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Nano-Composites and Mechanical Alloying Via the Ball Milling Technique

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Abstract

The ball milling technique has been utilized to produce nano-composites and to ascertain the fundamental parameters of the mechanochemical reaction and the mechanical alloying process. This is an innovative method of material synthesis and metallic coating that, compared to the current methods, is very cost-effective and environmentally friendly, although it has not been thoroughly analyzed. There are some general understandings of mechanical alloying, founded on the basic thermodynamics of the reaction, that have been widely accepted. These include heat energy generated by both the collisions between steel balls and the walls of the container and also between the balls themselves, heat transfer by the walls of the container, and heat absorbed by the layer of powder caught between the colliding surfaces. There are many fundamental parameters that require further study. Some parameters that have been investigated here include time of ignition or time of mechanochemical reaction; temperature change; and change of ignition time with respect to mass and number of steel balls, as well as with respect to powder mass. These theoretical parameters have been investigated and confirmed through experimental data. Knowledge of the fundamental parameters in turn helps the understanding of the ball milling process.

Keywords: Mechanical alloying, ball milling, nano-composites

1. Introduction

This work has been done at the condensed matter physics lab in the physics department of Goucher College. The intention was to investigate the process of mechanochemical reaction and to establish some of the parameters of the mechanical alloying that occurs during the ball milling process. This process involves placing reactant powders in the reinforced steel vial along with several steel balls and using a mixer to shake the vial. This shaking imparts kinetic energy to the individual balls within the walls of the vial. As these balls collide with each other, their kinetic energy is used to reduce the particle size of the powder caught between the colliding surfaces. As the milling time increases, the particle size decreases to the point that there are lattice defects in the molecular structure of the powder [1]. These lattice defects are called active sites where solid state diffusion between exothermic reactant particles takes place and releases thermal energy that creates large microscopic temperature changes [1,2]. Overall, however, the temperature change is very slow initially and remains relatively constant until ignition. During this process of creating lattice defects, the powder starts to coat the balls and the walls of the vial. Once this layer propagates through the vial to a certain thickness, the powder ignites and goes through the well-known process of Self-propagating Heat Synthesis (SHS) [3-5]. This ignition is an easily recorded and reproducible event that is used to ascertain certain fundamental parameters of the ball milling, as shown in Figure 1.

Although there is no complete analytical solution to the innovative method of ball milling, certain applications have already been successfully developed. It has been shown that ball milling can create metallic coating such as chromium on aluminum substrates to vastly increase micro-hardness and reduce

oxidation [6,7]. It has also been shown that using ball milling has produced nano-composites [8]. Ball milling can also be used to produce alloys, which are ultimately more useful than individual elements because composite alloys are more homogenous than metals and are less corrosive, and have higher melting points and hardness. The ball milling technique is more environmentally safe than the current method of chemical synthesis, producing far less chemical waste. Mechanical alloying can also be very easily scaled up to the tonnage proportion and is far more cost effective than chemical synthesis [9,10].

2. Materials and Methods

Ball milling was employed to impart mechanical energy to the exothermic reaction of $3\text{NiO} + 5\text{Al} \rightarrow 3\text{NiAl} + \text{Al}_2\text{O}_3$, with $\Delta H = 242 \text{ KJ/mol}$, using a SPEX 8000 mixer mill. Steel balls of different sizes obtained from Small Parts, Inc. were used and designated as such: L ($1/2''$ diameter and 8.25g); M ($3/8''$ and 3.48g); S ($1/4''$ and 1.02g); and XS ($3/16''$ and 0.44g). A cylindrical, round-ended hardened steel vial with inner diameter of $1\ 1/2''$ and an inner height of $2\ 1/4''$ was used. The mixer and vial were both made by SPEX-Centriprep. NiO powder at 99% purity and Al powder at 99.5% purity were obtained from Alfa Aesar. An Argon atmosphere glove-box was used when adding the powders to the vial so that no external oxygen or other contaminants from the air would interfere with the reaction. A thermocouple was attached to one of the SPEX 8000 machines and a QuickLog data acquisition program was used to read and record the temperature of the vial. Several different experiments were carried out to gain a sense of the fundamentals of ball milling; a more thorough explanation of the experiments will follow in the next section. In the first trials the mass of the powder was held constant, while the number, and more directly the mass, of the balls was altered, in the hopes of achieving a direct correlation between ball mass and ignition time based on the laws of thermodynamics. The change in temperature was also recorded during these trials, with the expectation that the ΔT would stay constant with respect to the mass of the balls. To establish accurate error bars, one of the trials was repeated numerous times. The error bars then became one standard deviation above and below. After these relationships were established, the mass of the balls was held constant while the mass of the powder was altered, with the expectation that there would be a logarithmic relationship between the powder mass and ignition time, based on earlier findings in literature [5,11]. It was also expected that ΔT would now have a direct relationship with the powder mass rather than stay constant. A final experiment was done, keeping the mass of the powder and the mass of the balls constant, to see how the number of balls altered the ignition time.

Following the experiments at the Physics Department of Goucher College, several samples were taken to the Physics Department at Towson University. X-ray diffraction was performed on our samples using a Bruker Axs diffractometer. Sherrer's equation was then manipulated to obtain the particle size of our samples.

3. Results and Discussion

In order to understand the fundamentals of ball milling, it was necessary to perform experiments under controlled conditions with controllable variables. The ignition of the powder under SHS is a controllable and reproducible event, and as such was a good way to track the events in the vial while in the SPEX 8000. It was expected that if the powder mass was held constant, ignition time would be directly related to ball mass. With the caveat that velocity is relatively constant since the number of balls is small, as the mass of the balls is increased, kinetic energy is likewise increased.

As the kinetic energy of the system is increased, the activation time necessary for reaction is decreased. As the ball mill is running, the particle size is constantly getting smaller and smaller. There is a point at which if the size of the particle becomes any smaller, then lattice defects occur, creating an active site. Solid state diffusion occurs at these active sites, releasing incredible heat at the microscopic level and forming products of the reaction. If there is enough material in the area of the active site, the heat will propagate through the entire vial, creating an ignition that can be easily recorded. This process is well known in literature and is referred to as SHS, or Self-propagating Heat Synthesis. SHS requires a powder layer to form before ignition can take place because the powder layer is essential for local diffusion to propagate the heat. The powder layer increases exponentially with respect to powder mass. As the number of balls is increased, kinetic energy is increased linearly. The powder should then be reduced to active sites

in a linear fashion, and therefore the time necessary for ignition should be reduced linearly. Our experimental data indicates this linear behavior as shown in Figure 2.

The next property that was established was the relationship between ΔT and the number of balls. It was expected that there would be no relationship between ΔT and the number of balls since activation energy is defined as 242 KJ/mol of the reactant powders. Indeed, ΔT stayed relatively constant as the number of balls was changed, as shown with the zero-slope average line in Figure 3. This is because the powder mass was held constant, and so even though the time for ignition was decreased as the number of balls was increased, the same energy was released by the powder during ignition.

Next, the relationship between powder mass and ignition time was observed. The kinetic energy of the system was held constant, and the mass of the powder was altered. It was expected that the ignition time would have a logarithmic relationship with the powder mass. In earlier work published by our group and elsewhere, it has been shown that the powder layer grows exponentially with respect to the powder mass. Therefore, as the powder mass was increased, the powder layer necessary for SHS was growing at an exponential rate with respect to time. The time versus powder mass should then follow a logarithmic relationship. This relationship is demonstrated by our data as shown in Figure 4. In looking at Figure 4, the ignition of 0 seconds means that no ignition took place; in fact at 0.5 grams of powder, no ignition was recorded, while at 1 gram, an ignition at 265 seconds was recorded, signifying that there is a minimum powder mass necessary for ignition with the kinetic energy that was supplied.

For the reason explained above, ΔT was expected to have a direct relationship with powder mass. As the powder mass is increased linearly, the energy given off during SHS should also increase linearly. This is precisely what our data indicates as shown in Figure 5.

For a final experiment, the mass of the powder and the mass of the balls were held constant and the size and number of balls were changed to see how this would effect the time necessary for ignition. As expected, by keeping the mass of the balls constant and changing the size, the number of balls increased pretty rapidly. This should also affect the terminal velocity of the individual balls. As the number of balls is increased, the mean free path between any consecutive collisions should be diminished, which will reduce the terminal velocity. The reduction in terminal velocity in turn will reduce the kinetic energy and is expected to increase the time for ignition. Therefore it is expected that when smaller and smaller balls are used to keep the mass constant, the time for ignition should increase. Our data clearly indicates such a relationship as shown in Figure 6.

We have also investigated the production of nano-composites as a useful application of the ball milling technique. In order for ball milling to be useful in producing nano-composites, it is necessary to ascertain if nanometer-sized particles are indeed produced. One way to estimate the particle size of a powder is through x-ray diffraction. X-ray diffraction is also an excellent tool to identify what elements or compounds are present in the powder that is the result of ball milling [12]. Literature shows that when a powder ignites through SHS, the chemical reaction takes place instantaneously. X-ray diffraction of the powders that we produced confirms this, as shown in Figures 7 and 8. Figure 7 is an x-ray diffraction taken on a sample of NiO and Al that did not ignite, while Figure 8 is an x-ray diffraction taken on a sample of NiO and Al that did ignite. It is clear that after ignition there are NiAl and Al_2O_3 products, while before ignition there are only the original NiO and Al reactants.

By using Scherrer's equation, particle size can be estimated using data gained through x-ray diffraction [13]. However, more detailed analysis could be done by going one step further and including the crystalline micro-strain in addition to Scherrer's equation. We have measured the domain size of our NiAl composite using the Williamson-Hall technique which incorporates the crystalline micro-strain and instrumental broadening [14]. Two profiles were used for this calculation: the Cauchy profile, equation (1), and the Gaussian profile, equation (2).

$$B_{size+strain} = B_{obs} - B_{inst} \quad (1)$$

$$B_{size+strain}^2 = B_{obs}^2 - B_{inst}^2 \quad (2)$$

In both of these profiles $B_{size} = \frac{K\lambda}{L \cos \theta_B}$ and $B_{strain} = \eta \tan \theta$.

K is a constant approximately equal to 0.9, λ is the $Cu - K_{\alpha 1}$ wavelength of the Bruker-Axs XRD instrument, L is the particle size, θ_B is half of the Bragg angle, and η is the micro-strain. B_{inst} has been estimated to be a maximum of 0.1° [14]. By using the Cauchy profile with values from two peaks, it is possible to solve the system of equations for L and η . Our calculations show that the maximum particle size using the Cauchy profile is 110 nm, but while using the Gaussian profile is 51 nm, and the micro-strain using the Cauchy profile is 0.00406 rad, but while using the Gaussian profile is 0.00248 rad.

4. Conclusion

These experiments have lent more understanding to the process of mechanical alloying via the ball milling process. Several relationships have been determined that will allow more precise predictions about mechanochemical reactions in the future. A useful metallic nano-composite has also been produced using this technique. Other systems, specifically the system of $SiO_2 + Al$, have been considered for future investigation. The system of $SiO_2 + Al$ merits further investigation because of the possibility of producing pure silicon as a result of a mechanochemical reaction. Further understanding of estimation of particle size should also be investigated.

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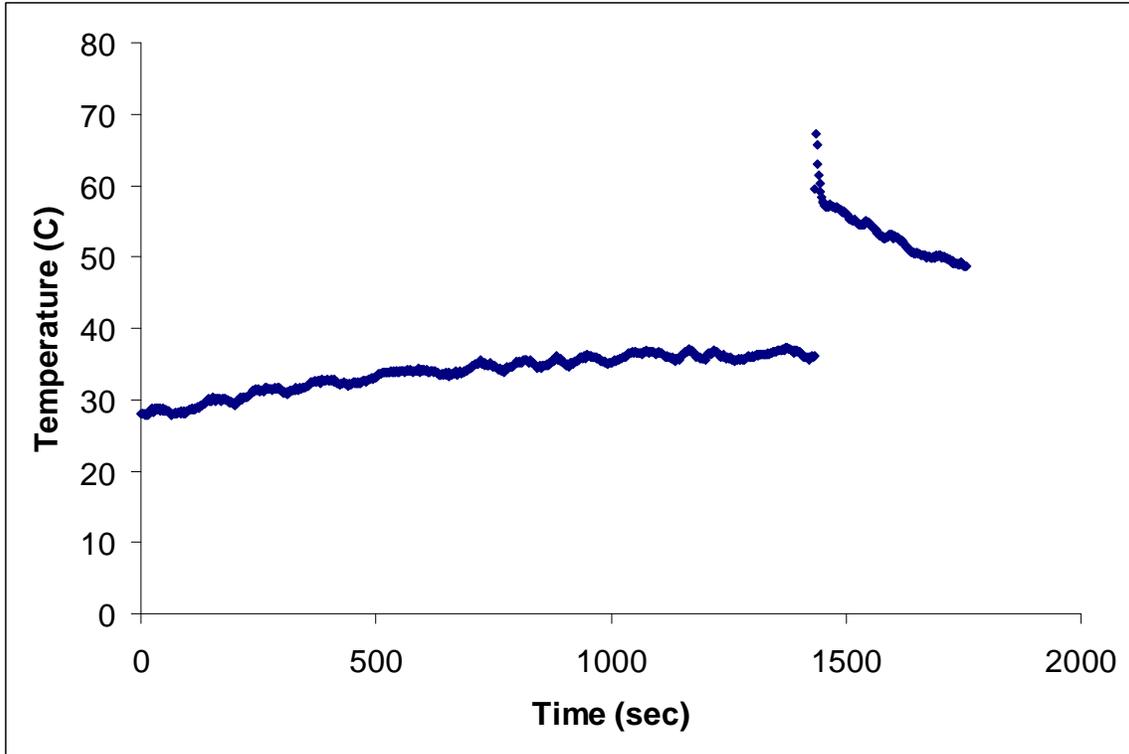


Figure 1: Ignition graph obtained from Quicklog, showing ΔT and ignition time.

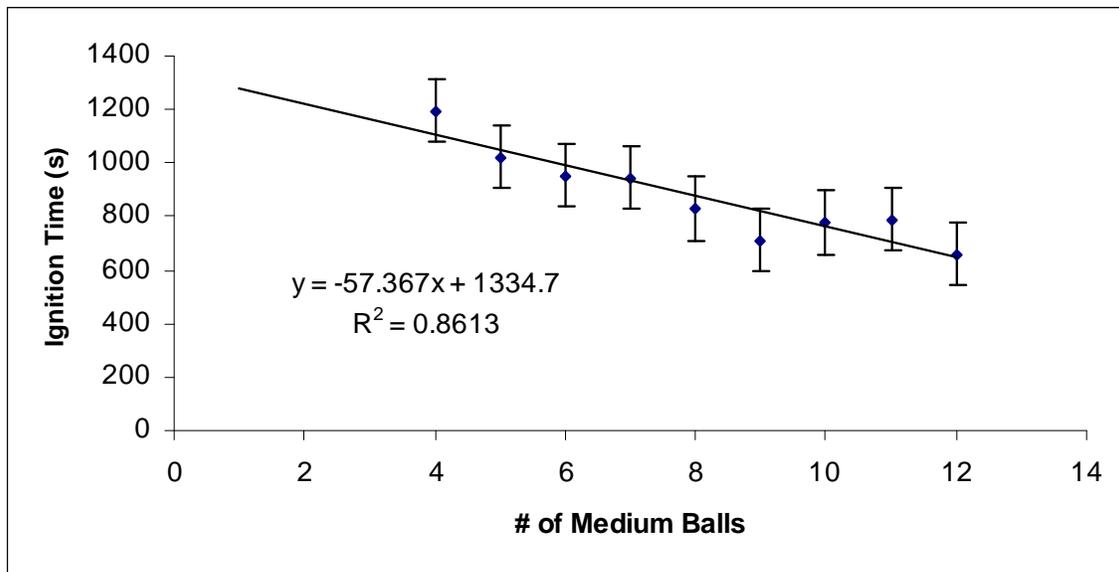


Figure 2: Ignition time vs. the number of medium balls with a constant 3g powder mass.

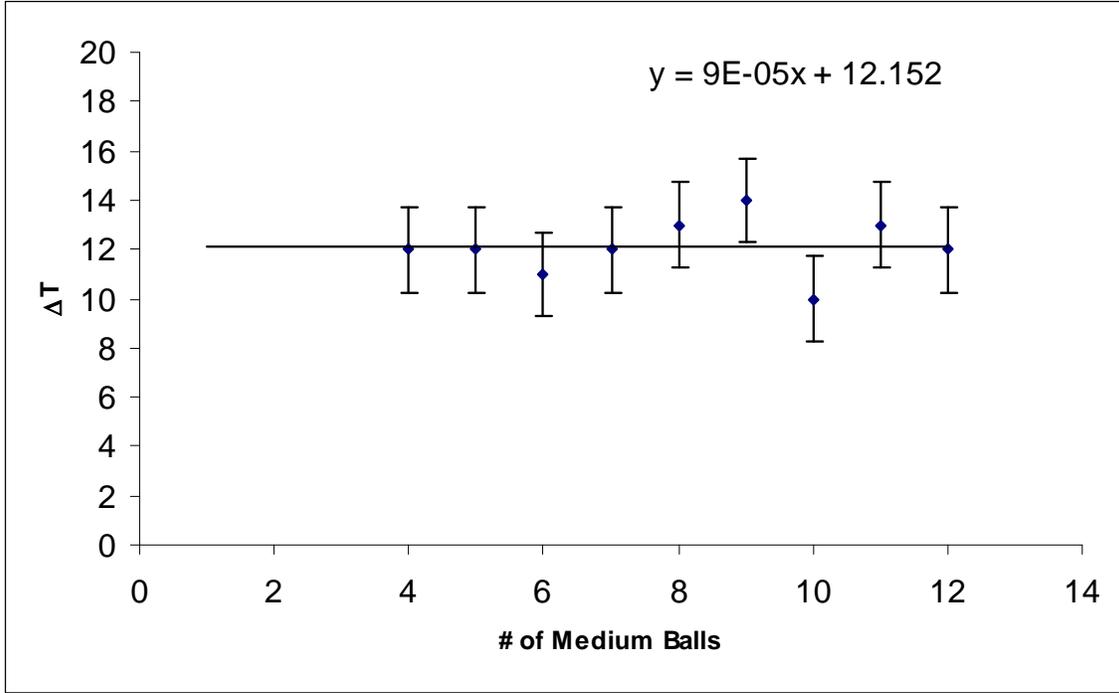


Figure 3: ΔT vs. the number of medium balls with a constant 3g powder mass.

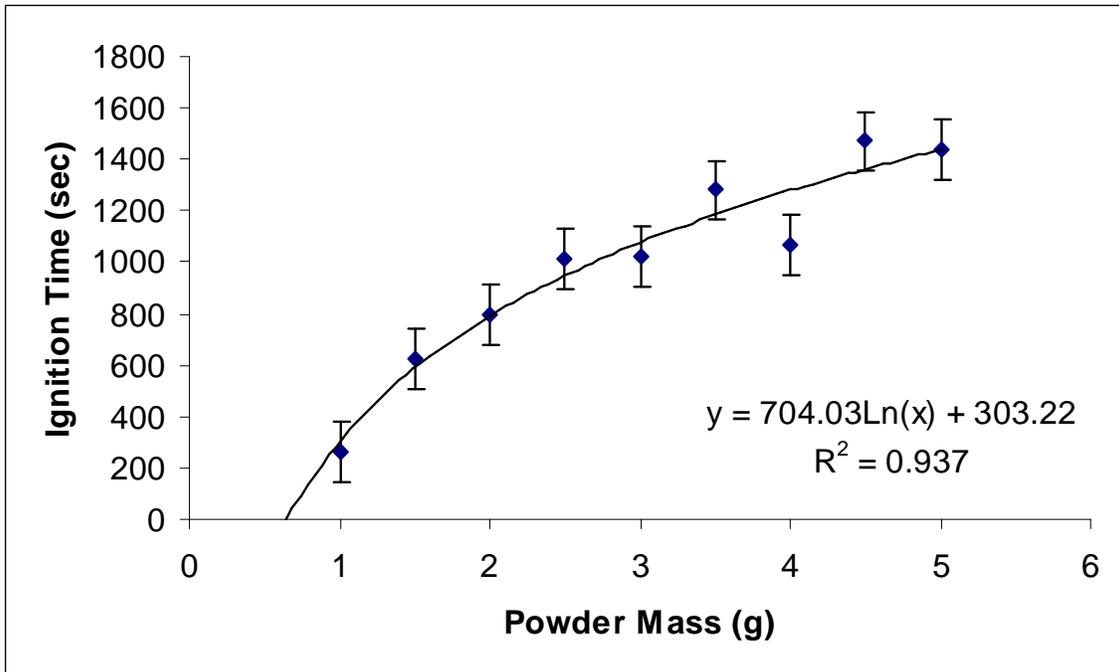


Figure 4: Powder mass vs. ignition time with constant 3g powder mass and 5M balls.

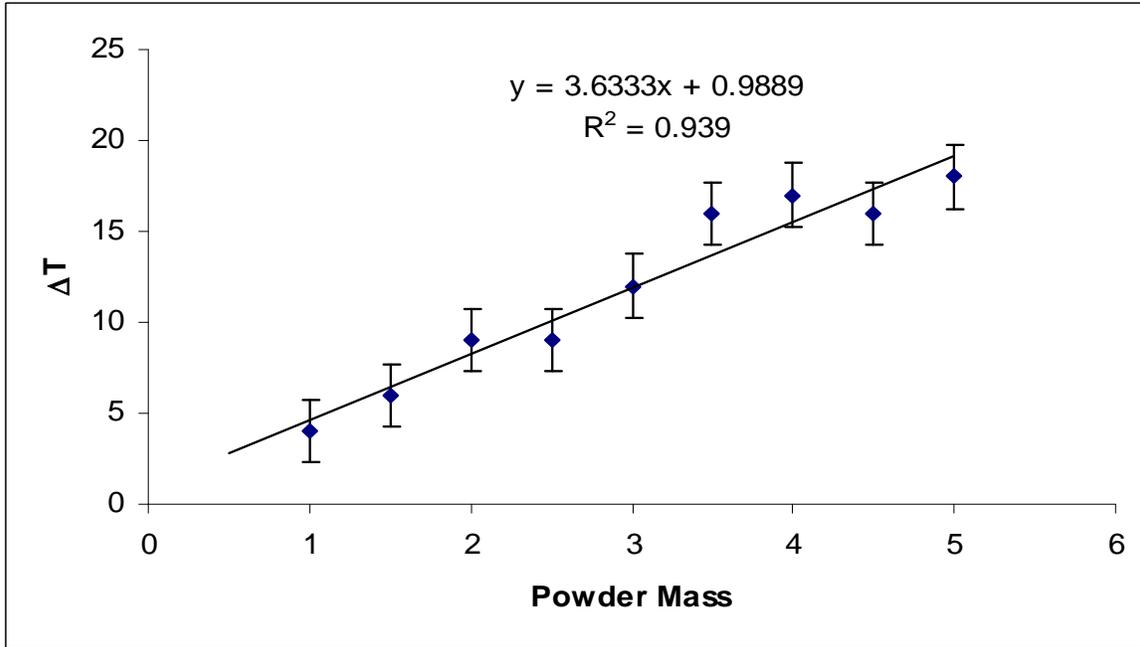


Figure 5: Powder mass vs. ΔT with constant 3g powder mass and 5M balls.

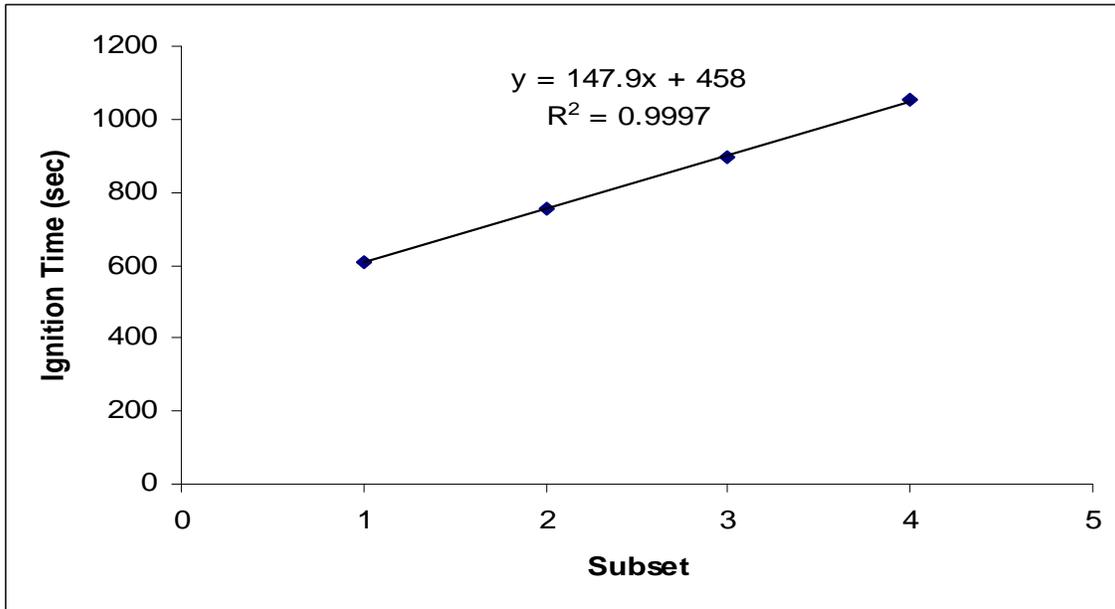


Figure 6: Number of Balls vs. ignition time with constant 3g powder mass. Subset 1 contains 5L Balls with a mass of 40.584g, Subset 2 contains 20M and 1XS Ball with a mass of 40.531g, Subset 3 contains 40S and 1 XXS Ball with a mass of 40.527g, and Subset 4 contains 94 XS, 1 XXS, and 1 XXXS Ball with a mass of 40.633g.

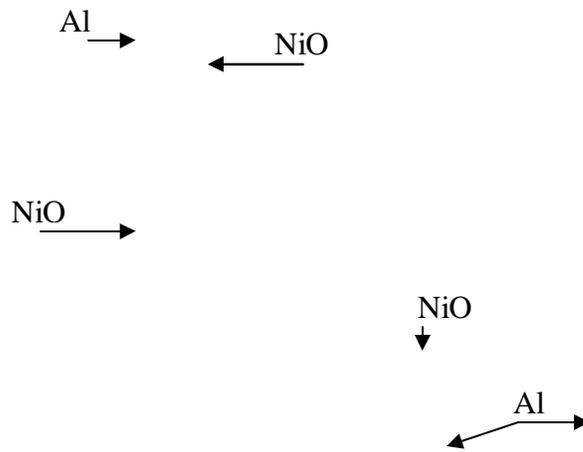


Figure 7: XRD of unreacted NiO and Al.

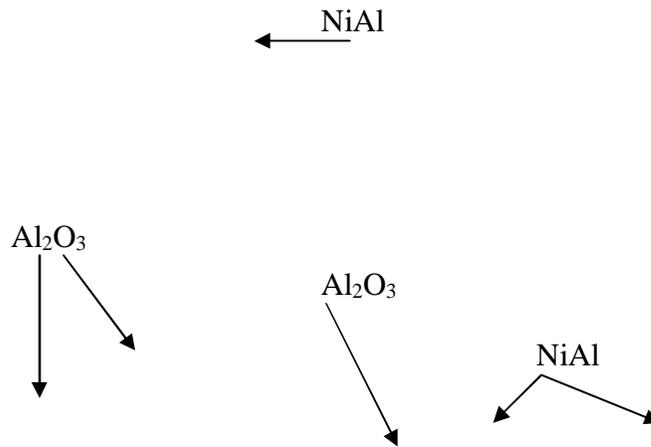


Figure 8: XRD of reacted NiO and Al