

Mechanical activation of hematite in different grinding mills

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ABSTRACT

Mechanical activation by grinding is a complex process involving alteration of structure, chemical composition, phase transformation and solid reactivity. The concentration of the mechanically-induced defects and their spatial distributions depends upon the condition of the energy transfer in the mill. The creation of defects enhances the stored energy (enthalpy) in the solids and consequently causes a decrease of activation barrier for the process and/or subsequent processes.

In this paper, the effects of milling on the structural changes of hematite have been investigated using wet milling in a stirred media mill and dry milling in a vibratory mill and in a planetary mill. The structural changes have been characterized using a combination analysis of BET surface area measurements and X-ray diffraction (XRD) scans. Besides, the hydrogen reduction behaviors of mechanically activated hematite and the initial sample were studied using simultaneous thermal analysis (STA). The dry grinding was extended in the planetary and the vibratory mills for 9 h and the wet milling in the stirred media mill was prolonged for 5 h. The Warren-Averbach method was used to resolve and extract the microstructural characteristics of hematite phases.

It was found that the BET surface area, X-ray amorphous phase content and XRD line breadths increase and XRD reflection intensity decreases with increasing of grinding time in the mills. It was concluded that hematite did not undergo a significant phase transformation or physico-chemical changes during milling whatever milling devices were applied. The

microstructural evolution occurred rapidly at the initial stages of milling and continued to develop slightly in the later stages of milling. The particle size and the BET surface area analysis indicated that the agglomeration of finely ground particles takes place at prolonged stages in the planetary mill. The use of stirred media mill resulted in a larger BET surface area, smaller particles, more XRD line broadening and subsequently greater structural distortions compared with the planetary and the vibratory mills for a given grinding time. The maximum BET specific surface area from the grinding in the stirred media mill was around $26.2 \text{ m}^2/\text{g}$ for 5 h of milling. Grinding in the vibratory and planetary mills for 9 h produced BET surface areas of about 5.2 and $4.4 \text{ m}^2/\text{g}$ respectively. The X-ray amorphous phase contents of 58 and 72 % obtained after 9 h of milling in the vibratory and planetary mills respectively. For the sample ground in the stirred media within 5 h of milling, the X-ray amorphization degree exceeded 83 %. After 9 h of milling in the vibratory and planetary mills, the surface weighted crystallite size reached 29.6 and 16.5 nm respectively. The surface weighted crystallite size in the sample ground for 5 h in the stirred media mill was smaller than 6 nm. The maximum lattice strains, $\langle \varepsilon_{L=10\text{nm}}^2 \rangle^{1/2}$, in the grinding with the vibratory and planetary mills for 9 h of milling were found about 2.58×10^{-3} and 3.01×10^{-3} respectively. A value of 4.5×10^{-3} obtained for the sample ground in stirred media mill for 5 h. The comparison of the results indicates that the efficiency of the stirred media mill in energy transfer to the particles being ground is higher

than that of the other mills, in spite of wet operation in the stirred media mill. In addition, STA analysis revealed a positive influence of mechanical activation on the reduction of hematite in particular at the first step of reduction. The results are discussed in details.

1. INTRODUCTION

The applications of treatment of minerals in milling devices are numerous and can roughly be divided into three categories: coarse grinding, fine grinding and mechanical activation. The most important goal in coarse grinding is size reduction. In contrast, the objective of mechanical activation is the changes in the structure, tension state and chemical composition, phase transformations in polymorphic materials, ionic exchange and reactivity (Zoltan Juhasz, 1998). The fine grinding limit is determined by ductile-brittle transition state (Boldyrev et al., 1996). The concentration of the mechanically induced defects and their spatial distribution depend upon the condition of the energy transfer in the mill. The concentration and distribution of the mechanically induced defects can also be influenced by varying the external conditions of stress. The creation of defects enhances the stored energy (enthalpy) in the solids and consequently causes a decrease of activation barrier for the process and/or subsequent processes (Steinike and Tkacova, 2000).

Several attempts have been made to understand the relationships between grinding factors and changes in structure during mechanical activation. Karagedov and Lyakhov (2003) investigated the influence of the density of milling media in mechanical activation of inorganic oxides. Dry grinding was found to be more effective than wet milling in the dissolution of tantalite despite the generation of a larger specific surface in wet milling (Welham, 2001). Welham and Llewellyn (1998) reported that the crystallite size decreased exponentially and strain increased by extending of milling periods during the mechanical activation of ilmenite. Baláz et al. (1988) carried out a comparative study to investigate mainly the influence of mill types (attritor, ball and vibratory) on the reactivity of sulphide minerals.

At present, mechanical activation exhibits a wide range of potential applications. It has been reported that mechanical activation substantially accelerates the leaching kinetics of several sulphide and oxide minerals, even at ambient pressure and temperature. The enhanced effect is attributed to the increase of specific surface area and structural disorder (Baláz, 1996), enhanced strain (Baláz, 2000), amorphization of mineral particles (Tkáčová et al., 1993), and formation of new phases more amenable to leaching (Welham, 2001).

The goal of this paper is to investigate the structural changes in hematite concentrate during wet stirred media and dry vibratory and planetary millings using Warren-Averbach analysis. Several structural characteristics such as BET surface area, amorphization, crystallite size, lattice strain, surface properties and hydrogen reduction behaviors of the ground samples and the initial sample are studied and discussed in details.

2. EXPERIMENTAL

The high purity hematite concentrate containing about 97.91% Fe_2O_3 was supplied by the LKAB (Luossavaara Kiirunavaara Aktiebolag) Company in Sweden. The XRD pattern of hematite concentrate (hereafter referred to as initial hematite) only showed the hematite reflection peaks.

Dry grinding tests were carried out using a planetary mill and a vibratory mill. For dry grinding, a mixture of ball steel media with dimensions between 6 mm and 22.2 mm and with apparent density of $4875 \text{ m}^3/\text{g}$ was used as grinding media. The grinding tests were performed in closed condition, i.e., the lids of the mills were kept bolted during the grinding. A stirred media mill which was operated in a re-circulated mode at a fixed flow rate was used for wet grinding. It consists of a 200mm×90mm stainless steel cylinder chamber (0.95 l of net grinding chamber volume) and an agitator with six perforated discs installed on a horizontal driven shaft. The grinding chamber is lined with ceramic walls (SiC) and the stirrer is equipped with discs of polyurethane (PU). The ground suspension is discharged from the mill chamber through a sieve cartridge which permits passing the particles smaller than 0.05 mm. Yttrium–

stabilized zirconia beads of 0.5 mm diameter with density of $6065 \text{ m}^2/\text{g}$ were used. Samples ground in the stirred mill were diluted with distilled water and the pH was adjusted at 3 (1 M HNO_3) before sonication for 3 min with an ultrasonic probe to ensure a homogeneous mixing. The experimental conditions are given in Table 1.

The XRD patterns were obtained using a Siemens D5000 powder diffractometer with Bragg-Brentano geometry equipped with a curved graphite monochromator in the diffracted beam arm and using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). The XRD patterns of the samples were recorded using a step size of 0.02° and a counting time of 5s per step. To characterize the microstructural characteristics encountered during the mechanical activation of specimens, Warren-Averbach analysis were applied (Pourghahramani and Forssberg, 2006a, b). The specific surface areas of the samples were determined by the BET method with the Flow Sorb II 2300 (Micromeritics). Samples were degassed by heating at 200°C for 90 min immediately prior to measurements, from which the equivalent particle diameter assuming spherical shape for particles was determined. Simultaneous thermal analysis (STA) was conducted using a NETZSCH STA 409C instrument at a heating rate of $10^\circ\text{C min}^{-1}$ to 800°C . The high temperature furnace was heated by graphite heating elements, which were protected by injection of inert argon gas. The temperature of furnace was controlled by a tungsten thermocouple. The heating was

performed under highly pure hydrogen as reduction gas with a rate of flow of 100 mlmin^{-1} . The mass of samples was almost 95mg.

3. RESULTS AND DISCUSSION

3.1 Changes in the particle size and surface area

The specific surface areas of the samples after different milling times are shown in Figure 1. The most obvious feature is that the stirred media mill brings about higher specific surface area than the other mills. No significant difference exists between the products of planetary and vibratory mills. Furthermore, the specific surface area in the initial stages of grinding increases rather sharply and continues to rise gradually. However, the BET surface area in the products of the vibratory and planetary mills increases marginally in the prolonged milling in spite of the stirred media mill products, which continues to increase sharply. This may be related to the ability of stirred media milling to reduce particle size. The ground samples in the planetary and vibratory mill indicate the formation of soft agglomerates during extended milling. The maximum specific surface area in the milling with vibratory, planetary and stirred media mills ranged to 5.2, 4.4 and $26.2 \text{ m}^2/\text{g}$ respectively, after 9, 9 and 5 h of milling. The trend in the BET surface area of the stirred media mill suggests that the production of more surface area is still possible with extending of milling.

Table 1: Experimental milling conditions and mill types

<i>Milling conditions</i>	<i>Stirred</i>	<i>Vibratory</i>	<i>Planetary</i>
Specific input energy (kJ/kg)	410-26400	2160-20000	9680-88000
Power density (kWh/m^3)	1150	70	2980
Media filling (%)	46.2	70	23.4
Milling time (h)	0.11-7.5	1,3,9	1,3,9
Ball to powder weight ratio	7	16.92:1	19.1:1
Speed (RPM)	2220	1000	100 (axle), 200 (drum)
Media apparent density (kg/m^3)	6065	4875	4875
Amplitude (mm)	---	8	--
$L \times \phi \text{ mm}$	200×90	320×185	87×115
Grinding mode (<i>wet/dry</i>)	Wet	Dry	Dry

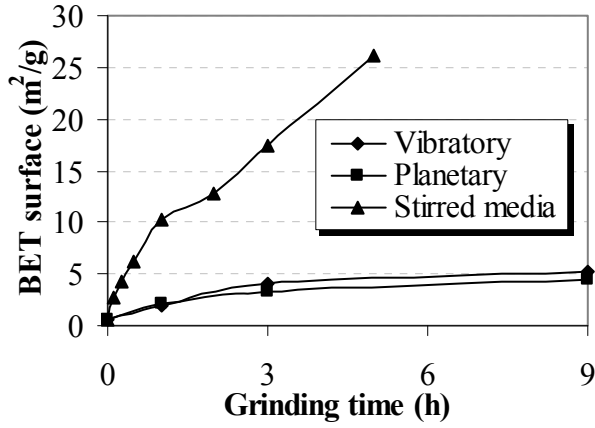


Figure 1: Changes in the specific surface area of hematite ground in three mills as a function of grinding time.

From the BET measurements, the particle size was determined via surface area by using the well known equation:

$$d_{av} = 6/(\sigma S) \quad (1)$$

where d_{av} is the equivalent spherical particle diameter (μm), σ is the density (g/cm^3) and S is the specific surface area (m^2/g). Figure 2 shows changes in the BET particle size in samples. The mean BET particle size decreases as the grinding progresses. The particle size decreased remarkably in the initial stage of milling in the stirred media mill rather than the other mills. Over the grinding periods, the stirred media milling exhibits smaller particles compared to the vibratory and planetary mills. The smallest particle size in the final products of the planetary, vibratory and stirred media mills are calculated about 159, 220 and 44 nm respectively.

3.2 Structural changes

The structural changes and the characterization of the microstructure characters were

investigated using XRD analysis. The X-ray diffraction patterns were collected for all activated and non-activated samples. An example of the XRD patterns for the samples ground in the stirred media mill is given in Figure 3. The diffraction peaks for mechanically-activated samples are lower and broader than of those for non-activated samples, mainly due to a disordering process of hematite crystal structure by intensive grinding. The reduction of diffraction peaks intensity implies the formation of amorphous material. The decrease of X-ray diffraction intensities is accompanied by a general broadening of the XRD patterns. The increase of the XRD line breadths is due to the plastic deformation and disintegration of hematite. The XRD patterns showed only the hematite reflections, indicating that hematite did not undergo significant reaction and physico-chemical changes. The presence of small, but remarkable, reflection peak after intensive grinding in the grinding mills can be taken as a further indication of the high milling resistance and mechanical strength of the submicron hematite crystallites.

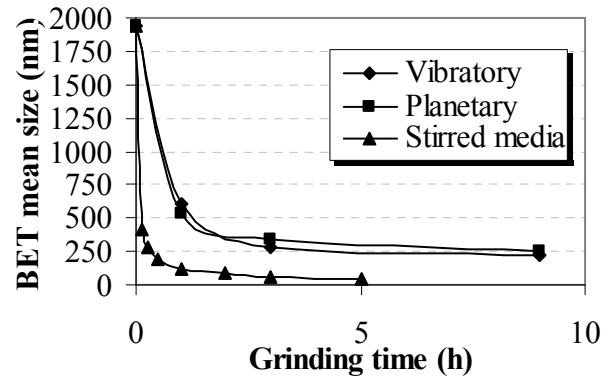


Figure 2: BET mean particle of activated hematite concentrate using different milling devices as a function of grinding time.

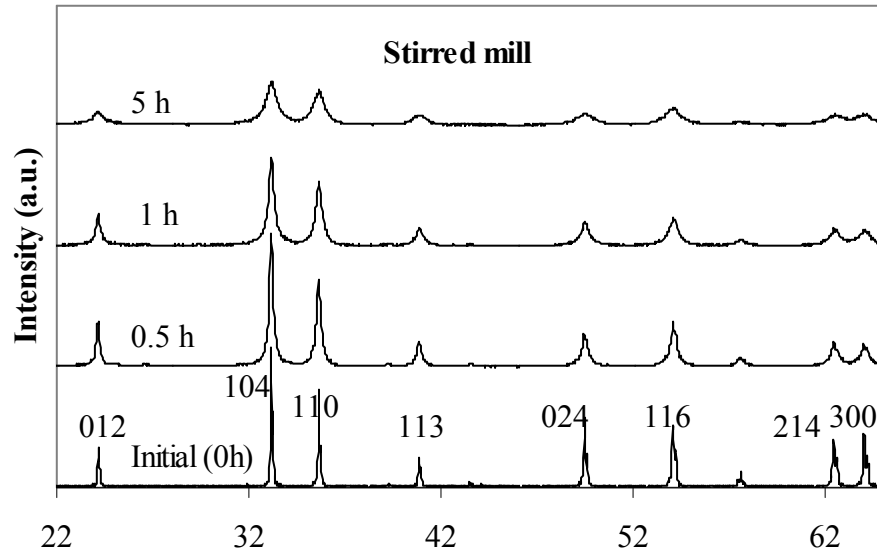


Figure 3: The X-ray diffraction patterns of hematite samples ground in the stirred as a function of the grinding time.

From the intensity of the reflection peaks and their background, the degree of X-ray amorphization is estimated and the results are depicted in Figure 4. The content of X-ray amorphous phase in hematite depends on both grinding mill and stress energy field. The portion of X-ray amorphous phase in the ground hematite with the stirred media mill is higher than of those ground in the planetary and vibratory mills over the grinding periods. The lowest X-ray amorphous phase content is calculated for the samples ground in the vibratory mill. The fraction of the X-ray amorphization increases steadily with progress in milling despite the particle size reduction in the mills and the BET surface area values during the grinding in the planetary and vibratory mills. The amorphization degree increased to 58, 72 and 83 % by grinding in the vibratory, planetary and stirred media mills respectively, after 9, 9 and 5 h of milling. These results show that more energy is needed in the vibratory and planetary mills than the stirred media mill to produce the same amorphization degree. The increase of X-ray amorphous phase due to intensive milling was reported for calcite and quartz (Heegn, 1986) and sulphide minerals (Balaz, 2000). The amorphization is in fact a highly distorted periodicity of lattice elements, and it is often characterized as a short range order in contrast to the long order of a fully crystalline structure.

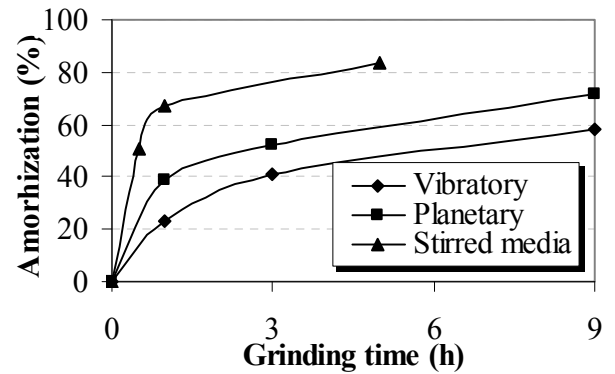


Figure 4: Variation of amorphization degree with the time of mechanical activation in the mills.

To obtain the microstructural characteristics, the Warren-Averbach method based on Fourier analysis, which can precisely determine microstructure characters, was used for direction [012]. From the Warren-Averbach method, the root mean square strain (RMSS), $\langle \epsilon^2_L \rangle^{1/2}$, and surface weighted crystallite sizes were calculated. The surface weighted crystallite size of the ground samples in the mills are compared in Figure 5. It is evident that the ground samples in the vibratory mill have larger crystallites than the ground samples in the planetary and stirred media mills. It can be observed from Figure 5 that the planetary mill products yield smaller crystallite than vibratory mill products when hematite is subjected to intensive grinding. The stirred media mill gives smaller crystallites than the other mills over the

grinding periods. With the vibratory, planetary and stirred media mills, the hematite crystallites refined up to the values of 29.6, 16.5 and 5.8 nm, respectively, after 9, 9 and 5 h of milling.

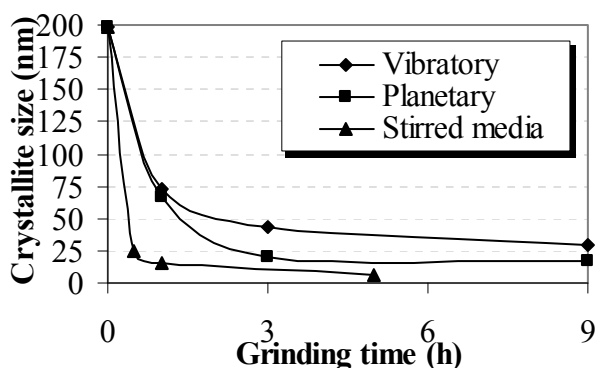


Figure 5: Changes in the surface weighted crystallite size as a function of grinding time.

The root mean square strain values, $\langle \varepsilon_{L=10nm}^2 \rangle^{1/2}$, for activated hematite in the mills are displayed in Figure 6. There is only minor difference between planetary and vibratory mills in deformation of hematite lattice. The stirred media mill exhibits higher microstrain compared with the other mills. The maximum lattice strain, $\langle \varepsilon_{L=10nm}^2 \rangle^{1/2}$, in the grinding with the vibratory and planetary mills was found at about 2.58×10^{-3} and 3.01×10^{-3} respectively. A value of 4.5×10^{-3} obtained for the sample ground in stirred media mill for 5 h. The steady state was not observed for grinding in the mills, suggesting that the production of smaller crystallites is still possible with increasing the grinding intensity. The comparison of the results indicates that the efficiency of the stirred media mill in energy transfer to the particles being ground is higher than that of the other mills, in spite of wet operation in the stirred media mill.

3.3 Effects of mechanical activation on the reduction behaviors

In order to obtain additional information about the weight loss of the samples during reduction, a TG analysis and a DTG analysis were performed. Hydrogen was used as reducing gas.

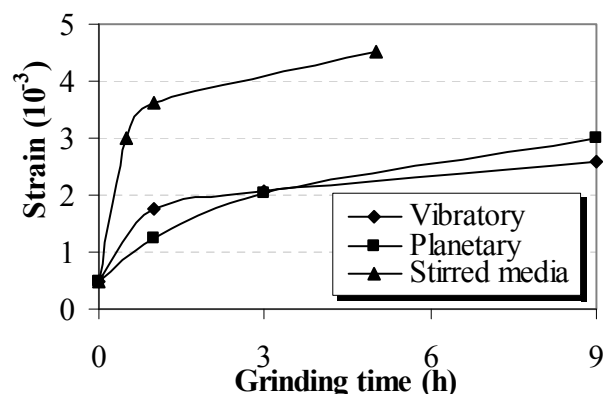


Figure 6: Changes in the lattice strain of the samples ground in the mills as a function of grinding time.

The results are given for the samples ground in the vibratory mill (Figs. 7, 8). Generally, the TG curves for the reduction of hematite exhibit a two-step weight loss that can be identified from changes in the slope of the curves. The first step of weight loss, corresponding to the reduction of hematite to magnetite, occurs at the lower temperatures. The second step (main step) of weight loss, the reduction of magnetite to iron, extends toward higher temperature sides up to 680°C. The total weight loss for all of the samples is 30%, which corresponds to the complete conversion of hematite to iron metal according to the following reactions:

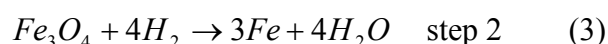
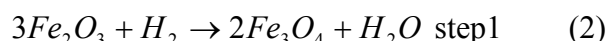


Figure 7 shows mass changes in the initial sample and in samples ground in the vibratory mill as a function of temperature. For the hematite ground in the vibratory mill, the TG curves shift toward lower temperatures with increasing grinding time up to 3 h. However, the curve corresponding to prolonged milling for 9 h moves to higher temperatures compared with the sample ground for 3 h. This is especially true for the second step of the weight-loss process. The results are consistent with observations from thermal studies of ground pyrophyllite (Perez-Rodriguez, 1991; Temujin et al., 2003). This effect is probably a result of the formation of agglomerates during extended dry milling, which accelerate the sintering of the particles at higher temperatures. The formation of a dense layer due to the sintering processes

hinders the reduction of magnetite to iron. The onset temperature of 421 °C in the initial sample

decreased to about 341 °C in the sample ground in the vibratory mill for 9 h.

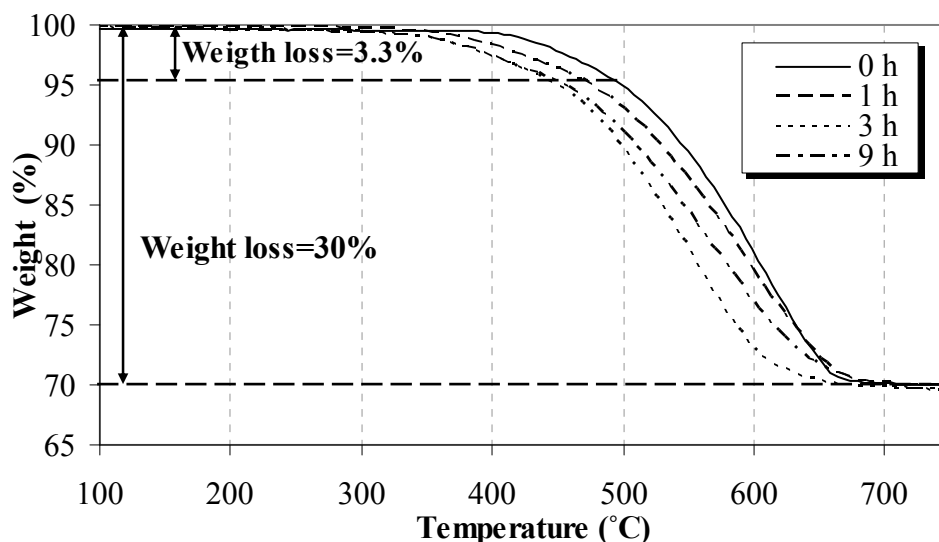


Figure 7: TG curves for the initial sample and for the samples ground in the vibratory mill for various grinding times as a function of temperature.

The DTG curves corresponding to the heating rate of 10°C/min for the initial sample and the samples ground in the vibratory mill for different grinding periods are shown in Figure 8 as a function of temperature. The DTG curves also represent a two-step weight loss which can be easily identified from the changes in the slope and the peaks of the curves. Interestingly, the first step of mass loss is more pronounced for mechanically activated samples compared with the initial sample. In addition, a plateau between the two steps of reduction process can be observed indicating different stapes during reduction processes. It is apparent that the resolution of the two events is greater for mechanically activated samples than for the initial sample. This is a consequence of the reduction of the energy required to destroy the crystalline structure of hematite. The energy supplied by milling causes structural disorder through the distortion or breakage of the crystalline network. This was evident from the reduction of the intensities of XRD peaks. Once more, this emphasizes that the mechanical activation results in improved resolution of overlapping reduction events. Moreover, the area of peak in the second step of reduction decreases concomitantly as the area of peak in the first weight loss step centered approximately

between 300°C and 450°C increases, depending upon grinding time.

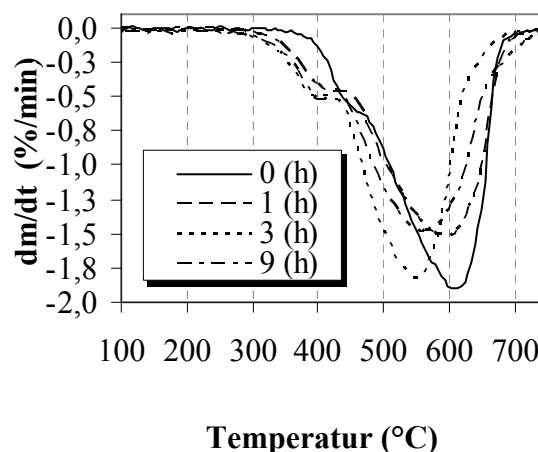


Figure 8: DTG curves for the initial sample and for samples ground in the vibratory mill for various grinding times as a function of temperature.

4. CONCLUSIONS

The use of prolonged grinding leads to higher specific surface area, X-ray amorphous material, XRD reflection broadening, microstrain, and smaller crystallites whatever mill types were applied.

The samples activated in the stirred media mill resulted the largest specific surface area among the mills used, being between 2.7 and 26.2 m²/g depending on the grinding time. The maximum amorphization degree, 85 %, was achieved from the milling in the stirred media mill after 5 h of milling. The vibratory mill produced the minimum X-ray amorphization material compared to the other milling devices over the grinding periods.

The Warren-Averbach method suggested that the stirred media mill products have smaller crystallites and higher microstrain than the products of planetary and vibratory mills. The final products of the stirred media mill contain crystallites smaller than 6 nm with the lattice strain, $\langle \varepsilon_{L=10nm}^2 \rangle^{1/2}$, of 4.53×10^{-3} . The comparison of the results indicates that the efficiency of the stirred media mill in energy transfer to the particles being ground is higher than that of the other mills, in spite of wet operation in the stirred media mill

The mechanical activation of hematite in the vibratory mill had a positive influence on the reduction of hematite with hydrogen gas. Mechanical activation of hematite concentrate led to the initiation of reduction at lower temperatures. The starting temperature of the reduction was decreased to about 80 °C. The reduction of hematite to magnetite was pronounced in the activated samples compared to the initial sample.

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