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Fabrication and Characterization of Thermoelectric $CrSi_2$ Compound by Mechanical Alloying and Spark Plasma Sintering

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A mixture of elemental Cr–Si powders has been subjected to mechanical alloying (MA) at room temperature to prepare $CrSi_2$ thermoelectric compound.The MA powders were sintered at 800–1000 °C Cunder 60 MPa using spark plasma sintering (SPS) technique. Due to the observed larger loss of Si relative Cr during ball milling, the starting composition was modified to $Cr_{30}Si_{70}$, $Cr_{31.5}Si_{68.5}$ and $Cr_{33}Si_{67}$ to get a single phase of $CrSi_2$ compound. The single phase $CrSi_2$ has been obtained by MA of $Cr_{31.5}Si_{68.5}$ mixture powders for 70 h and subsequently sintered at 1000 °C. X-ray diffraction data shows that the SPS compact sintered at 1000 °C consists of only nanocrystalline $CrSi_2$ compound with a grain size of 250 nm. The value of Seebeck coefficient of $CrSi_2$ compound increases with temperature and reaches maximum value of 245 μV/K at 300 °C.

Keywords: Thermoelectric $CrSi_2$ Compound, Mechanical Alloying, Spark Plasma Sintering.

1. INTRODUCTION

Chromium disilicide, $CrSi_2$ is reported to be thermally stable in air up 1050 K and therefore can be a candidate for thermoelectric power generation at elevated temperatures.[1, 2] In general, the so-called figure of merit of thermoelectric material can be improved by grain refinement due to decreasing thermal conductivity.[2–4]

Mechanical alloying (MA) based on solid state reaction through severe plastic deformation at room temperature has been proved to be an advantageous method for the synthesis of nano-structured alloy, amorphous phase, quasicystal and semiconducting thermoelectric compounds.[5–8] The method even allows the formation of those alloys which are difficult to obtain via solidification processes. The resulting powder material appears to be very homogeneous and, due to the large amount of induced grain boundaries and accumulation of crystal defects, compacts of MA thermoelectric materials show a comparable low thermal conductivity.[4] Therefore, MA process is believed to be very effective to get $CrSi_2$ thermoelectric material with high performance.

In the present work, $CrSi_2$ thermoelectric material has been prepared by MA coupled with spark plasma sintering (SPS). In particular, the milling parameters and SPS conditions are optimized so as to obtain the best thermoelectric properties. The effect of starting compositions on the formation of a single $CrSi_2$ compound was also investigated.

2. EXPERIMENTAL DETAILS

The MA was carried out at room temperature for a mixture of Cr (99.9%, 60 μm in size) and Si (99.999%, 150 μm in size) powders with the composition of $Cr_{30}Si_{70}$, $Cr_{31.5}Si_{68.5}$ and $Cr_{33}Si_{67}$. A planetary ball mill (Fritsch Pulverisette 5) was used with its vial rotation of 200 rpm. The vial and balls are made of the hardened steel (SKD11) and stainless steel (SUS304), respectively. The total mass of powders was about 15 g and the ratio of balls to powders was 7:1.

The structural changes of ball-milled powders have been studied by ordinary X-ray diffraction of continuous and step scanning mode with Cu-Kα radiation. Consolidation of the MA powders was performed in a spark plasma sintering (SPS) machine using graphite dies up to 800–1000 °C under 60 MPa with a heating rate of 100 °C/min.The sintered compacts were subjected to density measurement by Archimedes method.

The average grain size of $CrSi_2$ compound was also evaluated by the so-called Hall plot method using a diffraction line-width.[9, 12] X-ray diffraction line-broadening from the equipment was calibrated with the standard Si

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powders. More details are described in Refs. [9, 12]. Thermoelectric properties, such as electrical conductivity σ and Seebeck coefficient α were measured.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns for a mixture of Cr and Si powders with the composition of $Cr_{33}Si_{67}$ ball-milled for various time intervals. It can be seen that the diffraction lines associated with Cr and Si remain essentially unchanged after 20 hours of MA without any evidence for the formation of $CrSi_2$ compound. On the other hand, $CrSi_2$ compound begins to appear gradually after 50 hours of MA. Indeed, it can be seen that the formation of single phase $CrSi_2$ compound essentially completed after 100 h of MA. No trace of an impurity phase or secondary phase was observed. Webelieve that a substantial decrease in intensity coupled with broadening of the diffraction lines of $CrSi_2$ compound is caused by the refinement in grains and also by the accumulation of defects and strains.[9] An average grain size of $CrSi_2$ may be evaluated from the so-called Hall plot using the half-width of the diffraction lines in Figure 1.[9, 12] Here the half-width β of the diffraction line is expressed as:

$$\beta \cos\theta/\lambda = (2\eta \sin\theta/\lambda) + (1/\varepsilon)$$

where θ is the Bragg angle, λ is the X-ray wavelength, η is the internal strain and ε is an average grain size.

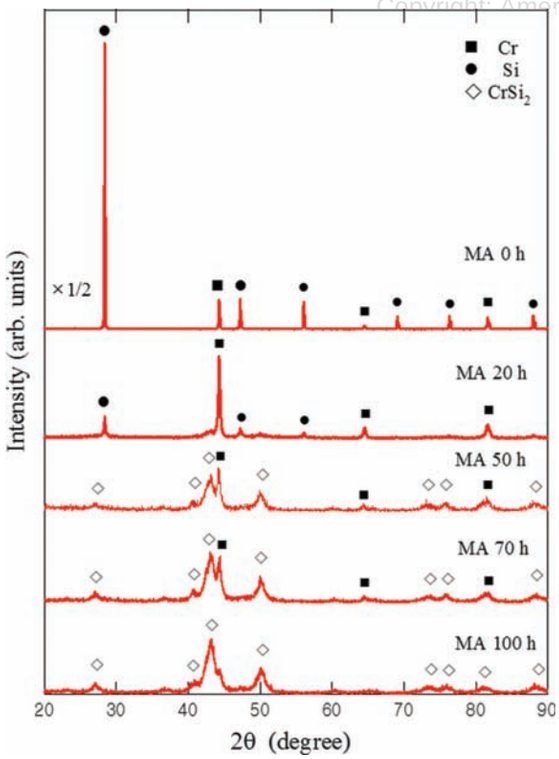

Figure 1. X-ray diffraction patterns of $Cr_{33}Si_{67}$ MA powders as a function of total milling time.

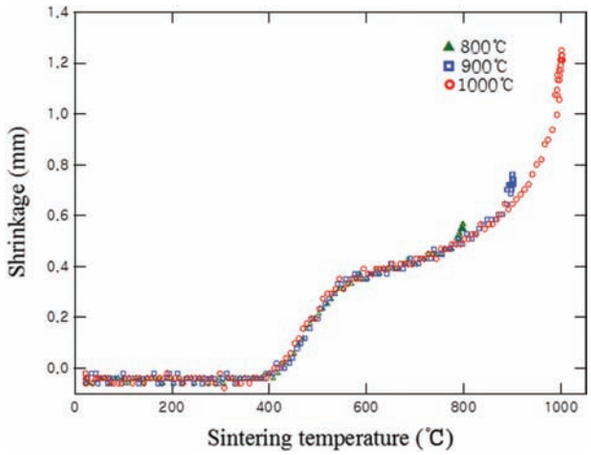

Figure 2. The variation of shrinkage during SPS of $Cr_{33}Si_{67}$ MA powders heated up to 800 °C, 900 °C and 1000 °C, respectively.

It is found that the average grain size of $CrSi_2$ compound by MA is estimated to be 50 nm by broadening of the diffraction line-width.

Spark plasma sintering of the $Cr_{33}Si_{67}$ powders ball-milled for 70 h was carried out at various temperatures. The shrinkage behaviors during heating up to 800–1000 °C Care shown Figure 2. The shrinkage of MA samples during SPS consolidation process increases gradually with increasing temperature and significant at about 550 °C. It can be seen that compact body sintered at 1000 °C has a high relative density above 96% with metallic glare on

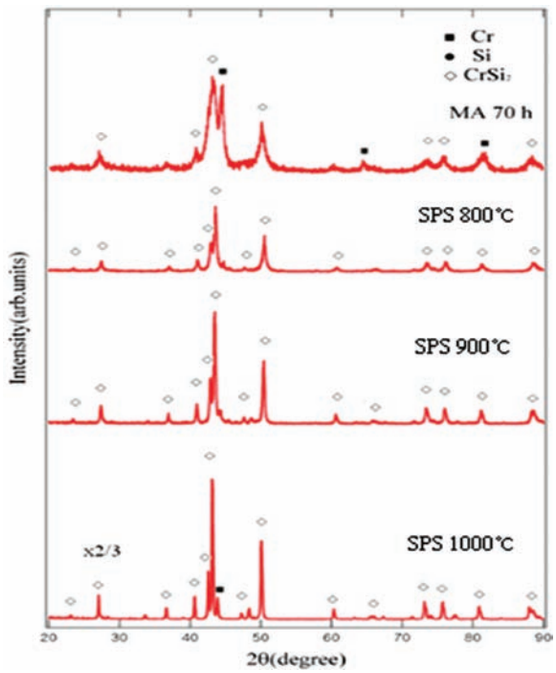

Figure 3. X-ray diffraction patterns for SPS sintered body of $Cr_{33}Si_{67}$ MA powders heated up to 800 °C, 900 °C and 1000 °C, respectively.

the surface. Optical observations of the sample sintered at 1000 °C also showed no voids on the polished sections.

Figure 3 shows the XRD patterns for the SPS sintered body of $Cr_{33}Si_{67}$ MA powders heated up to 800 °C, 900 °C and 1000 °C, respectively. It is seen from Figure 3 that all diffraction lines of SPS compacts sintered at 800 °C and 900 °C can be identified as $CrSi_2$ compound without any trace of other phase. However, it is rather surprising that apparently the diffraction line of Cr remains even after SPS processing at 1000 °C. It is clear from Figure 3 that a single $CrSi_2$ phase cannot be formed from a $Cr_{33}Si_{67}$ MA powders. So we investigated the dependence of the starting composition on the formation of a single $CrSi_2$ compound.

Figure 4 shows X-ray diffraction patterns for SPS sintered body of $Cr_{30}Si_{70}$, $Cr_{31.5}Si_{68.5}$ and $Cr_{33}Si_{67}$ MA powders sintered at 1000 °C. It is seen that a single $CrSi_2$ compound can be formed from $Cr_{31.5}Si_{68.5}$ MA powders ball-milled for 70 h, while the diffraction lines associated with Si and Cr still remains for $Cr_{30}Si_{70}$ and $Cr_{33}Si_{67}$ MA powders, respectively. This suggests that Si element relative to Cr tend to loss during MA process. The diffraction lines of single $CrSi_2$ compound sintered at 1000 °C are still broad, suggesting that the grain size of the sintered body remains very fine. The average grain size of this sample, estimated from Hall plot of line-width is found to be 250 nm.[9, 12] It is worth noting that the grain size of $CrSi_2$ compound is 250 nm even after sintering at a temperature of 1000 °C.

Figures 5(a)–(c) show the measured electrical conductivity σ, Seebeck coefficient α and power factor PF for

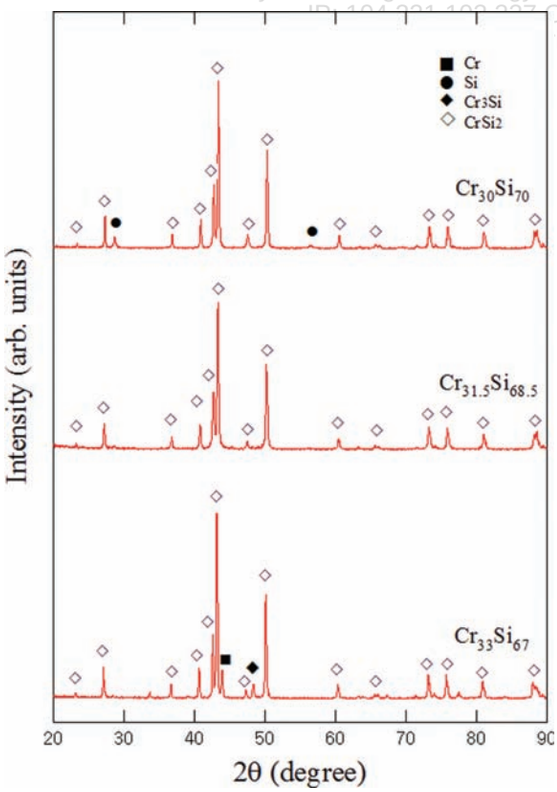

Figure 4. X-ray diffraction patternsfor SPS sintered body of $Cr_{30}Si_{70}$, $Cr_{31.5}Si_{68.5}$ and $Cr_{33}Si_{67}$ MA powders ball-milled for 70 h.

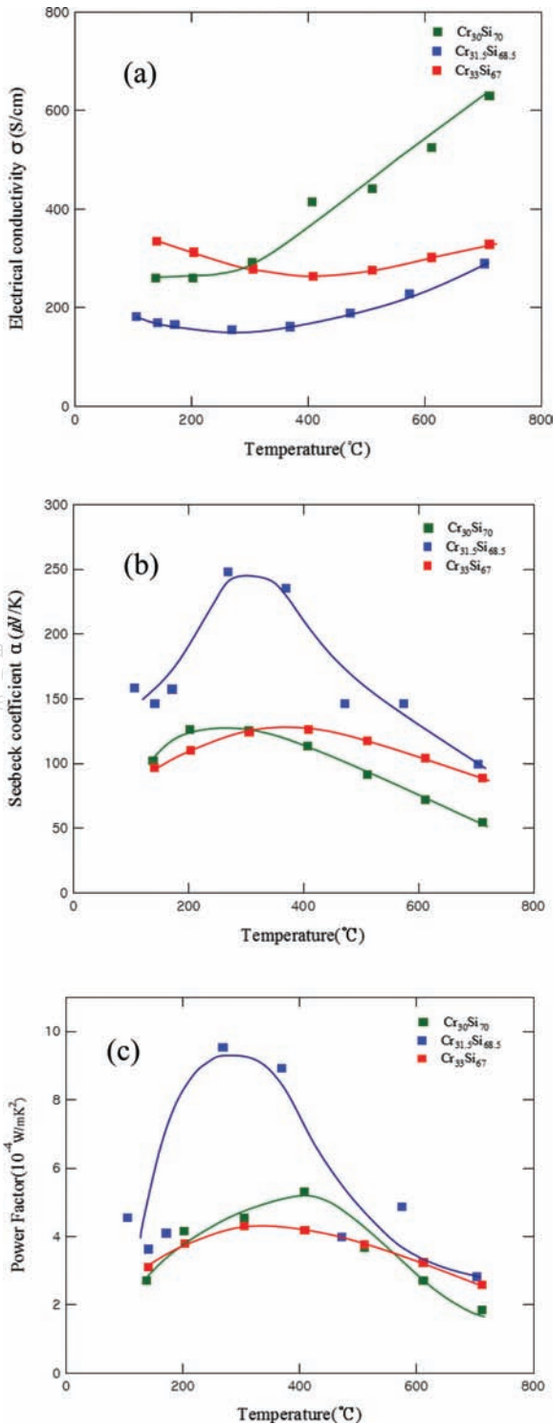

Figure 5. Temperature dependence of (a) Electrical conductivity, (b) seebeck coefficient and (c) power factor for SPS compacts of $Cr_{30}Si_{70}$, $Cr_{31.5}Si_{68.5}$ and $Cr_{33}Si_{67}$ MA powders sintered at 1000 °C.

SPS compacts of $Cr_{30}Si_{70}$, $Cr_{31.5}Si_{68.5}$ and $Cr_{33}Si_{67}$ MA powders sintered at 1000 °C as a function of temperature. The PF ($\alpha^2\sigma$) was calculated from measured α and σ values. The magnitude of σ for SPS compacts of $Cr_{30}Si_{70}$ and $Cr_{31.5}Si_{68.5}$ increases with increasing temperature, indicating the semiconducting behaviors. In addition, Seebeck coefficient α for SPS compacts of $Cr_{31.5}Si_{68.5}$ increases with increasing temperature and reaches maximum value of 245 μN/K at 300 °C. The thermoelectric power factor for SPS compacts of $Cr_{31.5}Si_{68.5}$ shows similar behavior, reaching peak value of 9.3×10^{-4} W/mK^2 at 300 °C, which is comparable to conventional thermoelectric materials.[2] Therefore, thermoelectric $CrSi_2$ compound by MA can be a promising candidate for thermoelectric power generation at elevated temperatures.

4. CONCLUSION

The effect of mechanical alloying on the formation of $CrSi_2$ thermoelectric compound was investigated. The single phase $CrSi_2$ can be obtained by MA and subsequently SPS sintering for a Si-rich composition of $Cr_{31.5}Si_{68.5}$ mixture powders, suggesting the constituent Si loss during MA process. It is found that the grain size of $CrSi_2$ SPS compact analyzed by Hall plot method is reduced to 250 nm. The present $CrSi_2$ sample possesses good thermoelectric properties, with a Seebeck coefficient of 245 μN/K and power factor of 9.3×10^{-4} W/mK^2 at 300 °C. Therefore $CrSi_2$ thermoelectric compound is a good candidate for intermediate and high temperature applications. Further study is underway to examine in more detail the thermal conductivity related to the present nano-structured $CrSi_2$ compound.

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