

University of Nevada, Reno

**Mechanochemistry of Titanium Dioxide**

A thesis submitted in partial fulfillment of the  
requirements for the degree of Master of Science in  
Metallurgical Engineering

by

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THE GRADUATE SCHOOL

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## Abstract

Mechanochemical processing of solids is a relatively new application of using mechanical energy (i.e., impact) to affect a chemical change. The process has been successfully used to alter natural minerals into different crystalline materials. Thermodynamic models can be a good way to predict the probability of two substances forming new compounds through mechanical impacting. A study was initiated to look into the mechanical alloying of titanium dioxide with various reactants and conditions in a dry ball mill. Using free energy models to look at reaction spontaneity, aluminum, bismuth(III) oxide, and barium peroxide were selected as candidates to react with the  $\text{TiO}_2$ . Each was individually added to a ball mill with titanium dioxide and allowed to roll for up to 24-hours to investigate the possibility of recovering metals or spinels from the blend. X-ray diffraction (XRD) was used to evaluate the effectiveness of the reactions by comparing the XRD scans of the feed material with the “reacted” blends to see if new crystalline structures could be made.

The resulting XRD scans showed that the peaks for the resulting product had almost identical peaks with the head scans, suggesting no reactions took place. Although thermodynamic models predicted spontaneous reactions, little effect was noted when

TiO<sub>2</sub> was impacted with Al, Bi<sub>2</sub>O<sub>3</sub> or BaO<sub>2</sub>. The blends were impacted in air, and in a vacuum to no avail. The absence of a reaction could be due to a number of factors. The most likely is that the mechanical energy was not sufficient to overcome the activation energy required to complete the reaction.

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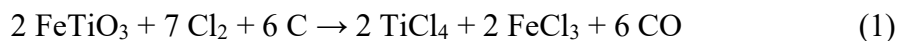


## Introduction

Titanium is a highly sought-after material typically alloyed with readily available materials such as aluminum, iron, and molybdenum to produce alloys that are lightweight and strong. The application for titanium alloys can be found in many aspects of modern civilization such as the automotive, aerospace, and medical industries.

Titanium has been refined starting as early as in the 1910s using the Hunter process, where an intermediate compound of titanium is reduced in a high temperature environment using elemental sodium. This gave way to further developments which resulted in the more economical Kroll process in the 1940s. Lower working temperatures and alternative reducing agents (i.e., magnesium) lead to the Kroll process being the leading method to be used in titanium production even today (Turner et al.).

Due to its affinity with oxygen in the atmosphere, the batch production of titanium starts out with the reduction of a mixture of ilmenite ( $\text{FeTiO}_3$ ) and carbon in chlorine gas at  $900\text{ }^\circ\text{C}$  as shown in Equation (1).



This will produce titanium tetrachloride ( $\text{TiCl}_4$ ), used in the Kroll process, where the  $\text{TiCl}_4$  will be subject to a reduction using molten magnesium at 1100 °C in a vacuum, as shown in Equation (2).



In more recent years, the FCC Cambridge process has been developed and has shown to be a more efficient method in titanium production as compared to the more conventional Kroll process. The FCC Cambridge process employs an electrochemical reduction using a carbon anode and titanium oxide cathode immersed in a molten  $\text{CaCl}_2$  bath (Fenn et al.). This process is likened to the Hall-Heurrott process in which aluminum is electrowon from  $\text{Al}_2\text{O}_3$  dissolved in cryolite ( $\text{Na}_3\text{AlF}_6$ ) solutions. (Newton 1952)

The various methods and techniques that are used to produce titanium can be boiled down to pyrometallurgical and electrochemical processes. The production of titanium from its readily available ores, namely ilmenite ( $\text{FeTiO}_3$ ) and rutile ( $\text{TiO}_2$ ), is very costly due to the nature of the process and resources needed to reduce the metal. This cost is often passed down to alloy producers and consumers of the various products that require titanium.

Mechanical alloying (MA) is the solid-state process where the energies within a ball mill are involved in the repeated fracturing and rewelding of particles. Mechanical alloying, is

“capable of producing true alloys from elements that are not either easy to form by conventional means or sometimes even impossible to prepare, e.g., elements which are immiscible under equilibrium conditions” (Suryanarayana 151).

In comminution theory, the main goal is to break down solid material through fractures induced by tensile and compressive stresses. This would lead to material that is more responsive to other processes that is to be done on the material. As Wills describes, “When fracture does occur, some of the stored energy is transformed into free surface energy, which is the potential energy of atoms at the newly produced surfaces. Due to this increase in surface energy, newly formed surfaces are often more chemically active, being more amenable to the action of flotation reagents, for example” (Wills 114). The empirical Bond model, as shown in Equation (3) is an energy-based comminution model that is still widely used today.

$$W = 10 * Wi \left( \frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) \quad (3)$$

Where W is the energy in kilowatt hours per short ton,  $W_i$  is the work index in kilowatt hours per short ton,  $P_{80}$  is the size where 80% of the product will pass through a screen at in micrometers, and  $F_{80}$  is the size where 80% of the feed will pass through a screen, also in micrometers.

The driving force that governs mechanical alloying has largely been contributed to two models revolving around enthalpy and the free energy of the systems. As Suryanarayana notes, “a substantial amount of enthalpy can be stored in nanocrystalline materials due to the large grain boundary area. It was also suggested that the enhanced solid solubility might be due to the high dislocation density produced during milling” (Suryanarayana 57). This enthalpy-based model suggests that the increased number of possible dislocation densities could further help store enthalpy between the interface of the components. On the other hand, Suryanarayana writes, “... the chemical enthalpy associated with the interface between the elemental components can enhance the free energy of a composite above that of the related solid solution thus providing a driving force for alloying in systems with a positive free energy of mixing” (Suryanarayana 57). As compared to the former, this model suggests that chemical composites may form before any alloying happens. It should be noted that Suryanarayana was modelling “alloying” in which two metal powders are “blended” by impact energy.

Mechanochemistry, is a branch of chemistry that involves the possible synthesis of materials from two different compounds through the aid of mechanical energy. This branch of chemistry has seen a steady increase in application within the mineral processing industry and is proven to be useful as described by Baláž when he wrote that, “chemical reactions and phase transformations take place because of the application of mechanical energy. As a consequence, reactions which normally require high temperature will occur at low temperature without any externally applied heat. Mechanochemical processing belongs among the routes which can effectively control and regulate the

course of solid-state reactions” (Baláž 5101). Baláž has shown that mechanochemistry can be used to develop processes that aid in the extraction of metals such as gold, silver, and copper from sulfide ores.

In particular, mechanochemical processing has proven to be effective when used to improve the recovery of gold and silver from sulfidic minerals. Sulfidic ores tend to cause significant problems when cyanide leaching is used to extract the precious metals from the ore. Baláž has verified that pretreatment via mechanochemical processes is “an effective tool for gold and silver extraction from refractory sulphidic ores” (Baláž 5097).

While enthalpy does provide more information regarding stabilities of reactants and products in a reaction, the free energy of a reaction is used to determine how spontaneous any reaction would be. In deciding whether a reaction will happen, the free energy of a reaction should be considered firsthand to decide if a reaction is favorable. While there is more work done on mechanical alloying with a focus on enthalpy, there is not enough work done on mechanical alloying, with regards to the thermodynamics, to agree on what drives the reaction within the mills.

With these considerations, the purpose for this study was to examine whether titanium dioxide can be mechanically alloyed with suitable reactants to produce alternate forms of titanium, perhaps forms that are more easily transformed into metallic titanium. Using free energies as a guide to determine if a reactant is suitable for spontaneous reactions to occur, the present study investigated possible reactions suitable for  $\text{TiO}_2$  processing.

## Considerations

In thermodynamics, free energy indicates the spontaneity of a reaction. As shown in Fig. 1, a  $\Delta G^\circ < 0$  would mean that the reaction in question should react to completion due to its free energy. In other words, if the free energies of the reactants (at 1 in the figure) are higher than the free energies of the products (at 3 in the figure) the reaction should be favorable to proceed spontaneously. That is, if sufficient “activation energy” is supplied (shown at point 2 in the figure).

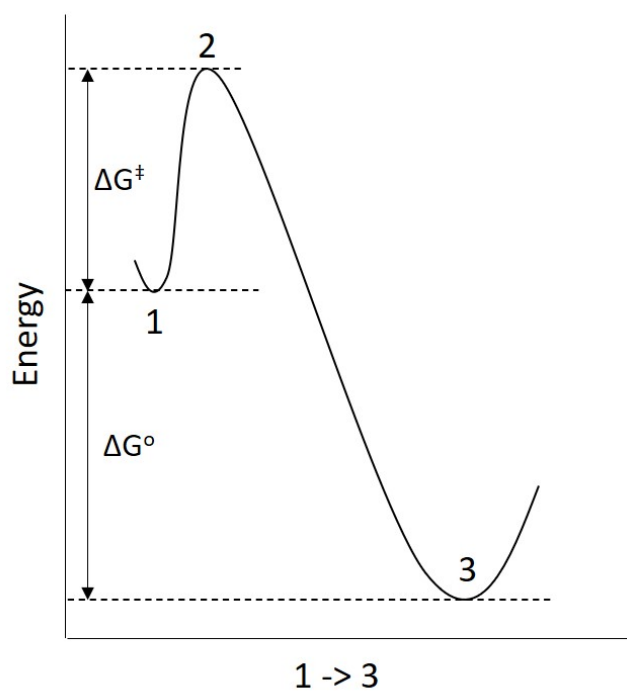


Fig. 3 Free Energy of a Reaction

Prior work done on mechanical alloying seem to indicate that while considering free energies, there has been indications that change does occur after a combination of samples are impacted.

Through personal communication with Dr. Carl Nesbitt, prior work was done to see if there were ways to use mechanical alloying to help liberate copper from chalcopyrite ( $\text{CuFeS}_2$ ). Chalcopyrite is a mineral well-known for its refractory nature in leaching processes. Dr. Nesbitt's team was investigating if mechanical alloying could be used to alter the minerals to improve copper recovery by leaching. Several promising reactants were identified and entered into the HSC chemistry program (HSC Chemistry 7.1) to retrieve the relevant thermodynamic data. Sodium peroxide was determined to be the best candidate as it offered a relatively large negative free energy ( $\Delta G$ ) throughout a range of temperatures as shown in the Table (1). It is also a "strong oxidant" which would suggest a complete conversion of the sulfide component of the mineral. Table I shows the various thermodynamic values for one chemical reaction between chalcopyrite and sodium peroxide. As seen in the table, the  $\Delta G$  appears to be quite favorable for this reaction.

<b><math>1.5\text{O}_2(\text{g}) + \text{CuFeS}_2 + \text{Na}_2\text{O}_2 = \text{CuS} + \text{FeO} + \text{Na}_2\text{SO}_4</math></b>					
<b>T, °C</b>	<b><math>\Delta H</math>, kcal</b>	<b><math>\Delta S</math>, cal/K</b>	<b><math>\Delta G</math>, kcal</b>	<b>K</b>	<b>Log(K)</b>
0	-241.3	-60.4	-224.8	7.214E+179	179.858
10	-241.3	-60.4	-224.2	1.096E+173	173.040
20	-241.3	-60.5	-223.6	4.857E+166	166.686

30	-241.3	-60.5	-223.0	5.647E+160	160.752
40	-241.3	-60.5	-222.4	1.570E+155	155.196
50	-241.3	-60.6	-221.7	9.635E+149	149.984
60	-241.3	-60.6	-221.1	1.214E+145	145.084
70	-241.3	-60.6	-220.5	2.953E+140	140.470
80	-241.3	-60.6	-219.9	1.310E+136	136.117
90	-241.4	-60.7	-219.3	1.009E+132	132.004
100	-241.4	-60.7	-218.7	1.291E+128	128.111

*Table 1. HSC Chemistry Data for Chalcopyrite Reaction with Sodium Peroxide*

Powder, reagent-grade sodium peroxide was added to chalcopyrite and blended in an open-air ball mill to facilitate airflow as the reaction proceeded. Under normal circumstances, a mild solution of sodium peroxide would be ineffective when trying to liberate copper from chalcopyrite. However, the X-ray diffraction (XRD) results from the impacted sample seem to indicate that the chalcopyrite has been affected by the test as shown in Figure 2. The scan of the finished sample suggests that, as compared to the head sample, there were new peaks that formed indicating a new compound was “derived” from the impacts. In the previous study with the chalcopyrite, a simple leach test was used to verify that the  $\text{CuFeS}_2$  was sufficiently altered. It was determined that less than 1% of the copper was solubilized from unaltered chalcopyrite in a 0.1M sulfuric acid solution. However, after several hours of impacting the  $\text{CuFeS}_2$  with sodium peroxide, there was as much as 60% of the copper recovered from the same leaching solution. This work has not been published, but is in preparation, as the identity of the “new products” are yet to be determined by XRD analyses.



(Coupled TwoTheta/Theta)

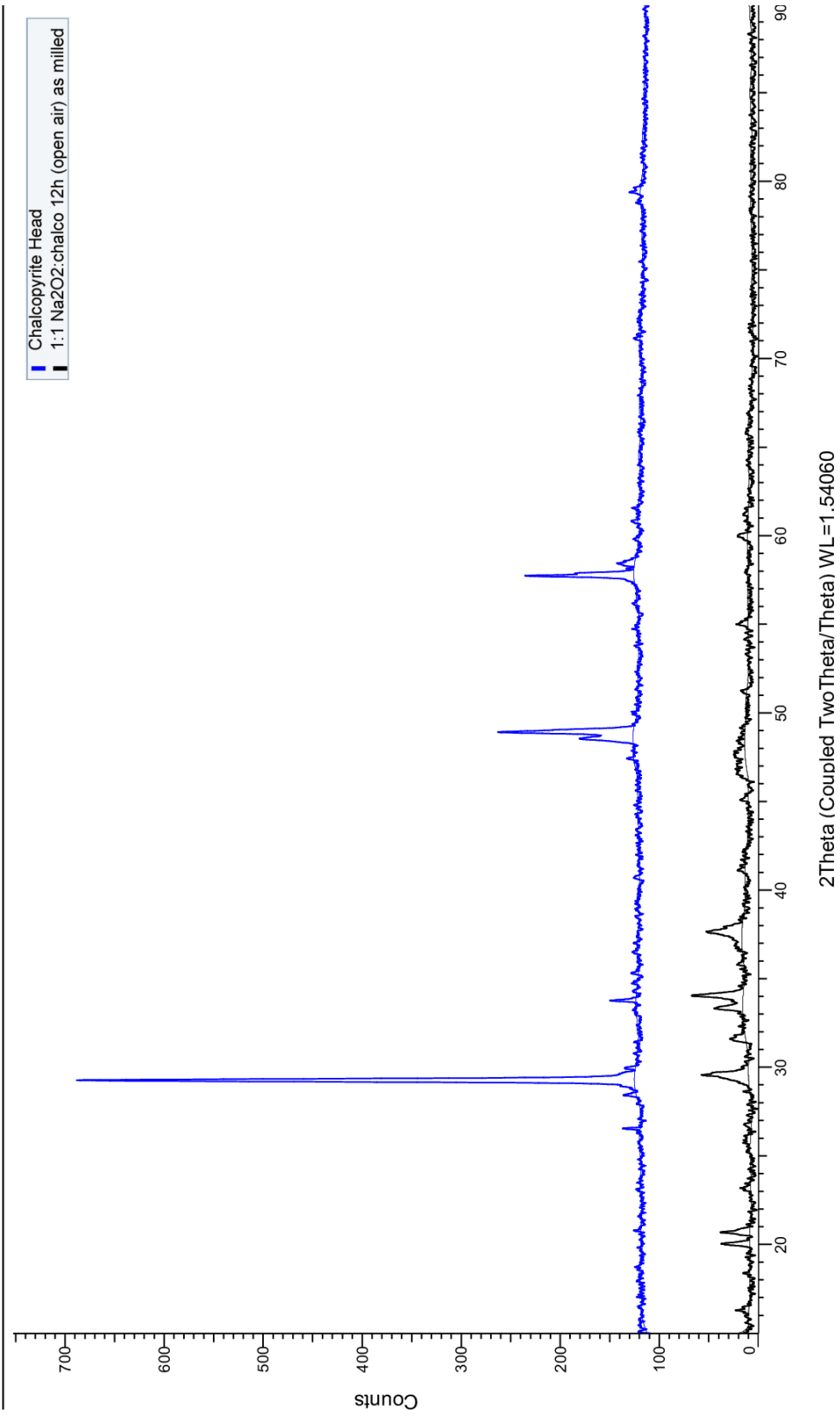


Fig. 4 Chalcopyrite and Sodium Peroxide XRD Scan Compared to Head Sample

In looking for things that have favorable  $\Delta G$ , the focus was initially on reactions that might result in “reduced” titanium. Several candidate metals were put into the model, including iron, copper, calcium, sodium, zinc, etc. Of these, only sodium and calcium showed promise. However, the cost to attain powders of these for a full-scale process would be too expensive. But aluminum worked too; this led the study to focus primarily on mixing an oxidizing metal (Al) with the  $\text{TiO}_2$  to form elemental titanium ( $\text{Ti}^0$ ) and a slag ( $\text{Al}_2\text{O}_3$ ). However, as the processes were investigated, other important components were determined to be viable “final” products of titanium spinels or mixed oxides of titanium. Compounds that can be written in the form  $AB_2\phi_4$ , have a spinel structure. Typically grouped by the B cation, spinel structured compounds are generally of cubic close packed systems (Biagioni and Pasero).

Spinel have a wide range of applications in industry. An example would be magnesium aluminate spinels (MAS) as noted by Ibram. The material has been used in optically transparent applications, neutron radiation applications, and refractory applications to name a few (Ibram). There are many options when it comes to spinel production. For the commercial production of magnesium aluminate spinels, the solid-state sintering of magnesium aluminate spinels is a popular method (Ibram). There are other routes, “such as coprecipitation, spray drying, freeze drying and spray pyrolysis by which MAS can be synthesised at par low temperatures” (Ibram 66). However, these have not proved to be commercially viable.

## Equipment

The milling was performed in a ball mill with an interior diameter of 19.5 centimeters, and 17.5 centimeters in length (See Figure 3). A steel ball charge with a total mass of 1815 grams was used in each of the milling cycles. The ball charge mimicked a “seasoned” charge with a distribution of grinding media similar to that used in Bond Grindability experiments. The steel vessel containing the steel charge and reactants was placed on a milling table powered by a 3/4 horsepower motor that brings the vessel to a constant 48 rotations per minute. For each experiment, a total charge of 100-g of material was weighed in stoichiometric ratios consistent with the reactions. For example, 69 g of  $\text{TiO}_2$  and 31 g of Al were mixed in the mill (100-g total charge, but a 1.5:2 stoichiometric ratio.)

Due to the lack of available work done to determine the energy generated by the laboratory ball mill setup used, an estimate would need to be derived. A 3/4 horsepower motor running with the available drivetrain of the mill would be running at 0.075 horsepower if an estimate of 10% efficiency is to be used. The 0.075 horsepower will roughly translate to 51 kcal over an hour of mill time.

In some cases, when the evacuation of air from the vessel was deemed necessary, the lid for the vessel was swapped out for a lid that has a flow valve tapped onto it (Fig 3). Using the valve, the air was evacuated using a vacuum pump through a hose. Additional

precautions to prevent air leakage was taken through the use of a silicone rubber gasket that was applied between the lid and the shell.



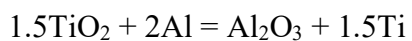
*Fig 3. Regular Mill Lid (left) and Tapped Mill Lid with Valve (Right)*

The X-Ray diffractometer used was a Bruker Phaser D2 and it was set to operate at 30 kV and 10 mA, to let the equipment run at 300W. A copper target with a K-alpha of 1.5418 Å was used in all the scans. The Bruker EVA program was used to determine the compositions of the “head” and “reacted” compounds.

## Experimental Procedure

The data collected at this phase was gathered in two main steps. First and foremost, identifying potential reagents that could displace the oxygen from titanium oxide by looking at the free energy of the reactions. These elements or compounds would then be added into a ball mill and run for a specified time. The resulting powder mixture would then be scanned using an X-Ray diffractometer.

Using data from HSC Chemistry program (HSC Chemistry 7.1) as shown in Table (2) with special considerations to possible end products, there were several reactions that could potentially work. Titanium dioxide with aluminum and iron, titanium dioxide with bismuth(III) oxide, and titanium dioxide with barium peroxide.

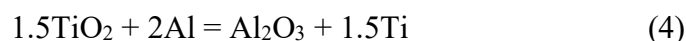


T, °C	ΔH, kcal	ΔS, cal/K	ΔG, kcal	K	Log(K)
25	-61.800	-8.356	-59.309	$3.007 \times 10^{43}$	43.478
50	-61.896	-8.666	-59.096	$9.344 \times 10^{39}$	39.971
75	-61.990	-8.944	-58.876	$9.164 \times 10^{36}$	36.962
100	-62.078	-9.189	-58.649	$2.254 \times 10^{34}$	34.353

Table 2. HSC data of Aluminum and Titanium Oxide

The reaction of titanium dioxide and aluminum in air, as shown in Equation (4) below, had a ΔG of -59.309 kcal at 25 °C. To keep the stoichiometry constant, 68.94 grams of

titanium dioxide and 31.06 grams of aluminum were added to a ball mill charged using steel balls of varying sizes. Three different runs were done for six, twelve and twenty-four hours before being extracted and scanned in the X-Ray diffractometer. Due to concerns that elemental titanium has an affinity for oxygen, a separate run with titanium dioxide and aluminum was performed in a vacuum for twenty-four hours. In the separate run, air was extracted from the vessel through a tapped lid fitted with a valve using a vacuum pump.



For the bismuth(III) oxide reaction, 79.55 grams of bismuth(III) oxide and 20.45 grams of titanium dioxide were added to a ball mill charged with appropriately sized steel balls. Air inside the cavity of the ball mill was extracted using a vacuum pump, as a precautionary step to help prevent atmospheric oxygen from reacting and contaminating the sample. An initial run time of twelve hours was decided on and the final product was extracted from the mill and scanned in the X-Ray diffractometer.

Finally, 67.952 grams of barium peroxide and 32.04 grams of titanium dioxide was measured out and added to a ball mill charged with the appropriate mix of steel balls. Like the bismuth(III) oxide sample, atmospheric air was evacuated from the mill chamber to help eliminate the possibility of contamination from external atmospheric air. The

mixture was processed in the mill for twelve hours before being extracted and scanned in the X-Ray diffractometer. Due to a slight variation in the results, a second sample with similar mass of reactants was run in the same conditions but through a longer time period of twenty-eight hours. Similarly, the second sample was scanned using an X-Ray diffractometer.

For comparison, all the head samples (i.e., unreacted solids) were scanned using the X-Ray diffractometer so that visual comparisons of the crystal structures of the materials could be made to identify any possible changes within the sample.

## Results

### Aluminum

For the three runs that had titanium dioxide and aluminum in air, the duration of each run was six, twelve and twenty-four hours. The XRD scans for each are shown in Figures (4), (5) and (6), respectively. In these graphs, the location of the peaks was almost identical to the “as received” material scans. When all three scans are combined and offset as shown in Figure (6a), it is evident that the duration of those runs had no effect on the final outcome.

Figure (7) shows the scan for the titanium dioxide and aluminum run in a vacuum. The peaks are similar to that of the runs that were done in air. Through these few runs, it is shown that with the given parameters, the atmosphere within the mill did not matter. It was estimated that the formation of  $Al_2O_3$  in a vacuum would be an indicator of some reaction in case the titanium recombined with air to form  $TiO_2$ , upon opening the mill. None was detected, however.



### Bismuth(III) Oxide

The scan of the bismuth(III) oxide and titanium dioxide run, as shown in Figure (8), has peaks that line up with the head bismuth(III) oxide sample scan. Superimposing and offsetting the head titanium dioxide and bismuth (III) oxide scan showed that while most of the peaks remained identical, some of the peaks from titanium dioxide seemed to be very suppressed or disappeared. This, however, does not give much evidence to indicate that a reaction occurred.

### Barium Peroxide

The barium peroxide and titanium dioxide sample produced the graph in Figure (9). While the resulting scan shows comparatively similar peaks, it was noted that they have slightly shifted off by a slight margin and a second run with longer run times was performed and produced a scan as shown in Figure (10). The scan showed that the longer run did not change much as to what was already shown in Figure (9). The peaks remained in the same spots without much variance, indicating that even after 28-hours of continuous impacting, no reaction occurred.

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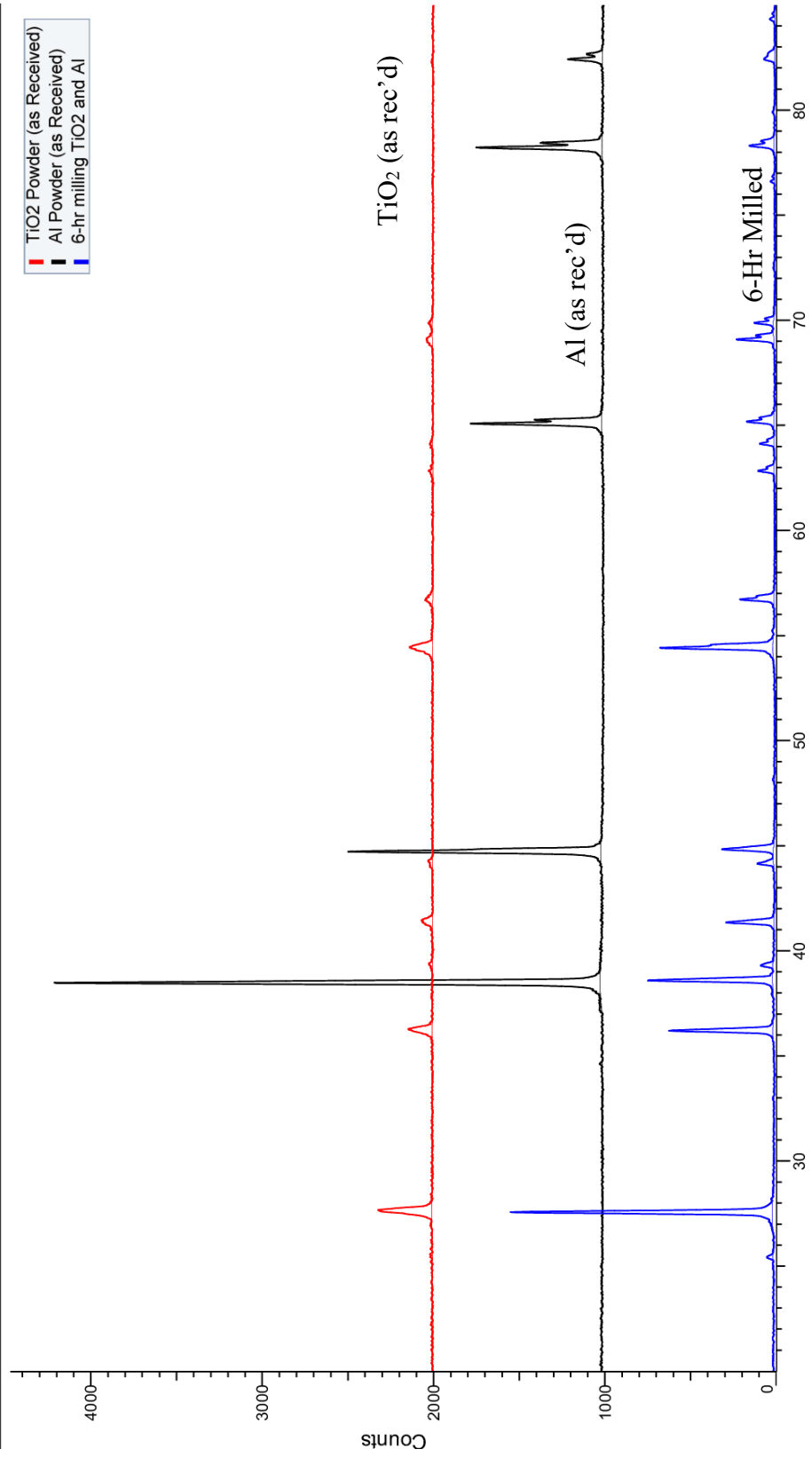


Fig. 4 XRD Scan of Titanium Dioxide and Aluminum Run (6 Hours)

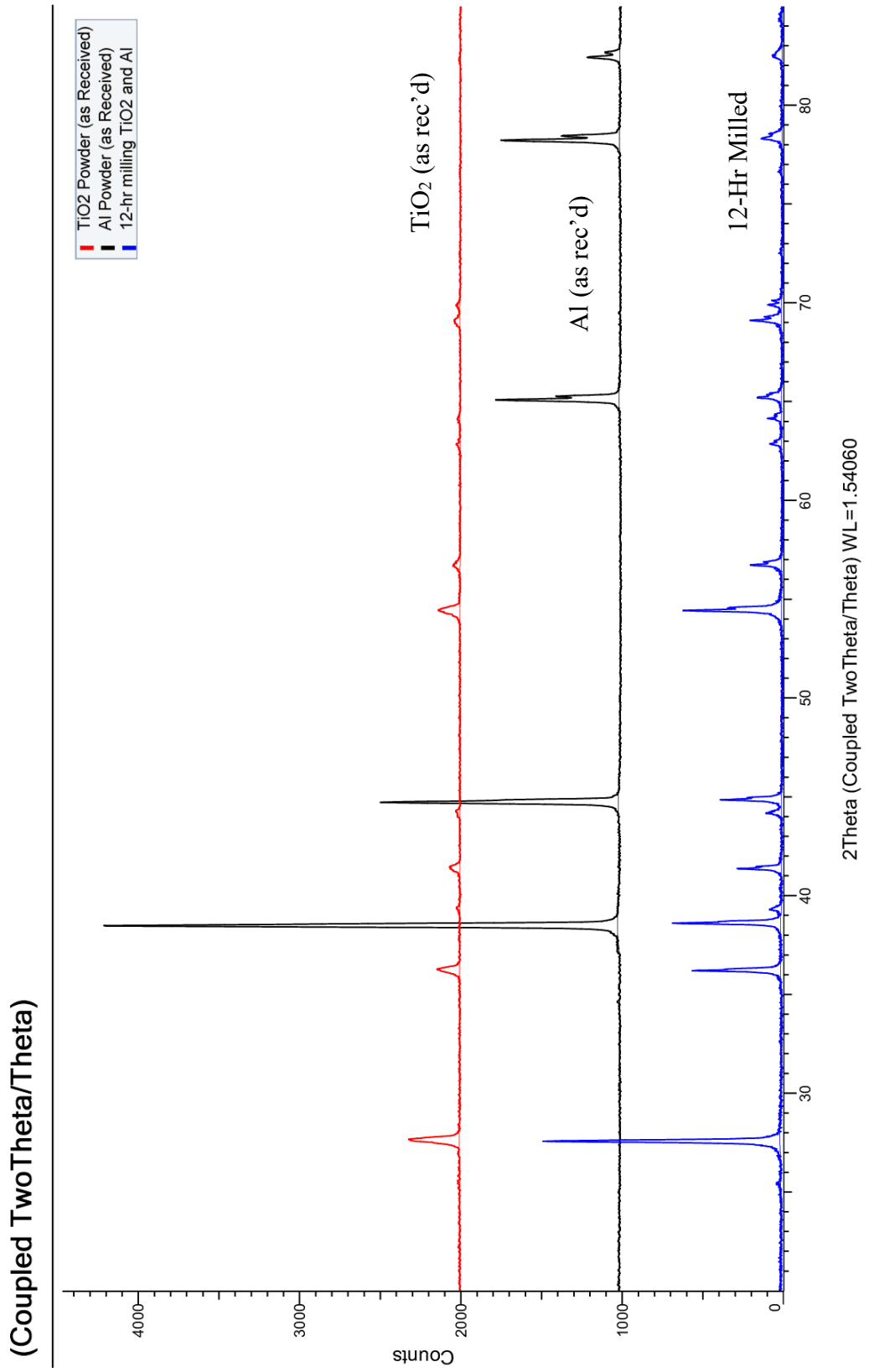


Fig. 5 XRD Scan of Titanium Dioxide and Aluminum Run (12 Hours)

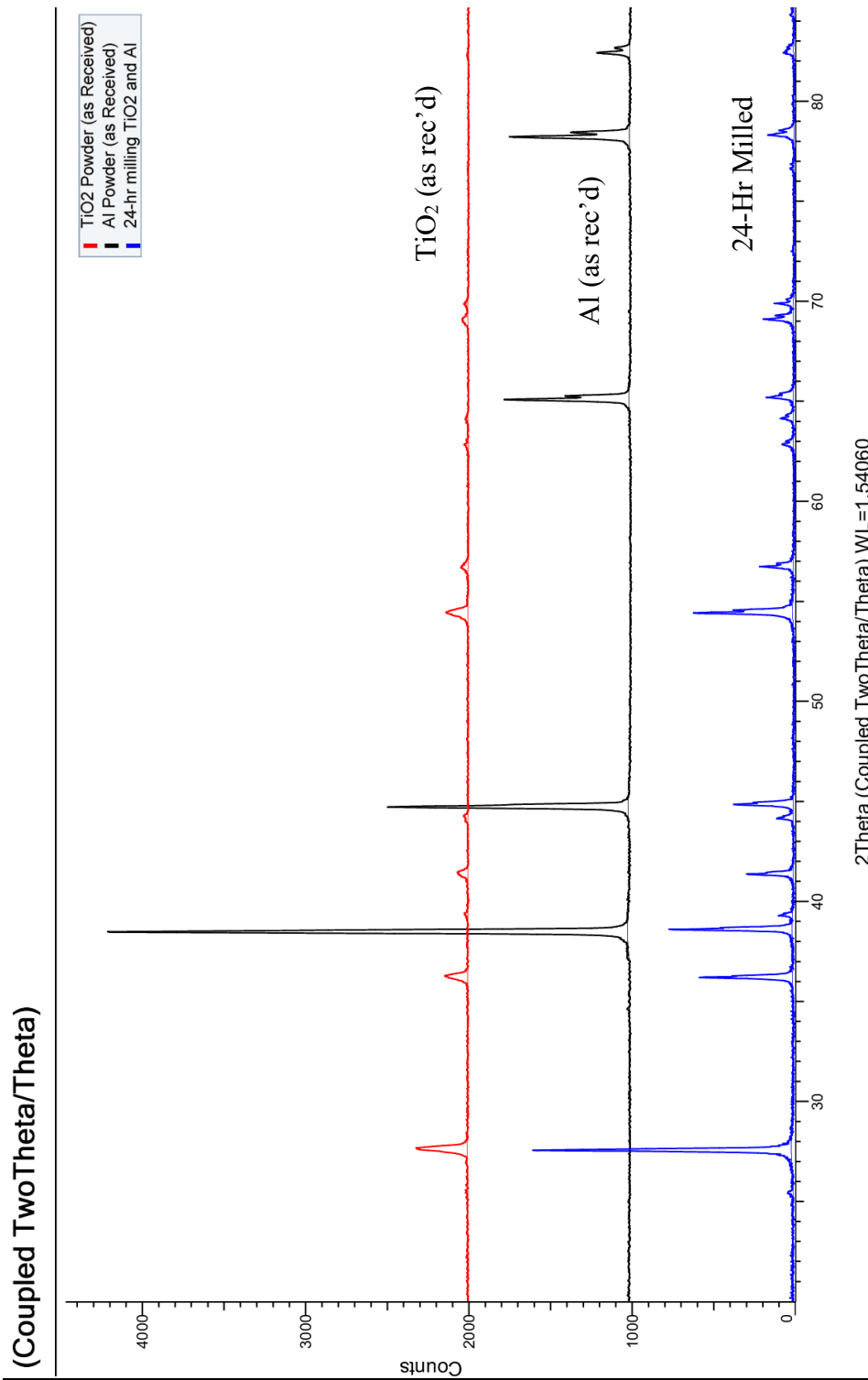


Fig. 6 XRD Scan of Titanium Dioxide and Aluminum Run (24 Hours)

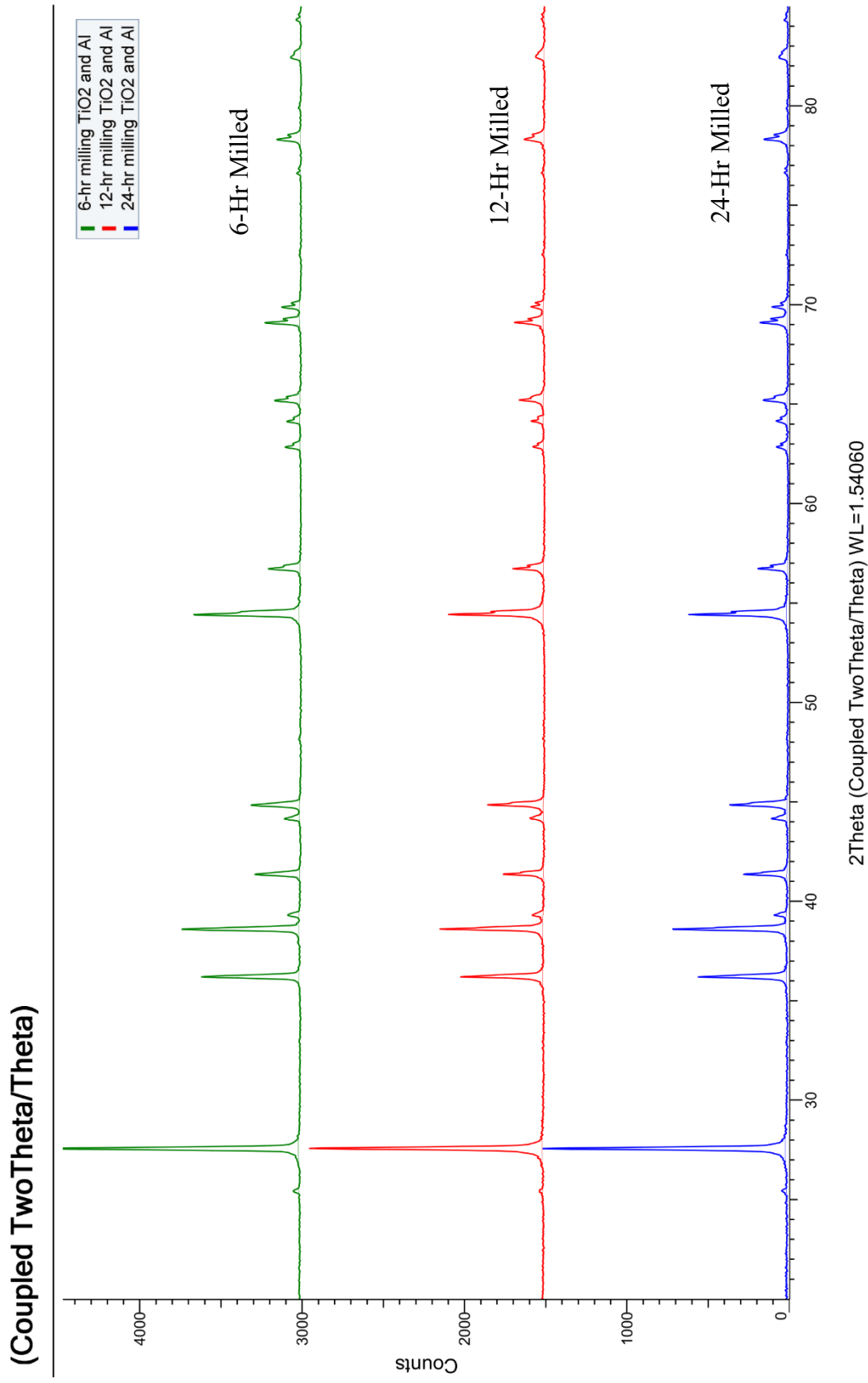


Fig. 6a All Three Al Open Air Scans (Offset)

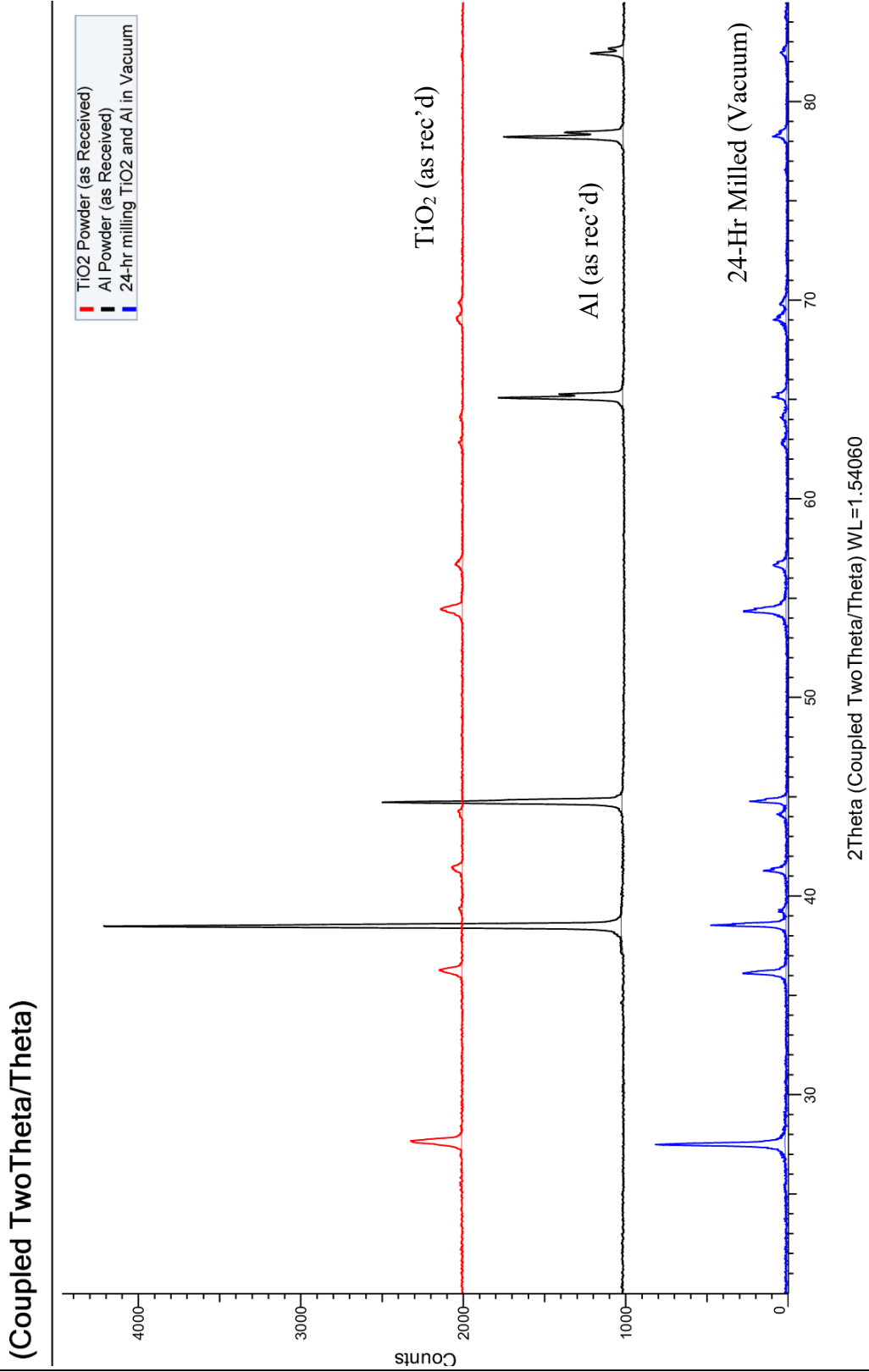


Fig. 7 XRD Scan of Titanium Dioxide and Aluminum Run in Vacuum (24 Hours)

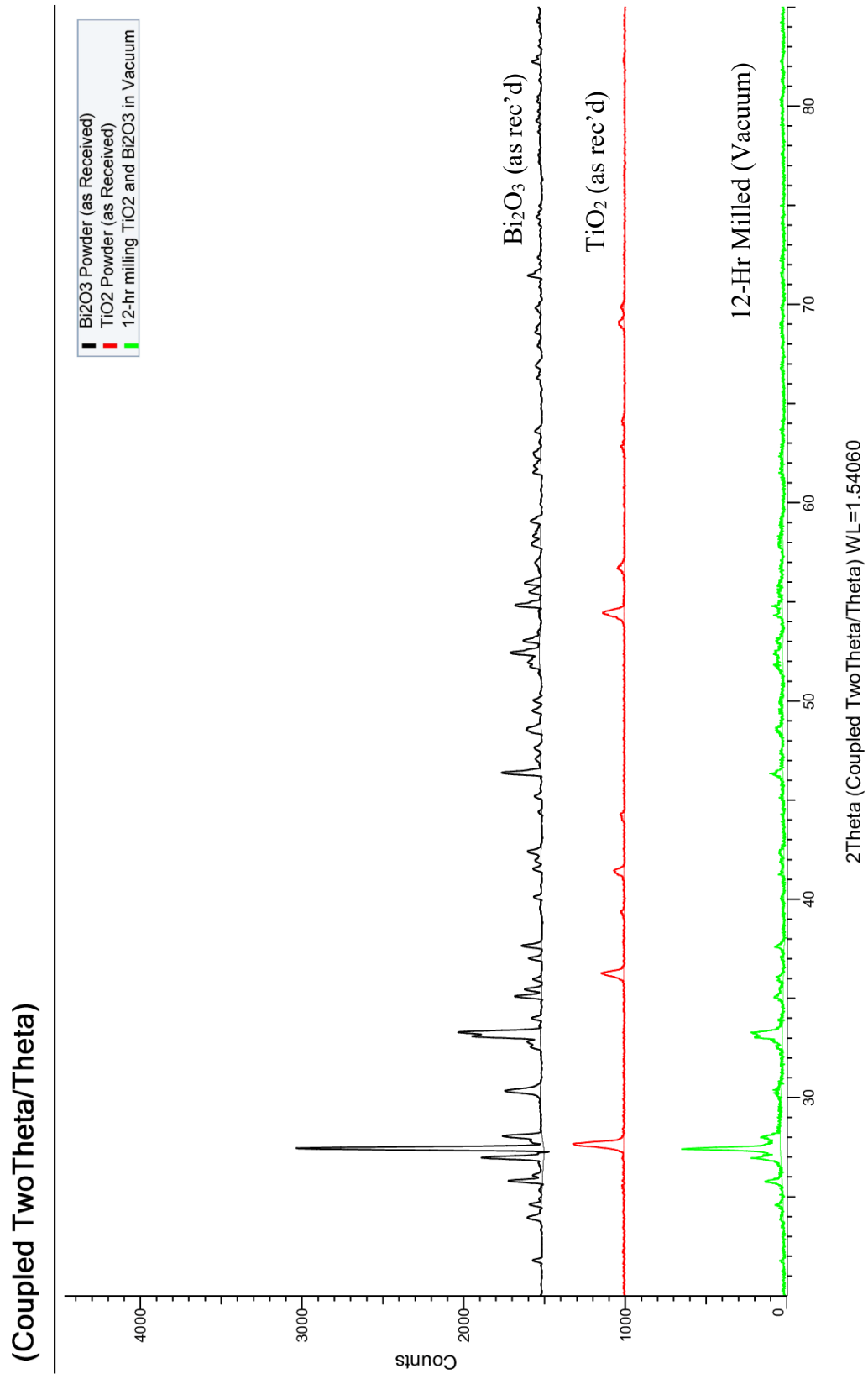


Fig. 8 XRD Scan of Bismuth(III) Oxide and Titanium Dioxide Run

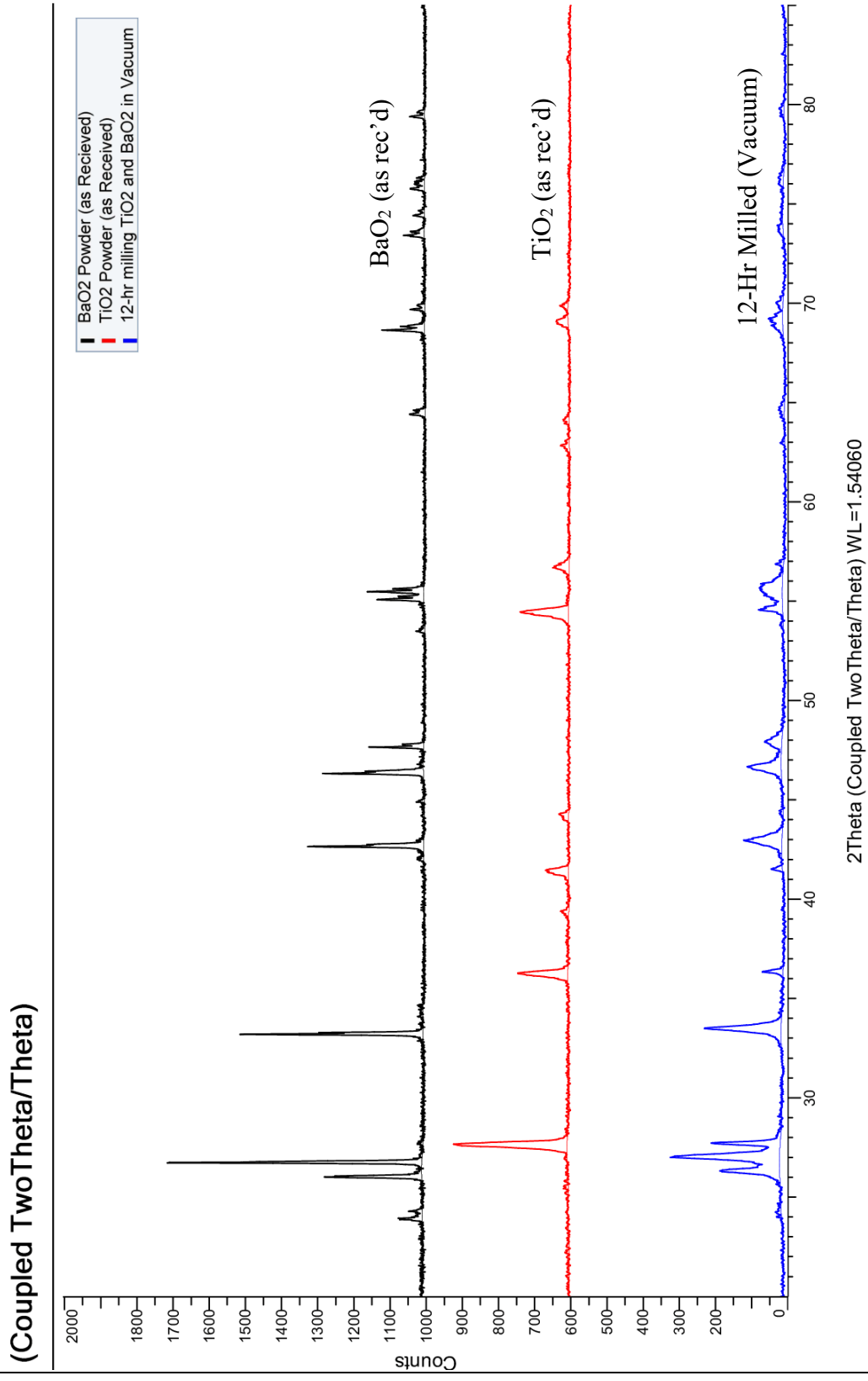


Fig. 9 XRD Scan of Titanium Dioxide and Barium Peroxide 12 Hour Run



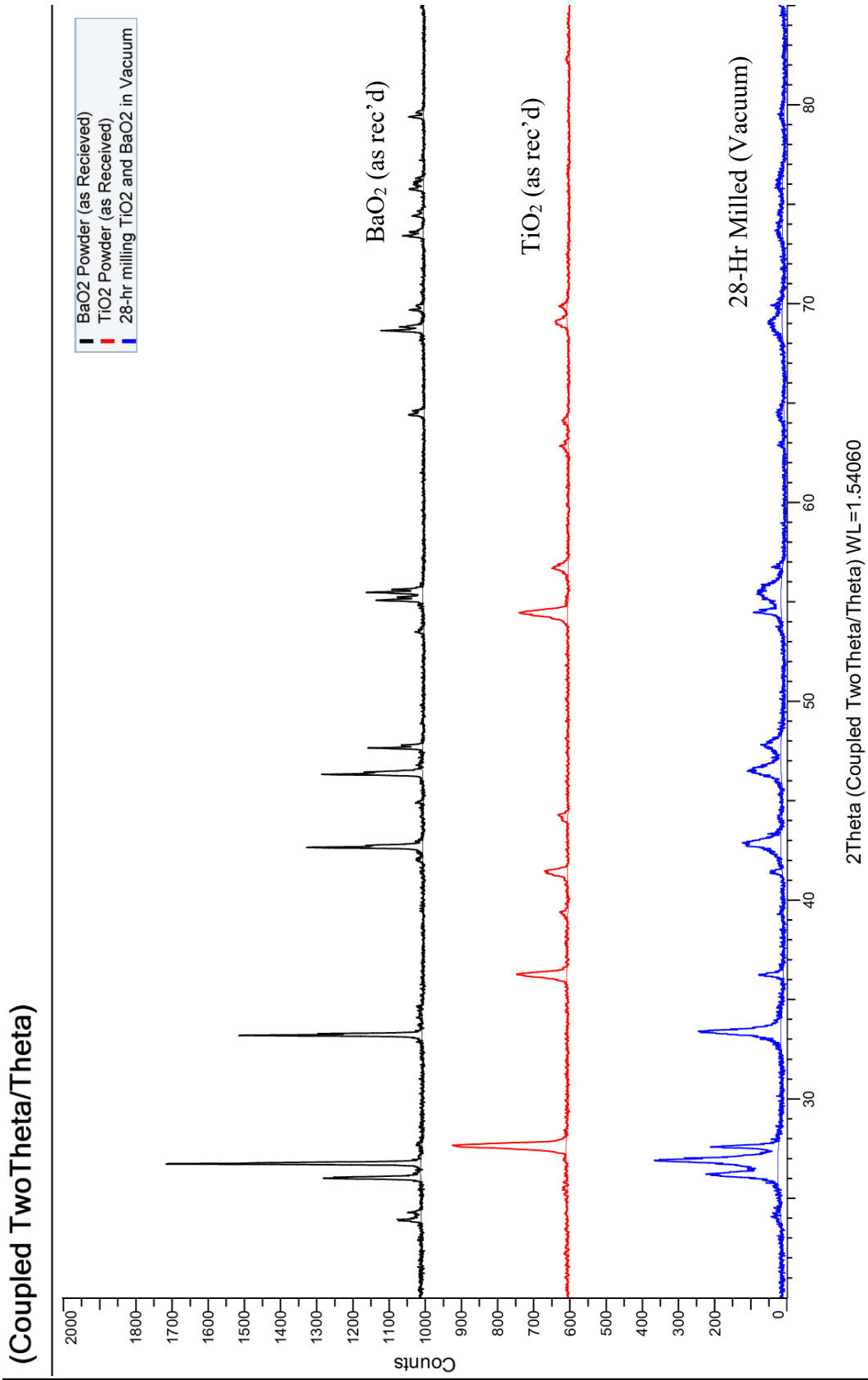


Fig. 10 XRD Scan of Titanium Dioxide and Barium Peroxide 28 Hour Run

## Discussion

The run with the aluminum shown in Figure (4) seemed to indicate that none of the original reactants changed in any way. The peaks of the original scans and the final scans were identical when imposed over one another. The  $\Delta G$ , as calculated using the HSC Chemistry program, indicated that the resulting reaction would be spontaneous, but nothing happened, and this could be due to a much higher activation energy being required. Much more impact energy may be required than what the ball mill setup used in this test could provide, thus prohibiting the progress of the reaction.

The HSC chemistry program does not contain data for either bismuth titanate or barium peroxide, so no  $\Delta G$  could be determined. However, given that the processes for these spinels are much less complicated than the process for making metallic titanium, it was thought that the  $\Delta G$  for this reaction might be favorable. The scans of the bismuth(III) oxide sample showed similar results to the aluminum and titanium dioxide tests.

Matching the peaks with the head sample did not show enough evidence of a reaction happening. This can also be said for the barium peroxide sample scan as shown in Figure 5 and 6. While a slight shift in peaks was observed, it was not enough evidence to say that a reaction did occur during both runtimes.

Another consideration is the time the reactants had in the ball mills. Mechanochemical synthesis of materials could take mere seconds to happen (Baláž et al, “Mechanochemistry of copper sulphides”), or it could require sessions of up to or more than 80 hours (Kanevskii 666). The duration of runs performed in this study ranged from 6 hours to 28 hours, there might be a possibility that the duration of the experimental runs was insufficient. However, it was considered that even if the reactions needed more time to complete, more evidence from “partial” reactions would have been evident in these shorter runs.

Future work could be done using high energy mills with tungsten carbide balls that are able to impart higher energies into these reactions to see whether the activation energy is a factor when it comes to working titanium dioxide mechanically. The duration of these reactions could also come into play and longer runtimes might be a factor to consider.

## Conclusion

While the free energies of the selected reactants showed promising results in terms of spontaneous reactions. The resulting scans of the runs determined that reactions did not occur for all the runs; the resulting X-Ray diffractometer scan had the same resulting peaks as the head scans.

The absence of a reaction could be attributed to a number of factors. One of the biggest possibilities could be insufficient energy in the ball mill to overcome the activation energy peak to start the reaction. Further work could be performed to see whether activation energies could be a contributing factor to these reactions.

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