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Spark plasma assisted *in-situ* phase evolution and densification of nano-crystalline magnesium silicide – silicon germanium thermo-electric composite: Pulse current effects and densification mechanisms

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ABSTRACT

The current work reports on the investigation of mechanisms involved during spark plasma assisted *in-situ* nano-crystalline magnesium silicide (Mg_2Si) phase evolution and the simultaneous densification with the substantial increase of nano-structured silicon-germanium alloy (SiGe) inclusion. The anisothermal sintering was carried out up to 650 °C with an applied pressure of 50 MPa in the vacuum atmosphere (~10 Pa). X-ray diffraction and electron microscopy studies conceded the formation of Mg_2Si matrix phase and presence of SiGe inclusion. The synthesized thermo-electric composite demonstrated the superior density (>95%). The synthesized TE composites shows the benchmark hardness values >0.97 GPa.

The scarcity of the fossil fuel supply and an associated environmental pollution are become the greater threatening to the human fraternity. It has created the strong alarming to eradicate the energy escalation and global warming. Therefore, the globe is on the quest to find an alternative, renewable and sustainable energy resources to face the future energy demands [1]. In the past couple of decades, the significant attention is being turned towards an eco-friendly energy harvesting from waste heat resources through solid state energy conversion using thermo-electric generators (TEGs) [2]. Several potential merits including simplicity in energy conversion, lesser investment cost, eco-friendliness, longer life time etc., have made thermo-electrics (TE) as the promising and potential technology to resolve the existing issues in tandem [3]. In order to make the TEGs highly reliable and utilizable for wider domestic applications, the several factual considerations such as material cost, toxicity, higher figure of merit, working temperature range etc., are the notably factors to be satisfied. In addition, TEGs are subjected to employ under fluctuating temperature cycles thus an excellent physical robustness is highly anticipated to avoid the physical failure such as cracks and degradation which resulting in catastrophic failures [4]. Surmounting these practical prospectus, TE technology can ever more become attractive and evidentially competitive in large scale applications including automobile, industrial, space, defense, fabrics sectors etc., Among several thermo-electric systems, semiconducting silicides are the natural candidate for TEG applications, especially eco-friendly, magnesium silicide (Mg_2Si) with FCC CaF_2 antiflurorite crystallographic structure with narrow bandgap (Eg 0.3–0.6 eV) [5]. In addition, it possess an excellent physical properties such as lower density (1.95 g/cm^3), higher melting temperature (1081 °C), higher compressive strength (1640 MPa) and Young's modulus (120 GPa). Remarkably the constituent elements (Mg and Si) are eco-friendly, highly abundant and inexpensive [6]. According to the classical thermo-electric theory, $m^{*3/2}\mu/\kappa_{ph}$ factor is the key criterion for selecting the potential thermo-electric materials for functional TEG applications, where m^* represents the density of states effective mass μ represents the carrier mobility and κ_{ph} is the thermal conductivty attributed by the phonons. This criterion factor value is 14 for Mg_2Si which is higher than Fe_2Si (0.8) and Mn_2Si (1.4) [7]. The conversion efficiency of thermo-electric materials is termed as an unitless figure of merit (ZT) represented by $ZT = (S^2\sigma/k)T$. Where S-Seebeck coefficient, σ- electrical conductivity and k- thermal conductivity contributed by lattice waves (phonons) and charge carriers at an absolute temperature T. The approach towards engineering the interdependency transport properties is the greater challenge that warrants both material design and processing attention. In this context, several tailoring strategies such as doping, nanostructuring, energy filtering, resonant energy and second phase nano inclusions are being exercised towards the enhancement of the power factor with substantial lowering of the thermal conductivity to obtain higher ZT [8].

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In the current research, the constituent phases of thermo-electric composite (nanostrutured Mg-Si and SiGe powders) with varying weight percentage was intimately mixed and densified by the spark plasma sintering (SPS). During SPS, the correlation of *in-situ* nano-crystalline Mg_2Si synthesis and simultaneous densification with the substantial inclusion of nano-structured SiGe alloy powder are discussed.

Magnesium (Mg) (particle size: −325 mesh, purity: 99.76%), silicon (Si) (particle size: −325 mesh, purity: 99.50%) and germanium (Ge) (particle size: −325 mesh, purity: 99.999%) were chosen as the starting materials to synthesis Mg_2Si-SiGe novel composite. Mg and Si powders were procured from M/s.Whole Win (Beijing) Materials Science and Technology Company Limited, Beijing, China. Germanium powder was supplied by Loba Chemie, Mumbai, India.

Mg and Si powders were taken in the suitable stoichiometry ratio and milled in the high energy ball mill (Fritsch Pulverisette, Germany). The mechanical milling parameters and conditions were reported elsewhere [9]. Si and Ge were taken in the stoichiometry ratio of 80:20 at.% with phosphorus (P) doping of 2.0 at.%. The dry milling was carried out for 10 h in tungsten carbide vials and balls (10 mm) in the high purity argon (99.999%) atmosphere. The ball to powder ratio was maintained to 15:1. The stearic acid of 1 wt% was taken as process control agent.

The milled Mg-Si powder was mixed with nano-structured SiGe alloy powder with varying weight percentage (5–20%). The intimately mixed Mg-Si and SiGe-$P_{2.0}$ powder was sintered using spark plasma sintering (Dr. Sinter Lab, Japan) at 650 °C with the heating rate of 50 °C per min in the vacuum atmosphere (~10 Pa). The instantaneous densification rate of the powder mixture ρ_n was estimated using the following relation [10].

$$\rho_n = \frac{d\rho_n}{dt_n} = \frac{\rho_{n+1}-\rho_{n-1}}{t_{n+1}-t_{n-1}};\quad \rho = \frac{L_0}{L}\rho_0 \tag{1}$$

where, ρ (%) is an instantaneous relative density per time t_n(s). The relative density ρ (%) was estimated from the variation in the initial height L_0 (mm) to the instantaneous height L (mm) and an initial density ρ_0. The high-resolution transmission electron microscope (JEM-2100, JEOL Electron Microscope, Japan) and X ray diffractometer (ULTIMA-III, Riagaku, Japan) with CuKα radiation ($\lambda = 1.54056$ Å) were used to understand the phase and structural evolutions after milling and SPS. Williamson and Hall relation was used to estimate crystallite size and strain of milled powder and sintered composite [11]. Differential thermal analysis (DTA) of mechanically milled Mg-Si and SiGe alloy powders were conducted up to 650 °C using simultaneous thermal analyser (STA 449 F3 Jupitor, Netzch Instruments, USA) with the heating rate of 10 °C/min in nitrogen atmosphere. The elemental quantification of the sintered bulk Mg_2Si-SiGe alloy composite was determined using energy dispersive spectroscopy (EDS) (Ultradry, Thermofisher, USA) and the relative density was determined by Archimedes principle using density measurement kit (AY220, Shimadzu, Japan). Micro-hardness indentation test was conducted on the sintered composite using Vickers hardness tester (Vickers 402MD, Wilson hardness, China) for the applied load of 0.300 Kg with the dwelling period of 10 s.

XRD patterns of Mg-Si and SiGe powder after milling and sintering conditions are shown in Fig. 1a. XRD pattern of mechanically milled Mg-Si powder reveals the distinct peaks corresponding to its parental elements (i.e. Mg and Si) with the crystallite size of 28.4 ± 0.05 nm and 48 ± 0.1 nm respectively. On the other hand, Si-Ge powder milled for 10 h results in the alloying of SiGe with the crystallite size of 35 ± 0.5 nm. The occurrence of peak broadening after milling refers to the reduction in crystallite size and the induced lattice strain in the SiGe alloy powder. Fig. 1b portrays the TEM images of ball milled powders (Mg-Si and SiGe alloy). It is understood that the milled Mg-Si powder are very fine and intimately mixed. The Si-Ge powders become alloy with nano-crystallite structure after milling. The corresponding SAED images show the poly-crystalline rings with finer white spots thus confirms the nanocrystalline features. The XRD pattern corresponding to the bulk nanocrystalline (Mg_2Si-SiGe) TE composites confirms the *in-situ* evolution of Mg_2Si compound phase with an antifluorite structure with the lattice parameter value of 6.33 Å. The experimental estimation from the XRD and TEM observations conceded to the reference JCPDS source [9]. Therefore, the discussion strongly attests that the Mg_2Si phase is reactively synthesized by spark plasma and simultaneously densified along with nano-structure SiGe alloy. The XRD peaks (Fig. 1a) corresponding to the bulk samples of $(Mg_2Si)_{95}$-$(SiGe)_{05}$ and $(Mg\text{-}Si)_{80}$-$(SiGe)_{20}$ primarily indicates the phases such as Mg_2Si and SiGe. Thus it confirms the presence of distinct phases Mg_2Si and SiGe in the sintered thermo-electric composite.

Figure 1c shows the DTA curves pertaining to the milled Mg-Si and SiGe alloy powders. It is well clear that Mg-Si powder mixture undergoes significant exothermic reaction in the temperature range RT to 650 °C. This can be understood from the variation in the onset and offset temperatures in DTA curves. The first exothermic peak in Mg-Si powder mixture is observed at 241 °C corresponding to the transition temperature of Mg. Further increasing of temperature, it can be seen the second exothermic peak with the onset and offset temperatures at 386 and 472°, respectively. The temperature required for the reaction to cause the combustion of Mg-Si powder mixture is 477 °C [12]. The estimated standard formation enthalpy to form Mg_2Si from Mg and Si is −77.8 KJ/mol (−25.9 kJ/g-atom) [13].

From the DTA curve, it is understood that the combustion temperature is lowered to 396 °C. It is due to the reduction in the crystallite size to nanoscale and the corresponding evolution of newer surfaces with the strong mechanical inter-mixing attributed by high energy milling. Furthermore, the surface of powder particles are cleaned by pulse current during SPS which facilitates the lower activation energy to initiate the combustion reaction in the combustible Mg-Si powder mixture. At the same time, no significant observation is noted for alloyed nano-structured SiGe alloy powder till 650 °C.

Notably, the SPS temperature and the pressure play a vital role as it is a driving force during *in-situ* phase evolution and simultaneous densification of the Mg_2Si-SiGe thermo-electric composite. As suggested by Bernard-Granger and Guizard, pressure assisted sintering is similarly termed as creep of materials [14]. This is due to the consideration of fact that the Mg-Si and SiGe powder mixture is subjected to the behavior like sinter forging and the densification occurs by power-law creep. The deformation rate (ε) of the powder particles under a stress (σ) which is expressed by the Norton law [15]

$$\varepsilon = \frac{d\varepsilon}{dt} = A_0 \exp\left(\frac{Q}{RT}\right)\sigma^n \tag{2}$$

where, A_0-material constant, Q-activation energy and n-stress exponent. The relative density and an instantaneous densification rate profiles as the function of SPS temperature showcase the variation in the Mg-Si densification kinetics with varying weight percentage of nano-structured SiGe alloy powder inclusion (Fig. 2). The densification profiles demonstrate the increasing trend during anisothermal sintering. In the current study, the combustion of Mg-Si powder mixture and densification are manifested by three sequential steps. During step 1, the imposed pressure is attributed towards the compaction of the powder mixture. This helps in the inter-particle re-arrangement and substantial reduction from the initial pores volume. Therefore, the ramping in the densification profile is observed. From RT till 150 °C, the notable thermodynamical kinetics are not witnessed and thus the surface energy is observed in control. The particle packing due to interparticle arrangement enhances the integration of the powder contacts. Therefore, it confirms the uniform and increase in the pulse current flow path network. The uniaxial pressure is uniformly distributed to the powder particles in the die mold. The localized pressure bear by each spherical particle can be explained by the theory of elastic contact $P_{max} = (3F_N/2\pi a^2)$, where F_N is an effective force on single particle. This is the ratio