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# The Effect of the Grinding Time on the Mechanical Activation of $MnO_2$ Ore and Tea Plant Waste Carbonization Product

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**Abstract:** In this study, pyrolusiteore ($MnO_2$) was subjected to mechanical milling with a high-energy mill with carbonized tea plant wastes and the effect of grinding time on the crystal structure of the material was investigated. The ratio of Mn/Fe was 8/1, the ratio of C/($MnO_2$ + $Fe_3O_4$) was 2 and the ratio of ball to ore was 10/1. The samples were mechanically ground at 10, 15, 20, 30, 60, 90 and 120 hours. In the processes performed on the attritor, the rotation speed of the mill shaft was determined to be 350 rpm. The results were characterized by TG-DTA, SEM and XRD analyzes. As a result of the experimental studies, it was observed that the samples subjected to mechanical grinding for 120 hours were gradually reduced due to the increasing grinding time at all the diffraction peaks when the XRD peaks were compared with the grinding times. In the thermogravimetric analysis, the sample milled for 120 hours, 50% weight loss was observed at 470 $^{o}$C, weight loss of up to 56% was observed at progressive temperatures.

**Key words:** Tea plant wastes, carbonization, mechanical grinding, pyrolusite ore.

## 1. Introduction

The manganese is found to be the most commonly used metal after iron, aluminum and copper, with being the twelfth most frequently found element in the earth's crust. It is the most important of the alloy elements used in steel construction. And 90-95% of the manganese produced in the world is used as ferromanganese or silicomanganese in the iron-steel industry. Ferromanganese is added to the steel to prevent adverse effects of sulphate. In the production of abrasion resistant steel, however, it is necessary to use it as a manganese alloy element [1, 2].

Manganese ores have been processed for many years with the use of pyrometallurgical methods. Among these methods, the carbothermal reduction method is the most important industrial method known and intensively applied in the process of manganese ores. During this process, the reduction process develops very slowly and requires high temperatures [3].

In the first model, which is presented as Magma-Plasma Model in Mechanochemistry, large amounts of energy are emitted at the contact points of the particles that collide with each other. This energy is sufficient for the formation of a specific plasmatic state characterized by the emission of electrons and photons from the portions of the solid material that have gone up to an upper energy level. The surface of the contacted particles is highly irregular and the local temperatures can exceed 10,000 $^{o}$C [4, 5]. The primary effect of mechanical activation on the mineral is disintegration. Thus, fresh, clean surfaces that have not been exposed to any effect before, resulting in semi-stable species [4, 5, 6]. (1) Vibrokinetic energy mill, (2) Planetary moving mills, (3) Centrifugal mills, (4) Eccentric vibratory mills, (5) Mixed ball mills and (6) Jet mills are used for the mechanical activation (Fig. 1) [7-13].

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The most important parameter in mechanical grinding is grinding time. The grinding time depends on the type of grinder used, the grinding speed, the ratio of the ball to the particle, and the grinding temperature [15]. If the temperature increase associated with the high diffusivity rate during milling of the metal particles in the mechanical grinding is too high, the resulting alloy will recrystallize and produce stable intermetallic phases. If the increase in temperature is small, amorphous or nanocrystalline structures are formed instead of recrystallization [15]. Mechanical activation by high-energy milling can ensure that chemical reactions that normally occur at higher temperatures occur even at room temperature. The mechanical activation process should be from 1 to 200 µm for the starting material dimensions [7, 15].

## 2. Experimental Studies

### *2.1 Material and Method*

In this study, tea plant waste supplied fromRize-ÇAYKUR, carbonization product (Table 1), magnetite ore (Table 2) supplied from Elazığ region and manganese oxide ore (Table 3) supplied from Karaman region were used.

The XRD analyses reveal that the ferrous manganese ore is in the form of pyrolusite ($MnO_2$) (Fig. 2). Manganese ore, magnetite ore and carbonized tea plant waste samples-125 µm in size were mixed at certain ratios to investigate the effect of mechanical milling on the crystal structure of material. And 250 gr of the mixture was weighed and placed in the attritor to perform mechanical milling. Mn/Fe, C/Mn, and ball/ore ratios of the mixtures in the attritor were taken as 8, 2 and 10, respectively. The samples were then subjected to mechanical milling for 10, 15, 20, 30, 60, 90 and 120 h. Stainless steel balls with a diameter of 8 mm and weighing approximately 2.04 gr/piece were used for this process. The mill shaft speed was determined at 350 rpm in the processes performed in the attritor and milling processes were carried out under dry milling conditions (Fig. 3). After the grinding, the XRD images of the samples were recorded and their DTA/TG graphs were obtained.

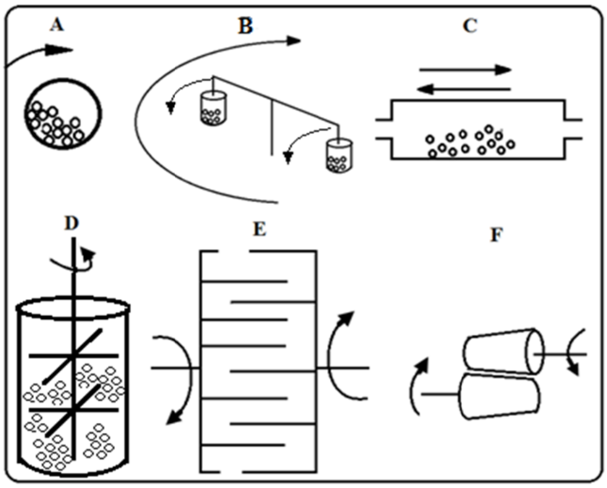


**Fig. 1 Mill types used for mechanical activation, A-Ball Mill, B-Planetary Mill, C-Vibratory Mill, D-Mixed Ball Mill (Attritor), E-Shaft mill and F-Rolled mill [14].**

**Table 1 Carbonized tea plant waste analysis.**

| Component | % |
|---|---|
| C | 70.63 |
| S | 0.32 |
| Calorie | 7,293 kal/gr |

**Table 2 Analysis of Elazığ-Keban region magnetite ore.**

| Component | % |
|---|---|
| $Fe_3O_4$ | 88.75 |
| $SiO_2$ | 6.65 |
| $MnO_2$ | 0.13 |
| CaO | 1.15 |
| $Al_2O_3$ | 0.22 |
| MgO | 0.20 |

**Table 3 Analysis of Karaman region manganese ore.**

| Component | % |
|---|---|
| $MnO_2$ | 49.73 |
| $Fe_2O_3$ | 1.796 |
| $SiO_2$ | 40.77 |
| CaO | 1.293 |
| $Al_2O_3$ | 2.727 |
| MgO | 0.476 |
| BaO | 1.167 |

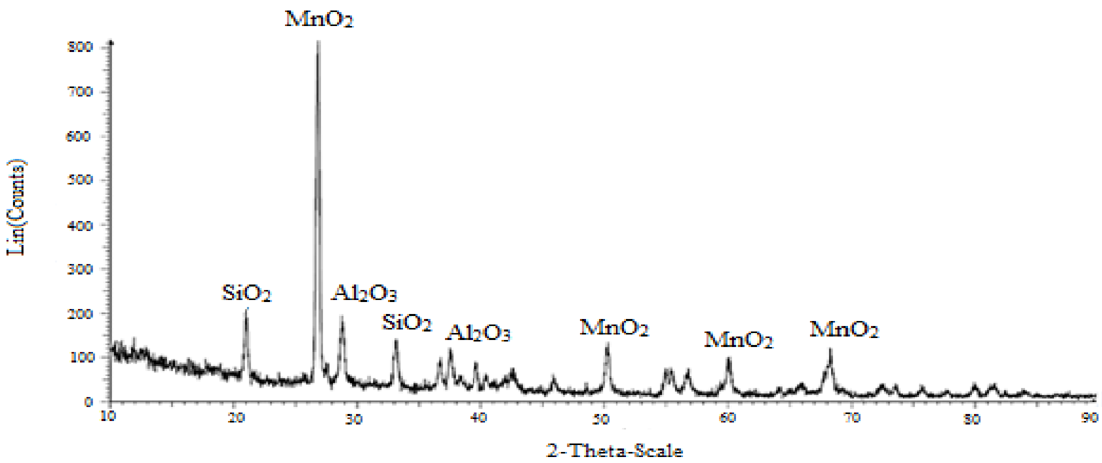


**Fig. 2 XRD image of the used manganese ore.**


**Fig. 3 Attritor mill used for mechanical grinding.**

## 3. Experiment Results

### *3.1 XRD Analyzes*

Mechanical milled mixture samples were analyzed by XRD. Fig. 4 shows the XRD analysis of the mixture made at different grinding times. The comparison of the XRD peaks for different milling durations (Fig. 4) indicates that all diffraction peaks gradually decreased with an increase in milling duration. It is considered that the decrease in peak length was caused by the amorphous structure and mechanical energy transferred from structural irregularities, and that partial alloys were formed in the later stages of milling process.

Mechanical milling increases dislocations in the structure, which leads to the formation of stress fields and deterioration in cage structures. These structures showing shrinkage in X-ray diffraction peaks can be regarded as semi-stable amorphous phases. Compared to various minerals, mechanical activation of the pyrolusite mineral seems to require much longer times. Since both the pyrolusite and the magnetite mineral have Mohs hardness grades between 6 and 6.5, the amorphous state of this hard material requires longer times than the minerals with lower hardness grades [12].

### *3.2 DTA-TG Analyzes*

The DTA-TG analyses of the mixture before grinding and after grinding are shown in Figs. 5-7. Both in the original mixture and in the milled sample, an endothermic reaction first took place, and after a certain temperature, it was determined that exothermic reactions occurred.

On the sample subjected to mechanical activation for 120 hours, a symmetrical change similar to the Gaussian function was observed. It is inevitable that the mechanical grinding process will cause a large increase in surface areas of the particles. This increase in surface area can be attributed to the material growing

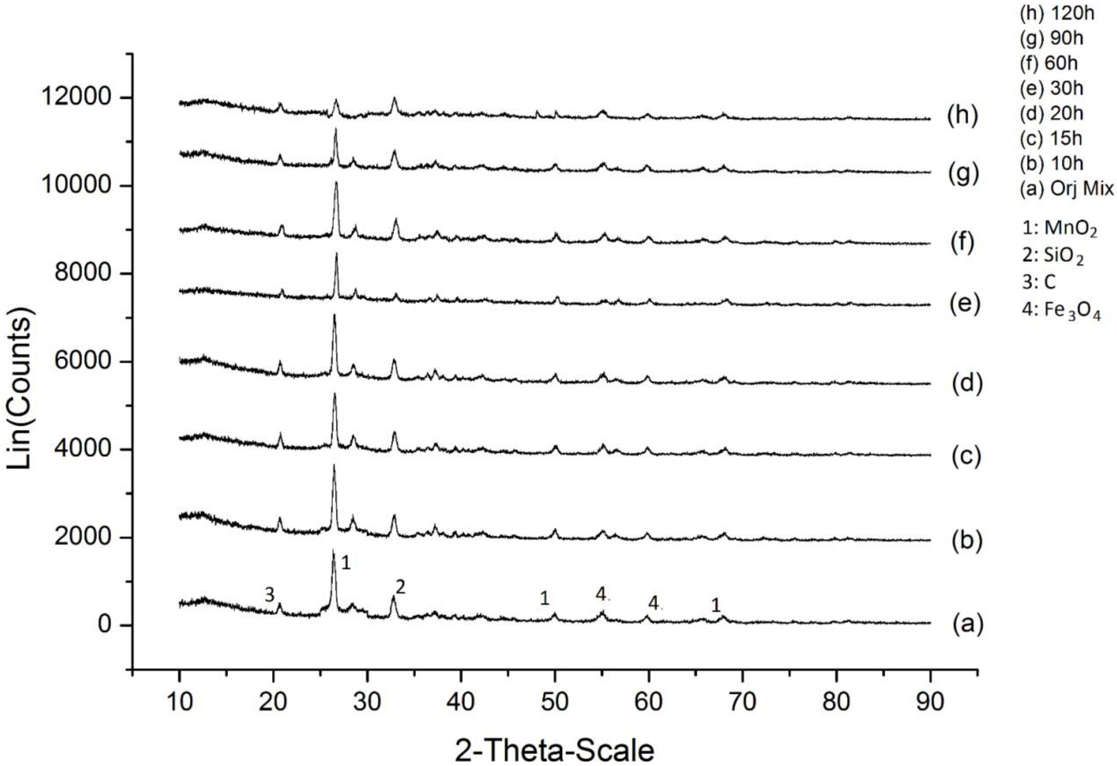


**Fig. 4 XRD images of samples subjected to mechanical grinding at different times.**

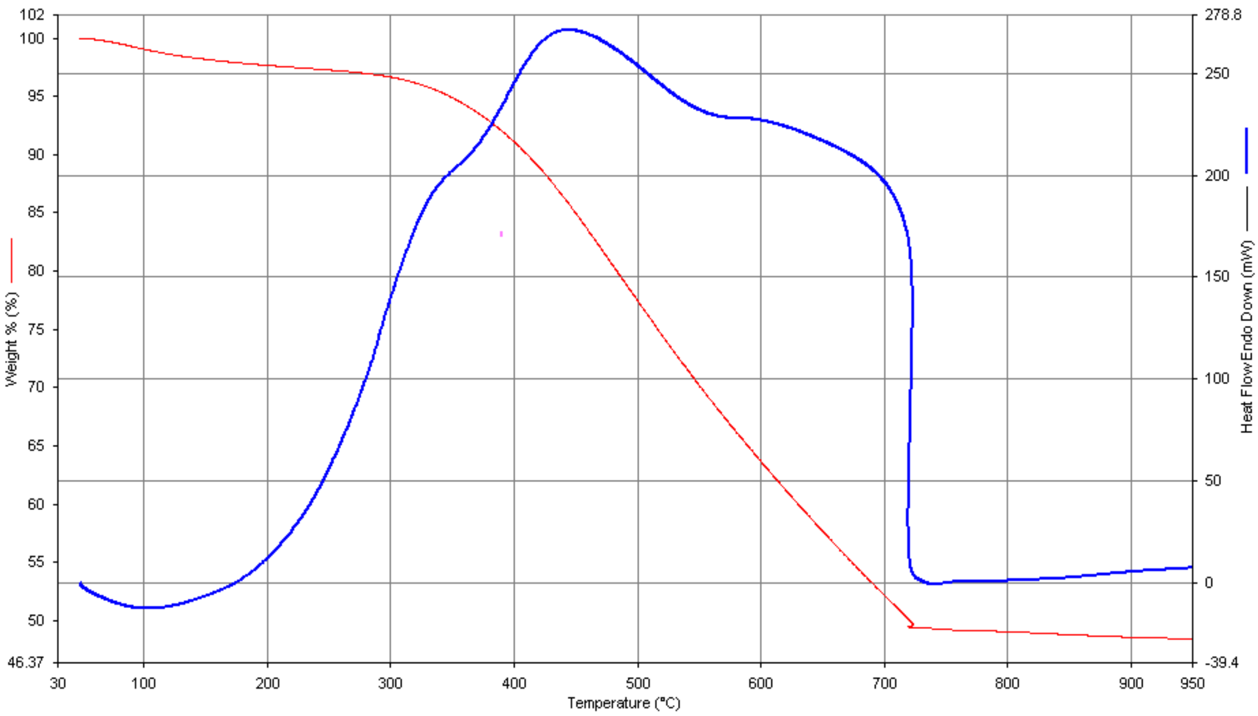


**Fig. 5 DTA-TG analysis of the un-grinding mixture.**

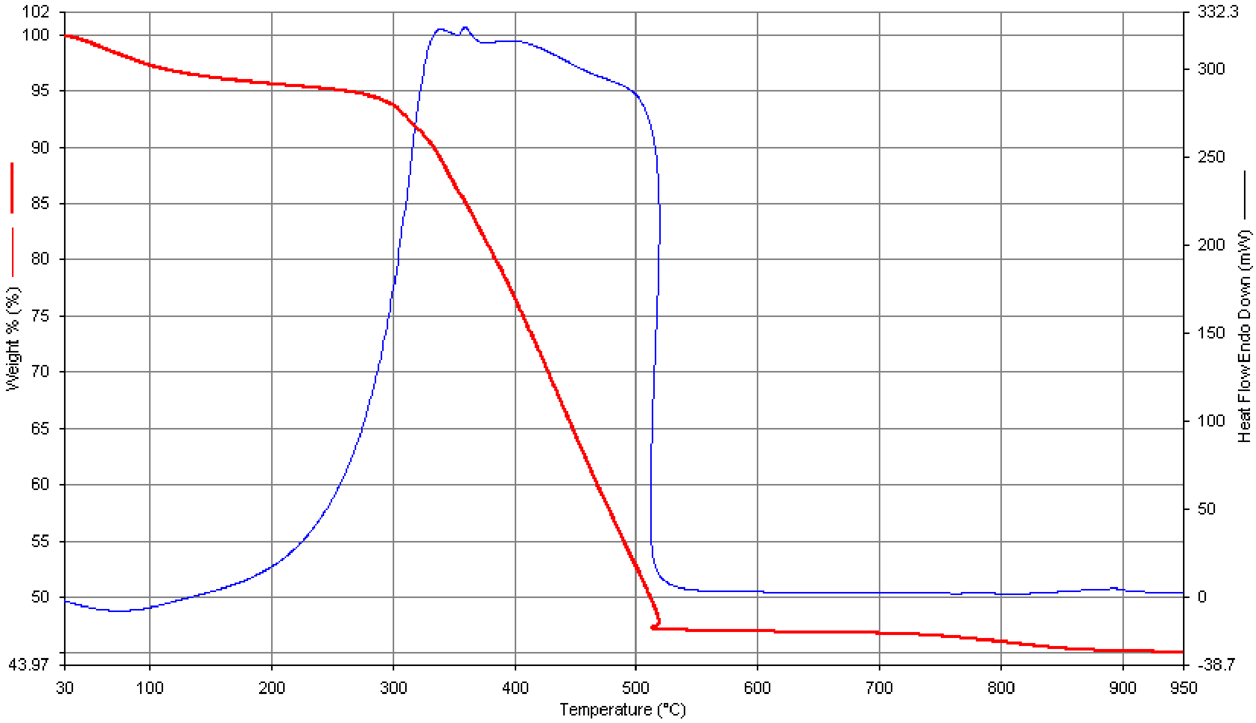


**Fig. 6 DTA-TG analysis of the mixture subjected to 10 hours milling.**

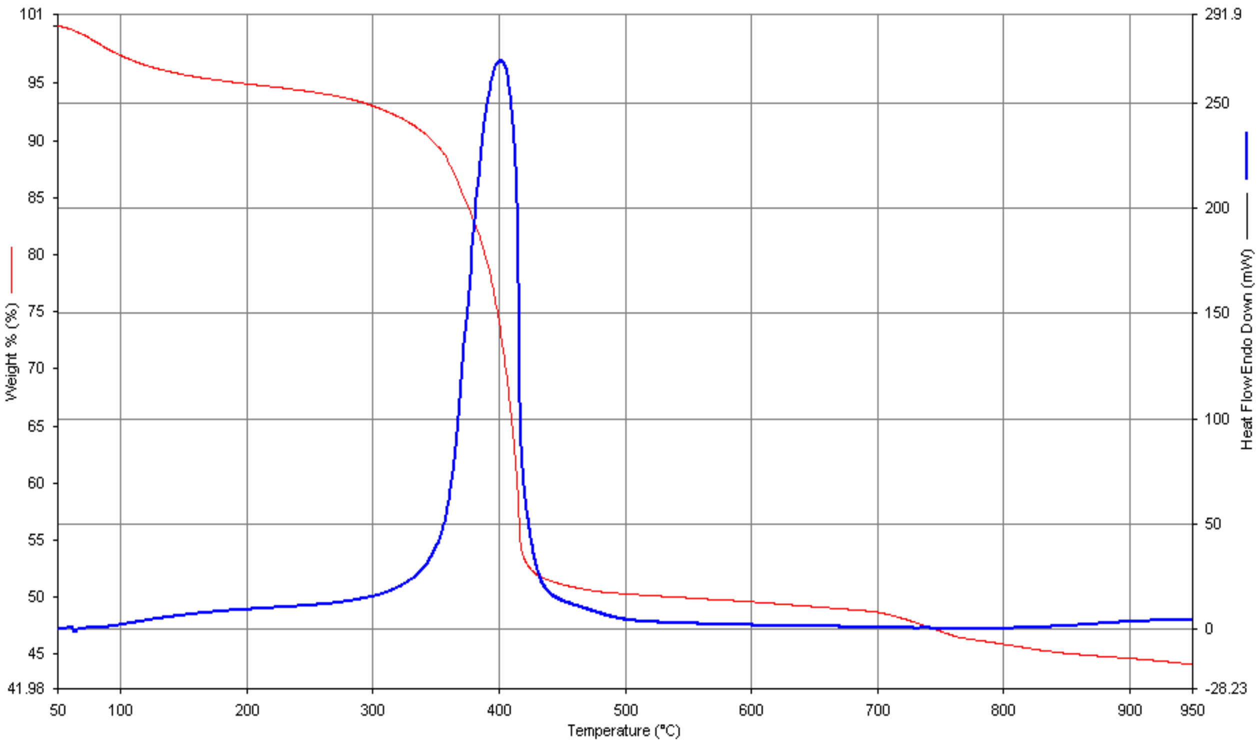


**Fig. 7 DTA-TG analysis of the mixture subjected to 120 hours milling.**

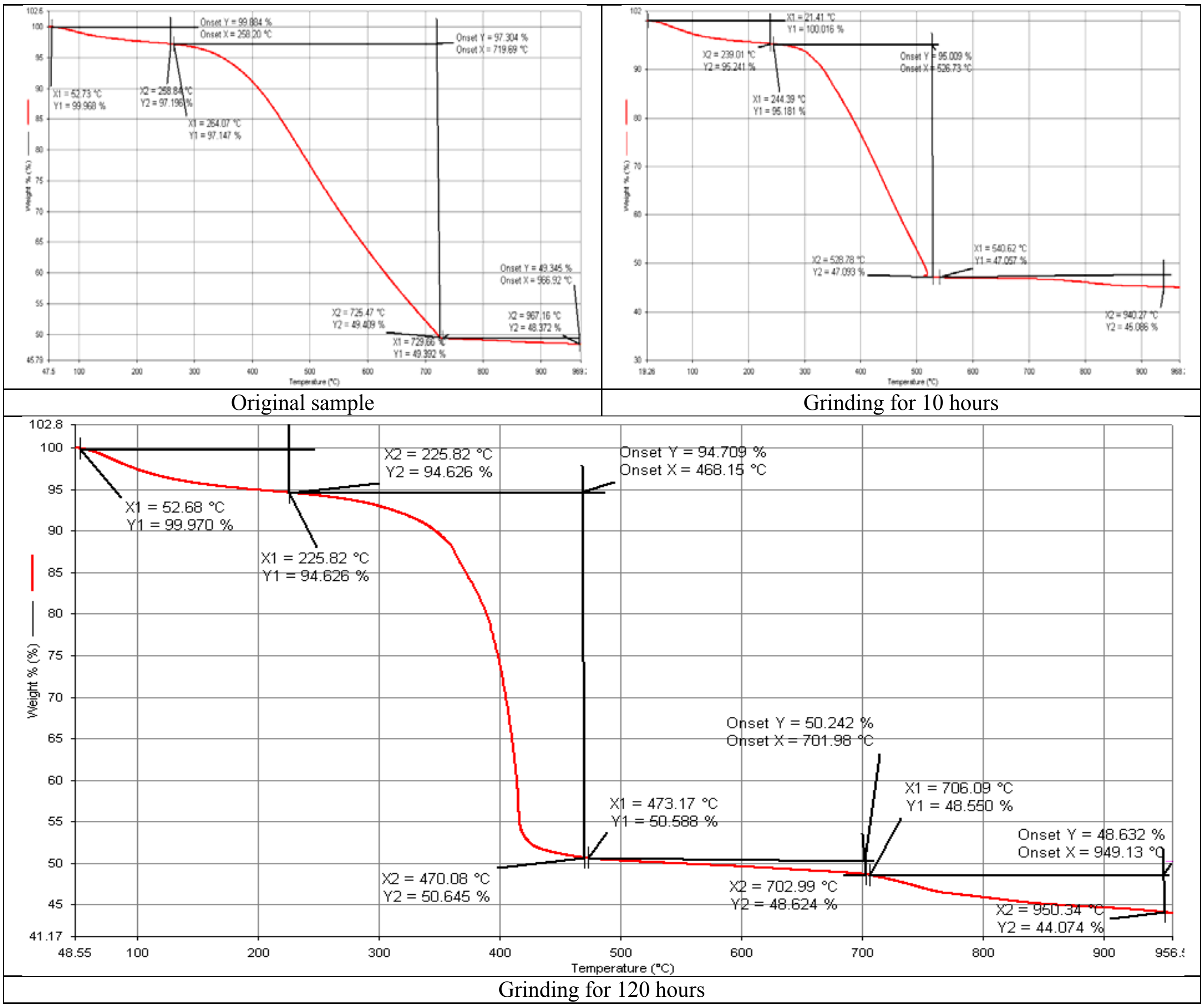


**Fig. 8 Comparison of TG graphs based on milling times.**

at much lower temperatures and the reduction in activation energy achieved by the reduction process. It is also possible to see in Fig. 8 that the change in the size of the grain forms a change on the thermogravimetric analysis.

The thermogravimetric analyses show three different weight loss steps in the 10 h milling and four different weight loss steps in the 120 h milling. There was a 3% weight loss in the original sample up to 260 °C. This may be due to surface moisture both on the surface and in the capillary channels. However, there was a 6% weight loss in the 120 h milled samples up to 245 °C. At later temperature stages, there was a 51% weight loss in the original sample up to 730 °C, a 53% weight loss in the 10 h milled sample up to 540 °C, and a 50% and 56% weight loss in the 120 h milled sample up to 470 °C and at later temperatures, respectively.

## 4. Results

In this study, pyrolusite ore ($MnO_2$) was subjected to mechanical milling with a high-energy mill with carbonized tea plant wastes and the effect of grinding time on the crystal structure of the material was investigated and the following general results were achieved.

Mn/Fe, C/($MnO_2$+$Fe_3O_4$) and ball/ore ratios of the mixture in the attritor were taken as 8, 2 and 10, respectively and the mixture was subjected to mechanical grinding for periods ranging from 10 to 120 hours. The turning speed of the mill was determined to be 350 rpm and the milling was carried out in a dry environment. The TG-DTA and XRD analyzes of the obtained samples showed that the samples subjected to mechanical grinding for 120 hours gradually decreased with increasing grinding time at all the diffraction peaks when the XRD peaks were compared to the grinding times.

It was observed a 6% weight loss in the 120 h milled samples up to 245 °C. At later temperature stages, there was a 56% weight loss in the 120 h milled sample up to 470 °C.

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