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Original Research Paper

Densification and alloying of ball milled Silicon-Germanium powder mixture during spark plasma sintering

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ABSTRACT

In this research, the influence of process parameters such as sintering temperature and current during alloying and densification of silicon-germanium (Si_{80}-Ge_{20}) powder mixture using spark plasma sintering (SPS) was reported. Si_{80}-Ge_{20} powder mixture was consolidated at the temperature range 900–1200 °C with 40 MPa pressure for 5 min. soaking. X-ray diffraction (XRD) study was made on sintered compacts to confirm the Si(Ge) alloy formation. Scanning electron microscope (SEM) was used to understand the morphology, particle size and distribution of un-milled and milled Si_{80}-Ge_{20} powder mixture. Transmission electron microscope (TEM) study was made on milled Si_{80}-Ge_{20} powder mixture and bulk SiGe alloy to confirm the nano-crystallinity and alloy formation. Fracture toughness of sintered bulk SiGe alloy was determined from Palmqvist cracks geometry model using Vickers hardness testing. It is understood that, during spark plasma sintering nano-structured Si_{80}-Ge_{20} powder simultaneously increases the densification and reaction kinetics. It helps to achieve homogenous nanostructured SiGe alloy of near theoretical density. The superior hardness and benchmarked fracture toughness (K_{IC}) values of 630 VHN and 2.19 MPa$\sqrt{m}$ was achieved for SiGe alloy sintered at 1200 °C, respectively.

1. Introduction

With decreasing of fossil fuels, energy saving has become major issues around the globe. The expectation for alternative energy technologies to reduce dependency on traditional fossil fuel is becoming an utmost important regime of research [1,2]. Thermo-electric devices are capable of converting heat directly into electricity or vice versa through simple structures [3–5]. The factors driving the renewed interest towards thermo-electric materials include solid state operation, absence of toxic residuals, vast scalability, maintenance free operation, absence of moving parts, no chemical reactions and reliable operation for long life span [6]. Among semiconducting materials family, increasing interest towards group IV elements, especially, Si-Ge alloy is considered potentially superior due to their desirable thermo-electrical power harvesting at high temperature range of 900–1200 °C [7,8]. However, still there is a greater scope and efforts are being made towards the improvement on thermo-electric properties of SiGe alloys with enhanced carrier concentration levels to increase the power factor values [9]. In this context, nanoscale approaches were proposed to improve the thermo-electric phenomena such as enhancement in the Seebeck coefficient, electrical conductivity and decreasing the thermal conductivity thus increases the thermo-electric efficiency for functional applications [10]. The nano-structuring in SiGe based devices is expected to reducing the amount of Ge in the SiGe alloy, paving the way for their large scale commercial utilization [11]. The preparation of Si-Ge alloys for thermo-electric applications is usually achieved through various synthesis techniques including melting and solid state routes. The liquid metallurgy processing methods are zone leveling, Czochralski technique, unidirectional solidification, vacuum melting, chill casting, arc melting, Bridgeman method and induction melting [7,12]. But, there is a difficulty and challenge in synthesis of Si-Ge alloy in melting route due to the existence of wide separation between the liquidus and solidus state which leads to structural inhomogeneity [13]. Solid state synthesis of SiGe alloy through mechanical alloying is an ideal method to achieve single phase SiGe alloy. It is appreciated as an effective and cheapest method of synthesis of nanostructured powders. However, the contamination from the milling media/atmosphere due to excessive milling and/or processing parameters that includes type of mill, material of milling medium, milling speed, duration of milling, extent of vial filling, wet or dry medium, temperature of

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milling and milling atmosphere are the inherent shortcoming of the technique [14]. Inclusion of residuals while processing the SiGe could drag down the thermo-electric properties [15]. On the other hand, fabrication of bulk SiGe alloy with close theoretical density with nanostructure features for end use applications still seems a challenging task. Recent decades, spark plasma sintering (SPS) [16] is considered as an advanced and prospective technique with high potential for processing of advanced materials that includes ceramics, semiconductors, composites and compounds. It carries the advantages such as higher heating rate, higher density, retention of nano-crystalline features etc., Several review papers [17,18] on thermo-electric materials highlighted the importance of rapid synthesis of semiconductors using SPS to minimize the grain growth in order to fabricate the nanostructured semiconductors of close theoretical density. During SPS, pulsed electric current passes through the graphite die and powder compact thus causes the joule heating for promoting rapid densification [19] than the conventional sintering techniques such as hot pressing, hot isostatic pressing (HIP), microwave energy [20,21]. In summary, it is well understood that, during the preparation of SiGe alloy requires utmost attention and sincere effort to produce a homogeneous SiGe alloy. Also, selection of suitable synthesis technique and processing conditions are inevitable in reproduction of thermo-electric materials of desired stoichiometry and physical properties [22]. Recently, Bathula et al. [23] reported on synthesis of $Si_{80}Ge_{20}$ alloy powder by adapting mechanical alloying for prolonged period of 90 h in the high energy ball mill and further densification by SPS. In this current research, the 10 h milled nanostructured Si-Ge powder mixture was alloyed and simultaneously densified in SPS at the temperature range 900–1200 °C. The alloying and densification kinetics were reported. The proposed method is an alternative to the previously reported SiGe synthesis methods and carrying the advantage of synthesizing the homogenous and nanostructured SiGe alloy of superior density and physical properties in rapid and effective manner.

2. Experimental procedure

2.1. Starting powders

Silicon powder (Particle size: −325 mesh, Purity: 99.50%) and germanium powder (Particle Size: −325 mesh, Purity: 99.999%) were chosen as starting materials. The powders were procured from M/s Whole Win (Beijing) Materials Science and Technology Company Limited, Beijing, China. Si_{80}-Ge_{20} powders were milled in a high energy planetary mill (Fritsch Pulverisette, Germany) for 10 h to obtain nano-structured Si-Ge powder mixture. The vials of ball mill and balls were made of tungsten carbide. The ball to powder ratio (BPR) was maintained to 15:1 and the milling speed was 300 rpm. The milling was conducted in wet (Toluene) medium. The milling cycle was 10 min milling and 20 min cooling. The powders handling were made inside the glove box in high purity (99.999%) argon atmosphere to avoid the oxidation and contamination of powders.

2.2. Spark plasma sintering of Si-Ge powder mixture

Spark plasma sintering (SPS) technique was used to consolidate the ball milled Si-Ge powder mixture. The pulse sequence was maintained with 12 pulses with 2 periods of no current which termed as 12:2. SPS process was conducted using Dr. Sinter, SPS Syntex Inc., Japan. Si-Ge powder mixture was consolidated at varying temperature (900–1200 °C). The schematic representation of SPS is shown in (Fig. 1).

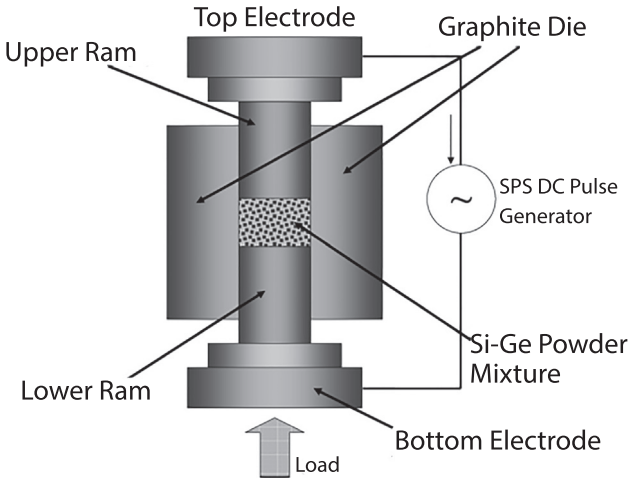

Fig. 1. Schematic representation of Spark Plasma Sintering.

The sintering temperature was continuously monitored using digital pyrometer. However, the measuring temperature is not the direct temperature of compacted SiGe powders. As reported [24] the temperature difference between the die and powder mixture was higher than 50 °C. As soon as heating programme was completed, the SiGe alloy was cooled to room temperature.

2.3. Characterization of Si-Ge powders and sintered Si(Ge) alloy

The morphology of as mixed and 10 h milled Si-Ge powders were studied using FEI SEM Quanta 200. Phase identification and crystallite size determination of Si-Ge powder mixture and SPS processed bulk SiGe alloy at different sintering temperatures were studied using XRD analysis. XRD patterns were recorded using ULTIMA-III, Rigaku Corporation, Japan with Cu Kα radiation and 2Θ range of 20–80° with the step size of 0.05°. Williamson and Hall relation was used for the deconvolution of crystallite size (D) and strain of milled Si-Ge powder mixture and sintered bulk SiGe alloy at different sintering temperatures and the same is expressed as follows in Eq. (1)

$$D = \frac{K\lambda}{\beta_{hkl}\mathrm{Cos}\theta} + 4\varepsilon\tan\theta \quad (1)$$

where D is the crystallite size, K is the shape factor (K = 0.9); λ is the wave length of X-rays (λ = 1.54056 Å for Cu Kα radiation), β_{hkl} is the value of full width half maximum from hkl planes (in radians), ε is the lattice strain and Θ is the diffraction angle.

The strain ε induced in Si-Ge powders during milling and bulk sintered SiGe alloy due to combined effect of thermo-mechanical effect in SPS was calculated using the formula expressed in Eq. (2)

$$\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \quad (2)$$

Transmission electron microscope (JEM 2100, JEOL) equipped with Energy dispersive studies (EDS) was used to understand the crystallinity and size of the milled Si-Ge powder mixture and the SiGe alloy formation after SPS. The EDS was used to quantify the Si and Ge elements in the sintered bulk SiGe alloy. Prior to the analysis, Si-Ge milled powder mixture were dispersed in ethanol and ultrasonicated for 360 s duration to avoid the clustering due to mechanical attraction. Then the powders was dispersed and dried in the copper grid. Bulk samples were diced and thinned to 100 μm thickness. Then it was prepared to 3 mm dia with through hole in the middle by ion milling.