

Proceedings of The National Conference
On Undergraduate Research (NCUR) 2007
Dominican University of California
San Rafael, California
April 12-14, 2007

An Anomalous Reaction of Silicon Oxide and Aluminum via Ball Milling

Michelle Marx
Department of Physics
Goucher College
1021 Dulaney Valley Road
Baltimore, MD 21204, USA

Faculty Advisor: Dr. Ali Bakhshai

Abstract

Previous studies have shown that the ball milling technique, which mechanically heats and releases energy, often causes a displacement reaction between various metals and metal oxides. Sometimes ball milling causes a self-propagating heat synthesis reaction (SHS) to occur. This study was undertaken to see whether the ball milling technique could provide a method to extract pure silicon from silicon oxide. Since silicon oxide and aluminum are readily available materials, the ball milling process would be an easy and cost-efficient way to produce silicon. The parameters tested in this study included varying the amount of aluminum, total powder mass, number of balls (kinetic energy), and milling atmosphere. Parameters also tested were additions of acetone and alcohol. X-ray diffraction was used to determine what elements and compounds were present before and after ignition. This study discovered that when silicon oxide and aluminum are milled SHS does not occur despite the reaction being highly exothermic. It does not appear possible to slow down the localized reactions to the point where SHS can occur.

Keywords: Mechanical alloying, Ball milling technique, Self-propagating heat synthesis (SHS)

1. Introduction

Mechanical alloying is a powder processing technique, requiring the use of ball mills, which was first developed for oxide-dispersion strengthening but is now being used to produce alloys, nano-composites, and metallic coating.¹ The many advantages of mechanical alloying over chemical synthesis include being safer for the environment, occurring at lower temperatures, having the ability to be scaled up to tonnage proportions, and being more cost-efficient.²⁻⁵

The process of ball milling involves using a vial containing balls and powder mixtures, which are shaken at high speeds by a mixer in order to activate mechanochemical reactions and mechanical alloying. The mixer provides kinetic energy to the balls inside the vial. The collision of the balls with the walls and powder reduces the powder's particle size. The reduction in particle size eventually causes lattice defects to form in the atomic structures which create active sites.

Studies have shown that the ball milling technique causes the displacement reaction of metals and metal oxides to have either a gradual change in temperature or an abrupt increase in temperature. A sudden jump in temperature has signaled that SHS has taken place, shown in Figure 1.

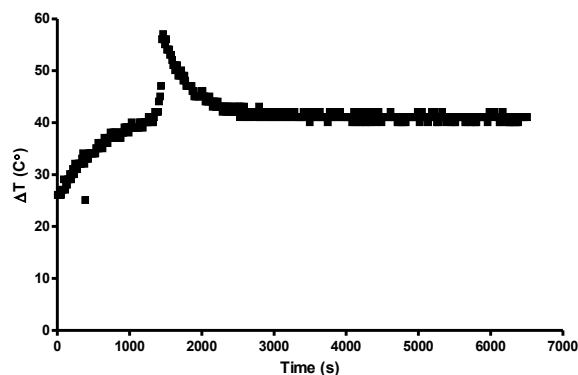


Figure 1: Ignition graph showing ΔT vs. time.

SHS has usually resulted if a reaction is exothermic, such as the reaction between nickel (II) oxide and aluminum ($\Delta H = -119$ kJ). Prior to SHS the particles have become smaller, the number of active sites is increasing, and upon collision mechanical energy is being released. In order for ignition to take place there had to be enough material causing heat to propagate through the vial.^{3, 6-8} SHS had taken place when the particle size reaches a certain value and requires the formation of the powder layer to a certain thickness. This combustion reaction had been initiated after some activation time in which the reactants were converted to products.

The objective was to determine if it is possible to slow down the localized reactions enough to allow for SHS to occur and produce pure silicon. Our studies have shown that the combination of silicon oxide and aluminum, a highly exothermic reaction ($\Delta H = -242$ kJ)⁹, does not lead to the occurrence of SHS. We theorized that SHS does not occur because the localized reactions are happening too fast without enough active sites in close proximity to form the critical amount of powder layer between the colliding bodies within the vial.

2. Materials and Methods

The milling experiments were done using a SPEX 8000 mixer mill and a cylindrical, flat-ended steel vial also made by SPEX. The milling balls used in our study were obtained from Small Parts, Inc., and were small (1/4", 1.012g), medium (3/8", 3.447g), and large (1/2" diameter, 7.996g). The starting materials were silicon oxide powder (SiO_2 , 99.5%, -400mesh) and aluminum powder (Al, 99.5%, -325mesh) obtained from Alfa Aesar. Other materials used were reagent alcohol (R-OH), composed of ethyl alcohol, methyl alcohol, and isopropyl alcohol, and acetone ($(\text{CH}_3)_2\text{CO}$), both obtained from Fisher Scientific.

The powders were added into the vial containing the balls in either an argon atmosphere glove-box or an oxygen open-air atmosphere. The stoichiometry of the powders was consistent with the equation (1).



However, in one experiment we increased the aluminum by 4% at each step in order to add impurities and change the rate of the reaction.

In the argon atmosphere the variables tested were the amount of aluminum, powder mass, and number of balls (amount of kinetic energy). In the oxygen atmosphere the variables tested were the powder mass, number of balls, acetone and number of balls, alcohol and powder mass, and alcohol and number of balls. In order to determine whether SHS would occur, we changed one of the parameters at a time and kept the others constant as control variables.

Temperature values were obtained using a thermocouple attached to the mill and a QuickLog data acquisition program. When the pressure inside the vial made it too difficult to open, a hydraulic press made by Fred S. Carver, Inc., was used to diminish the excess pressure on the vial cap before opening.

Several samples were then taken from the Physics Department at Goucher College to the Physics Department at Towson University as a result of research collaboration with Dr. Rajeswari Kolagani and Dr. Grace Yong. X-ray diffraction was performed using a Bruker Axs diffractometer with $\text{Cu K}\alpha$ radiation. By using x-ray diffraction it was possible to determine which elements or compounds were present in our powder samples.¹⁰ X-ray diffraction

made it possible to determine whether the reaction went to completion, which is converted from reactants to products.

3. Results and Discussion

Previous studies have shown that ignition of the powder under SHS is a controllable and reproducible event.³ Therefore, it was necessary to first perform experiments testing parameters that are known to cause ignition and the process of SHS between other metals and metal oxides, which have a less exothermic reaction than silicon oxide and aluminum. Then the hypothesis could be tested by adding impurities to the mixture in order to slow down the rate of the reaction and cause SHS to occur.

In both the argon and oxygen atmosphere, the first property established was the relationship between ΔT and powder mass. The number of large balls was held constant at six. If SHS had occurred, then the temperature would have increased linearly as the powder mass was increased. However, since ignition did not take place the change in temperature remained relatively constant, as shown in Figure 2.

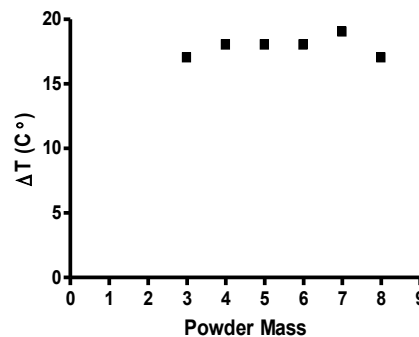


Figure 2: ΔT vs. powder mass with 6 large balls in an O_2 atmosphere.

In both atmospheres, the second property established was the relationship between ΔT and the number of balls. The powder mass was held constant at 3g in the argon atmosphere and held constant at 5g in the oxygen atmosphere. The temperature increased linearly, as expected, since the kinetic energy was increased, as indicated in Figures 3 and 4.

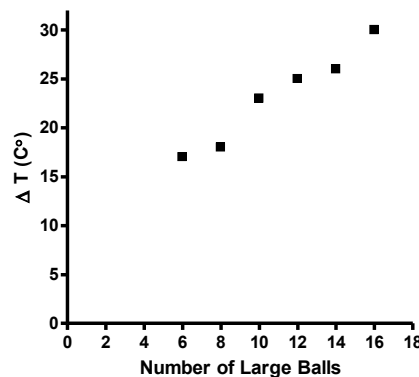


Figure 3: ΔT vs. number of large balls with constant 3g powder mass in an Ar atmosphere.

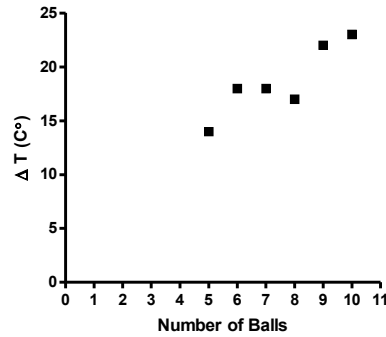


Figure 4: ΔT vs. number of large balls with constant 5g powder mass in an O_2 atmosphere.

Next the relationship between ΔT and the off-stoichiometry aluminum increase was examined in the argon atmosphere. The powder mass of silicon oxide was held constant at 1.876g and the number of balls was held constant at six (1 small, 4 medium, 1 large). By increasing the aluminum by 4% at each step, the rate of the reaction was changing as a result of impurities being added. The expected result was that the change in temperature would remain relatively constant since ignition did not occur, which is seen in Figure 5.

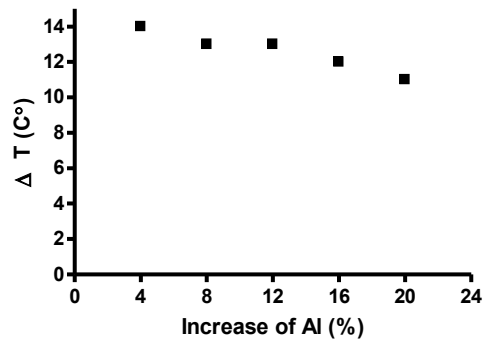


Figure 5: ΔT vs. off-stoichiometry Al with constant 1.876g SiO_2 and 6 balls (1S, 4M, 1L).

Next, in the oxygen atmosphere, the relationship between ΔT and number of balls with acetone as an additive was observed. The powder mass was held constant at 3g and the amount of acetone was held constant at 1.0cc. The temperature increased linearly, as expected, due to the increase in kinetic energy as can be seen in Figure 6.

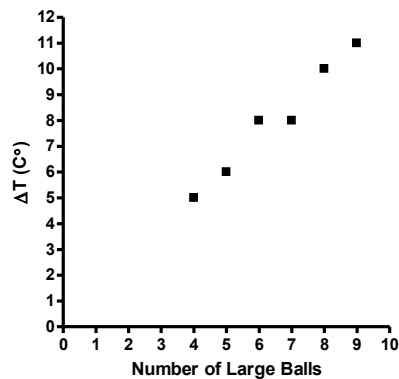


Figure 6: ΔT vs. number of large balls with constant 3g powder mass and 1.0cc $(CH_3)_2CO$.

As the vial was opened and the powder was exposed to oxygen, the powder caught fire. Since acetone is a flammable substance and SHS did not occur, its composition may have remained unchanged or changed minimally, which would account for why the powder caught fire.

The above experiment was then repeated using alcohol as an additive. The addition of alcohol slowed down the localized reactions allowing for ignition to take place. The relationship between ΔT and the number of balls was linear, while there is an inverse relationship between ignition time and the number of balls, which is consistent with the increase in kinetic energy. This inverse relationship is shown in Figure 7.

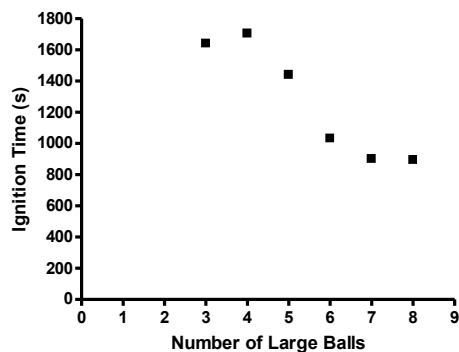


Figure 7: Ignition time vs. number of large balls with constant 3g powder mass and R-OH.

Since ignition occurred, the relationship between ΔT and powder mass was expected to be linear, which is confirmed in Figure 8.

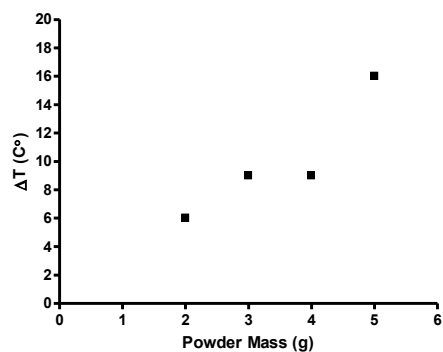


Figure 8: ΔT vs. powder mass with R-OH and 6 large balls.

The number of large balls was held constant at six. There was no sudden increase in temperature at 1g. Tests were not conducted past 5g for safety precautions, i.e., the temperature change and pressure were so high.

Next, the relationship between ΔT and the amount of alcohol added was observed. The amount of large balls was held constant at six. The temperature changed linearly, which is illustrated in Figure 9.

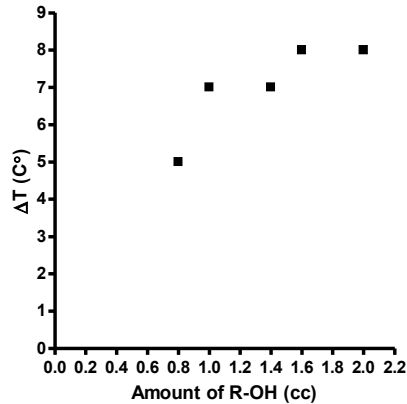


Figure 9: ΔT vs. amount of R-OH with constant 3g powder mass and 6 large balls.

This linear relationship is as expected since as more alcohol is added the reaction becomes slower. If the amount added was below 1.0cc, then the powder would catch fire when it became exposed to oxygen. Like acetone, alcohol is a flammable substance. If the composition remained unchanged or changed minimally, then the exposure to air would have caused the powder to catch fire.

Some of the samples' compositions were then studied using an x-ray diffractometer to determine which elements or compounds were present. This process is done by an incident beam striking the powder sample and causing diffraction. Diffraction occurs if constructive interference has taken place. Constructive interference is described by Bragg's equation (2).

$$2d \sin \theta = m\lambda \quad (2)$$

A sample of silicon oxide, aluminum, and alcohol was milled for a period of 10% of the ignition time and examined. Samples of reacted silicon oxide, aluminum, and alcohol were also examined. Since ignition had occurred in the reacted samples, products were expected to be found in those samples. However, the x-ray diffraction pattern showed that products had not been formed in the reacted samples. The x-ray diffraction patterns of pre-ignition and post-ignition samples can be seen in Figures 10 and 11 respectively.

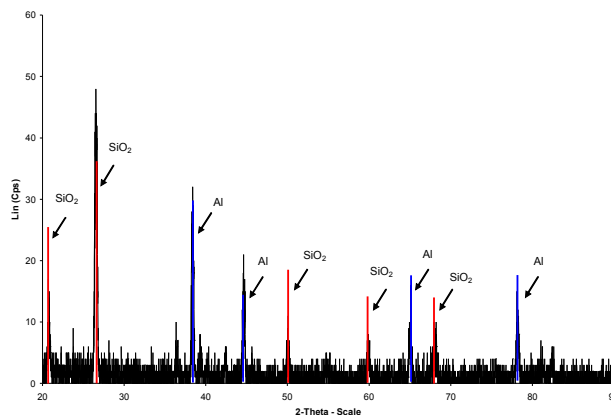


Figure 10: XRD pattern of SiO₂, Al, and R-OH milled at 10% of ignition time.

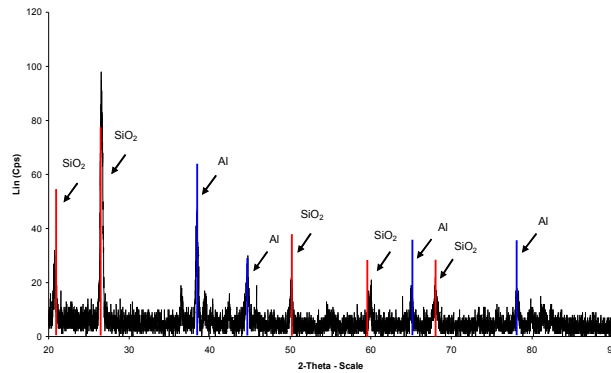


Figure 11: XRD pattern of SiO₂, Al, and R-OH after ignition

Based on these findings, experiments were then conducted using alcohol alone, alcohol with silicon oxide, and alcohol with aluminum. These tests revealed that a combination of alcohol and aluminum caused ignition.

Varying the amount of alcohol was then repeated while keeping the aluminum powder mass constant at 1.124g and the number of large balls constant at six. As in the earlier experiment, the temperature change increased linearly.

Next, the relationship between ΔT and aluminum powder mass with alcohol as an additive was examined. The number of large balls was held constant at six and the alcohol was held constant at 2.0cc. The values of aluminum corresponded to the stoichiometric amounts of aluminum in the silicon oxide - aluminum samples of 3g, 4g, 5g, etc. The smallest value of aluminum used was 0.374g. Ignition did not take place at that value. However, when 0.748g was used ignition did occur. There appears to be a minimum amount of aluminum necessary to cause ignition. At amounts larger than 0.748g the quantity of aluminum becomes irrelevant because the temperature change remained relatively constant, as shown in Figure 12.

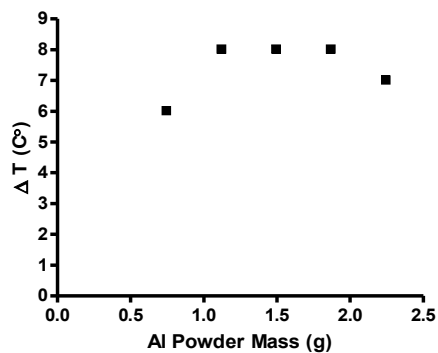


Figure 12: ΔT vs. Al powder mass with constant 2.0cc R-OH and 6 large balls.

These findings indicate that aluminum might be acting as a catalyst for the alcohol.

These results were further examined by looking at the composition of the sample of the reacted aluminum and alcohol by using an x-ray diffractometer. If aluminum was acting as a catalyst, then the presence of aluminum was expected to be seen in the x-ray diffraction pattern of the sample after ignition. The amount of Al and R-OH used was 1.124g Al and 2.0cc R-OH. Figure 13 shows that aluminum is a catalyst in the reaction.

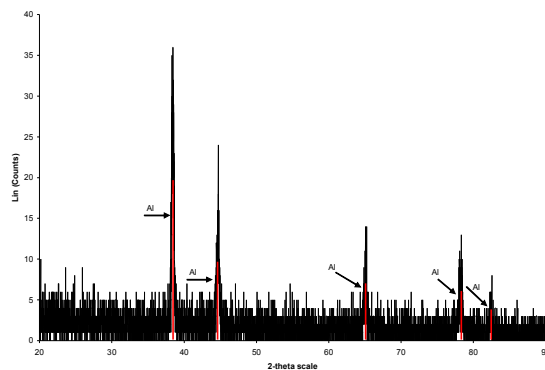


Figure 13: XRD pattern of reacted Al and R-OH.

Each individual run took approximately two hours, which accounts for why the graphs do not contain error bars. If there had been more time, each run would have been repeated four or five times. Since that was not the case, the main point was to discover the various trends from each experiment for further study.

4. Conclusion

The expected outcome of exothermic reactions, that is, the occurrence of SHS between metals and metal oxides, does not always occur. The reaction between silicon oxide and aluminum is one instance where SHS does not occur. The original prediction of the reaction was incorrect; however, the reaction that does occur requires further study. It was determined that aluminum is acting as a catalyst in the reaction. A gas was produced when the pressure inside that vial was released. This gas could have been H_2 , ethene, or propene. Although no instrumentation was available to determine which gas was produced, there was a 'pop' that indicates it was most likely hydrogen gas.

5. Acknowledgements

We would like to thank Towson University, especially Dr. Rajeswari Kolagani and Dr. Grace Yong, for use of their x-ray diffraction instrumentation. This work was supported by the Academic Dean's office of Goucher College.

6. References

- 1 C. Suryanarayana, *Progress in Materials Science* **46**, 1-184 (2001).
- 2 A. R. Torosyan, N. H. Zulumyan, Z. H. Hovhannisyanyan, and S. E. Ghazaryan, *The Minerals, Metals, and Materials Society*, 2004.
- 3 J. Sergeant and A. Bakhshai, *Proceedings of the National Conference on Undergraduate Research (NCUR)*, 2006.
- 4 C. C. Koch: *Annu. Rev. Mater. Sci.* **19**, 121-143 (1989).
- 5 L. Lü and M. O. Lai, *Mechanical Alloying* (Kluwer Academic Publishers, Boston, 1998).
- 6 V. Rusanov and C. Chakurov, *Journal of Solid Chemistry* **89**, 1-9 (1990).
- 7 C. Tschakarov, G. G. Gospodinov, and Z. Bontschev, *Journal of Solid State Chem.* **14**, 244 (1982).
- 8 A. Bakhshai, R. Pragani, and L. Takacs, *Metallurgical and Materials Transactions A* **33A**, 3521-2526 (2002).
- 9 F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema, and A. K. Niessen, *Cohesion in Metals: Transition Metal Alloys* (North-Holland Physics Publishing, Amsterdam, 1989).
- 10 B. D. Cullity, *Elements of X-Ray Diffraction* (Addison-Wesley Publishing, Reading, MA, 1978).