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Study on the Obtaining of MnSi$_{1.75}$ Intermetallic Compound by Mechanical Alloying

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Abstract. Thermoelectric higher manganese silicide (HMS) having the composition MnSi$_{1.75}$ material was obtained by mechanical alloying after 18 hours of milling. As starting materials, manganese and silicon elemental powders were used. After 18 hours of milling beside the HMS in the powders, MnSi phase was obtained as well. After only 4 hours of milling, both binary MnSi phases are found in material besides a significant amount of non-reacted elements. Milling up to 10 hours leads to the silicon characteristic peaks disappearance and the HMS and MnSi phases amount increase. Subsequent annealing of the milled powders was performed in order to promote internal stresses removal. The 4 hours annealing of the powder at the temperature of 350°C under high vacuum ($10^{-6}$ Torr) leads to stress release and an increase in the MnSi phase quantity. The particle size analysis shows that the powder diameter is in 0.1-125 μm range. A large amount of powder is in the range of 15-125 μm, but there is also a small amount that is in the 0.1-15μm range. Scanning electron microscopy (SEM) was used to characterize the powders morphology.

1. Introduction

The thermoelectric materials can convert a temperature difference into electrical energy. This conversion is possible due to the Seebeck effect. The performance of the thermoelectric materials is characterized by the Seebeck coefficient alongside with the figure of merit (ZT). The figure of merit of a thermoelectric material depends on the Seebeck coefficient, electrical conductivity, temperature and respectively thermal conductivity of the material [1, 2].

Higher manganese silicide (HMS) is one of many thermoelectrical materials intensively studied today. The thermoelectric materials in the Mn-Si system are attractive because the constituent elements have a widespread in the earth’s crust, are not toxic and have good chemical stability [3]. HMS is a thermoelectric compound with $p$-type conduction [4]. HMS have the general formula MnSi$_y$ where ($y$=1.67-1.77) and crystallized in tetragonal structure with manganese in corners and silicon inside of tetragon in the form of a spiral. The currently studied HMS compounds from the Mn-Si system are Mn$_{13}$Si$_{19}$, Mn$_{26}$Si$_{45}$, Mn$_{15}$Si$_{36}$, Mn$_{27}$Si$_{47}$, Mn$_{3}$Si$_{7}$ [5-7].

The preparation of HMS by conventional arc melting is difficult due to the high melting points of the elements and the high time required to obtain the structural homogeneity [4, 8]. Mechanical alloying represents an alternative technique to obtain HMS. The obtaining of the HMS compounds by mechanical alloying is studied in several articles, where different milling parameters (ball to powder ration, vials...
and/or main disk speed etc.) are varied, leading to the complete formation reaction being spanned in the range of 3 to 24 hours [9-11].

In the present study, using a planetary ball mill, the formation of the HMS compound was studied for milling times up to 18 hours. The phase evolution, the morphology, and the particle size distribution as the milling time increase are discussed.

2. Experimental
For obtaining the HMS compound manganese powder (purity 99.3% and -325 mesh particle class) and silicon powder (purity 99.9% and -100 mesh particle class) from Alfa Aesar was used. The amount of each component was weighed with an analytical balance in order to obtain the following chemical composition: MnSi$_{1.75}$. The homogenization of powders was performed using a Turbula spatial homogenizer for 15 minutes. The blended powder was loaded in a stainless steel vial with 89 stainless steel balls (14 mm). The milling was performed in a Fritsch Pulverisette 6 planetary ball mill under argon atmosphere. The ball to powder ratio was 10:1 and the main disk rotation speed was 400 rpm. The process was carried out in an argon atmosphere. Sampling was made inside of glove bag with argon atmosphere to avoid the oxidation. A thermal treatment for stress releases was performed at 350 °C for 4 hours in high vacuum.

X-ray diffraction (XRD) studies were carried out with a Buke D8 Advance diffractometer using Cu Kα ($\lambda = 1.54183$ Å) radiation in the angular range: $2\theta=20$-110°. To record high-resolution data, the acquisition time for the X-ray patterns was 12 hours. The particle size analyzer Analysette 22 Nano Tec was used to record the particle size distribution of the powders mechanically milled. From the particle size distribution the D10, D50, and D90 parameters were determined. D10, D50, and D90 represent the mean powder particle diameter of the 10, 50 and 90 % of the total powder volume [12]. The JEOL-JSM 5600 LV scanning electronic microscope (SEM) was used to study the morphology of powders.

3. Results and discussion
The XRD patterns for MnSi$_{1.75}$ are presented in figure 1 at different milling time and for the initial mixture of powders. In the diffraction pattern of initial mixture, only the characteristic peaks for silicon and manganese elements are identified. After 4 hours of mechanical alloying, the corresponding peaks of silicon decreases in intensity and widens due to the reduction of the crystallite size [13]. On the other hand, the manganese peaks increase in intensity and width. At the same milling time, the HMS compound and an undesired MnSi phase appear as a consequence of solid state reaction initiation.

![Figure 1](image1.png)

**Figure 1.** X-ray diffraction patterns for the initial mixture of powders and for 4, 10 and 18 hours milled powders.

![Figure 2](image2.png)

**Figure 2.** X-ray diffraction patterns for milled powders and subsequently annealed at 350 °C for 4 hours.
The diffraction patterns for 10 hours milled powder shows the HMS, MnSi and initial elements (Mn and Si) peaks. The unreacted amount of initial elements quantity is small. The majority phase in the material is the HMS compound. The complete reaction of elements was achieved after 18 hours of milling. However the 18 hours diffraction patterns contains both Mn-Si phases (HMS and MnSi). The amount of MnSi phase at this milling time is smaller compared to the samples milled for 10 hours. It is not clear what process leads to decreasing the MnSi phase quantity, but it can be possible that this phase transforms under high stress induced by milling process into the HMS phase. The analysis of the X-ray diffraction patterns, did not evidenced any oxidation of the powders, as reported in [8], since the milling and the sampling was performed in high purity argon atmosphere.

Shin et al [7], using a planetary ball mill (Fritsch, Pulverisette5) with ball to powder ration 20:1 and balls with 5 mm in diameter obtain a complete reaction of elements after 12 hours at 400 rpm. Comparing the results obtained in this paper and the results presented by Shin it is concluded that the use of more energetic conditions (as compared to our milling conditions) can reduce the time needed for alloying. It can also be seen that the steps through which the powder passes are comparable only at slightly higher times. Therefore, it can be said that the use of a higher ball to powder ratio conduct to reducing the time needed for alloying. Figure 2 shows XRD patterns for the samples mechanically milled for different duration and subsequently subjected to a heat treatment. In comparison with the peaks for as-milled powder, after heat treatment, the peaks become narrow because the internal stresses removal. Heat treatment at 350 °C for 4 hours has also the effect of enhancing the compound formation. In the case of 10 hours milled samples and heat treated, the disappearance of the silicon maximum (2θ ≈ 28.4°) and the maximum of manganese (2θ ≈ 43°) is observed. This can be assigned to the complete reaction of those phases. In the diffraction patterns corresponding to powders milled 18 hours and heat treated there are not significative changes.

In figure 3 the SEM images for mechanical milled powders and for elemental powders (as reference sample) are presented. In the figure 3.a, the image for manganese elemental powders is shown. The irregular shape and sharp edges of manganese powder are evidenced. Manganese powder contains particle sizes ranging from a few micrometers to several tens of micrometers. In contrast, the silicon powders presented in figure 3.b, contains only large particles. The morphology of silicon powders is approximately the same as the manganese powder. In the image presented in figure 3.c) it can be seen that smaller manganese particles are well mixed with larger silicon particles. After 4 hours of mechanical milling, the morphology of particles is completely modified, sharp edges disappears and small, agglomerated particles are noticed.

Figure 3. SEM images: a) Mn powder, b) Si powder, c) 0h-MA milled powder, d) 4h-MA milled powder, e) 10h-MA milled powder and f) 18h-MA milled powder
In figures 3.d, 3.e and 3.f, it can be seen that the milled powders consists in agglomerates of smaller, fine particles. The dimension of agglomerates increases with milling time. At the milling time investigated, it can be noticed that the particle size is below 10 μm, but the size of the agglomerates exceeds a few tens of micrometers. Particle size are comparable to those reported in [9], with the difference that no agglomerated particles were reported in the reference.

In the image 4 is shown the particle size distribution for powders milled for 4, 10 and 18 hours, respectively. At all of these milling times, it’s possible to identify that in the milled powders exist a very small amount of fine powders and a large amount of large particles. This result is in concordance with SEM images. The curve corresponding to 4 hours of milling is Gaussian type distribution. The curves for 10 and 18 hours of milling are slight asymmetrical.

![Particle size distribution for powders milled 4, 10 and 18 hours.](image)

Using the particle size distribution data, the average of particle size was calculated and this is presented in figure 5. The D10 parameter and remains constant up to 18 hours of milling, with a value of about 29 μm. The decrease of parameter D10 in the range of 4 to 10 hours is attributed to the fragmentation processes, especially in the silicon large particles.

![D10, D50, and D90 parameters for powders milled 4, 10 and 18 hours.](image)

In the case of a D50 parameter, the powder particle size increases more visible in the 4 to 10 hours interval and slightly in 10 to 18 hours interval. The D50 parameter is ranging from 47 μm corresponding to 4 hours of milling to 54 μm at 18 hours of milling. This trend is also observed for D90 parameter. Increased growth in the range of 4 to 10 may be due to the fact in this milling time range a large powder
quantity reacts and the welding process are slightly higher than the fracture ones. In the range 10 – 18 hours, agglomeration of particles containing the HMS phase is more significant.

4. Conclusions
HMS having the composition MnSi1.75 was obtained after mechanical alloying up to 18 hours of milling. The prepared powders are not single-phase powders, the HMS phase being accompanied by a minor MnSi phase. The quantity of MnSi impurity phase is reduced via increasing of the mechanical milling duration. Heat treatments at 350 °C for 4 hours are sufficient to conduct to stresses release. After 18 hours of mechanical alloying material shows agglomerates of very fine powders.

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