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A SOLID STATE APPROACH TO THE PRODUCTION OF KILOGRAM QUANTITIES OF $Si_{80}Ge_{20}$ THERMOELECTRIC ALLOYS

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Abstract

An important consideration in the development of improved materials for thermal-to-electrical power generation is whether a research-scale process or methodology is amenable to production of kilogram quantities. Research efforts on the solid state technique of mechanical alloying have shown that both n- and p-type Si-20 at. % Ge alloys can be produced which have improved thermoelectric properties compared to state-of-the-art MOD-RTG materials. Studies on the production of large quantities of mechanically alloyed powder alloys using a planetary mill indicate that properties similar to those observed in alloys prepared in smaller quantities by a vibratory mill can be obtained. The characterization of several p-type alloys doped with 0.8 at. % B in the form SiB_4 by X-ray diffraction, scanning laser mass spectroscopy, Hall effect, and high temperature electrical resistivity and Seebeck coefficient measurements are described. The transport properties of these alloys are shown to be comparable to those measured on similar samples prepared in small quantities by a research-grade vibratory mill.

INTRODUCTION

Mechanical alloying (MA) is a high energy ball milling technique originally developed in the early 1970s for the production of dispersion-strengthened superalloys. Since then, numerous other applications of this technology have been explored and developed including the preparation of unique metastable alloys (Han et al. 1992 and Fecht et al. 1990), extension of normal equilibrium solid solubility limits (Eckert et al. 1990 and Sui et al. 1992), synthesis of homogeneous alloys from liquid-immiscible systems (Sundaresan and Froes 1987), and amorphization of intermetallic compounds (Kobayashi et al. 1990 and Gaffet 1991). Preparation of alloys by MA at relatively low temperature precludes some of the difficulties in obtaining homogeneity such as dendritic segregation which can accompany conventional cast metallurgy and loss of dopant by vaporization. In addition, this technique creates new possibilities for additions that are not amenable to a melting process. The preparation of doped silicon-germanium alloys by mechanical alloying has been demonstrated and shown to yield properties comparable to or better than those of state-of-the-art MOD-RTG alloys (Cook et al. 1991). Production of research quantities (5 to 10 grams) utilized a Spex 8000 vibratory mill (Spex Industries, Edison, NJ) in which the components were prepared in 195 cm^3 vials. The vial is agitated in three mutually perpendicular directions at a frequency of 1200 Hz. This approach typically produced a homogeneous powder alloy in 4 to 5 hours of operation. While ideal for research applications, the capacity of this system is far too small to be of practical use in the hot pressing of thermoelectric materials for unicouple or multicouple devices in which 0.4 to 0.5 kg of powder are required. The vibratory mill is but one type of design; other large-scale configurations, such as attritors and planetary mills, have been used to produce multi-kilogram quantities of oxide dispersion-strengthened material but little information is known about the applicability of these systems to prepare homogeneous, doped thermoelectric alloys. The kinematics of these large-scale devices differs significantly from that of the vibratory mill in that rotation of the vial, rather than agitation or vibration, is the dominant activity. In an effort to address this question, a scale-up project was initiated to prepare and analyze alloys of Si-20 at. % Ge doped with 0.8 % B (target composition) using a planetary ball mill. The properties of alloys having this composition as prepared by a Spex 8000 are reasonably well understood and thus meaningful comparisons between techniques are possible. A ten-fold increase in the mass of powder produced, from 5 grams to 50 grams (as compared to the Spex 8000), was arbitrarily chosen. The maximum capacity of the vessels used in this study is 500 grams. Various amounts of milling time and grinding media configurations were evaluated. The powder was analyzed for phases, lattice parameter, and homogeneity by X-ray diffraction. Scanning laser mass spectroscopy (SLMS) was used to identify possible contamination of the powder by wear debris from the collisions. Room temperature Hall effect and high temperature electrical resistivity and Seebeck coefficient measurements were performed on hot pressed samples as a further means of verifying homogeneity. The results show that formation of alloys having nearly identical properties can be accomplished. This paper summarizes the progress in developing one approach to the production of large-scale, good quality silicon-germanium alloys by mechanical alloying.

METHODS

A Fritsch planetary ball mill (Pulverisette 5) was chosen to study the large scale production of Si-Ge alloys by MA. This type of planetary mill operates with a ratio of vessel angular velocity (ω) to platform angular velocity (Ω) of 2:1. There are three primary forces acting on the grinding media during processing: a centripetal force due to the rotation of the platform ($\Omega^2 \bullet R$ where R = radius of the platform), a centripetal force due to the rotation of the vessel ($\omega^2 \bullet r$ where r = radius of the vessel), and a coriolis force due to the combined rotational effects ($2(\omega x r) x \Omega$). Depending on the value of the ratio ω/Ω, the grinding media are either pinned to the inner wall of the vessel or the movement of the vessel causes an apparent curved trajectory causing an impact between the media and the vessel walls. Two types of vials were used, tungsten carbide and steel. In both types of vials a 50 gram charge was prepared consisting of powdered silicon (Hemlock, Hemlock, MI), germanium (Cabot, Boyertown, PA), and a sufficient quantity of SiB_4 (Electronic Space Products International, Agoura Hills, CA) to yield a target composition of 0.8 at. % B. In the WC vials, WC balls were added as grinding media with a ball to powder mass ratio of 5:1. Two different grinding configurations in the steel vials were studied, both having a charge ratio of 4:1. The number and size of steel balls in both configurations differed significantly from that used in the WC vials. The vials were all sealed under helium and milled at a speed setting of 3.5 (maximum speed = 10) for 66 hours followed by an additional 30 hours at 5.5. Visual inspection of the contents revealed the formation of a hard "impression" of material in the bottom of the vials which was easily broken up and removed from the containers. Samples were taken from various locations within each vial for X-ray diffraction analysis. The analysis was performed using a Scintag powder diffractometer and Cu Kα radiation. The samples were spun to reduce the chance of a preferred orientation.

Five grams samples from the original 50 gram charge were removed for consolidation by hot pressing. The powder was loaded into a graphite-lined die which was in turn loaded into an RF induction-heated hot press. The alloys were hot pressed in a 1.33×10^{-4} Pa (10^{-6} torr) vacuum at a temperature of 1473 K with applied pressures of 140 to 160 Mpa (22 to 22.7 ksi) for 20 minutes. The samples were allowed to furnace cool over a period of several hours and were removed by cutting the liner away from the compact. Samples for property measurements, X-ray diffraction, and scanning laser mass spectroscopy were obtained by sectioning the compact with a low speed diamond saw.

RESULTS AND DISCUSSION

Samples of the 50 gram charge prepared in the tungsten-carbide planetary mill vial (PM2) were analyzed by x-ray diffraction after 96 hours of processing. A typical diffraction pattern, shown in Fig. 1, indicates that alloying has occurred since only single, broad peaks are observed.

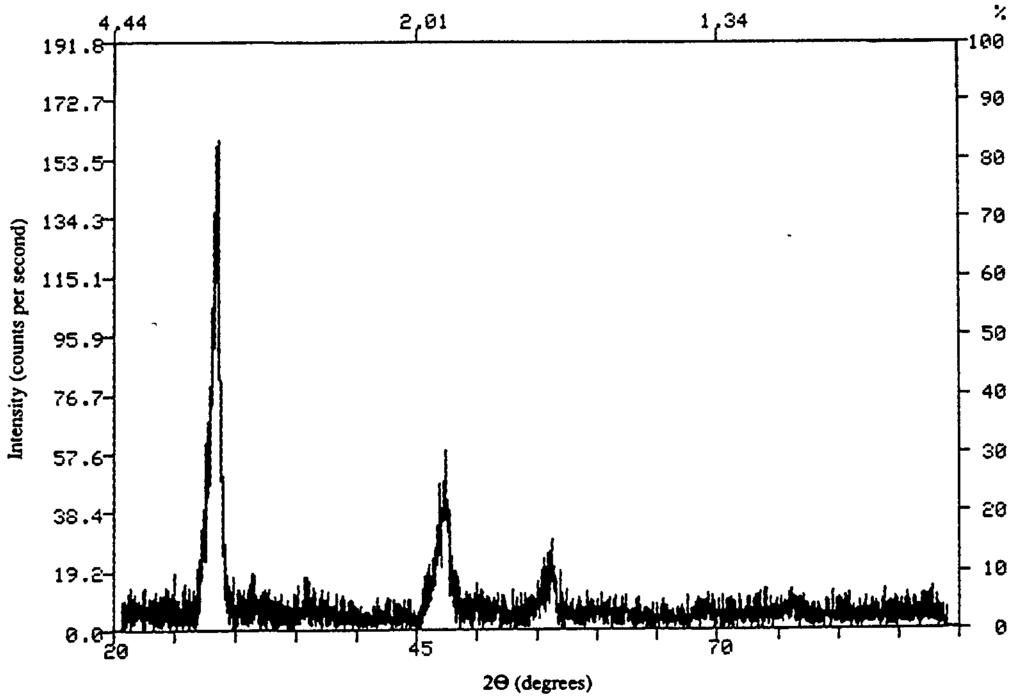

FIGURE 1. X-Ray Diffraction Pattern of a 50-g Charge of Si-20 at. % Ge Doped with 0.8 at. % B and MA for 96 Hours in a Planetary Ball Mill.

The pattern suggests that not only has alloy formation taken place, but that a considerable degree of amorphization has also occurred. The effective grain size of the powder was obtained by use of the Scherrer formula,

$$\Phi = (0.91\lambda)/B\cos\Theta \qquad (1)$$

where λ is the wavelength of radiation and B is the line width at half maximum intensity (in radians). The calculation of this parameter translates to an effective grain size of 8.9 nm. Similar results were obtained previously on smaller quantities of undoped silicon-germanium alloys in a planetary mill (Gaffet et al. 1991). Precision lattice parameter determination of the hot pressed alloy using a Nelson-Riley extrapolation routine gives a value of $a_o = 0.54661$ nm which yields a composition of Si-17.2 at. % Ge. Due to the nearly amorphous nature of the as-milled powders, it was not possible to obtain sufficient accuracy in the determination of the d-spacing parameter to estimate composition. Slightly different results were observed in the steel vials. No evidence of alloying was observed after 50 hours of processing. After 91 hours of milling, the material was stratified into three distinct regions: loose powder, which showed evidence of nearly complete amorphization, plus two layers of hard, compacted material. An x-ray pattern of the top layer of compacted material showed that the powder had been completely alloyed but that it was not amorphous. The bottom layer as well as a mixture of all the material, ground to a powder and X-rayed, showed distinct silicon and germanium lines suggesting that the bottom layer was composed of un-alloyed material. The temperature rise inside the vial during milling may be an important factor. It has been observed during these studies that the hotter the vial the more completely alloyed and homogeneous the powder. The temperature rise of the outer surface of the WC vial appears to be greater than that of the steel vial and the corresponding powder is homogeneous and completely alloyed after 96 hours. A thermocouple was attached to the outside wall of each vial immediately after 50 hours of continuous operation. The largest temperature rise above ambient was observed in the tungsten carbide vial which reached a maximum temperature of 45°C to 50°C. The temperature rise of the outer surface of the steel vials was slightly less, 35°C. Use of a simple thermodynamic model predicts that the temperature rise of trapped powder due to colliding media varies as the square of the ball velocity, which in turn is inversely proportional to the total number of balls in the vessel. Since the total number of balls in the steel vials exceeded that in the WC vials, it is likely that their average velocity was lower, producing a smaller instantaneous temperature rise during impact. This would account for the observed increase in alloying time in the steel vessels. It was not possible to configure both types of vials with identical numbers and masses of grinding media with the same charge ratio because of the difference density between steel and tungsten-carbide.

Due to the intrinsically brittle nature of silicon and germanium only minimal wear on the vessel walls compared to the milling of metallic components was expected. Samples of the as-pressed compacts were submitted for chemical analysis by scanning laser mass spectroscopy to confirm this assumption. The most significant metallic contaminant found was tungsten at a measured value of 1200 ppma or 0.12 at. %. This level of metallic impurity is not expected to cause measurable changes in the thermoelectric properties of these alloys. It has been pointed out that oxygen contamination can have significant effects on the transport properties of Si-Ge alloys (Cook et al. 1992). There is some question as to the best technique for the determination of non-metallic impurities (particularly oxygen) in Si-Ge and ongoing research is directed at resolving this issue.

The room temperature Hall effect was measured on a disk sectioned from one of the hot pressed compacts and gave a carrier concentration, n, of 2.4×10^{20} per cubic cm, a resistivity, ρ, of 0.86 mΩ-cm, and a carrier mobility, μ, of 30.5 cm^2/V-s. A second 50-g load prepared in another WC vial and hot pressed under similar conditions gave hot pressed values of $\rho = 0.80$ mΩ-cm, $n = 2.6 \times 10^{20}$ cm^{-3}, and $\mu = 31.3$ cm^2/V-s showing reasonably good duplication. These are typical values for p-type Si-Ge alloys with high figures of merit. Values for comparably doped alloys having similar carrier concentrations and similar amounts of second phase oxygen prepared in a Spex 8000 are $\rho = 0.80$ mΩ-cm, $n = 2.5 \times 10^{20}$ cm^{-3}, and $\mu = 31.0$ cm^2/V-s, nearly identical to that measured on samples prepared in large scale quantities.

Figure 2 shows the electrical power factor (S^2/ρ) as a function of temperature between room temperature and 1000°C of the hot pressed compacts prepared in a WC vial.

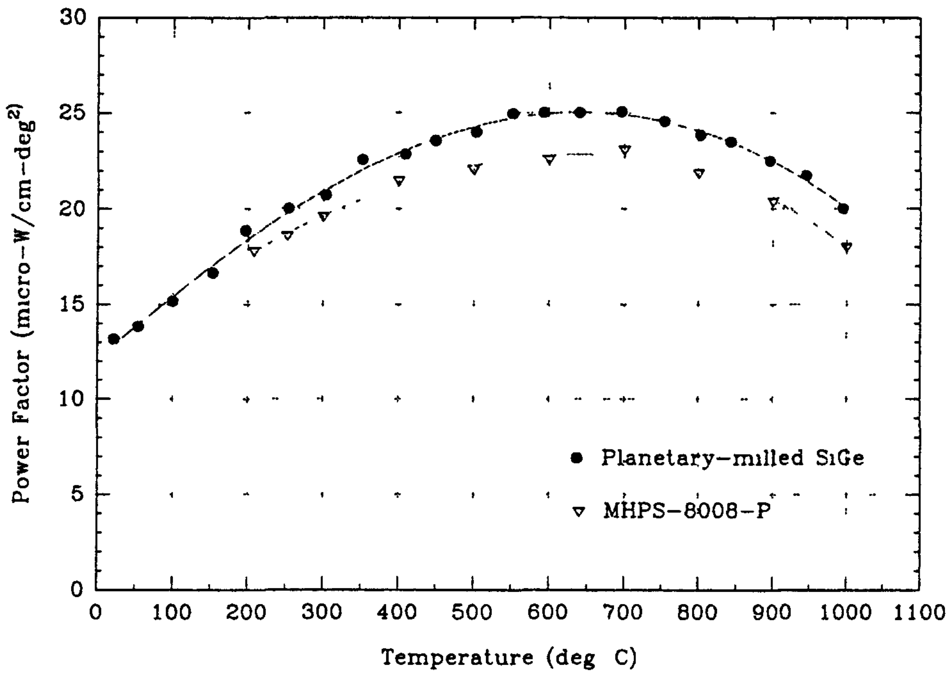

FIGURE 2. Electrical Power Factor (S^2/ρ) versus Temperature for Mechanically Alloyed p-type Si-20 at. % Ge Shown With Typical MOD-RTG Data.

The maximum power factor of 25.1 μW/cm-°C^2 occurs at a temperature of 700°C and decreases to 20 μW/cm-°C^2 at 1000°C. The 300 to 1000°C integrated average power factor is 23.3 μW/cm-°C^2 which is nearly equal to that measured on similar alloys prepared in a Spex 8000 mill. Data obtained previously on a MOD-RTG sample, MHPS-8008, is also shown on the graph for comparison which yields an average power factor over the same interval of 21.2 μW/cm-°C^2. The MHPS-8008 data corresponds to an average value of the results of measurements performed by four laboratories on this alloy during a 1988 round robin study. It is expected that the thermal conductivity, and hence the figure-of-merit of the planetary-milled alloys will also be comparable to that previously measured on smaller-scale research materials since no significant differences are observed in carrier concentration or microstructure. Studies are currently underway at the General Electric AstroSpace Division (King of Prussia, PA) to develop a process for the consolidation of large quantities of Si-Ge powder (both n and p-type) prepared by MA. In an initial test using 425 grams of p-type Si-Ge powder produced in a vibratory mill at the Ames Laboratory, a 10 to 15 percent improvement in the 300 to 1000°C integrated average figure of merit (Z) was observed in material hot pressed at GE, mainly due to a lower thermal conductivity. Similar improvements in Z were found in control samples taken from the 425 gram lot and hot pressed at Ames, however, a higher electrical power factor, not lower thermal conductivity, was responsible for the improvements observed in the small scale hot pressed samples. It is believed that either a slow cooling rate between 1240°C and 900°C in the GE-pressed compact caused precipitation of nanophase B_3Si particles within the grains or that the powder picked up a significant amount of oxygen during handling, either which would manifest itself in a lower thermal conductivity. Low mobilities measured on slices of the GE-pressed compact (28 to 30 cm^2/V-s compared to 32 to 34 cm^2/V-s on the Ames-pressed material) suggest that oxygen pick-up may have occurred. Neutron activation analysis of a slice of the material indicated that 2.1 at. % O was present in the bulk which is four times the expected value. The detrimental effects of oxygen on the thermoelectric properties of n-type Si-Ge alloys has been reported (Cook et al. 1992). A test hot pressing of 425 grams of material similar to that reported in this paper, prepared by the planetary mill, employed a faster cooling rate and resulted in a compact with a large number of cracks due to thermal stress. Additional work continues to obtain an optimum process which will preserve high carrier mobilities by minimizing oxygen pick-up and to incorporate mechanisms intended to lower the lattice thermal conductivity.

CONCLUSION

It has been shown that the large-scale production of mechanically alloyed p-type Si-20 at. % Ge thermoelectric alloys is possible through the use of a planetary mill. Electrical properties nearly identical to those reported on samples prepared in a Spex 8000 vibratory mill are obtained. Results of chemical analysis indicate that negligible amounts of metallic impurities are introduced by this technique. Efforts to extend the improvements in Z previously observed on small scale research samples to large 425 gram compacts have produced a 10 to 15 percent improvement in Z.

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