WHERE DOES THE ENERGY GO IN HIGH ENERGY MILLING?

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Abstract

An attempt is made to analyze as to how the energy is dissipated, stored and distributed in the material during the process of high energy milling. The manifestation of the enhanced potential energy in different forms (point, line and volume defects, surfaces and interfaces, strain and structural disorder) is determined through direct energy measurements, calorimetry, surface area and surface energy measurements. X-ray line broadening analysis employing the Hall-Williamson method is used to estimate the non-uniform elastic strain and grain size and the extent of structural disorder is evaluated from integral peak areas of XRD. A close packing of crystallites approximating a tetrakai-decahedron configuration is used to calculate the grain boundary area. The strain energy is calculated using the theory of elasticity. The energy of amorphisation is calculated from the enthalpy of fusion and specific heats of solid and liquid. Mechanical activation of zircon is chosen for the study of the energetics of the process. For the milling of zircon, the energy transferred to the material is found to be 13% of the specific energy input in 6 h of milling in a planetary mill. It is observed that a large part of the energy transferred to the material is lost during the breaking of the bonds and only a small fraction goes towards enhancing the potential energy mainly as elastic strain energy and structural disorder. The energy stored in point and line defects, additional surfaces and grain boundaries are comparatively lesser.

Introduction

The process of mechanical activation involves the enhancement of potential or stored energy of a material through mechanical forces. The various possible ways in which the potential energy of a solid can manifest itself is given in Fig. 1. The kinetic energy input or the mechanical work done on the solids through compression, shear and impact is partly stored in the solid as chemical and strain energy and a large part of the mechanical energy transforms to heat, some energy is dissipated as sound as well as electromagnetic emissions. Shear and compressive stresses possibly result in accumulation of structural defects at the surface and in the near-surface layers whereas the impact stresses possibly results in defects that are uniformly distributed through the entire volume of the material. The strain energy stored could be elastic which is recoverable or plastic, which is irreversible. The chemically stored energy can manifest through bond energy changes such as in structural rearrangement, or result in new structures or complete disordering as in amorphisation or through defect energy associated with point, line, surface and volume defects or result in a change in

electronic state or Fermi energy. Mechanical activation can also result in various types of electromagnetic emissions [1-3]. The large numbers of excitation processes that occur due to mechanical activation are characterized by different relaxation times [4-6]. The electromagnetic effects, lattice vibrations and the surface effects are short lived whereas the additional surfaces, interfaces and lattice defects that are introduced during the high energy milling process have long relaxation times.
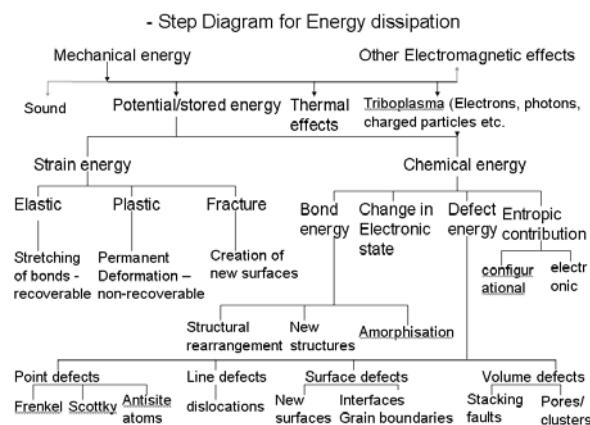

Figure 1. Various modes of energy dissipation in the mechanical activation process

The energy balance for the mechanical activation process (occurring without a change in chemical composition) can be deduced from the law of conservation of energy. If the acoustic and electromagnetic energy losses during the high energy milling process are ignored, the mechanical work done (W) can be given as:

$$W = \Delta E_M + \Delta E_G - (-Q) \tag{1}$$

where, Q is the heat evolved, ΔE_M and ΔE_G is the internal energy change of the milled material and grinding media respectively. The total heat evolved during the process can be determined by adiabatic calorimetry. The internal energy change of the milled material can be determined from the overall energy change and the heat losses in the absence of the material in separate experiments or from the individual processes that occur within the material subject to mechanical activation. If the mechanical activation process is assumed to occur at constant pressure and if no work is done against external pressure, the change in internal

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energy is same as the change in enthalpy. The internal energy increase in the material can then be written as:

$$\Delta E_M = \Delta s.\gamma_s + \Delta g_b.\gamma_{gb} + \varepsilon.\Delta E_\varepsilon + f_{amor}.\Delta H_{s\rightarrow l} + f_{def}.\Delta E_{def} + f_{trans} \Delta H_{trans} \tag{2}$$

Where

Δs	change in surface area during milling	γ_s	material surface energy
Δg_{gb}	change in grain boundary area	γ_{gb}	grain boundary energy
ε	lattice strain induced during milling	ΔE_ε	strain energy
f_{amor}	fraction of amorphisation	$\Delta H_{s\rightarrow l}$	enthalpy of fusion at the amorphisation temperature
f_{def}	defect concentration;	ΔE_{def}	defect energy
f_{def}	defect concentration	ΔE_{def}	defect energy
f_{trans}	extent of other structural transformations	ΔH_{trans}	enthalpy change for other structural transformations

It is possible to broadly evaluate the various parameters given in Eq. (2) separately. The total effects can be divided to that resulting from an increase in surface area and energy on milling and the rest of the parameters result from structural effects. For mechano-chemical activation, the energy associated with the change in chemical composition has to be included.

The total mechanical work done during milling as well as the energy that is stored in the material will depend on the stress number and the stress intensity. These in turn depend on the nature of the mill, the dynamics of the impact processes, impacting material and their mass as well as the properties of the material being milled and it's mass. Depending on the mode of transfer of external energy, mechanical activation can be achieved in a variety of mills such as planetary mills, attrition mills, vibratory mill, tumbling mill, jet mill, ball mill etc., both in dry and in wet medium. However, the specific mill power and the specific energy transferred to the solid particles will depend upon the type of mill, milling parameters, the grinding medium of milling and the material being milled. For a ball ball mill, the specific mill power is 30-50 kW/tonne, for a vibratory mill it is 250-4500 kW/tonne, for an attrition mill it is 900-14000 kW/tonne and for the planetary mill it is 9000-36000 kW/tonne [6]. It is estimated that about 10-15% of the specific mill power can be transferred to the material being milled, which redistributes as surfaces and structural defects [5,6].

In an earlier study [7], the energetics of the mechanical activation of ilmenite with specific reference to the energy transferred to the material *vis a vis* the specific energy consumption, the amount of potential energy stored in the material and its manifestation in various forms such as increase in defect density, additional surfaces and interfaces, elastic strain and structural disorder was reported. The specific energy consumption, the amount of energy transferred to the material, the increase in potential energy and the manifestation of the stored energy in various forms will depend on the hardness and physical properties of the material. Therefore, in this study, zircon ($ZrSiO_4$) is chosen for the analysis of the energy balance of the mechanical activation process.

Experimental

A zircon concentrate obtained from Indian Rare Earths Limited located at Chatrapur (Orissa, India) region is used for mechanical activation. The bulk chemical composition of the zircon sample used in this study is given in Table 1.

Table 1. Chemical composition of the zircon sample used in the present study

Compounds	Wt. %
ZrO_2	64.80
SiO_2	32.30
TiO_2	0.30
Fe_2O_3	0.30
P_2O_5	0.12
Total	97.82

A Fritsch Pulviresette-5 planetary mill having agate bowl and balls (Fritsch GMBH, Germany) is employed for the mechanical activation. The pulverizer is coupled with a high sensitive power meter (YOKOGAWA WT 3000 with sensitivity better than 0.2%) to measure the energy input into the mill during the milling operation. The power meter is connected in parallel with the planetary mill to ensure that only the power input to the mill is measured. The bowl and balls used for milling is of agate. For each milling experiment, two bowls comprising of fifteen agate balls of 20 mm diameter (160 g) in each bowl are used. The samples (40 + 40 g in each bowl) are subjected to dry milling in ambient atmosphere. The ore to ball ratio in the bowl was maintained at a ratio of 1:4 by weight for all the experiments. Milling is carried out at 200 rpm for all the batch experiments. No other additives are used during the milling. The samples are activated in the planetary mill for 60, 120, 240 and 360 minutes in separate experiments. The milling experiments are carried out in a cyclic mode (i.e. the direction of rotation is changed every 15 minutes) to minimize the aggregation of powder samples and their sticking to the bowls and for effective transfer of energy into the material.

The effect of mechanical activation on the unit cell parameters, crystallite size, strain and degree of amorphization are analyzed by x-ray powder diffraction technique and line broadening analysis using standard methods reported in the literature [8, 9] and integral peak area analysis [10]. The x-ray diffraction measurement is carried out using a Siemens D-500 diffractometer. The samples are analyzed with Co-K$_\alpha$ radiation (λ=1.79026 A) at a scan rate of 1°/min.

The heat evolved during the process of relaxation of defects by the milled ilmenite samples is measured in distilled water (pH=7) using an isothermal conduction calorimeter (Thermometric AB, Sweden) with a sensitivity of 0.1 mW. The samples were stored in ice immediately after milling until the calorimetric experiment to minimize relaxation effects during the storing period. In the present study, the activated samples of zircon are subjected to relaxation for periods up to 5 hours at 27°C. The differential power between the sample and an alumina reference is continuously recorded. No changes are observed in the power vs time plots beyond 1 hour. The heat evolved is determined from the integral of the power *vs* time plot. The instrument has a facility to load several samples simultaneously.

Thus the unmilled and activated samples (60, 120, 240 and 360 min) are subjected to the calorimetric measurements simultaneously.

The particle size distribution of the milled and as received zircon samples was determined using a laser particle size analyzer (CILAS 1180). The surface area of the milled powders is measured using a multipoint surface area analyzer (MICROMERETICS ASAP 2020). The surface energy of zircon before and after milling is measured by the capillary rise method (KRUSS Tensiometer K100). The capillary rise through a packed bed of the bulk powder measured by the increase in weight as a function of time is correlated to the advancing contact angle between the liquid and solid through the Washburn equation:

$$\frac{W^3}{t} = \frac{\left[(c.\bar{r})\varepsilon^2(\pi R^2)\right]\rho^2\gamma_L\cos\theta}{2\eta}. \tag{3}$$

where, W is the weight of penetrating liquid, t is the time of flow, σ_l is the surface tension of the liquid, (c.r) is the material constant, θ is the advancing angle, η is the viscosity of the liquid. If the viscosity and surface tension of the liquid are known, the advancing angle (contact angle) can be determined from knowledge of the material constant (c.r) which is determined through a calibration experiment using a completely wetting liquid (n-hexane). The measurements are carried out with five liquids (n-Hexane, formamide, water, di-chloromethane and ethelene glygol) for each sample. The surface energy of the powder is then determined from the measured contact angles in different liquids using the Young's equation and the equation of state [11]. The surface energies of the experimental liquids are taken from the compilation of Kwok and Neumann [11].

Results and Discussion

Direct Energy Measurements

The energy transferred to the material (zircon) was deduced from the energy input to the pulverizing mill with material and in absence of the material (all the other conditions remaining same). The applied energy to the mill and the energy transferred to the material are shown in Fig. 2 as a function of milling time. It is observed that the specific energy consumption in 6 hours of planetary milling under the conditions of milling adopted in this study is 18 kWh/kg (11877 kJ/mol) and the energy transferred to the material is found to be 2.38 kWh/kg (1572 kJ/mol) i.e., about 13% of the energy input to the mill is transferred to the material in 6 hours of mechanical activation. The specific energy as well as the stored energy is significantly higher for zircon than for ilmenite. For ilmenite, the specific energy consumption was 11.1 kWh/kg (6074 kJ/mol) and the energy transferred to the material is found to be 0.66 kWhr/kg (360 kJ/mol) in 4 hours of mechanical activation under identical milling conditions resulting in about 6% of the energy input to the mill being transferred to the material. Zircon has a Mho's hardness of 7-8 whereas ilmenite has a hardness of 5-6 [12].
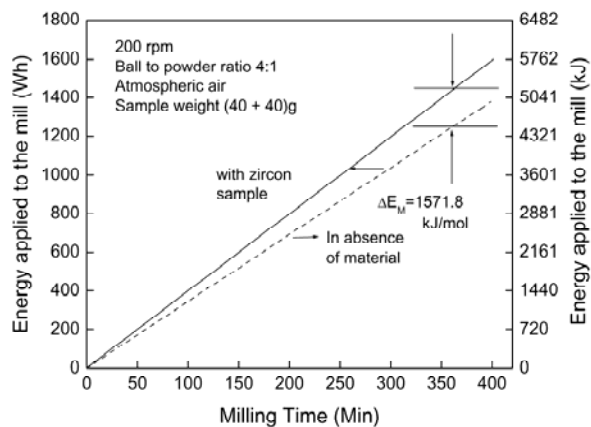

Figure 2. Variation of energy applied to the mill with time of milling

Isothermal Calorimetry

Assuming that there is no change in pressure and neglecting the work done against external pressure ($P\Delta V$) during the mechanical activation process, the change in internal energy (ΔE) during the milling process can be assumed to be the change in enthalpy. In the process of mechanical activation, the energy is stored in the material through increased surfaces, enhanced grain boundaries, increased defect density (point, line, stacking faults and volumetric defects) and structural transformation to higher energy structures including disordering. The stored energy is subsequently released through relaxation processes [4-6]. The relaxation times range from 10^{-9} seconds for lattice vibrations to more than 10^7 seconds for metastable structural states and surfaces [4, 5]. However, during the time scale of the calorimetric experiment only partial relaxation of defects occurs and the extent of relaxation depends both on temperature and time. The relaxation kinetics for the various micro-processes given by Balaz [5] indicates that the point, line and surface defects relax within 10-1000 seconds. The timescale of the calorimetric experiment at room temperature is expected to correspond to the energy of relaxation of the point and line defects especially at the surface.

The variation of power in the calorimeter as a function of time of relaxation in distilled water at 27 °C is shown in Fig. 3 for the as received and activated zircon samples. The enthalpy of relaxation derived from the area under the curve corresponding to 5 hours of relaxation is shown in Fig. 4. It is observed that the enthalpy of relaxation increases linearly with time of activation; it is 16 kJ/mol for the zircon sample subjected to 6 hours of planetary milling. The finite relaxation enthalpy for the unmilled sample results from the experimental uncertainty of the isothermal calorimeter. The magnitude of the defect relaxation energy in zircon measured from calorimetric experiments (16 kJ/mol in 6 hours of milling) is comparable to that obtained for ilmenite (14 kJ/mol in 4 hours of milling).
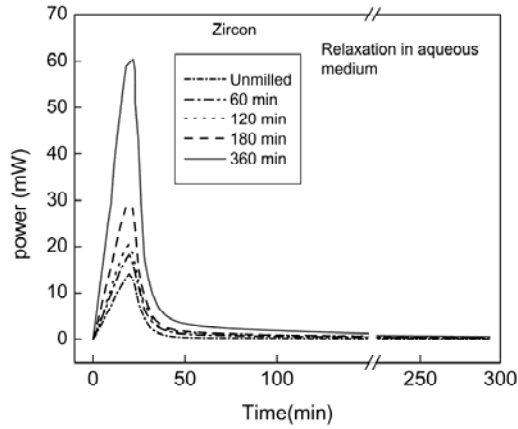
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Figure 3. Calorimetric results on variation of power with time of relaxation
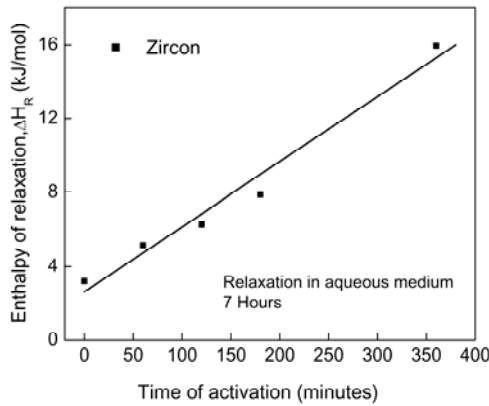

Figure 5. Variation of mean particle size and surface area with time of milling

Figure 4 Variation of enthalpy of relaxation with time of activation
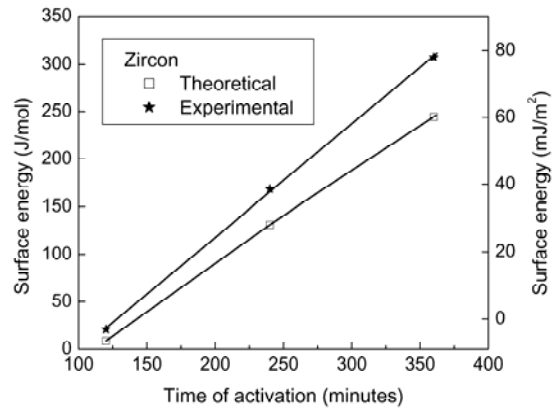
Figure 6. Variation of experimental and calculated values of surface energy with time of activation

Surface Energy

The increase in surface energy (ΔE_{SE}) of the material by mechanical milling can be estimated from surface area and specific surface energy measurements:

$$\Delta E_{SE} = \gamma_s . \Delta s . M \qquad (4)$$

where, γ_S is the specific surface energy, Δs is the increase in surface area by mechanical milling and M is the molecular weight of zircon. The variation of the mean particle size and BET surface area as a function of milling time for zircon is given in Fig. 5. Both, the average particle size and the surface area show an exponential variation with activation time and a surface area of 19 m²/g is achieved in 480 minutes of activation. The variation of the energy stored in surfaces with time of activation is shown in Fig. 6.

The surface energy increases linearly with the time of activation. In 6 hours of activation, a surface energy of 80 mJ/m² (307
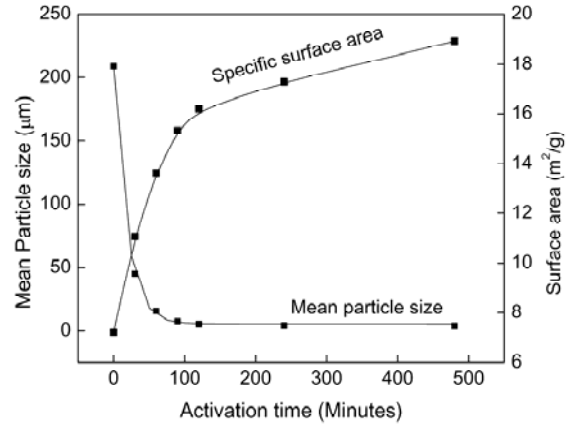
J/mol) is achieved for zircon. This is higher than that obtained for ilmenite (45 mJ/m² i.e., 37 J/mol in 4 hours of mechanical milling). The molar surface energies are derived by combining the specific surface energy with the measured specific surface area. An expression has been proposed by Tromans and Meech [13] for the increase in surface energy per unit mass (ΔE_S):

$$\Delta E_{SE} = \frac{6 F_r \gamma}{\rho} \left[\frac{1}{D_f} - \frac{1}{D_i} \right] \approx \frac{6 F_r \gamma}{\rho D_f} \qquad (5)$$

where, ρ is the mineral density (gm⁻³), D_i is the initial average particle diameter, D_f is the final average particle diameter, γ_S is the fracture surface energy (Jm⁻²), F_r is the surface roughness factor (>1) allowing for non-spherical morphology of milled particles. The calculated values of surface energy determined from data derived in this study using the equation of Tromans and Meech [13] is compared with the direct measurements of surface area and surface energy in Fig. 6. The calculated values are somewhat lower than the experimental values because the porosity and surface defects caused by mechanical activation are not taken into account in the expression of Tromans and Meech.

Grain Boundary Energy

The energy stored in the grain boundaries of the material can be given as:

$$\Delta E_{Sgb} = \gamma_{GB} . \Delta A_{GB} . M \tag{6}$$

where, γ_{GB} is the specific grain boundary energy, ΔA_{GB} is the change in grain boundary area of the material by mechanical activation and M is the molar weight of the sample. The variation of average crystallite size of zircon as a function of time of activation measured from X-ray line broadening measurements using the Hall-Williamson method is shown in Fig. 7.
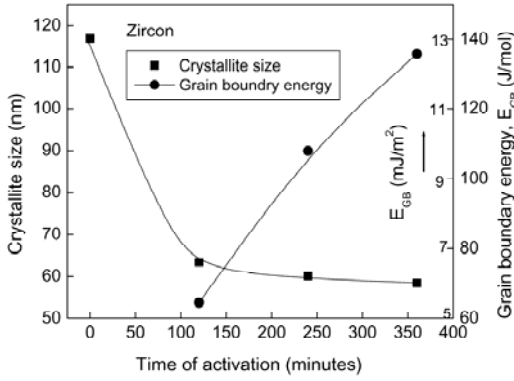
Figure 7. Variation of crystallite size and grain boundary energy with time of activation

The measured crystallite size decreases exponentially with time of activation and reaches a critical value after which it remains constant. The mean crystallite size achieved by milling zircon (58 nm) is larger than that obtained for ilmenite (30 nm). The total grain boundary area is determined using the mean crystallite size of the zircon sample obtained from XRD line broadening analysis (D) assuming the crystallites to have a tetrakai-decahedron configuration [9]:

$$\Delta A_{GB} = N * 47.569 * (D/3)^2 \tag{7}$$

where N is the number of grains per unit volume. In general, the specific grain boundary energy for minerals is approximately 40% of the specific surface energy [14]. The variation of total grain boundary energy with time of activation calculated from the measured grain boundary area and specific grain boundary energy is also depicted in Fig. 7. The total grain boundary energy of zircon in 6 hours of milling is estimated to be 13 mJ/m^2 (136 J/mol derived by combining the specific grain boundary energy with the measured grain boundary area).

Strain Energy

Eshelby has proposed an expression for the elastic strain energy from the theory of elasticity [15]:

$$E = \frac{18\mu K \varepsilon^2}{4\mu + 3K} \tag{8}$$

where μ is the shear modulus of the material, K is the bulk modulus of the material and ε is the strain..

The strain energy is calculated with the assumption that there is no change in shear and bulk modulus of the material during the process of mechanical activation. The bulk modulus and shear modulus of zircon are taken to be 229 GPa and 107 GPa respectively [16]. The elastic strain induced by mechanical activation is obtained from the XRD line broadening measurements of five most intense reflections using the Hall-Williamson method. The variation of strain and strain energy of zircon with time of activation is illustrated in Fig. 8. Both the strain as well as the strain energy varied exponentially with time of activation. The 6 hours milled sample showed total elastic strain energy of 59 kJ/mol. The total strain energy in 6 hours of milling measured for zircon is significantly lower than that obtained for ilmenite (84 kJ/mol in 4 hours of milling).
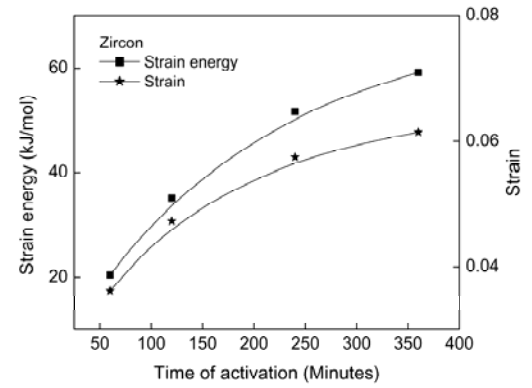
Figure 8. Variation of strain and strain energy with time of activation

Energy of Amorphisation

The energy of amorphisation of milled zircon can be determined from the extent of amorphisation (f_A) and the enthalpy of fusion at the reduced temperature of amorphisation (ΔH_F) using the following equation:

$$\Delta E_A = \Delta H_F . f_A \tag{9}$$

The enthalpy of amorphisation at temperatures below the melting point can be written as:

$$\Delta H^T_{Crys \leftrightarrow Amor} = \Delta H^{MP}_F - \int_{MP}^{T} \Delta C_P dT \tag{10}$$

where

$$\int_{MP}^{T} \Delta C_P dT = \int_{MP}^{T} \left[C_{P\,liquid} - C_{P\,solid} \right] dT \tag{11}$$

$$= \left[a(T - T_{MP}) + b\left(T^2 - T_{MP}^2\right) + c\left(\frac{1}{T} - \frac{1}{T_{MP}}\right) \right]_{Liquid}$$

$$- \left[a(T - T_{MP}) + b\left(T^2 - T_{MP}^2\right) + c\left(\frac{1}{T} - \frac{1}{T_{MP}}\right) \right]_{Solid} \tag{12}$$

where, ΔH^{MP}_F is the enthalpy of fusion at the melting point and *a, b,* and *c* are the thermodynamic coefficients for the specific heat (C_p) of zircon in solid and liquid states. Data on the enthalpy of fusion of zircon is not available in the literature. The enthalpy of fusion of zircon was estimated from that of ZrO_2 and SiO_2 assuming Hess law. The specific heat of zircon in solid state is taken from the database of the FACTSAGE software (Version 5.0). Since data on the specific heat of zircon in liquid state is not available in the literature, it is derived from the Kopp-Neumann rule using the Cp data of ZrO_2 and SiO_2 in the liquid state. Strictly, the Kopp-Neumann rule cannot be applied to liquids. The enthalpy of fusion and heat capacity data are derived at 300 K and the fraction of amorphisation is derived from the integral intensity of XRD peaks (Ohlberg, and Strikler, 1962). The fraction of amorphisation and the calculated amorphisation energy as a function of milling time is depicted in Fig. 9. It is observed that the energy of amorphisation increases exponentially with time of activation. Zircon when activated for 6 hours shows a change in amorphisation energy of about 53 kJ/mol. This is much higher than that estimated for ilmenite (12 kJ/mol in 4 hours of milling).
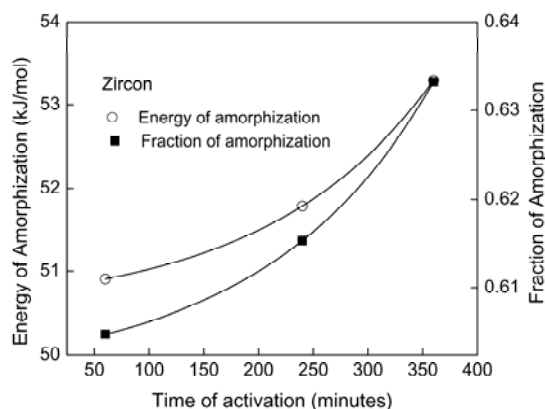

Figure 9. Energy of amorphization of zircon with time of activation

Estimation of the Stored Energy

The stored energy in the material is taken to be equal to the sum of energy changes contributed by the enthalpy of relaxation of defects, change in surface energy, grain boundary energy, strain energy and energy of amorphisation. This is 128 kJ/mol for the 6 hours activated zircon. Although the stored energy in zircon is higher than in ilmenite (96 kJ/mol), this accounts for only 1.1 % of the energy applied to the mill. In the case of ilmenite, the total stored energy in four hours of milling was found to be 1.6% of the applied energy. It is seen that a major part of the energy is stored as strain energy and structural disorder whereas the extent of energy stored in point and line defects, additional surfaces and grain boundaries are comparatively lower. It is clear that a large part (>90%) of the energy transferred to the material is lost possibly as heat during the process of breakage of bonds during the mechanical milling process.

The energy stored in the mineral samples also manifests itself through a reduction in activation energy (ΔE) and an increase in the rate of dissolution (Δk) in leaching studies. The decrease in

Table 2. Summary of the energy measurements in zircon

Time of milling (min)	Energy applied to the mill	Energy transferred to material (ΔE_M)	Energy lost in breakage of bonds	Manifestation of stored energy* in different forms				
				Surface (E_{SE})	Grain boundary (ΔE_{GB})	Elastic Strain (ΔE_ε)	Amorphization (ΔE_A)	Defects with short relaxation times (ΔH_{Defrel})
60	1820	241	169.6	---	---	20.5	50.9	5.2
120	3637	526	439.8	21	65	35.1	51.1	6.3
240	7204	959	855.4	168	108	51.6	51.8	7.9
360	10814	1571	1458.1	307	136	59.2	53.3	16.0

* in kJ/mole

activation energy (ΔE) for the sulfuric acid dissolution of zircon because of mechanical activation was determined by us [17] in a separate study. The reduction in activation energy (ΔE) for the dissolution in sulfuric acid of zircon milled for 6 hours was 14 kJ/mol. This value is much lower compared to the estimated stored energy (128 kJ/mol).

Conclusions

An attempt is made to evaluate the energy balance for the mechanical activation process. The specific energy consumption in 6 hours of planetary milling of zircon is measured to be 18 kWh/kg (11877 kJ/mol) of which 2.38 kWh/kg (1572 kJ/mol) is transferred to the material i.e., about 13% of the energy input to the mill is transferred to zircon. It is deduced that more than 90% of this energy transferred to the material is actually expended in the breakage of the bonds which is released mainly as heat and only the remaining energy is truly stored within the material. This energy is found to be stored in additional surfaces and interfaces, point, line and volume defects, high energy structures and non-uniform strain. A large part of the stored energy is reflected as strain energy and structural disorder. Part of the defect energy stored in the activated ilmenite samples is found to relax much faster. The energy stored through additional surfaces and grain boundaries is found to be much lesser. Table 2 shows the summary of the energy measurements. The knowledge of the distribution of energy in various forms in materials subject to high energy milling has enormous implications in the downstream application of nano-materials synthesized by the mechanical milling route.

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