Is Ball Milling An Innovative Technique For the Production of Zn From ZnO?

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Abstract

The process of mechanical alloying using ball milling transfers mechanical energy to reactants in powder form, causing the particle size of the reactant powders to be reduced until defects in the lattice structure of the reactants are created. For reactions of sufficient exothermicity, this facilitates a complete mechanochemical reaction through self-heat propagating synthesis (SHS). The oxide reduction reaction of ZnO with Al, which yields pure Zn as a product, cannot be induced using ball milling alone because of its low exothermicity. This study used a systematic combination of ball milling and annealing through heat treatment in order to induce the reaction. Parameters tested were milling time, annealing time, and annealing temperature with the purpose of establishing the importance of each of these variables in inducing a complete reaction in the sample. The completeness of the reaction was determined using x-ray diffraction analysis and inspection with an optical microscope. Results confirmed that neither ball milling nor heat treatment could induce the reaction individually; only ball milling followed by annealing could cause the reaction to take place. An optimal milling time and annealing temperature were also established. This study suggests that using ball milling in conjunction with heat treatment can produce Zn from ZnO in a less costly, more efficient, easier, and less wasteful manner than traditional methods.

Introduction

Ball milling is a materials synthesis technique that is a key process in many applications under the umbrella of mechanical alloying. In use since the 1970s during Chakurov's study of combination reactions[2], ball milling has become an innovative technique in the fields of materials synthesis and mechanochemistry. It has specific applications in the production of metallic coatings, nanocomposite materials, and alloys, often implicit in inducing oxide reduction reactions[1].

Mechanical alloying involves an alternative for a chemical process using a transfer of mechanical energy. Ball milling accomplishes this by catalyzing a chemical reaction in a controlled environment through transfer of kinetic energy. During ball milling, reactant powders are mixed inside a hardened steel vial containing several stainless steel balls. The vial is shaken rapidly inside a ball mill, thus causing the balls inside to collide with each other as well as the surface of the container. These rapid collisions decrease the size of the reactant particles until defects in the crystal lattice structure of the particles themselves are created. These defect areas, called *active sites*, facilitate the process of solid state diffusion by which the kinetic energy of the steel balls is transferred to the powder, causing the desired alloying reaction to take place. By this time, a thin layer of powder has formed on the balls and on the surface of the container,

bringing the active sites in close proximity to each other. Depending on the exothermicity of the reaction, the reaction then propagates throughout the vial in a gradual process or through self-heat propagating synthesis (SHS), a rapid process.

For certain reactions of low exothermicity, particularly copper oxide reduction reactions, *loose powder ignition* causes the powder to react gradually throughout the milling time[2]. However, if a sufficient amount of heat is released, SHS can be induced. During SHS, the heat released at each localized active site is transferred to a nearby site, thereby causing a rapid chain reaction to proliferate through the vial. This chain reaction is called *ignition*, and typically happens in less than three seconds. A variable of particular interest in the process of ball milling is the time after the beginning of milling that ignition takes place; the ignition time tends to vary depending on the constituent reactant particles, the mass of reactant powder, and the mechanical energy supplied by the balls.

Although ball milling is particularly useful in reactions where SHS occurs within the vial, research shows that it can also be used in conjunction with additional heat treatment for reactions of low exothermicity or endothermic reactions, where SHS does not occur[1]. In the oxide reduction reaction of ZnO with Al, ball milling is particularly useful because it causes lattice defects to form, thereby facilitating a solid state diffusion process that can be induced using heat treatment in a furnace at much lower temperatures than traditional chemical processes. Thermal dissociation of ZnO occurs above 1900 °C[4], and chemical methods of production such as pyrometallurgy processing and electrowinning require comparable temperatures as well as expensive chemical solvents that can be harmful to the environment[3]. Since Zinc has important industrial uses, including the production of brass for batteries, corrosion-resistant steel plating in the aerospace industry, skin treatment products, and energy-saving windows, ball milling in conjunction with heat treatment is an innovative process for the production of zinc because it is less costly, less wasteful, and requires much lower temperatures than traditional methods[3].

Materials and Methods

The experimental process was completed incrementally in five primary steps. First, the correct amounts of each reactant powder had to be measured out and placed in the vials in a LABCONCO controlled atmosphere glove box under minimal gauge pressure, in order to minimize the possibility of oxygen contamination that could disrupt the reaction. The reactant powders were then milled in a SPEX 8000 mixer mill for a set time period. Upon completion of the milling period, the composite powder was pressed into a one-half inch disk using a hydraulic press in order to facilitate the annealing process. Finally, heat treatment was performed in a tube furnace and samples were analyzed using one or more of the following instruments: an optical microscope, Goucher College's Atomic Force Microscope, and the Towson University Physics Department's x-ray diffractometer.

The reactants used were zinc oxide powder and aluminum powder supplied by Alfa Aesar. Three grams of the reactant mixture were used in each trial, with the individual amounts of each compound determined by stoichiometry of the following reaction:

$$3ZnO + 2Al \rightarrow Al_2O_3 + 3Zn, \Delta H = -632 \text{ kJ/mol}$$

The mixture was milled by placing it in a SPEX cylindrical hardened steel vial with five stainless steel balls of different sizes. For four trials, three large (one-half inch, 8.25 gram) and two medium (three-eighths inch, 3.48 gram) balls were used, manufactured by Small Parts Inc. For

the remaining sixteen trials, two large balls and three medium balls were used. This change was made in order to increase the kinetic energy transferred to the powder, since smaller balls travel faster within the vial due to the increased mean free path between collisions which results in fewer, but more energetic, collisions taking place. The variable of particular interest in the milling process was the time of milling; this took on a value of ten minutes to seventy-five minutes over all the trials. Milling time was determined to be an important factor in the degree of success of the combined ball milling and annealing process, since the formation of active sites within the powder depends on the number and severity of collisions that take place within the vial.

The ball milling technique described above is accompanied by several disadvantages in addition to the aspects that make it useful for experimental materials synthesis research. Due to the high number, intensity and frequency of collisions within the vial, small impurities will inevitably be introduced into the sample that are trace elements of the hardened steel vial and balls, and these impurities can cause experimental data to be skewed. However, one of the main reasons why the ball milling step is so useful in the experimental process is that it is dependable and produces consistent results; we expect that milling a set amount of a powder mixture for a set duration with the same intensity (ball mass) will cause a similar process to take place within the vial each time a trial is performed. For the purpose of this research, it was worthwhile to analyze the dependability of the ball milling technique more thoroughly, and this analysis was performed prior to the ZnO reduction reaction experiment by performing several trials using a reaction of high exothermicity:

$$Bi_2O_3 + 2Al \rightarrow Al_2O_3 + 2Bi, \ \Delta H = -1102 \text{ kJ/mol}$$

The bismuth oxide reduction reaction was exothermic enough to cause an SHS process to take place within the vial. Six trials were performed with the same powder mass and the same milling intensity of three large balls, with the objective of reproducing a consistent time of ignition across each trial. An Omega Engineering Inc. thermocouple was attached to the vial during milling in order to record the temperature of the vial and occurrence of ignition was indicated by a sharp increase in temperature as depicted in Figure 1. The results of this preliminary investigation, depicted in Table 1, indicated the reproducibility of the ball milling technique; the small standard deviation in ignition time across the six trials was clearly indicative of a consistent and predictable process taking place within the vial and we can reasonably conclude from this data that the technique should be as dependable for a set amount of a different substance.

Continuing with the ZnO investigation, after the milling cycle was completed, the powder was removed from the vial and pressed using a Carver Laboratory hydraulic press at a pressure of eleven metric tons. Samples were then placed in heat-resistant ceramic boats (Coors Ceramic Company) and placed in a Lindberg digital tube furnace for annealing in an argon gas flow. Up to three samples at a time were exposed to each heat treatment cycle.

Analysis of the milled and annealed samples focused on several properties which were indicative of the completeness of the reaction. Surface morphology of samples was analyzed using Goucher College's QScope Atomic Force Microscope; however, after performing many trials and noting the properties shared by the most successful samples the completeness of the reaction could be judged using a National DC2-155 Digital optical microscope or naked eye observation. The most accurate method of determining the chemical composition of each sample

involved analysis using the Broker AXS diffractometer in collaboration with Dr. Raj Kolagani at Towson University. This way, the presence of each expected compound (Zn, ZnO, Al, Al_2O_3) was detected and used to indicate whether the sample had completely or partially reacted (Figures 3 & 4).

The experimental process that we performed was a systematic approach involving observation of the effects of changing a particular variable while holding others constant over several trials. This approach allowed us to determine which variables were most important in causing a complete reaction to take place within the sample. The three main variables studied were milling time, annealing time, and annealing temperature. Successive trials were performed in order to minimize each of these variables while still producing a reacted sample.

Results and Discussion

This investigation was carried out using a systematic approach designed to resolve the role of key experimental parameters involved in catalyzing the desired reaction in the sample. Parameters tested were milling time, annealing time, and annealing temperature. The expectation was that milling of the sample for a sufficient period of time would allow for the minimization of the other variables of interest – that is, significant reductions in the temperature and length of the heat treatment. These reductions are desirable because they reflect the overall usefulness of the ball milling technique in the production of Zn from ZnO: waste reduction, increased efficiency and reduced cost. The results are depicted in Table 2, with the first five trials delineated from the rest because of the difference in milling intensity: these trials used three large balls and two medium balls for milling, while the rest of the trials were performed using two large balls and three medium balls in order to increase the mechanical energy transferred in each collision.

The samples which exhibited signs that a complete reaction had taken place were those milled for at least forty-five minutes and annealed for four hours at 425°C. As shown in Table 2, these optimal parameters were determined by holding one variable constant while testing several values of a different variable. More focus was placed on determining the interdependent relationship between milling time and annealing temperature than on determining a lower bound for the annealing time, although the samples which were annealed for less than four hours were at most only partly reacted.

The first set of trials processed samples with a milling time of 10, 20, and 30 minutes at an annealing temperature of 400°C. Analysis of these samples determined that a complete reaction had not taken place. In addition to these three trials, control trials were performed in order to confirm the relationship between the milling process and the annealing process; that is, that the latter complements the former in inducing a complete reaction in the sample. One control was a sample milled for sixty minutes with no subsequent heat treatment, and the other was a sample that was annealed for four hours at 400°C but did not undergo ball milling. Neither of these samples showed even slight signs that a reaction had taken place. This is because the reaction of ZnO with Al is not exothermic enough to trigger SHS during the milling process, so while some isolated reactions may take place the reaction does not propagate throughout the vial. Additional heat treatment is needed to trigger the SHS process. The reader may question, at this point, why ball milling followed by annealing causes the sample to react but annealing without milling is not sufficient, or why the ball milling and annealing processes could not be performed in reverse order. The answer has to do with the effects of the ball milling process itself. As described in earlier sections, the ball milling process causes lattice defects in the crystal structure

of the ZnO molecules. These areas, where the chemical bonds are broken, become "active sites" that facilitate the process of solid state diffusion between molecules. The solid state diffusion process causes the reaction to take place, and the additional heat treatment ensures that the SHS process will occur, by which the heat released in each localized reaction induces a reaction in neighboring regions. Without the active sites formed during the milling process, thermal dissociation of ZnO requires a much higher temperature. The formation of active sites within the crystal structure of the ZnO molecules allows the SHS process to occur at much lower temperatures – in this experiment, as low as 425°C.

Subsequent trials were performed at 425°C and a new range of milling times. The most successfully reacted samples analyzed came from this group, in which an optimal value for milling time was also established: samples milled for at least 45 minutes or up to 60 minutes had the most complete reactions. Lower milling times produced partly reacted samples while milling samples for longer than 60 minutes did not cause a noticeable increase in the completeness of the reaction.

After annealing, the samples were analyzed to determine the completeness of the reaction. This analysis was performed using x-ray diffraction, which indicated the presence of both the reactants and products within the sample (Figures 3 & 4). After performing several trials and noting which conditions allowed for the most complete reactions to take place, however, preliminary indicators of reaction completeness could be determined using naked-eye observation of the sample or an optical microscope. In samples where a reaction had taken place, the zinc was easily noticeable in the form of silver wiry strands or droplets on the surface of the sample. Samples that did not undergo a complete reaction remained dark greyish black with little or no indication that zinc was present.

As a result of this investigation, an optimal milling time and annealing temperature were established – 60 minutes of milling at 425°C produced samples with the most complete reactions. The explanation for these results lies in the combined microscopic effects of the ball milling and annealing processes. The idea is that in order to extract Zn from ZnO, chemical bonds must be broken requiring high temperatures. Ball milling causes small defects in the lattice structure of ZnO and Al molecules, allowing for the oxide reduction reaction to take place in small, localized regions during the milling process. In this way, trace amounts of Zn are present at these active sites after ball milling is completed and before annealing is performed. During heat treatment, once the melting point of Zn – 419.58°C – is reached, this small amount of Zn melts and soon afterwards reaches phase equilibrium with ZnO at 419.6°C[3]. At this point, an unknown reaction involving energy exchange occurs between the ZnO and melted Zn that causes SHS to occur during annealing. The equilibrium temperature of 419.6°C agrees closely with the temperature at which we observed the most successful reactions, 425°C. Future research can be done which examines the relevant phase shifts in greater detail to determine how exactly the SHS process is initiated by the energy exchange between ZnO and liquid Zn.

Conclusions

This investigation has demonstrated the consistency and dependability of the ball milling technique as a method of materials synthesis as well as its usefulness, when combined with moderate heat treatment, in producing pure Zn from ZnO via an oxide reduction reaction. Using x-ray diffraction analysis as well as naked-eye and optical microscope observations, analysis showed a dependent relationship between milling time, annealing temperature, and annealing

time in causing the sample to react fully during annealing. This method is an inexpensive, less time consuming and less wasteful alternative to Zn mining or chemical methods of Zn production. Further investigations can more closely hone in on optimum milling and annealing time, in order to make the process even more efficient.

References

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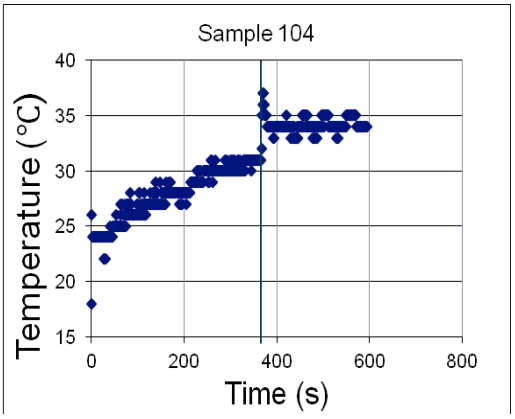

Figure 1: Temperature vs. time for one trial in the Bi_2O_3 investigation. Ignition occurs at 367 seconds.

Sample #	Duration (s)	Ignition time (s)
102	684	336
103	582	333
104	594	367
105	615	305
106	615	355
107	615	354
Mean ignition time	342 ± 22 sec	

Table 1: Results for the Bi_2O_3 investigation

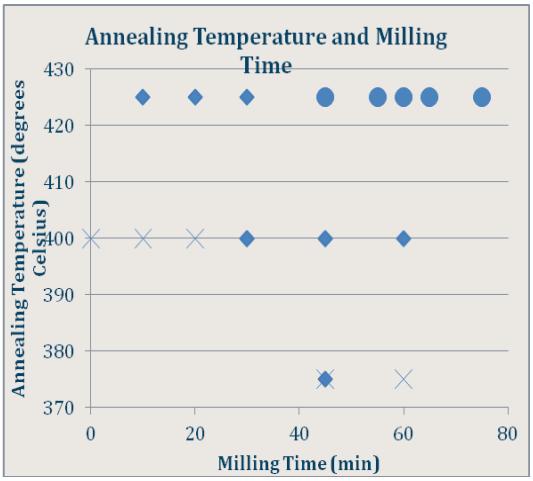

Figure 2: Completeness of reactions: a cross indicates no reaction, diamond partly reacted, circle full reaction

Sample #	Milling time (min)	Annealing time (hrs)	Annealing Temp. (°C)
8	0	4	400
9	10	4	400
10	20	4	400
11	30	4	400
12	60	0	~
16	30	4	425
17	20	4	425
18	45	4	425
19	60	4	425
20	75	4	425
21	10	4	425
22	55	4	425
23	65	4	425
24	75	4	425
25	30	4	400
26	45	4	400
27	60	4	400
28	45	1	400
29	45	1	375
30	45	2	375
31	60	4	375

Table 2: Results for the ZnO investigation. The shaded rows represent a different milling intensity.

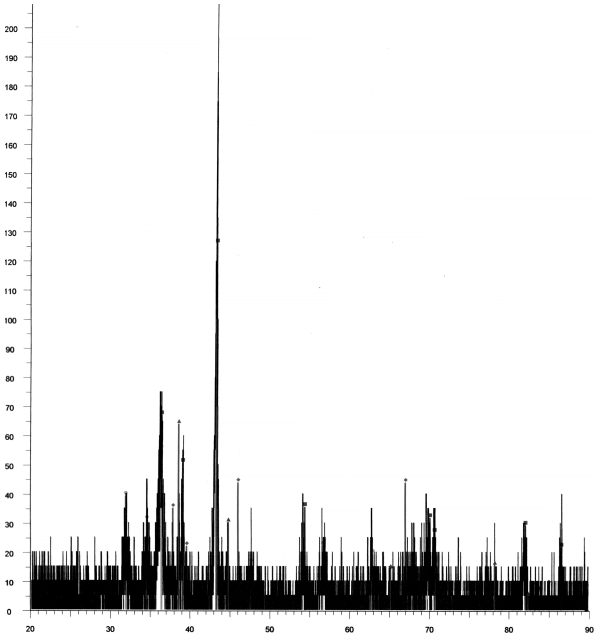

Figure 3: XRD data for a fully reacted sample. A high-intensity Zn peak is present.

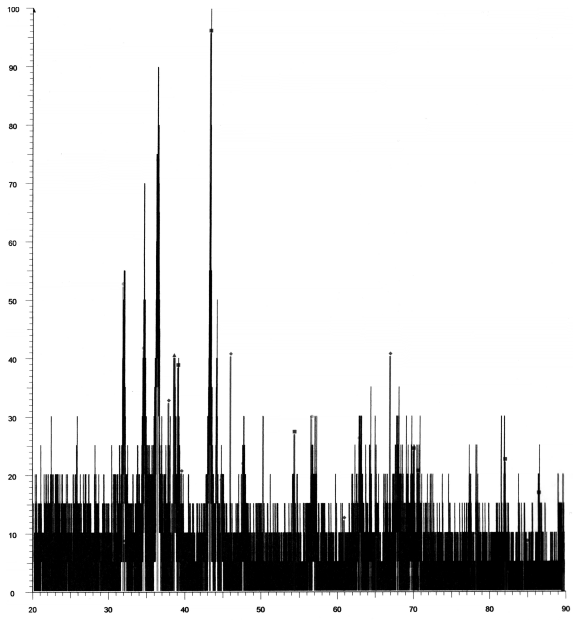

Figure 4: XRD data for a partly reacted sample. The peaks for Zn and ZnO are almost the same.