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MECHANICAL ALLOYING OF BRITTLE COMPONENTS: SILICON AND GERMANIUM

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Introduction

Mechanical alloying (MA) is a process whereby a blend of elemental or alloy powders is subjected to highly energetic compressive impact forces resulting in the formation of a composite powder (1). The resultant powder develops through the repeated cold-welding and fracture of the powder particles with a final composition corresponding to the percentages of the respective constituents in the original charge (2-3). This high energy ball milling technique is unique in that alloy formation is a solid state process where some of the restrictions of equilibrium phase formation may be overcome (2).

Heretofore, mechanical alloying has been mainly utilized in the production of dispersion strengthened alloys (2-6). While encouraging success has been met in this application of MA, true atomic level alloying as a result of this process is still a topic of much debate. However, recent experiments seem to indicate that the mechanical alloying technique can, in fact, be employed to create homogeneous alloys.

Benjamin (2) makes reference to the use of MA in the production of a true solid solution of Ni-Cr. Nickel, being ferromagnetic, and chromium, were blended and mechanically alloyed for 10-15 hours. The resultant powder demonstrated a magnetic response identical to that of a similar alloy formed by melting and working. More recently, McDermott and Koch (7) employed mechanical alloying to create ordered bcc beta brass from fcc copper and hcp zinc powders.

Until now, mechanical alloying has been applied to relatively ductile systems in which the mechanism of repeated cold welding and fracture has been well defined metallographically. While brittle components have been introduced into the MA synthesis of nickel-based superalloys (2-4), it is not apparent that mechanical alloying is feasible when all powder components are brittle. Extensive plastic deformation during the formation of the initial composites of the powder components has been experimentally observed (1,2) and may be essential to alloy formation by this method. To evaluate this possibility, several systems were subjected to MA in which both components were brittle at ambient temperature.

The following summarizes the initial results of a study aimed at using mechanical alloying to produce composite powders from elemental silicon and germanium. These brittle elements have been made to form a diamond-cubic substitutional solid solution by MA. Energy dispersive x-ray analysis, scanning electron microscopy, and x-ray diffraction were utilized to characterize the effects of the MA process with respect to this brittle alloy system.

Experimental Procedure

Two initial compositions were considered in the Si-Ge system; Ge-72 at.% Si and Si-50 at.% Ge. The silicon and germanium starting powders were obtained from Alfa products with a stated purity of 99.9% and 99.999%, respectively. The initial charge was loaded into a cylindrical, shock resistant (S5) tool steel vial (76 x 57 mm diameter) along with 440C stainless steel balls (7.9 mm diameter) as the milling media. The vials employed an o-ring seal to contain the internal atmosphere and the ball-to-powder weight ratio was held constant at 5:1. Mechanical alloying was carried out with the Spex Industries 8000 Mixer/Mill.

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Both compositions were ball milled in both air and inert argon atmospheres. The MA process was carried out over a period of 8 hours with a powder sample taken for analysis at 1 hour intervals. Care was taken to insure that the samples loaded under argon were not exposed to air during processing and sampling to eliminate oxygen contamination. At each sampling during the 8 hour MA run, a partial vacuum was encountered in those charges loaded in air. This indicated powder oxidation had occurred during processing. No such observation was made in the samples loaded under argon.

Since Si and Ge are isomorphous and exhibit a nearly linear composition dependence of lattice parameter, calculated lattice parameters were used to verify alloy formation and composition. Lattice parameters obtained were compared to those predicted by Vegard's "Law" as well as those provided by Olesinski and Abbaschian (8). X-ray diffraction was carried out using copper K-alpha radiation and a nickel filter in conjunction with a Debye-Scherrer powder camera. Scanning electron microscopy was used to analyze MA powder morphology. Energy Dispersive x-ray analysis, performed by the Tracor Northern TN5500 X-ray Analyzer, was utilized for both qualitative and semi-quantitative powder characterization. EDX samples were mounted and polished using standard metallographic procedures which facilitated compositional determination and reduced errors to within approximately 5%.

Results and Discussion

X-ray diffraction of the Ge-72 at.% Si air-loaded samples revealed that after 7 to 8 hours of MA, a solid solution had formed. With a measured lattice parameter of a = 0.54921 nm, deviation of this value from that of a similar melt-formed alloy (8) was -0.002%. Also present on the x-ray pattern were diffraction lines corresponding to SiO_2 and GeO. These oxides were detected as early as MA=1 hour and remained, although at low concentrations, throughout the course of the run.

MA in an inert argon environment yielded somewhat different results. While a Si-Ge alloy was produced after 4 to 5 hours, the calculated lattice parameters indicated a shift in composition from approximately 37-42 wt.% Si, balance Ge, during the remaining 4-5 hours milling time. Figure 1 demonstrates this compositional shift as well as the abrupt transition from elemental Si and Ge to the alloy. Oxides of the elemental constituents were not detected by x-ray analysis and also no partial vacuum was encountered during sampling.

At the composition corresponding to (Si-Ge) 50 at.% and MA=8 hours, the calculated lattice parameter of the composite powder formed in both air and argon atmospheres corresponded to an alloy having a composition of 20 atomic % Si, balance Ge, i.e., a larger than predicted lattice parameter. This deviation from Vegard's "Law" was also demonstrated after MA=8 hours for all compositions studied with less than 72 at.% Si as shown in Figure 2. Several attempts were undertaken to try to explain this peculiar alloying behavior which seems to be unique to the Si-Ge system. Similar investigations (2,7,9,17) into mechanical alloying have yielded expected results in that the final composite powders possessed correct compositions. Initial screening of the starting powders and subsequent MA of selected particle sizes indicated this anomalous alloying behavior was not a function of powder size. The presence of line broadening in the x-ray diffraction photographs indicated that residual stress could be affecting the ability to accurately resolve diffraction lines. The powder samples were subjected to a heat treatment designed to reduce the residual stress effects while avoiding temperature regimes favorable for noticeable diffusion. Subsequent x-ray diffraction analysis demonstrated a marked decrease in line width but calculated lattice parameters closely marked pre-annealed values. Recently, Politis and Johnson (18) utilized mechanical alloying to synthesize amorphous alloy powders from Cu and Ti. During their investigation they reported having to mechanically scrape the vial and balls to ensure homogeneous composition of the final powder. Similar procedures were incorporated into the MA of silicon and germanium with no positive results realized. It is assumed that the observed alloying behavior is caused by the reactivity of Si towards the milling media and vial walls. This leads to powder buildup and consequently a preferential loss of silicon which has been found not to be simply a by-product of powder oxidation. In fact, semi-quantitative energy dispersive x-ray analysis of powder taken from the vial walls indicate higher than expected silicon concentration levels.

Energy dispersive x-ray analysis was used to both identify the presence and relative amounts of impurities. In all samples tested, iron was detected at a maximum concentration of 0.5 at.%. Iron contamination is a result of vial and milling media wear. Enhanced

powder homogeneity has been achieved by the replacement of the steel milling media with transformation toughened ZrO_2 balls.

An interesting observation was made during this study while characterizing particle morphology. In every system containing brittle components in which mechanical alloying has been attempted, these being Si-Ge, Mn-Bi, and alpha quartz, numerous cases of interparticle necking have been observed. Figure 3 shows such necking in air-loaded Ge-72 at.% Si mechanically alloyed for 8 hours. These necks are present as early as MA=3 hours for air-loaded samples. Similar observations were made in argon-loaded samples where necking occurred as early as MA=1 hour. Similar necking observations have been made in which the initial components were ductile (12). This seems to indicate that inter-particle necking is a phenomenon not exclusive to brittle-brittle MA systems. While a great majority of the observed necks demonstrate a relatively smooth surface morphology, Figure 4 shows the internal structure of such a region. Rather than being a homogeneous particle, the MA powders appear to be composed of smaller particles cold-welded together.

The underlying mechanisms responsible for the inter-particle necking require further study for resolution. It may be that localized heating increases the plasticity of the material. This possibly initiates an extrusion process leading to the observed necks. However, calculations aimed at predicting bulk as well as microscopic temperature rises indicate otherwise. Using Schwarz's analysis (9), which assumes bulk temperature increases as a result of localized shear of powder particles trapped between two colliding balls, the temperature increase, ΔT, is given by

$$\Delta T = \frac{F}{2}\left(\frac{\Delta t}{\pi\, Ko\, \rho_p\, C_p}\right)^{\frac{1}{2}} \qquad [1]$$

where $F = \sigma_n v_r = 199.08\ MJ/m^2s$ is the dissipated energy flux, $\Delta t = 2d/v_s$ the stress state lifetime, v_s the longitudinal wave velocity, $v_r = 2$ m/s the relative velocity of the balls before impact, C_p the specific heat of the powder, Ko the thermal conductivity of the powder, $d = 0.0079$ m the ball diameter, ρ_p the powder density, and σ_n the normal stress developed by the head-on collision of two balls. Considering pure Ge, with Ko = 58.6 J/m·K·s, $\rho_p = 5324\ kg/m^3$, $C_p = 321.7$ J/kg·K, $\Delta T = 10.1$ K. Applying this method to pure Si, with Ko = 149 J/m·K·s, $\rho_p = 2330\ kg/m^3$, and $C_p = 677.96$ J/kg·K, $\Delta T = 6.57$ K. In the above calculations, the normal stress was taken to be the maximum compressive stress generated by the head-on collision of two balls. Under the given conditions, this value can be determined by the relation (14)

$$\sigma_n = \sigma_c = 0.616\left[PE^2\left(\frac{D_1 + D_2}{D_1 D_2}\right)^2\right]^{1/3} \qquad [2]$$

In equation 2, $E = 206.92$ MPa is the elastic modulus of the balls, $P = (1.01 \times 10^{-3})$ $a = 7.691 \times 10^{-4}$ kg the load, and $a = 0.762\ m/s^2$ the approximate ball acceleration. Substituting these values, σ_n is found to be 99.54 MPa.

Another method (10), which considers heating on the microscopic level as a result of sliding friction, gives similar results. This method considers a system in which a body is making contact with another over a limited area and moving over the surface of the other body at constant velocity. The contact area is considered to be square. Under these conditions, the microscopic temperature rise is given by

$$\Delta T = \frac{fW\, v_r}{4.24\, \ell J(K_1 + K_2)} \qquad [3]$$

Where $f = 0.6$ is the friction coefficient, W the load, l the half length of the side of the contact area, J the mechanical equivalent of heat, and K_1, K_2 the thermal conductivity of the respective bodies. Considering Si-on-Ge with K_1 and K_2 equal to 149 and 56.2 J/m·K·s, respectively, and $f = 0.6$, equation 3 reduces to

$$\Delta T = 1.4068 \times 10^{-4}\left(\frac{W}{\ell}\right) \qquad [4]$$

Using the normal load calculated above and $l = 0.025 \times 10^{-6}$ m, $\Delta T = 4.32$K.

These calculated values however are not consistent with measurements. Miller et al., using microsecond time-resolved radiometry, observed temperature increases on the order of 400 to 500°C upon impaction of NaCl crystals (11). More recently, McDermott and Koch (12)

have observed similar higher than predicted temperature rises during phase transition experiments.

Complex stress states in the compressed powder particles offer yet another possible explanation for the observed necks. It is known that some brittle materials under the influence of either a pure hydrostatic stress or a hydrostatic plus a superimposed tensile stress (15-16), can demonstrate ductile behavior. During the MA process, this may very well be the case. Easterling and Tholen (13) have suggested a parallel explanation. When two spherical particles come into contact and bonding occurs, stored elastic stress in the contact region can initiate diffusional currents that could lead to neck formation.

Summary

Mechanical alloying has been used to form a true solid solution from brittle, elemental starting Si and Ge powders. A Ge-72 at.% Si alloy was produced after 8 hours of ball milling with a calculated lattice parameter approximately equal to that of a similar melt-formed alloy. Compositions in the Si-Ge system with less than 72 atomic percent Si have also been alloyed with final compositions deviating from predicted values.

Inter-particle necking has been observed in the brittle systems Si-Ge, Mn-Bi, and in alpha-quartz after varying degrees of mechanical alloying.

Further work will focus on following the structural evolution of the Si-Ge solid solution from the brittle Si and Ge starting powders. Microanalytical tools including SEM and TEM will be used. The feasibility of MA brittle components opens up a wide range of possibilities for the synthesis of new materials.

Acknowledgements

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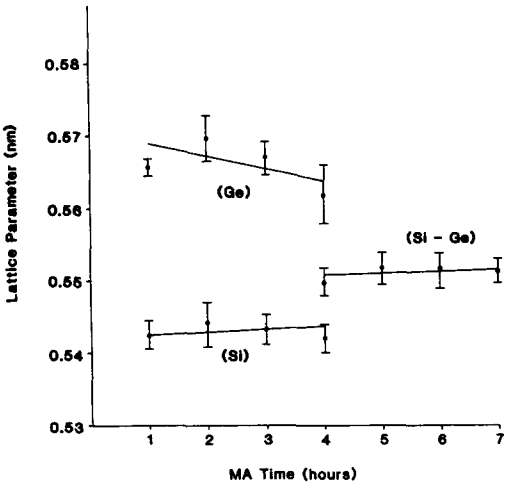

Fig. 1. Alloying behavior of argon-loaded Ge-72 at.% Si.

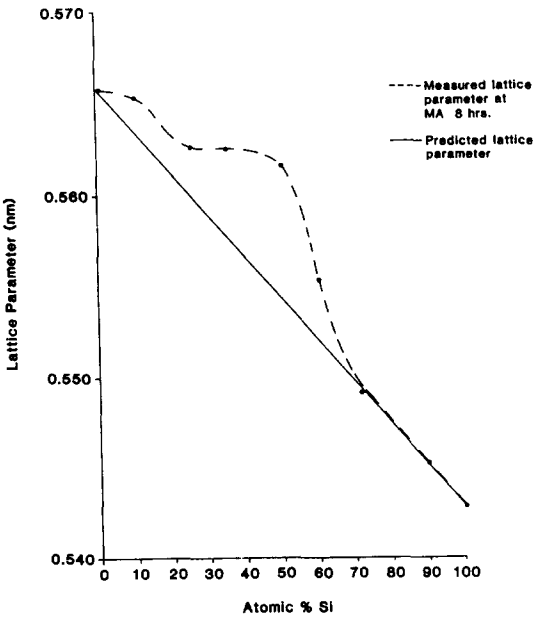

Fig. 2. Lattice parameter variation as a function of at.% Si.

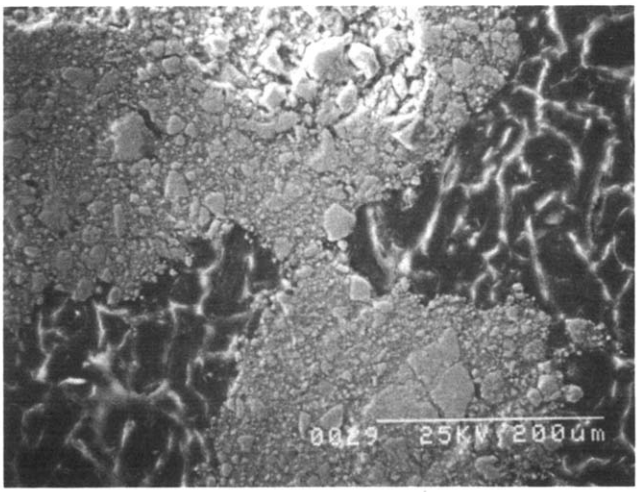

Fig. 3. Inter-particle necking in air-loaded Ge-72 at.% Si (MA = 8 h)

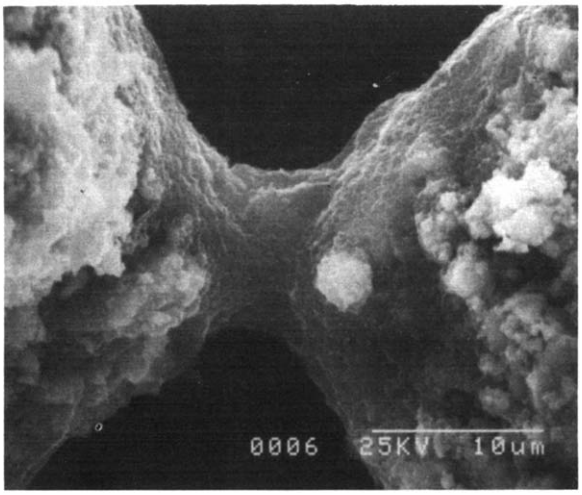

Fig. 4. Internal microstructure of air-loaded Ge-72 at.% Si (MA = 8 h)