

About opportunities of the directed modification a set of defects in the surface region of ZnO particles

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Abstract

Using of EPR the laws of formation of various defects during mechanical treatment (MT) of powders of zinc oxide were considered. Formation of six different types of paramagnetic centers was established. The quantitative analysis of the changes of intensity (concentration of the centers in the sample) of EPR signals I–VI depending on conditions of MT (speed of rotation of jars of a mill, duration of MT, amount of entered additives, etc.) has allowed to establish interrelation between defects formation and temperature processes, which develop during MT. In the work the opportunities of an obtaining of samples with a necessary set of surface defects are discussed.

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1. Introduction

Mechanical destruction of solid state is the extremal process, which is accompanied by formation of a neogenic surface containing a wide set of the defects with different properties [1,2]. Thus, from the most common considerations, the use of mechanical treatment (MT) of various materials for initiation in them of catalytic properties is possible. Naturally, the catalytic reactivity of material will be determined by a concentration of catalytic centers.

The present paper describes the regularities of EPR-defects formation in ZnO-samples depending on conditions of MT. The analysis allows formulating recommendations concerning a choice of the conditions of MT for creation of a necessary set of reactive defects in the sample.

2. Experiments

The starting materials were commercially available ZnO (>99% purity, Reasol, Milan, Italy; corresponds to the specification of the American Chemical Society). Electron microscope studies (scanning electron microscopy, model LEO 1450 VP, LEO Electron Microscopy Inc., Thornwood, NY) showed that the average size of particle was $d_{\text{ZnO}} \approx 0.25 \mu\text{m}$.

MT of samples was carried out in Planetary Ball-Mill (type PM 400/2, Retsch Inc.). Grinding jars (volume 50 ml) and balls (3 of 20 mm and 10 of 10 mm) from tungsten carbide were used. The ratio of the balls to powders was 7:1, 14:1, 28:1 and 56:1 by weight. The MT was carried out in air (in hermetically sealed jars) with a maximal (for this mill) rotation rate of 400 rpm. Duration of the milling, t_{MT} , of powders was: 1, 3, 6, 30, 90, 390 min. Note that one of two jars from tungsten carbide, delivery by Retsch Inc., has completely collapsed right at the beginning of our experiments.

Also, specimens were pressed on installation for fabrication of synthetic superhard materials (model D 0043) at pressures P from 1 to 8 GPa. Standard equipment with a high-pressure chamber (from BN_g) of the “anvil-toroid” type was used.

Electron paramagnetic resonance (EPR, SE/X 2547—Radiopan, Poznan, Poland) at room temperature was used for investigation of the formation different paramagnetic centers during MT of the ZnO powder.

3. Experimental results

The EPR signal in the initial ZnO powder was absent. The pressing of samples caused the occurrence of series of EPR signals from some structural electron–hole centers in ZnO lattice (Fig. 1). In Table 1 the parameters of a Spin – Hamiltonian and types of these centers are given. The centers were identified by comparing the obtained results with

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Table 1
Values of obtained parameters of EPR signals in pressed zinc oxide powder and parameters of signals of defects obtained in study of single crystals

Signal	Values of g-factors obtained in this work	Center	Values of g-factors obtained on single crystals	References
I	$g_{\perp} = 2.0190, g_{\parallel} < g_{\perp}$	$V_{Zn}^{-} : Zn_i^0$	$g_{xx} = 2.0185, g_{yy} = 2.0188, g_{zz} = 2.0040$	3
II	$g_{\perp} = 2.0130, g_{\parallel} = 2.0140$	V_{Zn}^{-}	$g_{\perp} = 2.0128, g_{\parallel} = 2.0142$	4
III	$g_1 = 2.0075, g_2 = 2.0060, g_3 = 2.0015$	$(V_{Zn}^{-})_2^{-}$	$g_{xx} = 2.0077, g_{yy} = 2.0010, g_{zz} = 2.0059$	3
IV	$g_{\perp} = 1.9965, g_{\parallel} = 1.9950$	V_O^{+}	$g_{\perp} = 1.9963, g_{\parallel} = 1.9948$	5
V	$g = 1.964$	SDC	$g \approx 1.96$	6
VI	$g = 1.956$	SDC_{imp}	$g_{\perp} = 1.956, g_{\parallel} = 1.957$	7

SDC, small donor centers.

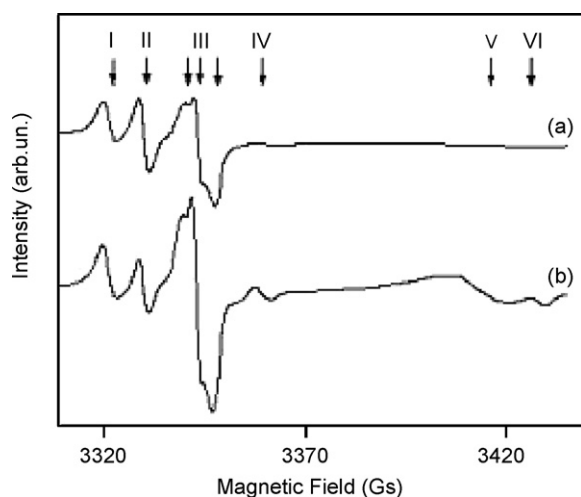


Fig. 1. EPR spectra initiated by a pressing of ZnO powders: (a) $P = 2$ GPa; (b) $P = 8$ GPa.

data for single crystal samples [3–7]. In Fig. 2 the dependence of the intensity of signals I–III on annealing temperature are given. This data allow to establish that signal II disappears after an annealing at $T_{treat} \sim 453$ K; signal I disappears after treatment at $T_{treat} \sim 493$ K; signal III disappears after treatment at $T_{treat} \sim 533$ K. Note that in the further we use these results for an estimation of temperatures developed during MT.

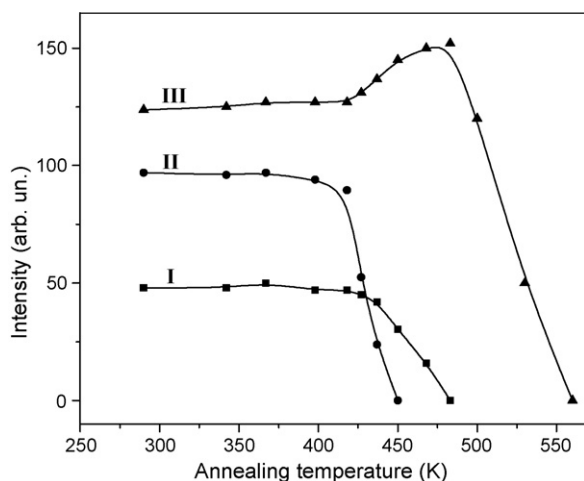


Fig. 2. Dependence of intensity of EPR spectrum of I, II and III centers in pressed ZnO ($P = 2$ GPa) on the annealing temperature.

Fig. 3 shows the evolution of EPR spectra of electron–hole paramagnetic centers I–III induced in ZnO during MT in mill depending on duration MT, t_{MT} , and amount of sample in a jar (the ratio of the balls to powders). These centers are formed in a zone of destruction. From the analysis of width of signals I ($\Delta B_I \approx 2.5$ Gs), II ($\Delta B_{II} \approx 3.0$ Gs) and III ($\Delta B_{III} \approx 2.7$ Gs) it is possible to conclude that local concentration of I, II and III centers does not exceed 0.1 at.%. Note that in these samples the formation of the V_O^{+} -centers (F^+ -center) and small donor centers (SDC) was not observed. Fig. 4 shows quantitative changes of intensity of these signals depending on t_{MT} and ratio of the

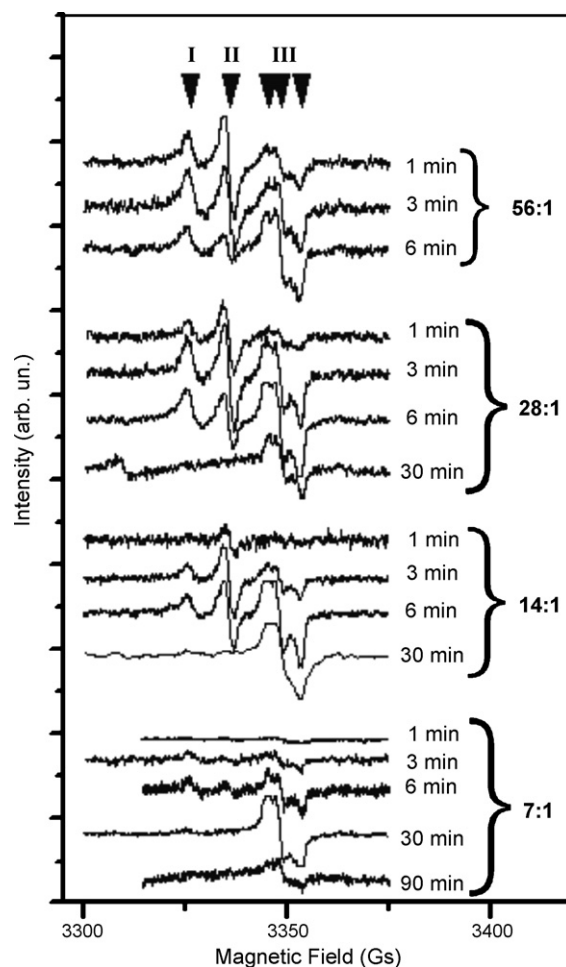


Fig. 3. EPR spectra of electron–hole paramagnetic centers I, II and III in ZnO powder depending on conditions (t_{MT} and the ratio of the balls to powder in weight) of MT.

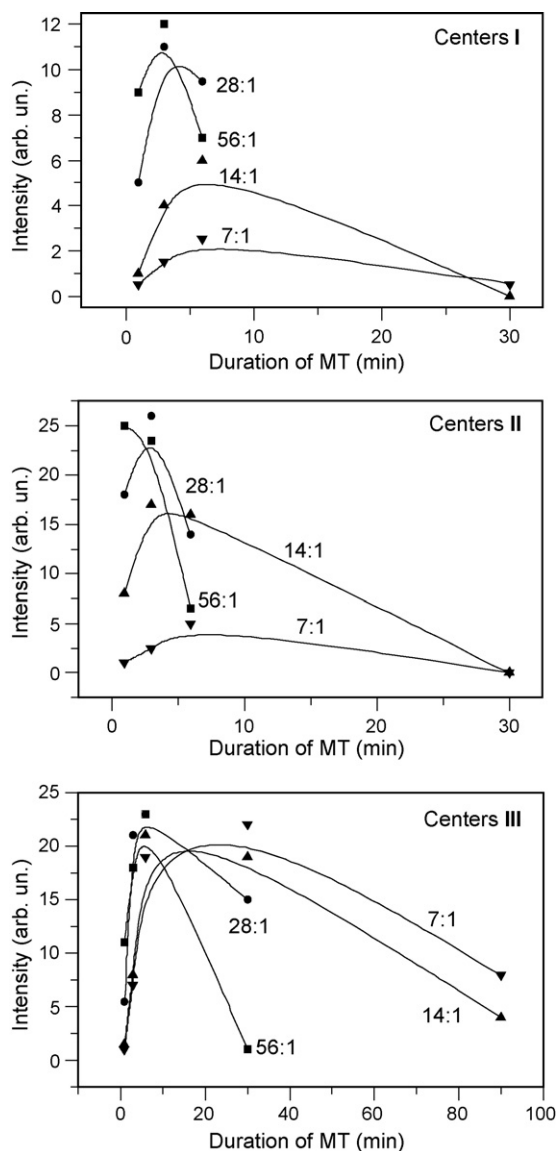


Fig. 4. The dependence of the intensity of EPR spectra of electron–hole centers I, II, and III on contentions of samples in jar and on duration of its MT.

balls to powders. It is easy to see that intensity of I, II and III centers essentially depends on conditions of processing.

4. Discussion

Let us consider results with a point of view of consecutive evolution of structure of defects in sample at prolonged MT. At the initial moment a mill (jars and balls) and the sample have room temperature. It is known that in a zone of destruction (and deformations) there is a formation of a wide set of defects, which have various physical and chemical properties [1,2]. In turn, the formation of defects is accompanied by development of various mechanothermic processes (impulsive, periodical, connected with rolling-process, and accumulative processes), which may actively modify a forming defects structure. Let us consider in more detail the thermal processes taking place during MT of powders.

4.1. The analysis of thermal processes at MT of disperse systems

The main areas of a heat release during a mechanic loading may be the zones of new surface formation, zones of dislocation development and displacement, zones of interparticle friction (i.e. zones of defects formation), and zones of friction between the grinder's working parts [1].

4.1.1. Interparticle friction

When the particles constituting the disperse system, i.e. the particles being in contact with each other, are in movement, the work being done against friction forces is transformed into a heat. It has been shown [8,9] that during sliding friction the temperature in contact areas increases up to the melting point of one of the substances. For an evaluation of local temperatures in the zone of contact of the bodies at friction a formula has been proposed:

$$\Delta T = T - T_0 = \frac{\mu P v}{4aI} \times (k_1 + k_2), \quad (1)$$

where μ is the friction coefficient, P the pressure at the contact surface, v the sliding velocity, a the radius of contact area, I Joules equivalent, and k_1 and k_2 are the thermal conductivities of the bodies in friction. According to the estimates [8], during this process the momentary temperature can jump up to 1300 K. The duration of such temperature pikes at the area of 10^{-7} to 10^{-9} m² is $\sim 10^{-4}$ s. T_0 is the initial temperature in a place of contact of the particles.

4.1.2. Thermal effects during deformation

The formation of deformation–destruction zones (i.e. zones of an active defect development) is characterized by the appearance of high-temperature spikes [8,10]. Theoretical analysis indicates that we may expect an increasing of temperature only in case of high-dislocation densities:

$$\Delta T = T - T_0 \approx \ln \left(\frac{n\Lambda}{\lambda} \right) \frac{b\sigma v n}{2\nu\pi K}, \quad \text{if } \lambda \ll \Lambda,$$

$$\Lambda = \frac{2\chi}{v}, \quad (2)$$

where b is the Burgers vector, σ the mechanical stress, K the heat conductivity, n the number of movable dislocations, χ the temperature conductivity ($\chi = K/c$, c is the specific heat), and λ is the mean distance between dislocations.

The formation of dynamic lines of sliding occurs over times of about several microseconds [10] and a time of relaxation of this heat peak, t_h , is several milliseconds [11]. The experimental observation of a temperature rise up to 1000 K in the process of the deformation has been reported [8,10].

4.1.3. Thermal effects at formation of a single micro-crack

The more general phenomenon of a cracking is accompanied by formation of a short-lived ultra-high-temperature peak. In the case of a high velocity of a fracture, which occurs under adiabatic conditions, the upper limit of temperature, which may be calcu-

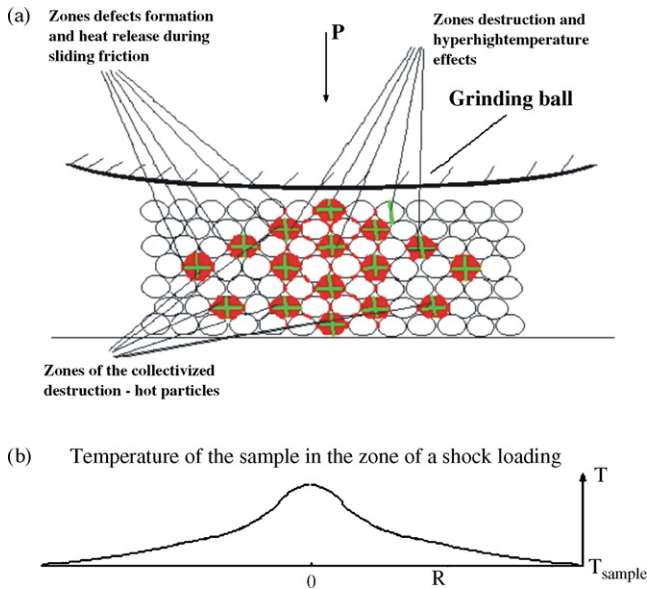


Fig. 5. Scheme of the defects formation and development of the temperature effects in powder sample during a shock loading by a milling ball (a) and space distribution of temperature in a loading zone in a moment of loading (b).

lated using Q (the heat released as a result of the irreversible plastic deformation dependent on the cracking resistance R : $Q = 0.6-0.9R$), is

$$\Delta T = T - T_0 = \frac{Q}{(c\rho \times 2\delta)}. \quad (3)$$

Here c is the specific heat, ρ the density, and 2δ is the width of the destruction zone [12]. This estimation shows that the maximum temperatures, which can be achieved at a cracking, significantly exceed 1000 K [12]. For glass and quartz the maximum temperatures may exceed 3200 and 4700 K, correspondingly [12]. This ultra-high-temperature excitation lasts about $\sim 10^{-9}$ s. In the case of a single micro-crack development, the shape of ultra-high-temperature spike depends on the thermal conductivity of the material and on the temperature conditions of MT.

4.1.4. Thermal effects at collectivized destruction of a single particle

In the case of formation of the destruction zone, which has a high-local density of micro-cracks (Fig. 5a), the transformation of a group of short-term ultra-high-temperature spikes into an averaged “collectivized high-temperature spike” with significantly larger duration of high-temperature excitation must take place:

$$\Delta T = T - T_0 = \sum Q_i / (c m_p). \quad (4)$$

Here Q_i reflects various thermal processes occurring at the moment of destruction of a particle, and m_p is the weight of a particle.

4.1.5. Thermal effects in a loading zone at MT

The process of the development of mechanothermal effects in grinders-activators has a space-heterogeneous and discrete

character. The basic processes of defects formation is accompanied by different thermal effects in a loading zone (Fig. 5a). The set of various elementary thermal processes, which have small duration, promotes the fast local heating of a sample in a loading zone (Fig. 5b). The value of the temperature effect depends on loading parameters, speed of defects formation, amount of material in a loading zone, etc. In general, $\Delta T = T - T_0 = \sum Q_n / mc$, where Q_n is various thermal effects and m is quantity of a material in a loading zone. The duration of thermal excitation in such zone will be determined by the thermal conductivity of elements surrounding this zone (jar, balls, and gas environment).

Now let us also introduce the parameter of cooling powder in compact state, $t_{cool,a}$. It characterizes an interval of time, which is necessary for cooling the materials in compact state in loading zone up to reference temperature.

4.1.6. The increase of average temperature of a sample

The combination of all local pulse-mechanothermal processes results in an increase of the average temperature, T_{av} , of the sample. In the case of prolonged MT exist the latency time for achievement by the system of thermodynamic equilibrium with the environment. Let us introduce a parameter of a loading, t_{load} (see Fig. 6a). It is an average interval of time, which characterizes the periodicity of presence of material in a loading zone. In a case $t_{load} < t_{cool,av}$ an increase of average temperature of a sample, T_{av} , takes place. In Fig. 6b the schemes of the increasing T_{av} for two various frequencies of loading are given.

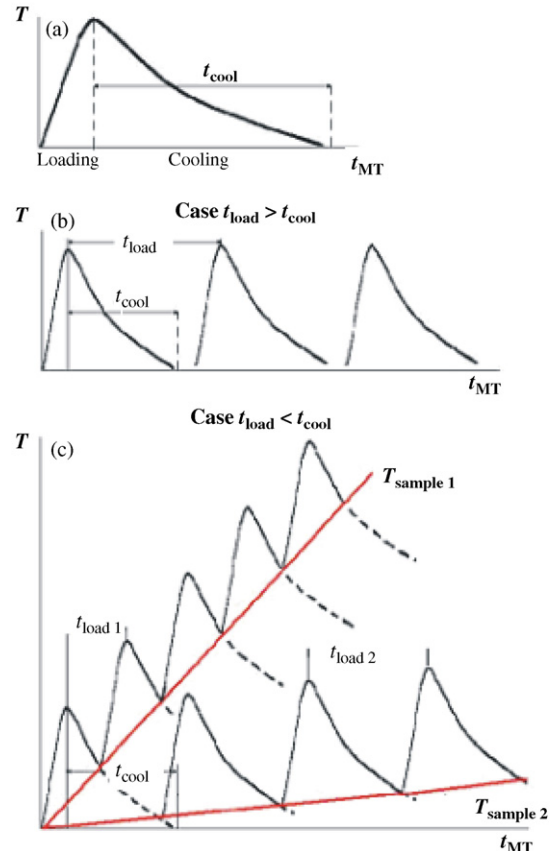


Fig. 6. Schemes of an increase of T_{av} for different frequencies of loading: (a) single influence; (b) case $t_{load} > t_{cool}$; (c) two cases for $t_{load} < t_{cool}$.

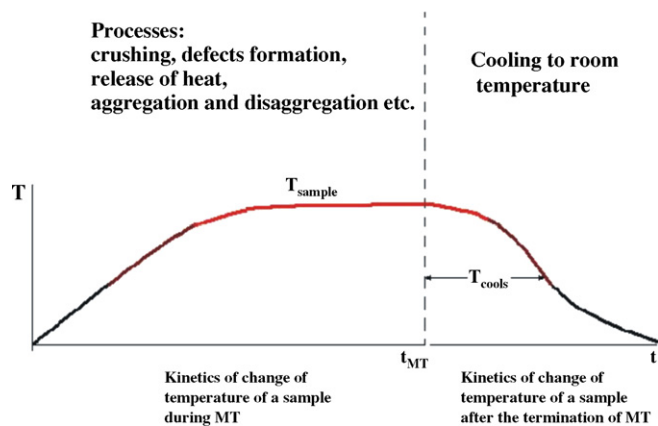


Fig. 7. The change of average temperature of a sample during work of a grinder-activator and after its stop.

The conducted analysis shows that mechanical reactor works simultaneously as a heat reactor. The heat released is being spent on the heating of the disperse system, working components of the mill and environment. At the prolonged MT in system the thermodynamic balance is established. The average temperature of a sample achieves the maximal meaning (equilibrium temperature, T_{eq}), which is characteristic for concrete conditions of the processing (Fig. 7). At that the conditions $t_{load} = t_{cool,av}$ are established. And only after switching off the grinder (the mill), the system grinder–sample is cooled down to ambient temperature. For the description of a temperature regime of a sample cooling we introduce the parameter $t_{cool,s}$ (Fig. 7).

4.2. Defects annealing in the average temperature field of a sample

At absence of significant changes in temperature of sample during MT it is possible to expect the proportional to t_{MT} an increasing of concentration of “primary” defects (Fig. 8a). It takes place during initial stage of MT or during work of a grinder in a discrete regime (opportunity of cooling of a sample up to initial temperature thus is given). However during work in a continuous regime the increase in T_{av} of a sample (Figs. 6c, 7 and 8b) occurs. In this case the consecutive annealing of defects befalls. The annealing of defects, which have a minimal value of E_{ac} , takes place first (Fig. 8c). Thus, the generated set of defects in a sample (Fig. 8c) is determined by concrete conditions of grinder work.

4.3. Hyper-rapid thermal defects annealing

Effect of hyper-rapid thermal defects annealing during MT is possible to observe during grinding of such material in the medium of other materials having a different thermal conductivity (Figs. 9 and 10). It was revealed by authors [13–16] on examples of a grinding of a ZnO (a), ZnO–TiO₂ (b), and ZnO–SnO₂ (c) samples. Significant qualitative differences in the shapes of the EPR spectra of ZnO for a, b, and c specimens (Fig. 9) [13–16] indicate that the destruction–deformation process does not represent the development of a single crack in

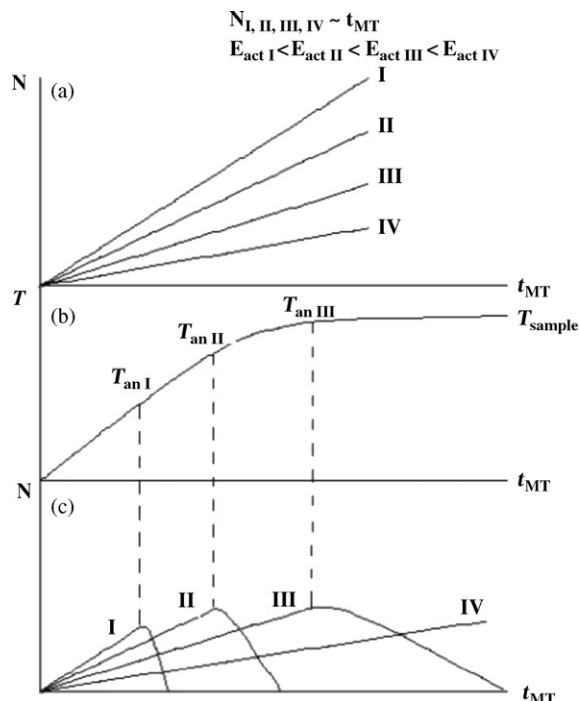


Fig. 8. The kinetic schemes of accumulation of defects at constant temperature of a sample (a), the change of temperature of a sample (b) and accumulation of defects in real conditions (c) during MT.

individual ZnO particle. The destruction–deformation process does not grow out of a series accumulation of such individual acts of destruction. In these cases the EPR spectra in a, b, and c specimens would be the same. The differences in the EPR spectra [13–16] indicate that in the disintegrating ZnO particles the collective process of the destruction–deformation takes

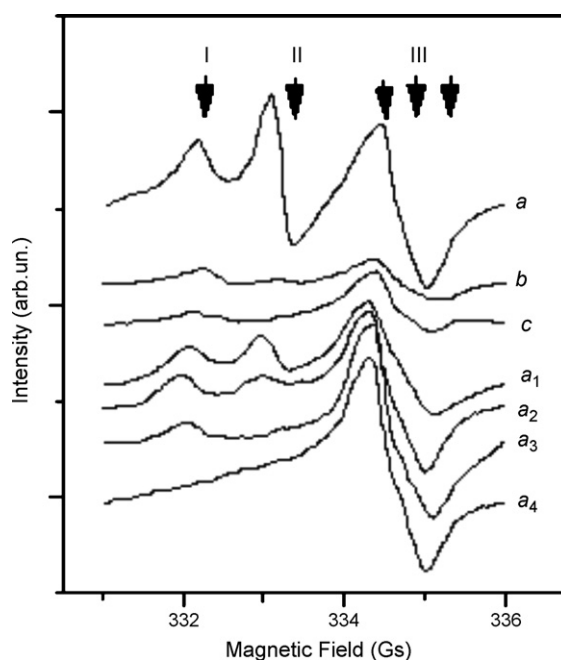


Fig. 9. EPR spectra in ZnO after MT of ZnO–SnO₂ (a), ZnO (b) and ZnO–TiO₂ (c) specimens and after temperature treatment of ‘a’ specimen ($t_{MT} = 5$ min): $T_{treat} = 428$ K (a_1); $T_{treat} = 443$ K (a_2); $T_{treat} = 453$ K (a_3); $T_{treat} = 493$ K (a_4).

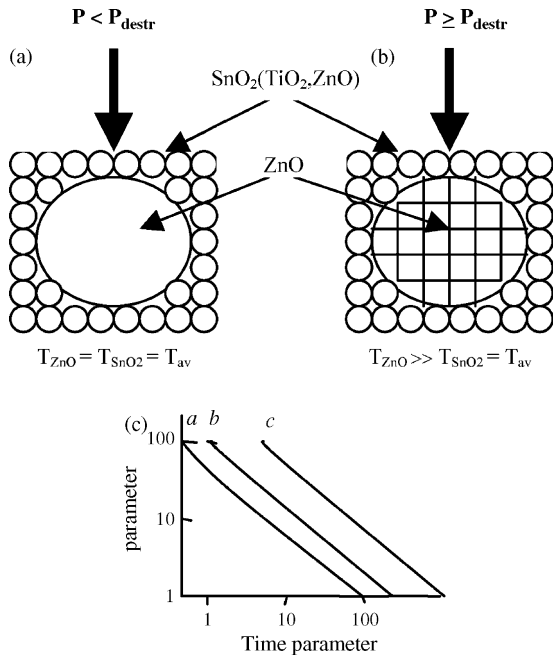


Fig. 10. Break-up model of an individual ZnO particle in environment of other (ZnO, SnO₂, TiO₂) particles: (a) before destruction; (b) at moment of destruction; (c) kinetics of the changes of temperature excitation (according to [17]) in ZnO particle surrounded by the particles of SnO₂ (a), ZnO (b), and TiO₂ (c).

place. We assume that at any specific moment of a loading time, the individual ZnO particles in “the most optimum states for destruction” are exposed to this process to the full extent. Intensive defect formation occurs in the particles, which then act as sources of heat release.

The analysis carried out allowed us to associate the differences in the EPR spectra of specimens a, b, and c (Fig. 9), the specific mechano-thermal process, that develops in an individual ZnO particle and the effect of hyper-rapid thermal defects annealing (HRTDA) on the defect structure that is formed [14]. A calculation such as that made [17] for the case of time decay of the local energetic excitation can be used. Thus

$$q = \frac{Q}{(4\pi\chi t)^{3/2}} \exp\left(\frac{-r^2}{4\chi t}\right), \quad (5)$$

where Q is the heat released at $t=0$ for point $r=0$, q the energy density of the excited solid, r the distance to the excitation center, t the time and χ is the temperature conductivity of the medium (for ‘a’ sample such environment is ZnO; for ‘b’ sample such environment is TiO₂; for ‘c’ sample such environment is SnO₂). Eq. (5) allows a qualitative description of the temperature regimes of the “thermoactive” ZnO particles in different samples. The duration, t_p , of the mechano-thermal spike of a particle is inversely proportional to the temperature conductivity of its environment, i.e. $t_p \sim 1/\chi$.

As the various defects have the different activation energies of annealing, E_{ac} , in the destroying particles depending on duration of a thermal pulse the various statistical set of the defect centers is formed. The given example illustrates also that, at least on the initial stage MT, the collectivized destruction of individual particles is preferable.

4.4. Influence of amount of a work material on thermal effects

The thermal processes, which developed during MT, lead to: (a) the heating of the sample; (b) the heating of a jars and balls of a mill; (c) the heating of a surrounding atmosphere. The use of peak changes of EPR signals I, II and III (see Section 3 and Figs. 1–4) as temperature probes allows monitoring the temperature changes in the work sample depending on its amount in a jar and duration of MT. Fig. 11 shows the temperature kinetics of the EPR spectra in the samples. The analysis of curves in Fig. 11 indicates that in an initial stage of MT the rate of temperature rise ($\nu_T = \Delta T/\Delta t_{MT}$) is: $\nu_T \approx 3.8 \text{ K min}^{-1}$ for the sample with the ratio of the balls to powders 7:1 by weight; $\nu_T \approx 6.2 \text{ K min}^{-1}$ for the sample with the ratio of the balls to powders 14:1; $\nu_T \approx 10 \text{ K min}^{-1}$ for the sample with the ratio of the balls to powders 28:1; $\nu_T \approx 16 \text{ K min}^{-1}$ for the sample with the ratio of the balls to powders 56:1. From here it is possible to make the conclusion that the rate of temperature rise at initial stage MT follows law:

$$\nu_T \sim \frac{1}{m^n}, \quad (6)$$

where m is the amount of sample in jar, $n \approx 0.7\text{--}0.6$.

4.5. Some opportunities of the directed creation of a necessary set of defects

- The change of initial temperature conditions of processing, on the one hand, can change a set of the formed centers (due to the change of the mechanism of destruction). On the other hand, can influence on temperature conditions of the sample during of MT.
- The high-energy processing, on the one hand, intensifies process of defects formation. However, on the other hand, the high-energy processing intensifies the fast increasing of tem-

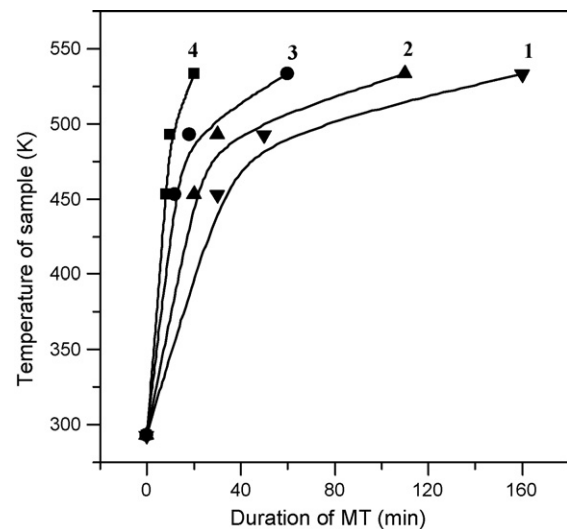


Fig. 11. The temperature kinetics of the powder ZnO samples depending on its amount in a jar of a mill. The ratio of the balls to powders by weight is (1) 7:1; (2) 14:1; (3) 28:1; (4) 56:1.

perature of the sample and considerably raises equilibrium temperature (T_{eq}) of the sample. It leads to fast annealing of defects with small values of E_{ac} and to accumulation in the sample of high-energy defects.

- (c) MT in a intermittent duty of a mill allows to use the initial stage of processing, when the temperature of the sample is still low enough and the annealing processes of low-energy defects do not yet work.
- (d) The change of quantity, the size and weight of balls, amount of a work material will allow to change both conditions of mechanical loading (thereby to realize the modification of a set of created defects) and to change a temperature regime of the sample.
- (e) The change of a material of a jar and its weight influences speed of a heat sink from the sample. As a result it tells on value of equilibrium temperature of the sample.
- (f) The change of type of additives (possessing various mechanical properties and heat conductivity) to a work material in a combination with an intermittent duty of MT allows to modify a set of defects due to realization described above effect of hyper-rapid thermal defects annealing, etc.

5. Conclusion

The results show that MT of disperse systems is accompanied by: (a) formation of wide set of the various defects, which have various properties and the different activation energy of annealing; (b) development of a wide set of various temperature effects. Thus, the ensemble of defects (the active centers) formed in a final material will be substantially defined by the temperature conditions developed in the used mechanical reactor. Modification of conditions of processing: frequency and intensity of

mechanical actions, duration of processing, the quantity, size and weight of balls, the amount of a work material, the weight of a jar, the heat conductivity of a material of a jar and environment, the additives (having different mechanical properties and different heat conductivity) to a work material, the initial temperature of a grinder and the sample and many other things allow directionally to optimize the obtaining of a set of the necessary active centers.

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