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Effects of vial shape on the rate of mechanical alloying in $Si_{80}Ge_{20}$

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The rate of mechanical alloying for doped $Si_{80}Ge_{20}$ alloys was studied using flat and concave ended hardened tool steel vials. Alloying was found to occur at significantly higher rates using a flat ended vial. It was also found by X-ray diffraction that the homogeneity of the alloy remained constant between 9 and 30 h for the flat ended vial and between 15 and 30 h for the round ended vial.

1. Introduction

Mechanical alloying (MA) is a high energy ball milling technique used to obtain a homogeneous alloy from elemental or pre-alloyed starting materials through solid state reactions. MA has been applied to brittle/brittle systems including Si–Ge [1, 2]. Si–Ge alloys doped with GaP and P are currently under study for use in thermoelectric generators for space applications. Cook *et al.* [3] have shown that MA can be used to produce heavily doped Si–Ge thermoelectric alloys in a vibratory shaker mill. Koch [2] indicates that MA in brittle/brittle systems is a thermally activated process, involving diffusion and cold welding between particles induced by temperature increases caused by grinding media collisions. Koch [2] reports that the rise in temperature is directly dependent on the kinetic energy obtained by the balls during milling.

Solazzi [4] has examined the milling characteristics of flat and concave ended vials for a vibratory shaker mill. Sand (SiO_2) was milled in both round and flat ended polystyrene vials with two methyl methacrylate balls. It was found that the concave ended vials produced finer particles as measured by a weight percentage of the milled material passing through a 43 μm screen for a given milling period.

Davis *et al* [5] studied MA in brittle/brittle systems including Si–Ge using a Spex 8000 mill and a flat ended vial. They found that alloy formation was due to thermal activation as indicated by suppressed alloying when milling was performed in a vial cooled by liquid nitrogen. Computer models of multiple ball systems indicated that head on or near head on ball impacts that could contribute substantially to the total powder particle heating were rare. It was suggested that alloying may be caused by temperature induced microdiffusion or temperature enhanced deformation.

Maurice and Courtney [6] have modelled MA on the basis of Hertzian impact theory which is perturbed by powder trapped between the milling tools. MA is viewed as an upset forging process between two parallel plates, but where only a small fraction of the kinetic energy is used to deform the particles. There are also additional components to the applied force when there are non-normal collisions in MA, unlike upset forging. In the present study, the interest in preparing a homogeneous alloy of heavily doped $Si_{80}Ge_{20}$ by MA has necessitated a thorough study of various parameters which affect the final hot-pressed material. This paper summarizes results obtained when two different shapes of vial were used.

2. Experimental procedure

Mechanical alloying was performed with a Spex 8000 mixer/mill. A hardened tool steel vial with flat ends and a hardened tool steel vial with round, dome shaped ends were obtained from Spex along with a set of three 8.35 g and three 1.04 g hardened steel balls for each vial. Two identical *n*-type alloys were prepared each having a nominal composition of $Si_{0.747}Ge_{0.187}Ga_{0.016}P_{0.05}$. Both samples used chunks of Si (99.9999% pure), Ge (99.999% pure), and GaP (99.9999% pure), all obtained from Aesar, along with P (99.99% pure) from Cerac. The Ge and P were used in the as-received form of approximately 0.3 cm chunks while the large chunks of Si and GaP were broken down to about the same size with the 20 mesh pieces removed. One alloy, designated 43–2, was milled in a flat ended steel vial and another, designated 51G, was milled in a round ended steel vial. The vials were loaded and unloaded in a He filled glove box with a small amount removed every three hours for X-ray diffraction. The X-ray diffraction was performed using a Scintag PAD-V powder diffractometer with CuK_α radiation, a step scan of 0.01° in 2 theta, and a preset time of 1 s at each step. Software routines were used to perform background noise correction and K_{α_2} stripping. The X-ray patterns were then smoothed.

3. Results and discussion

Expanded views of the (1 1 1) line of each sample were examined. This line shows the most detail concerning the progress of alloying for these diamond cubic samples of the F_{d3m} space group. Fig. 1 shows the X-ray

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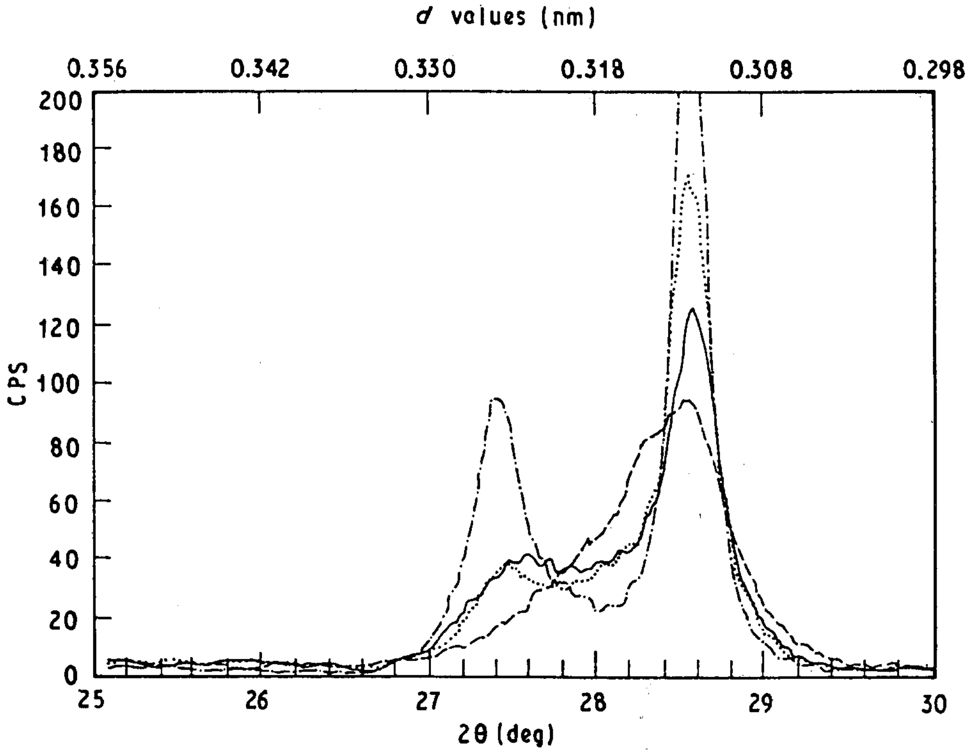

Figure 1 Diffraction line (1 1 1) of samples milled for: (–·–) 3 and (. . .) 6 h in the round ended vial (51G); (—) 3 h and (– – –) 6 h in the flat ended vial (43–2).

pattern for 43–2 and 51G following 3 and 6 h of milling. The 3 h pattern for sample 43–2, the sample prepared in the flat ended steel vial, indicates considerably more alloying than 51G after the same amount of time as can be seen from both the line shape and intensity. The line for sample 51G exhibits two intense peaks whereas the line 43–2 shows a peak attributable to Si and a hump on the Ge side of the peak. This hump can be attributed to Ge that has alloyed to some degree with Si, although not in the desired 80:20 ratio but rather in a range of compositions. It is apparent that samples milled in the round ended steel vial alloy at a much slower rate than samples milled in the flat ended vial. The line from 51G after 6 h is still more intense than both the 3 and 6 h lines from 43–2. The line exhibits a hump similar to that observed in the 3 h line of 43–2. There is still a slight peak on the Ge side which indicates that this material is not alloyed to the extent that 43–2 is after 3 h. The line for 43–2 is a single, asymmetric reflection after 6 h of milling, which indicates a more uniform alloy than after 3 h, but still not yet fully homogeneous. Fig. 2 shows the (1 1 1) line for 51G after 9, 12, and 15 h of milling along with the (1 1 1) line for 43–2 following 9 h of milling. Sample 51G exhibits a single peak after 9 h which is asymmetric like 43–2 was after 6 h milling, but it still has a higher intensity than 43–2. The line for 43–2 is more symmetric after 9 h when compared with the 3 and 6 h patterns in Fig. 1, which demonstrates that the alloy is more homogeneous. The intensity of the peak has changed very little between 6 and 9 h. The 51G pattern changes somewhat between 9 and 15 h of milling, demonstrating that further alloying is occurring. With continued milling, the line shape and intensity for 43–2 did not change between 9 and 30 h. The line shape and intensity for 51G did not change between 15 and 30 h. At each milling interval, the line for 51G is more intense than the corresponding line for 43–2. Even after 30 h milling, the line for 51G is more intense than the 9 h line for 43–2.

The round ended vial does not alloy material as fast as the flat ended vial for the Si–Ge system. Davis *et al.* [5] demonstrated that only normal or near normal collisions dissipate sufficient kinetic energy to raise the temperature of trapped powder significantly. In the milling systems they studied, it was found that impacts of ± 10° from the normal were comparatively rare. In a round ended vial one would assume a smaller percentage of ball–wall collisions would be normal or nearly normal, compared to a flat ended vial. The fractional change in kinetic energy available to the trapped powder would be reduced by a function of the angle between the ball's velocity vector at the instant of impact and a tangent to the surface of the wall at that point. If MA is assumed to be operated by a diffusion controlled Arrhenius process between the components, with the primary contribution to localized temperature increases originating from impacts of near 90°, one would infer from these data that there are more near normal collisions in a flat vial than in a round ended vial. One could estimate the difference in localized temperature increases between the two types of geometries by considering the alloying rates observed in this study. The standard form of the diffusion coefficient, D, is given by

$$D = D_{\infty}\exp[-\Delta E_a/kT]$$

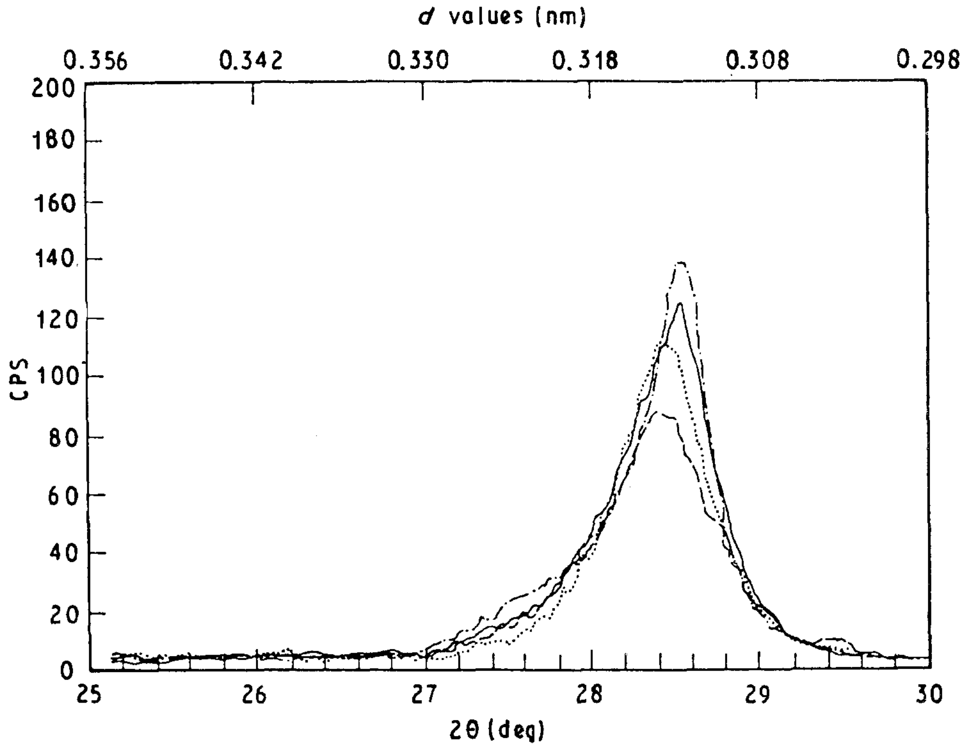

Figure 2 Diffraction line (1 1 1) of samples milled for: (–·–) 9, (—) 12, and (. . .) 15 h in the round ended vial (51G) and a sample milled for (– – –) 9 h in the flat ended vial (43–2).

where D_∞ is the apparent value of D at infinite temperature, ΔE_a the activation energy, T the absolute temperature, and k is Boltzmann's constant. If one defines D_F as the apparent diffusion coefficient of Ge in Si as observed in a flat ended vial and D_R similarly for a round ended vial, the results of our study suggest that

$$D_F \approx 2D_R$$

since the observed alloying rate in a flat ended vial was roughly twice that observed in a round ended vial and since alloying rates would be directly proportional to the rate of diffusion. Using this approximation one can write

$$\left[\frac{1}{T_F} - \frac{1}{T_R}\right] = \frac{-\mathrm{k}\ln 2}{\Delta E}$$

where T_F and T_R are the corresponding average localized temperature rises due to ball–wall collisions in each type of vial. Other researchers [5] have estimated the magnitude of T_F as anywhere from 100–350 K above ambient for powder particles during MA. This would place T_R anywhere from 98–344 K above ambient, in other words, only slightly less than T_F. This would indicate that if temperature induced microdiffusion is the sole driving force for MA, then small changes in temperature during milling will have a significant impact on alloying rates. The presence of additional species such as the GaP and elemental P no doubt affect the absolute diffusion rate but the ratio of D_F/D_R is expected to remain constant since both alloys were doped to the same degree. The present study indicates that ball–wall collisions are the dominant collision mechanism for alloying. Further studies should be conducted to model the kinematics of the ball–wall interactions in these vials so that the large differences in alloying rates can be more fully understood. In addition, a similar study should be initiated in which the alloying rates of a ductile–ductile and ductile–brittle binary system are examined using both types of vials. Such a study would contribute significantly to the understanding of mechanical alloying in general.

4. Summary

Heavily doped $Si_{80}Ge_{20}$ samples were mechanically alloyed using chunk starting materials in a flat and in a round ended steel vial. The resulting (1 1 1) reflection of the powders were analysed after every three hours of milling by X-ray diffraction. It was found that components milled in a flat ended hardened steel vial alloyed at a considerably faster rate than in the round ended vial. This was shown by a comparison of the (1 1 1) line shape and intensity at each milling interval, as well as, the increased time required to reach a constant intensity and shape of the peak; from 9 h in the flat ended vial to 15 h in the round ended vial. In both cases, additional milling up to 30 h did not change the intensity or line shape of the peak. A comparison of diffusion coefficients for each case suggests that localized temperature increases in a round ended vial are only slightly less than that generated in a flat ended vial.

Acknowledgements

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References

1. R. M. DAVIS and C. C. KOCH, *Scrip. Metall.* **21** (1987) 305.
2. C. C. KOCH, *Ann. Rev. Mater. Sci.* **19** (1989) 121.
3. B. A. COOK, B. J. BEAUDRY, J. L. HARRINGA, W. J. BARNETT, in Proceedings of the 24th IECEC (IEEE, Washington, D.C., August 1989) p. 693.
4. M. J. SOLAZZI, *Amer. Lab. October* (1983) 63.
5. R. M. DAVIS, B. McDERMOTT, C. C. KOCH, *Metall. Trans. A*, **19A** (1988) 2867.
6. D. R. MAURICE and T. H. COURTNEY, *ibid.* **21A** (1990) 289.

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