at room temperature and prevent the oxidation of silicon with oxygen. The ball milling method is suitable method for preparing composite powder. However, the condition of ball milling, such as speed and duration, need optimization. Because those parameters have an effect on micro structure of the samples and distribution of composite materials. Thus, the appropriate condition of time and speed for ball milling are studied in this work for the silicon and HMS composites.

Objectives of the study

1. To prepare the powders based on composite materials between silicon and manganese via ball milling method.
2. To study the influence of speed and time of ball milling method on phase and micro structure of the composite materials between silicon and manganese.

Methodology

A ball milling method is used to mix silicon and manganese powders. It is taken to cylindrical chamber and set into horizontal position. The zircronium ball with diameter 5 millimeter were loaded into the chamber and the ball per the material ratio of 20:1 was used. After that, the chamber was rotated on the horizontal axis. As shown in Figure 2, during rotation, the balls have impacts on powder. The powder size become smaller and powders were mixed well (Suryanarayana 2001). Then, the powder after ball milling was hot-pressed at 1273 K for 1 hr step by 10K/min and a pressure of 70 MPa. In this process, the bonding between silicon and manganese particles occurred and the HMS phase were obtained.

The speed and time of ball milling were adjusted as 50, 100, 200, 300 and 400 rpm and 0.5, 6 and 12 hr, respectively. The samples were characterized via X-ray diffraction (XRD) analysis and scanning electron microscope (SEM) for their phase and morphology. The optimized parameters (speed and time of ball milling) were chosen. Next, the concentration of

HMS in $Si_{100-x}(Mn_4Si_7)_x$ composites was studied, when x = 0, 10, 20, 30, 40, 50. Figure 3 and 4 summarizes the process and the diagram for this work.

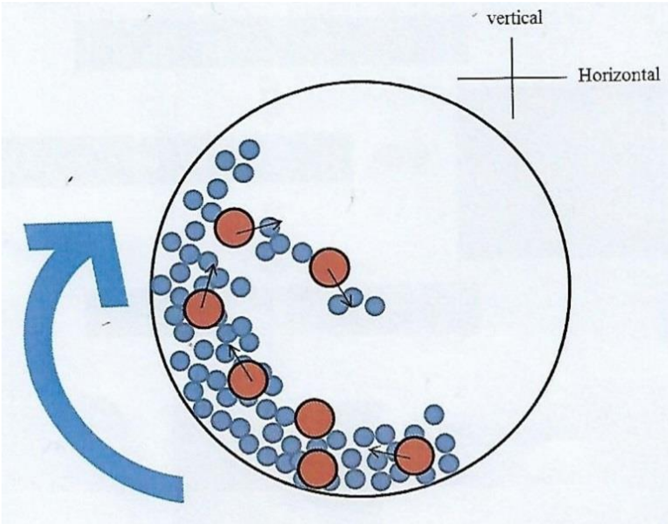

Figure 2 The principle model of ball milling machine.

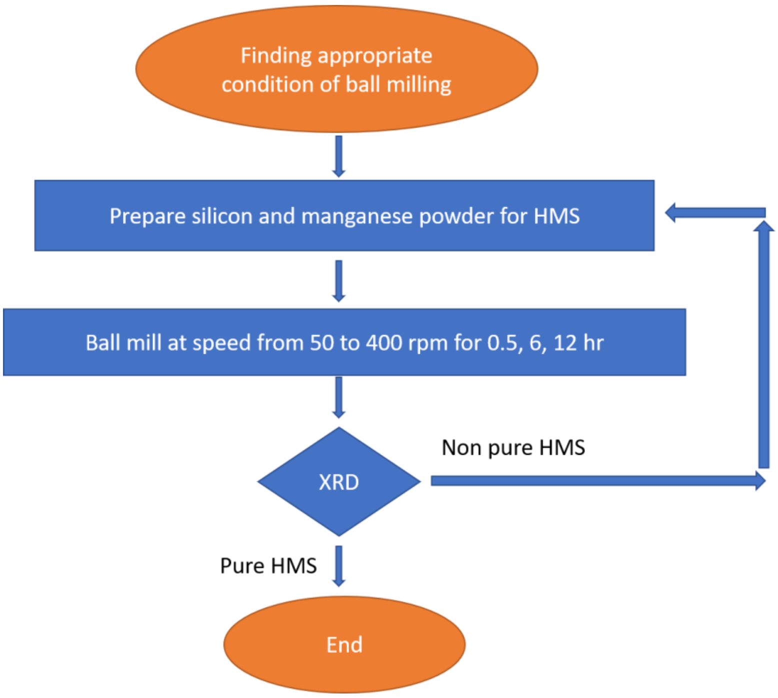

Figure 3 Steps for preparing HMS via ball milling method

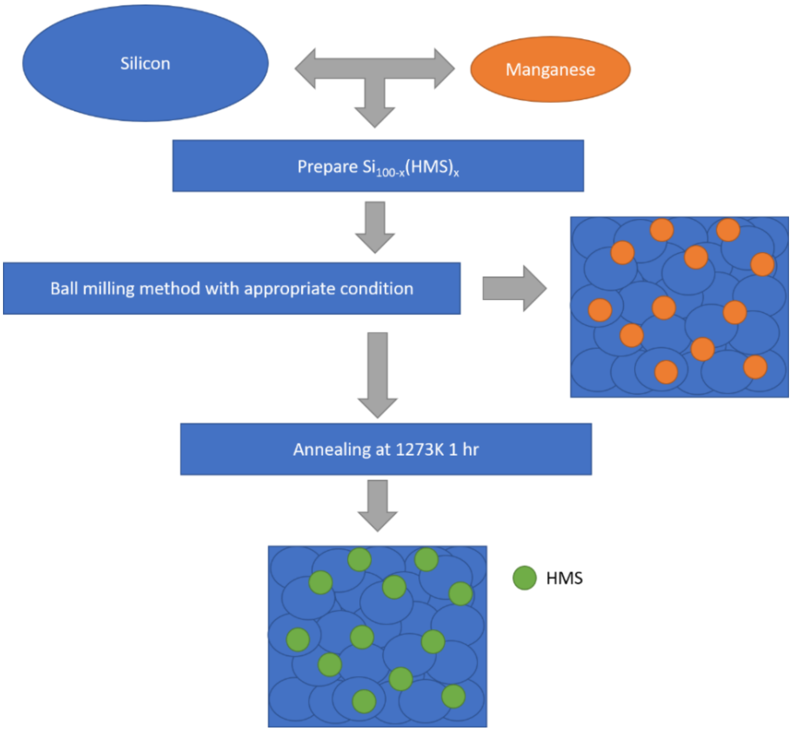

Figure 4 A diagram for synthesis composite thermoelectric materials between silicon and manganese.

Results

XRD analysis for the suitable conditions of ball milling is shown in Figure 5. The peaks of HMS appeared in all conditions. On the other hand, at the miliing duration of 30 minutes and 12 hr for all speeds, the pure phase of HMS could be obtained. The peak of silicon (circle) and MnSi (triangle) are presented at the lowest time (30minutes) for all speeds. Moreover, for the speed of 50, 100 and 200 rpm at 6 hr and 12hr, the peaks of silicon and MnSi are also presented. In contrast, for the speed of 300 and 400 rpm and the time of 6 hr and 12 hr, only the phase of HMS without silicon and MnSi was found. Therefore, the ball milling condition of 6 hr and the speed of 400 rpm were selected.

From XRD analysis, the condition of ball milling which have the duration of 6 hr and the speed as 400 rpm was appropriate for preparing powder of composite materials, $Si_{100-x}(HMS)_x$. XRD patterns of $Si_{100-x}(Mn_4Si_7)_x$ are shown in figure 6. The composite phases between silicon and HMS were observed for all of x without MnSi phase. When x increase, the peaks of silicon decrease, along with the increased HMS peaks. For each XRD pattern, the lattice parameters were calculated by Rietveld Refinement method (Rietveld 2011), as shown in Table 1. The lattice parameter of silicon in the composite material increased for the addition of HMS. In contrary, the increasing of HMS affects to reduce lattice parameter of silicon and HMS as well. But it still has more than theory. Moreover, the space between particle in composite materials have wider than base material. Thus, the heat transfers via particle oscillation is harder and the thermal conductivity may be decreased from the increasing of lattice parameter.

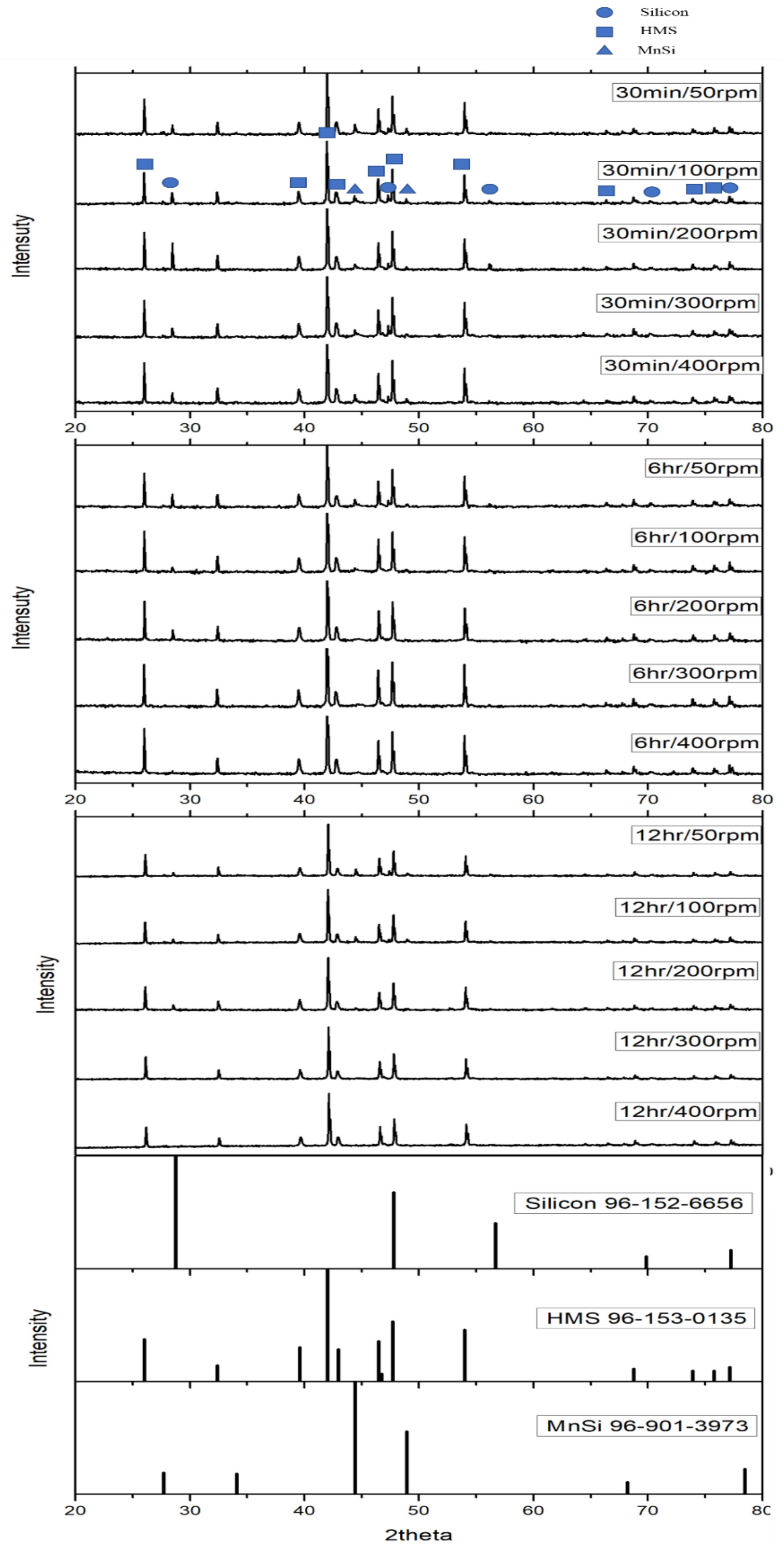

Figure 5 XRD pattern of HMS powder after ball milling and hot-pressing at speed 50, 100, 200, …, 400 for time A. 30 min, B. 6 hr and C 12 hr.

Table 1 the lattice parameter of composite materials between silicon and HMS for difference X parameter.

Material	$Si_{100-x}(HMS)_x$	x=10	x=20	x=30	x=40	x=50
HMS	a	5.530564	5.529297	5.528335	5.52817	5.52787
	c	17.47593	17.4748	17.46987	17.4745	17.46948
Silicon	a	5.43204	5.431287	5.430577	5.430021	5.429861

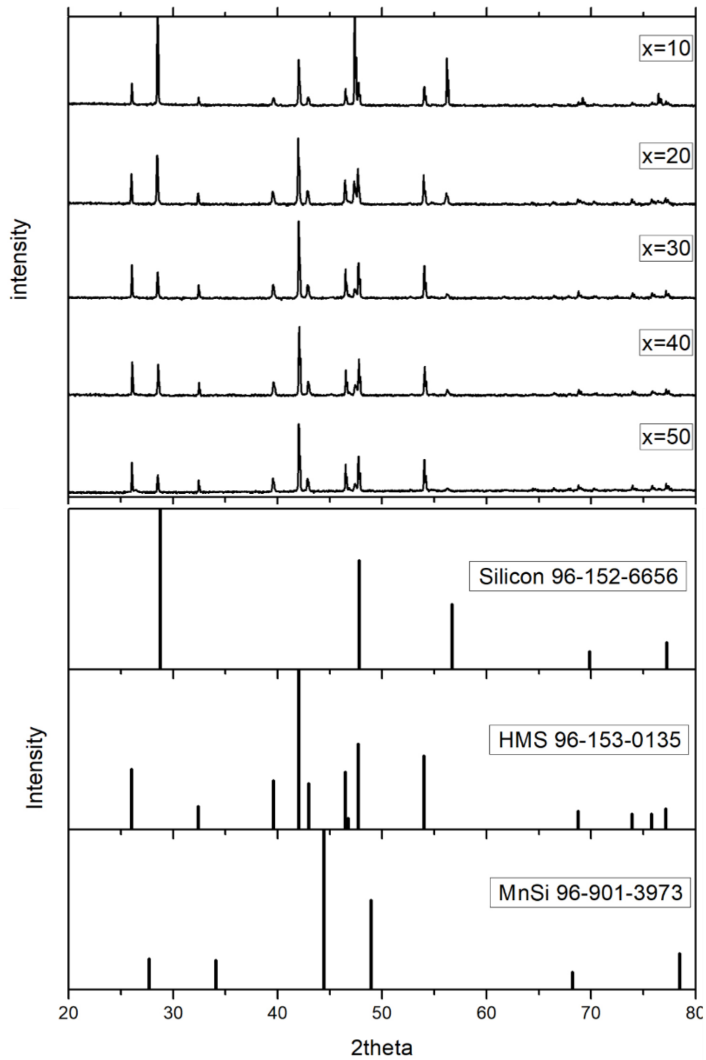

Figure 6 XRD pattern of composite thermoelectric materials $Si_{100-x}(HMS)_x$ where x = 10, 20, 30, 40 and 50

The SEM images of the fractured surface of the samples after ball milling and hot pressing are shown in figure 7. The grains of silicon were represented with the dark site and have the average size about 5 and 3 μm for x = 10 and 20 respectively, as shown in figure 7A and 7C. The image at high magnificent presented the dots on the grains of silicon. The dots had brighter than silicon because it had electrical conductivity more than silicon as shown in figure 7B and 7D. Thus, the dots were believed to be the HMS phase that dispersed in the silicon matrix. From the small size of the HMS dots about 100-300 nm, they can behave like the barrier for obstructing the phonon with a short wavelength and decrease thermal conductivity of the sample.

The SEM image at low magnificent of the polished surface are shown in the figure 8 for observing the overview of the sample after ball milling and hot-pressing. The 2 areas, dark and white, were presented. The dark and the white were silicon and HMS respectively. Furthermore, the HMS area expanded when the number of x increase from 10 to 50, as shown in figure 8A to 8E. The boundaries between phase act like the barrier to scatter the long wavelength phonons and the thermal conductivity could be reduced.

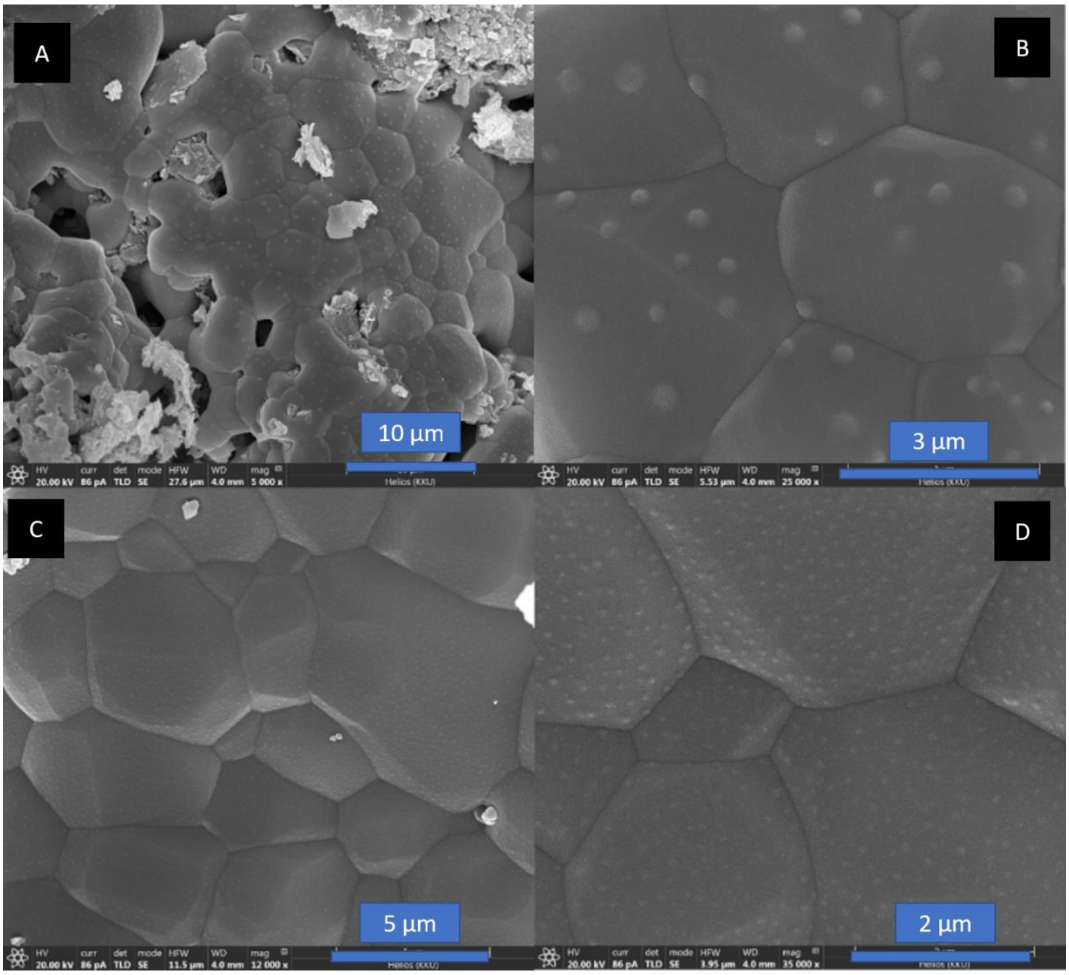

Figure 7 The SEM images of the crack sample after ball milling and hot-pressing (A). X=10 at 5000x, (B). X=10 at 25000x, (C). X=20 at 12000x and (D). X=20 at 35000x.

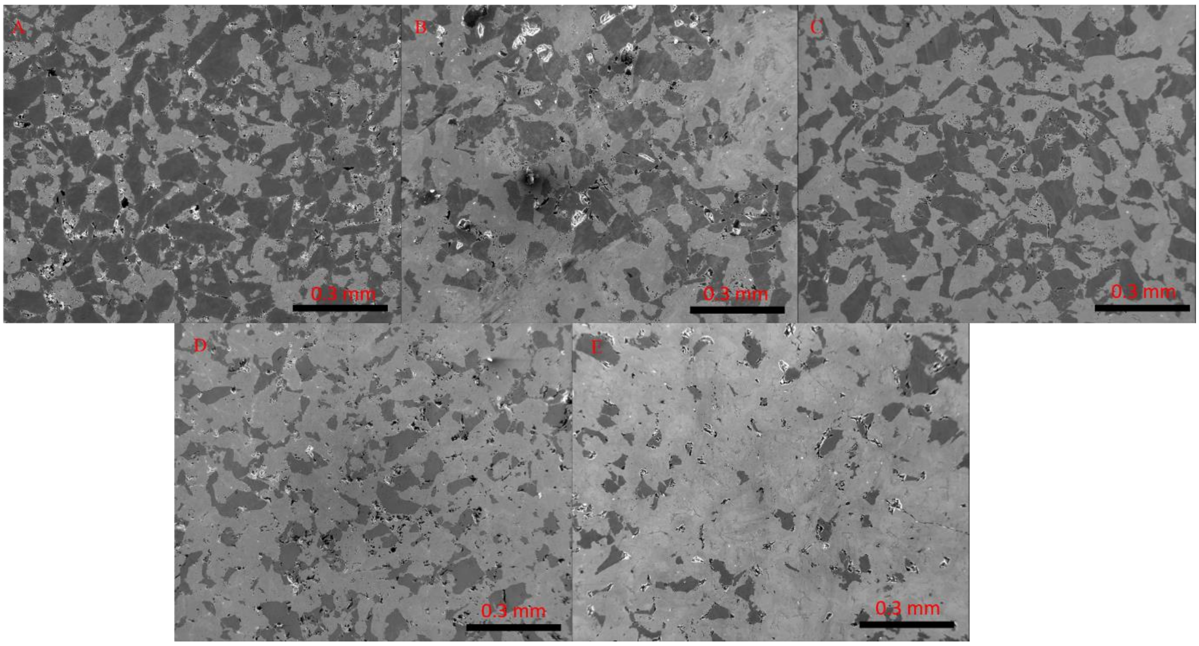

Figure 8 The SEM image of the polished surface area where A, B, C, D and E are for $Si_{100-x}(Mn_4Si_7)_x$ where x = 10, 20, 30, 40 and 50, respectively.

Discussion and Conclusions

In summary, the different conditions of ball milling affect the microstructure of the prepared powder of silicon and manganese for HMS before hot-pressing. After hot-pressing, XRD analysis showed that the appropriate condition of ball milling method was the speed of more than 300 rpm and time at 6 hr or 12 hr. The optimized condition, the speed of 400 rpm and the time of 6 hr are used for preparing composite powder of silicon and HMS (silicon and manganese) via ball milling. XRD analysis of the composite material represented the peaks of silicon and HMS. The additional HMS can raise lattice parameter from silicon from theory, but the trend of lattice parameter drops when increase the number of x parameter. The SEM image for internal structure showed the grains and grain boundaries, and a lot of dots on the surface of grains. The HMS dots were the possible ways to reduce the lattice thermal conductivity of the composite. Moreover, the overview image of sample surface showed the dispersion of HMS areas in silicon matrix. The mixed phases can obstruct the long wavelength phonon and improve the thermoelectric properties of bulk silicon.

Acknowledgements

The research was supported by the Science Achievement Scholarship Thailand (SAST), the Thailand Research fund (TRF) in cooperation with Khon Kaen University (RSA5980014), and the Institute of Nanomaterials Research and Innovation for Energy (IN-RIE), Khon Kaen University and the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its program of Research Network NANOTEC (RNN)

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