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The Production of Si from SiO₂ via the Ball-Milling Technique

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Abstract

The ball-milling technique employs mechanical energy to reduce the particle size of reactants to a size small enough to cause defects in the reactants' lattice structures and produce active sites. In exothermic reactions, solid-state diffusions within these active sites induce self-heat propagating synthesis (SHS), allowing a complete reaction via mechanical energy. However, extracting silicon from silicon oxide using aluminum is endothermic, and therefore milling alone does not complete the reaction. This study sought to supplement the solid-state diffusion via the lattice defects with energy supplied by moderate heat treatment as a method of producing pure silicon and to investigate the parameters of this method to maximize its efficiency. The parameters tested were annealing temperature, milling time, and annealing time. The relationship between annealing temperature and milling time was also investigated thoroughly. X-ray diffraction, as well as some comparison with Atomic Force Microscopy, was used to determine the presence of products in samples. The data confirmed that milling is necessary for the reaction to take place, and that even one minute of milling can change the products significantly. The use of milling, combined with a moderate heat treatment, can produce silicon in a way that is more environmentally friendly and cost-effective than current methods and can be used at tonnage proportions for industrial purposes.

Keywords: ball-milling technique, silicon oxide, aluminum, mechanical energy, moderate heat treatment

Introduction

The ball-milling technique is a well-known innovative process often used for metallic coating and nanocomposite materials synthesis^[1]. In general, this process involves placing balls inside a steel vial with reactants and using a mixer to impart mechanical kinetic energy to the balls within the vial. The balls collide with one another in the vial, as well as with the powder reactants and the sides of the vial. They impart this energy to the reactants, shown by the gradual rise in temperature of the vial. The collisions continually reduce the particle size of the reactants, eventually causing defects in the lattice structure of the powder reactants^[2-3]. These defects are often called "active sites"^[3]. When a critical layer of powder is formed on and between the colliding bodies such as the walls of the vial and the balls, self heat-propagating synthesis (SHS) occurs^[2] as a result of the solid-state diffusion of the active sites, and causes the whole layer of powder to ignite almost simultaneously. This is called "ignition" and can be detected by a sudden jump in the vial's temperature, easily detected on a temperature versus time chart. The solid-state diffusion of the active sites in layers produced by the milling causes this ignition and, if the reaction is exothermic, products can be expected in the vial. This ignition can be used as an indicator for knowing that SHS has occurred.

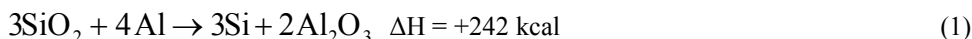
The most common applications of the ball-milling technique are metallic coating, metallic nanocomposites, and oxide reduction reactions^[3]. Without a mechanical energy method to perform these reactions, these processes require chemical synthesis and/or tedious and expensive methods to produce results, such as

various Vacuum Deposition techniques^[4-5]. The ball-milling technique is an attempt to make these processes both more environmentally friendly and more cost effective, as well as still capable of reproducing the method at tonnage proportions.

When working with oxide reduction reactions, most exothermic reactions will be induced by SHS when the ball-milling technique is used. However, some very useful reactions, such as combining silicon oxide and aluminum to form silicon and aluminum oxide, are *endothermic* and thus milling is not sufficient to complete the reaction. While milling still causes defects in the lattice structure, more energy is needed for solid-state diffusion, and hence SHS, to take place. Heat treatment from a furnace can be used to supply this missing energy and yield a complete reaction. Currently, heat is applied in some of the processes used to make silicon, causing a great harm to the environment and adding to the expense of making pure silicon. These processes include multi-step chemical purification^[6], silicon production on the Moon^[7], the chemical and heat purification of silicon wafers (requiring upwards of 1900°C)^[8], and heat treatment in an electric arc furnace with some chemical interaction (also requiring upwards of 1900°C)^[9]. However, the heat treatment used in this experiment requires temperatures almost one quarter that of the process commonly used to make silicon from silicon oxide today, making it a huge improvement that can be credited to the ball-milling part of the process.

Materials and Methods

The reactants used were silicon oxide powder (SiO₂, 99.5%, -400 mesh) and aluminum powder (Al, 99.5%, -325 mesh). Both were bought from Alfa Aesar. A SPEX 8000 mixer mill was used to mill the reactants in cylindrical, flat-ended hardened steel vials. Both the mixer and the vials were obtained from SPEX. The balls used came from Small Parts, Inc. and varied by size: small (1/4", 1.012 g), medium (3/8", 3.447 g), and large (1/2", 7.996 g). Heat-resistant aluminum oxide boats were obtained from Coors Ceramic Company and heat treatment was performed using a computer-controlled tube furnace manufactured by Lindberg. The milling products were pressed into a 1/2" disk before putting them into the furnace using a Carver Laboratory 3620 press that applied 11 metric tons of pressure to the powder. The heat treatment was done under a steady and continuous argon gas flow. The reactants were placed within a hardened steel vial with a set number of balls in an open-air atmosphere. The amount of each reactant was determined by setting a total mass of 4 g and using the following stoichiometry:



The vials were manually sealed and placed in the mill. A thermocouple ran from the vial's base to the computer, where temperature data from the vial was recorded in a QuickLog data acquisition program.

Variables tested were milling time, annealing temperature, the relationship between milling time and annealing temperature, and annealing time. Systematic studies were used to test variables independently, keeping the others as controls. The integrative nature of the milling time and annealing temperature parameters was also tested to find their relationship and to find the best possible combined effectiveness of the two parameters in order to reduce the input mechanical and heat energies. Reducing heat energy was, of course, much more important.

Samples were tested for completion with x-ray diffraction at the Physics Department at Towson University in collaboration with Dr. Rajeswari Kolagani and Dr. Grace Yong. A Bruker Axs diffractometer with Cu K α radiation was used to detect the elements and compounds present in the samples. This gave a means to determine which samples had completed their reactions, which had not, and which produced a mixed reaction. The Atomic Force Microscope (AFM) at Goucher College was also used to study the surface morphology of some of the samples after heat treatment.

Results and Discussion

The purpose of this investigation was to test the parameters of the reaction between silicon oxide and aluminum, including the following: milling time, annealing temperature, the relationship between milling

time and annealing temperature, and annealing time. Reducing annealing temperature and milling time to their limits is considered to be important in order to find out where these limits are and to make this method even more cost-effective and environmentally friendly. These limits are also important to explore the possibility of an existing relationship between annealing temperature and milling time, in the hopes of lowering the annealing temperature as much as possible. Finally, the lower limits of annealing time were also tested as a final measure to reduce harm to the environment, as well as to reduce cost.

The reaction was known to take place consistently under the following conditions: 60 minutes of milling time annealed at 600°C, for the duration of 4 hours. By keeping the mass of the powder and number and size of the balls constant, it was possible to test each of these three parameters as well as the relationship between milling time and annealing temperature.

Each sample had a reactant powder mass of 4g, 1.877 g of silicon oxide and 1.123 g of aluminum, as calculated from the stoichiometry of the reaction, Equation 1. While the number and size of the balls were usually kept consistent, changes had to be made due to a flower-patterned formation that occurred between the large-sized balls and the walls. Six large balls fit perfectly into this formation at the top of the cylindrical vial. The balls would get stuck in this pattern due to the reactions occurring in the powders, which would occur between the balls and the vial and between the balls themselves, causing them to get stuck in this formation. This would effectively stop these balls from participating in the milling process and reduce the amount of kinetic energy. It also would make the samples inconsistent, so eventually samples were prepared with 4 large and 6 medium balls consistently.

After the sample was prepared, the vial was placed into the mill and milled, keeping track of the temperature of the vial all the while. When the vial was removed, and the insides and balls were scraped for the milled powder. This powder was then pressed into a 1/2" diameter tablet with 11 metric tons of pressure, and this tablet was placed into an aluminum oxide boat. The boats were placed near the center of the furnace, which was programmed with an upward ramp of 10°C per minute to its desired temperature for a set amount of time (usually 4 hours) and had a downward ramp of 30°C per minute. Some of the samples were selected for investigation with the Atomic Force Microscope (AFM) at Goucher College, but almost all of the samples were taken to Towson University for x-ray diffraction (XRD) analysis.

Milling time was tested by first milling samples for 60, 40, 20 and 0 minutes and annealing them for 4 hours at 600°C. The zero-minute sample was created as a control and to establish that milling is necessary for the reaction to take place in the furnace. X-ray diffraction revealed that indeed, all three milled samples had completed the reaction, and the zero-minute sample was composed entirely of the reactant powders.


Therefore, 15, 10, and 5-minute samples were tested under the same controlled conditions, and they too yielded complete reactions. Then, 4, 3, 2 and 1-minute samples were tested, and their surface morphology was observed using the AFM after being annealed but before being ground for x-ray diffraction. While none of these samples yielded a complete reaction, all of them yielded a mixed reaction, showing both reactants and products were present in the sample (see Figures 1, 2, 3, and 4). Both their surface morphologies and their diffraction patterns showed that each minute of milling yielded a slightly more complete reaction. Even more important, this part of the experiment showed that even one minute of milling made the difference between no reaction taking place, and a partial reaction taking place at the same controlled conditions.

Some samples were also made for the AFM to see the difference in surface morphologies between 10, 30, and 60 minutes of milling. Many other samples were also selected for scans with the AFM, but it soon became apparent that any sample that was fully reacted had a surface too rough for the AFM to properly detect. The AFM tests confirm that samples that have completely reacted are much rougher than unreacted or mixed samples.

Though AFM and x-ray diffraction scans detected differences in the reacted and unreacted samples before annealing, no difference could be seen in the temperature vs. time graphs shown in Figure 5 between a 60-minute milled sample and a 4-minute milled sample. The change in temperature over time was usually

around the same for all samples, never showing sudden jumps like those found in SHS reactions. The results of the difference in milling time could not be seen in the products until after annealing.

Next, milling time was kept constant at 30 minutes, while annealing temperature was lowered. However, it was also suspected that annealing temperature and milling time were related integratively and thus several milling times were studied at each annealing temperature. It was soon found that 550°C worked for most milling times, so the next annealing temperature tested was lowered to 500°C. There, mixed reactions were observed above 10 minutes, and thus a lower limit for annealing temperature was established and the limit for a full reaction could now be sought between 500 and 550°C. Further investigations have shown that completed reactions are possible at a lower minimum annealing temperature of 525°C with as low as 7 minutes of milling time.

As mentioned before, to test the relationship between milling time and annealing temperature, different milling times were tested at each temperature. Besides just finding out where on the milling time vs. annealing temperature graph the reaction worked fully, many samples were also made to investigate where the lines were between full and mixed reactions and between mixed reactions and no reactions at all. Therefore, lower temperatures needed to be investigated as well as higher ones. For-hundred and seventy-five °C proved to be too low to produce any reaction at all. However, 500°C produced mixed reactions after 10 minutes. Our lowest combination of conditions that produced fully reacted samples continued to be 525°C and 7 minutes of milling time.  graph in Figure 6, produced from all the data points, shows phase trend lines to differentiate where a sample will be fully reacted, partially reacted (mixed reactants and products), or not reacted at all. All the samples on this chart were annealed for 4 hours, though their annealing temperatures and milling times differ.

One last parameter was tested briefly on its own to see if further research could be conducted. Three samples were made to test annealing time. All three were milled for 60 minutes and annealed at 600°C. The 3-hour, 2-hour, and 1-hour samples all yielded completed reactions. While there was not enough time to test the lower limit of annealing time further or to investigate the relationships annealing time might have with the other parameters, this leaves even more than the detailed limits of annealing temperature and milling time for further research to explore. By also lowering annealing time, the amount of heat used in this method could be reduced significantly, decreasing harm to the environment and cost even more.

Conclusions

This investigation has outlined the conditions necessary for using the ball milling technique followed by moderate heat treatment to create silicon from silicon oxide. X-ray diffraction and Atomic Force Microscopy have helped confirm a trend line of the relationship existing between the amount of time the reactants are milled and the temperature they are annealed at. Silicon is a desirable metal, not found on its own in nature, that is usually extracted using chemical means or methods requiring heat treatments exceeding 1900°C. These experiments have illustrated the possibility of the production of silicon from silicon oxide, a very common compound (sand), using mechanical energy to reduce the temperature of heat treatment significantly. This will make the production of pure silicon easier and, effectively, less costly. This method will also make silicon production more environmentally friendly. The precise boundaries of annealing temperature and milling time should be investigated in future research to find the exact lower temperature limits. In addition, annealing time should be investigated, as it shows promising results for using less heat in the production of silicon.

Acknowledgements

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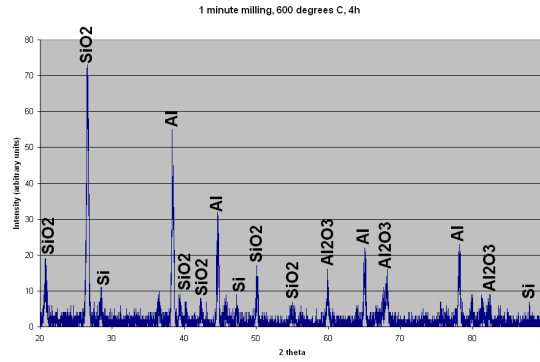
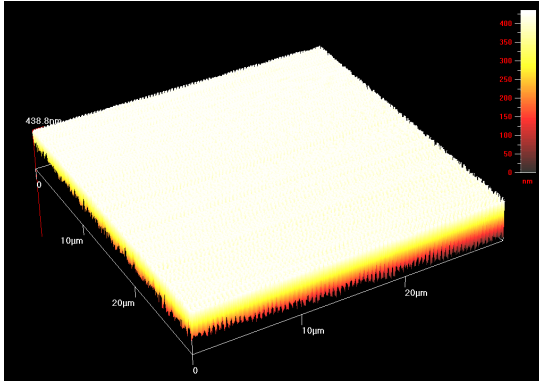


Figure 1: AFM and XRD results of sample milled for 1 minute, annealed for 4 hours at 600 ° C .

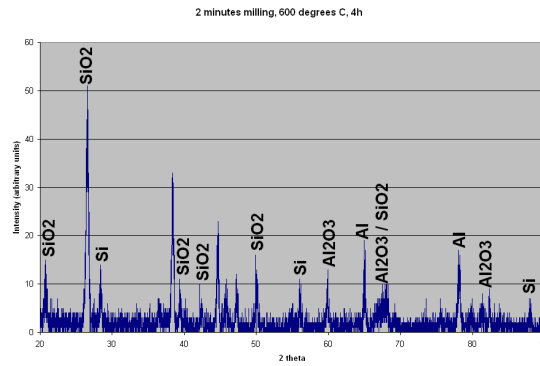
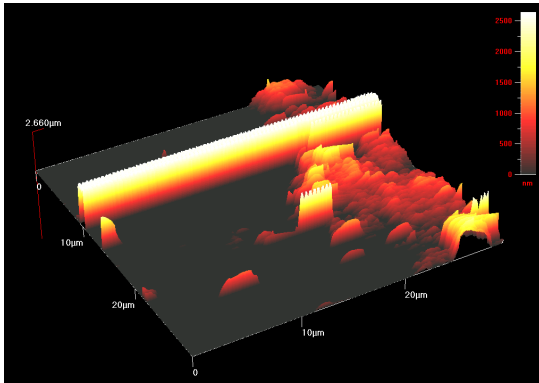


Figure 2: AFM and XRD results of sample milled for 2 minutes, annealed for 4 hours at 600 ° C .

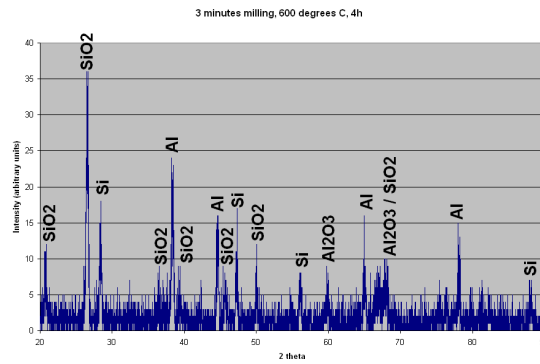
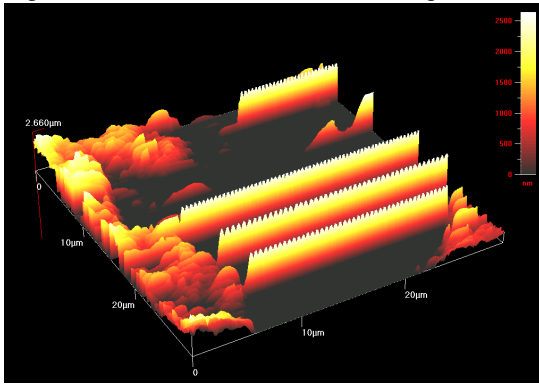


Figure 3: AFM and XRD results of sample milled for 3 minutes, annealed for 4 hours at 600 ° C .

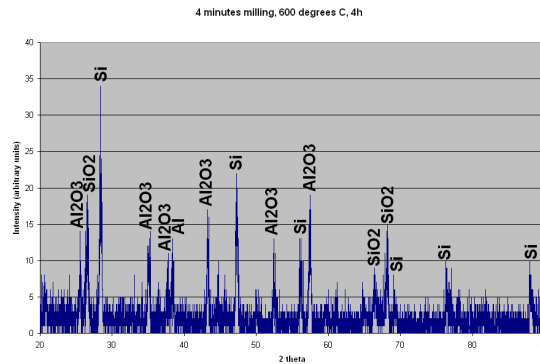
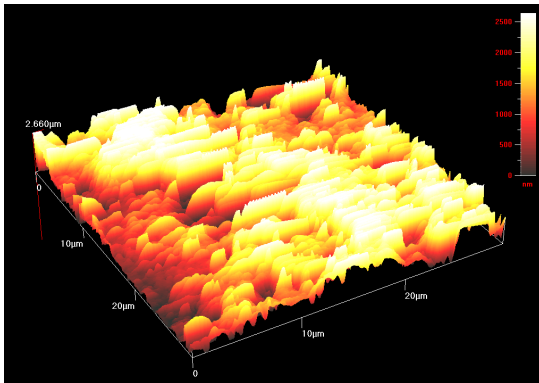


Figure 4: AFM and XRD results of sample milled for 4 minutes, annealed for 4 hours at 600 ° C .

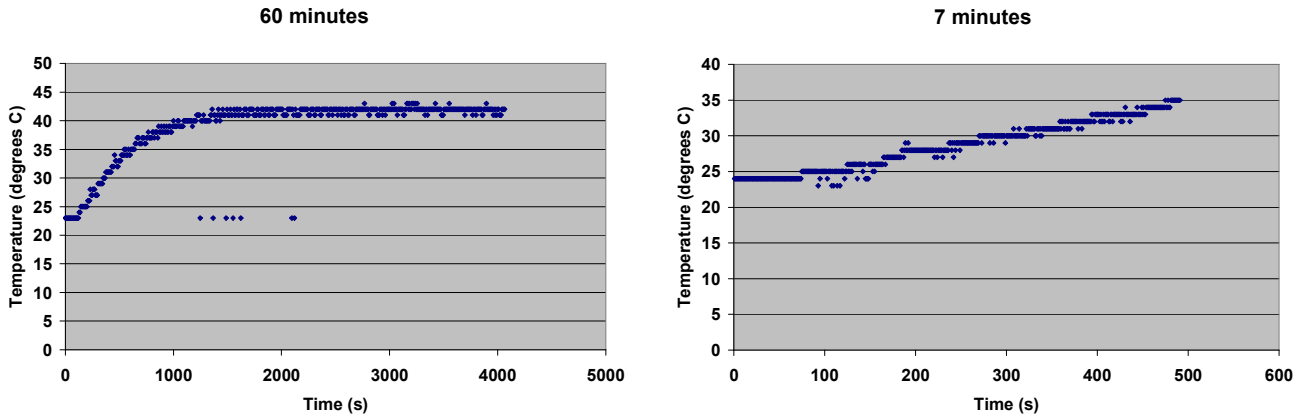


Figure 5: Whether milled for 60 minutes or for 10, trend of the temperature vs. time graphs is the same.

Annealing Temperature and Milling Time

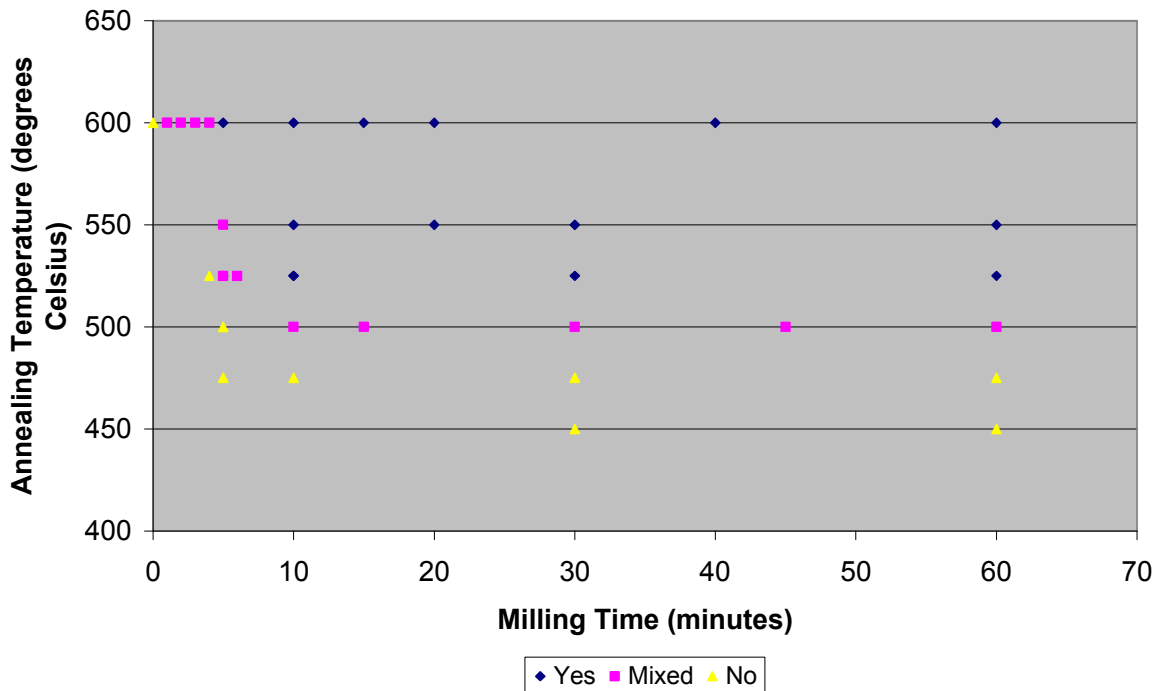


Figure 6: Annealing Temperature vs. Milling Time. Data points represented by triangles are unreacted. Those represented by squares are mixed reactions, and those represented by diamonds are complete reactions. The limits between regions begin to create phase lines for this reaction, indicating under what combinations of annealing temperature and milling time the reaction will be complete, will be mixed, or will not occur at all.