Science of Sintering, **36** (2004) 65-72

UDK 621.926.085:661.847.2:666.119.2

Electron Paramagnetic Resonance in the Research of Defect Formation and Thermal Processes During Grinding of ZnO Powders

M. Kakazey[1], M. Vlasova[1*], M. Dominguez-Patiño[1], G. Dominguez-Patiño[1], T. Sreckovic[2], N. Nikolic[2]

[1] CIICAp/FCQI, Universidad Autonoma de Estado de Morelos, Av. Universidad, 1001, Col. Chamilpa, C.P. 62210, Cuernavaca, Mexico,

[2] Joint Laboratory for Advanced Materials of SASA, 11000 Belgrade, Serbia and Montenegro

Abstract:

This work shows some possibilities for using electron paramagnetic resonance in an experimental study of the role of mechanothermal effects in the formation of defect structures in dispersed systems during prolonged mechanical treatment of ZnO powders. The use of EPR for this purpose is based on the known fact that initiation of a number of paramagnetic centers occurs during mechanical treatment of some materials. Such centers can serve as EPR-sondes of different thermal processes appearing during mechanical treatment of systems containing ZnO.

Keywords: *Zinc oxide, Mechanical treatment, Point defects, Annealing, Electron paramagnetic resonance*.

1. Introduction

The process of mechanical treatment (MT) of solids is accompanied by defect formation [1]. In turn, the formation of deformation-destruction zones (i.e. zones of active defect development) is characterized by the appearance of high-temperature spikes [2]. In particular, an experimental observation of a temperature rise up to 1000 K in the deformation process has been reported [3]. The more general phenomenon of cracking is accompanied by the formation of a short-lived ultra-high temperature peak [4]. However the problem of interdependence of a defect structure, formed during MT, and the developed thermal effects have practically not been considered in literature [1]. The main reason why little is known about this phenomenon important for materials science consists in: it is methodically difficult to precisely measure the temperature in a zone of destruction; with high localization and small duration of flowing processes.

This work shows some possibilities of using the EPR method in an experimental study of the role of mechanothermal effects in the formation of defect structures in dispersed systems during prolonged MT. The use of EPR is based on the known fact of initiation of a number of paramagnetic centers during MT of some materials [5]. As the EPR method showed, evolution of paramagnetic defects with increasing MT time took place during MT of ZnO powders [6]. Such a transformation could be caused by the development of

*) Corresponding author: kakazey@hotmail.com

mechanothermal processes in the treated system, i.e. by the processes of gradual increase of temperature in ZnO powder up to T_{eq}. The disappearance of one center and the appearance of others depend on the condition of MT. This is shown by different activation energy values. Thus, such centers can serve as EPR-sondes of mechanothermal processes in systems containing zinc oxide.

2. Theoretical model

ZnO powder and also ZnO particles surrounded by SnO_2 and TiO_2 particles were chosen as the object of the present study.

A commercial powder of ZnO with a specific surface area S_0 of about 3.6 m^2/g and commercial powders of TiO_2 (rutile, $S_0 \approx 4.8$ m^2/g) and SnO_2 with $S_0 \approx 2.9$ m^2/g were used in the present study. The mixtures (50:50 vol%) investigated were ZnO–SnO_2 (specimens ZS) and ZnO–TiO_2 (specimens ZT), and pure ZnO (specimens ZZ). The average size of ZnO particles was approximately 0.4 μm.

Thermal conductivities of ZnO, SnO_2, and TiO_2 at room temperature were ~17.5, 30, and 6.5 W/(m·K), respectively, and microhardness values of the powders were ~1500, 10 000, and 7800 MPa, respectively [7].

Specimens ZZ, ZS, and ZT were mechanically treated in a vibro-mill (type MN 954/3, KHD Humboldt Wedag AG) in open air with process time t_{MT} from 0 to 300 min. Also, specimens ZZ 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_r) of the "anvil-toroid" type was used.

The EPR spectra were measured at room temperature using an X-band spectrometer (SE/X 2547 Radiopan) in absorption mode and magnetic field modulation.

3. Results and discussion

The EPR signal was absent in the initial ZnO powder, but MT and pressing caused the occurrence of a series of EPR signals of structural electron-hole centers in zinc oxide samples ZZ, ZS, and ZT (Fig. 1). In Table I the parameters of a Spin - Hamiltonian of these centres are given as well as the types of centres that were identified by comparing the obtained results with published data for single crystal samples [8-12].

Table I Values of obtained parameters of EPR signals in pressed or MT zinc oxide powder and parameters of signals of defects obtained in the study of single crystals.

Signal	Values of g-factors obtained in this work	Center	Values of g-factors obtained on single crystals	References
I	$g_\perp = 2.0190$, $g_\parallel < g_\perp$	$V_{Zn}^{-} : Zn_i^0$	$g_{xx} = 2.0185$, $g_{yy} = 2.0188$ $g_{zz} = 2.0040$	8
II	$g_\perp = 2.0130$, $g_\parallel = 2.0140$	V_{Zn}^{-}	$g_\perp = 2.0128$, $g_\parallel = 2.0142$	9
III	$g_1 = 2.0075$, $g_2 = 2.0060$, $g_3 = 2.0015$	$(V_{Zn}^{-})_2^{-}$	$g_{xx} = 2.0077$, $g_{yy} = 2.0010$, $g_{zz} = 2.0059$	8
IV	$g_\perp = 1.9965$, $g_\parallel = 1.9950$	V_O^{+}	$g_\perp = 1.9963$, $g_\parallel = 1.9948$	10
V	$g = 1.964$	SDS	$g \approx 1.96$	11
VI	$g = 1.956$	SDS_{imp}	$g_\perp = 1.956$, $g_\parallel = 1.957$	12

A unique difference between the basic series of EPR signals detected in the pressed samples and MT, i.e. dispersed ZnO powder, is the occurrence of a relatively low EPR signal with g = 1.956 in samples pressed under high P values (Fig. 1., centre VI). This signal was attributed to shallow donor states (SDS_{imp}) connected with the presence of impurities in ZnO [12].

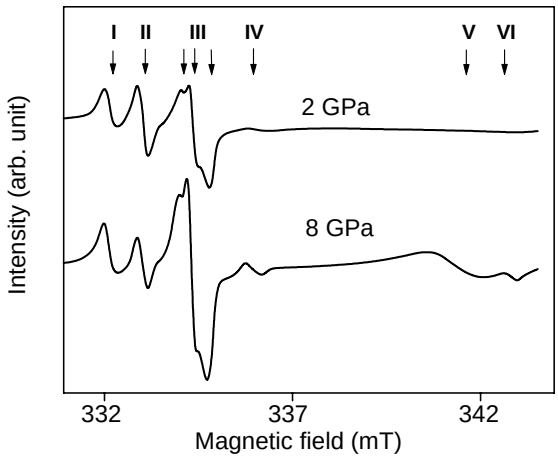

Fig. 1 EPR spectra initiated by pressing of ZnO powders with P = 2 GPa and P = 8 GPa.

Figure 2 shows that the linear rise of intensity of signals I, II and III is practically observed up to the pressure of P = 2 GPa. Under this pressure the intensity of signal II becomes maximal and further increase of pressure tends only to attenuate the signal [13].

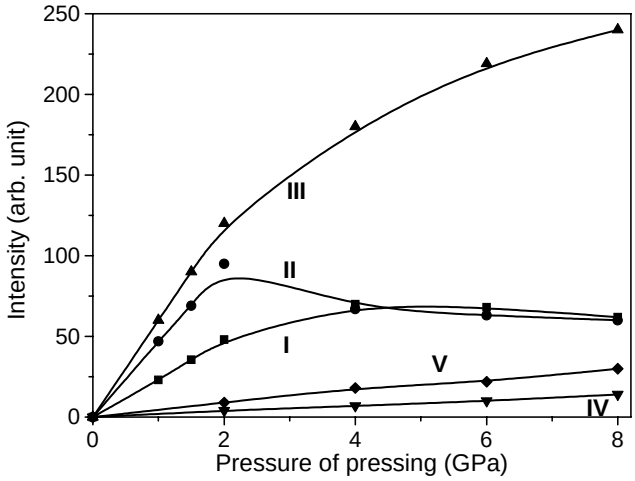

Fig. 2 Dependence of the intensity of EPR signals I - V in ZnO (a) on the pressing pressure P.

The intensity *I* of EPR signals I, II and III in ZnO (Fig. 3) for all three systems was proportional to t_{MT} at the initial stage of processing (Fig. 4) [14]. A correlation between the microhardness of the specimen components and the increments of signal III was observed (Fig. 4). The end of such proportionality with the increase of t_{MT} specifies the conclusion of the initial stage of MT. The duration of the initial stage t_1 is different for samples of various series. So, for the ZnO-SnO_2 system - t_1 = 5 min [15], for ZnO-TiO_2 - t_1 =10 min [16], and for

ZnO - t_1 = 30 min (see Fig. 4). The EPR signal from the centres II in samples ZnO-TiO_2 is absent.

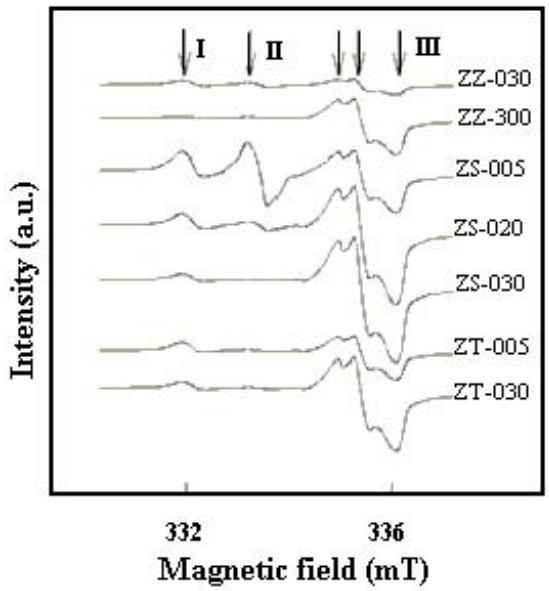

Fig. 3 EPR-spectra initiated in ZnO by the mechanical treatment of ZnO (ZZ), ZnO-SnO_2 (ZS) and ZnO-TiO_2 (ZT) specimens; t_{MT} = 5, 20, 30 and 300 min (denoted as 005, 020, 030 and 300 respectively).

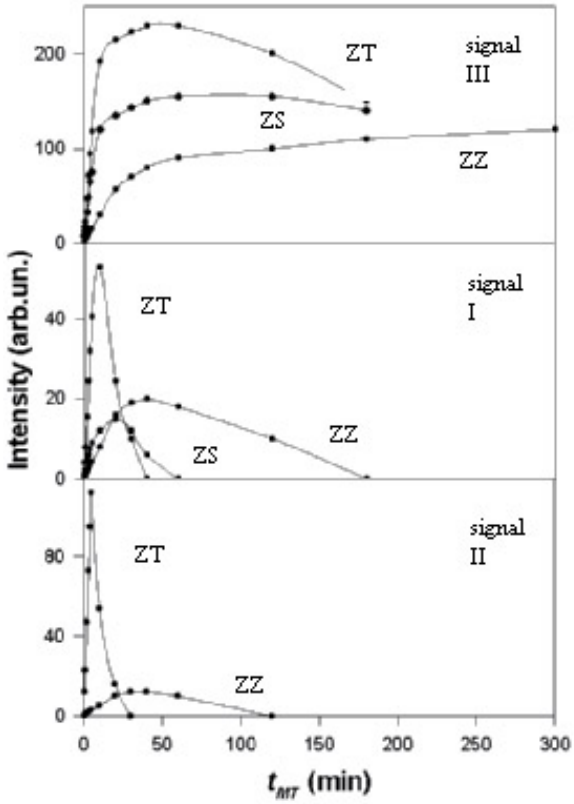

Fig. 4 Dependence of the intensities of EPR-signals III, I and II initiated in ZnO by mechanical treatment of ZnO (ZZ), ZnO-SnO_2 (ZS) and ZnO-TiO_2 (ZT) specimens with the treatment time t_{MT}.

In Fig. 5 the dependence of the intensity of signals I-III on annealing temperature are given.

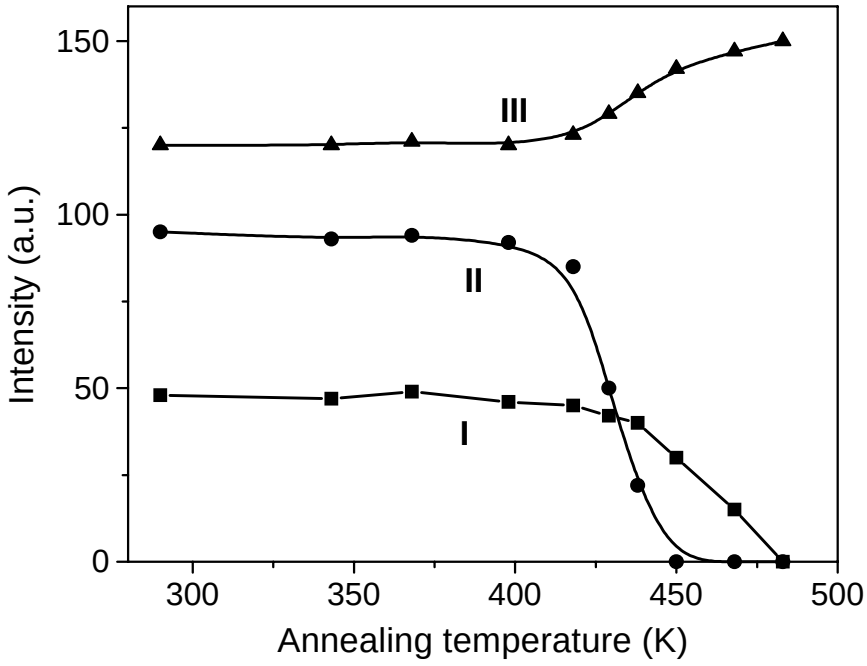

Fig. 5 Dependence of EPR spectrum in pressed ZnO (P = 2 GPa) on the annealing temperature.

4. Discussion

The main sources of heat release during mechanical treatment (MT) of disperse systems are zones of new surface formation, zones of dislocation, development and displacement, zones of interparticle friction (i.e. a zones of active defect formation), and zones of friction of the mechanical reactor's working parts [1]. Formation of deformation-damage zones is characterized by the appearance of high-temperature spikes (up to 1000 K) [2]. Crack propagation is accompanied by the formation of short-lived ($\tau \sim 10^{-9}$ s) ultra-high temperature spikes (up to 5000 K) [3, 4].

In the case of single micro-crack propagation, the time-dependent shape of the ultra-high temperature spike depends only on the thermal conductivity of the material. In the case of formation of a damage zone with a high local density of micro-cracks, many short-lived single ultra-high temperature spikes are averaged into a collective high-temperature spike; such a spike has a significantly longer duration ($\tau \sim 10^{-6}$ s). The shape of this high-temperature spike is determined by the thermal conduction in the neighborhood of the damage zone.

The combination of all local impulse-mechanothermal processes serves to increase the average temperature T_{av} of the sample as a whole. In the case of prolonged MT, t_{MT} is the time or latency needed for the system to reach thermodynamic equilibrium with the environment.

The qualitative changes in the EPR signals of the MT-samples are similar to those observed under heat treatment. This phenomenon allows us to associate the differences in the EPR spectra of specimens ZZ, ZS, and ZT with the specific mechanothermal process that

develops in an individual ZnO particle and the effect of hyper-rapid thermal defect annealing (HRTDA) [14] on the defect structure formed. A calculation such as the one made in [17] for the case of time decay of the local energetic excitation can be used. Thus,

$$q=Q/(4\pi\chi t)^{3/2} \cdot \exp(-r^2/4\chi t), \quad (1)$$

where Q is the heat released at $t = 0$ for point $r = 0$; q - energy density of the excited solid; r - distance to the excitation center; t - time; χ - temperature conductivity of the environment. Eq. (1) allows a qualitative description of the temperature regimes of "thermoactive" ZnO particles in different samples. The duration, τ, of the mechanothermal spike of a particle is inversely proportional to the temperature conductivity of its environment, i.e., $\tau \sim 1/\chi$. From this point of view, the shortest heat spike, which has the slightest annealing effect, must occur in specimens *a*, and the longest heat spike, with the greatest annealing effect, in specimens *c*.

Increasing of the duration of MT ($t_{MT} > t_1$) results in a change of the EPR signal shape and a change of the relative intensity of the various centers (Fig. 4). Type II centers are the first to decrease their EPR signal with increasing t_{MT}. In samples of ZnO this signal disappears after $t_{MT} \approx 120$ min. Shortly following there is a decrease of intensity of the signal from type I centers. In samples of ZnO-TiO_2 this signal disappears after $t_{MT} \approx 60$ min and in samples of ZnO this signal disappears after $t_{MT} \approx 180$ min. The intensity of the most stable signal from type III centers achieves maximal value in samples of ZnO-TiO_2 after $t_{MT} \approx 60$ to 120 min (in samples of ZnO after $t_{MT} \approx 300$ min) beyond $t_{MT} \approx 300$ min there is little change (Fig. 2).

Our thermal data lead to the hypothesis that the rate of increase of average temperature for a powder sample at the initial stage of MT is primarily determined by the defect formation rate; i.e. one may approximate $T_{av}(t_{MT}) \sim t_{MT} \cdot dI_{III}/dt$. Within limits of the given work $(dT_{av}/dt)_{ZnO\text{-}TiO2}/(dT_{av}/dt)_{ZnO} \sim H_{TiO2}/H_{ZnO}$. Steady state annealing begins at the threshold temperature (~ 428 K) marking the beginning of stage 2. This threshold temperature is lower than the peak temperatures of stage 1. Since $H_{TiO2} > H_{ZnO}$ the threshold temperature is achieved sooner in ZnO-TiO_2 than in pure ZnO. The defects formed during stage 1 are annealed in stage 2.

The maxima on curves I =f (p) (see Fig. 2) for EPR signals from centres I and II can be attributed to the development of mechanothermal processes promoting annealing of the defects created during pressing.

5. Conclusions

The prospects of using a paramagnetic sonde method in a study of processes of defect formation and thermal processes during MT of zinc oxide powder are shown.

A two-stage model of thermal annealing can be defined for MT of disperse systems of ZnO, ZnO-SnO_2 and ZnO-TiO_2 powders. The first stage is a collective process of break-up of individual particles. The defects formed (within a single particle) are located in high-temperature fields created by a set of short duration with ultrahigh-temperature spikes. Thus, hyper-rapid thermal defect annealing (HRTDA) takes place.

Heat accumulation processes explain the observed second stage of thermal annealing. Such processes occur at considerably lower temperatures than those during the first stage, but the duration of these heat accumulation processes is proportional to t_{MT}. The rate of defect formation and temperature (T_{av}) growth in the ZnO-TiO_2 system is approximately 5 times higher than that in a pure ZnO system. Hence, in the second stage, annealing of defects in the ZnO-TiO_2 system occurs much earlier than annealing of defects in a pure ZnO system.

Acknowledgement

This research was performed within the project No. 1832 entitled "Synthesis of functional materials from the 'synthesis-structure-properties-application' relationship", financed by the Ministry of Science and Environmental Protection of the Republic of Serbia and project No. 38318-U CONACYT (Mexico).

References

1. G. Heinicke, Tribochemistry, Akademie-Verlag, Berlin, 1984.
2. J.D. Eshelby, P.L.Pratt, *Acta Metallurg*. 4 (1956) 560.
3. F.P. Bowden, P.A.Persson, *Proc.Roy.Soc.* A260 (1961) 433.
4. K.B. Broberg, Cracks and Fracture, Academic Press, San Diego-London-Boston-New York-Tokyo-Toronto, 1999.
5. M.V. Vlasova, N.G. Kakazey, Electron Paramagnetic Resonance in Mechanically Destroyed Solids (in Russian), Naukova Dumka, Kiev, 1979.
6. N.G. Kakazey, T.V. Sreckovic, M.M. Ristic, J. Mater. Sci. 32 (1997) 4619.
7. G.V. Samsonov (Ed.), The Oxide Handbook, IFI/Plenum, New York/Washington/London, 1982.
8. B. Schallenberger, A.Hausmann, *Z.Physik* B23 (1976) 177.
9. D. Galland, A.Herve, Solid State Commun. 14 (1974) 953.
10. J.M. Smith, W.E. Vehse, Phys. Lett. 31A (1970) 147.
11. V.A.Nikitenko, J. Appl. Spectr. 57 (1992) 367.
12. P.H. Kasai, Phys.Rev. 130 (1963) 989
13. M.G. Kakazey, G.N. Kakazei, J.G. Gonzalez-Rodriguez, Cryst. Res. Tech. 36 (2001) 429.
14. M.G. Kakazey, M. Vlasova, M. Dominguez-Patiño, G. Dominguez-Patiño, G. Gonzalez-Rodriguez, B. Salazar-Hernandez, J. Appl. Phys. 92 (2002) 5566.
15. M. Kakazey, J.J. Sánchez Mondragón, J.G. Gonzalez-Rodriguez, M.Vlasova, T. Sreckovic, N. Nikolic, M. Ristic, Mater. Sci. Eng. B 90 (2002) 1.
16. M. Kakazey, J.G. Gonzalez-Rodriguez, B. Salasar-Hernandez, M. Vlasova, M. Ristic, T. Sreckovic, Int. J. Fract. 113 (2002) L13.
17. R. Shone, Chem.Ing.Techn. 41 (1969) 282.

Резюме: *В данной работе представлены некоторые возможности использования электронного парамагнитного резонанса в зкспериментальных исследованиях роли механотермических воздействий на образование дефектной структуры дисперсных систем в течение продлиненной механической обработке порошка окиси цинка. Использование при этом ЭПР основано на известном факте, что при механической обработке некоторых материалов образуется множество парамагнитных центров. Такие центры в качестве ЭПР-зонда могут быть использованы для различных химических процессов, возникающих в течение механической обработки системы, содержащей ZnO.*

Ключевые слова*: окись цинка; механическая обработка; точечные дефекты; нагревание; электронный парамагнитный резонанс.*

Садржај*: У овом раду показане су неке могућности коришћења електронске парамагнетне резонанције у експерименталном истраживању улоге механотермијских*

ефеката у формирању дефектне структуре дисперзних система током продуженог механичког третмана праха цинк-оксида. Коришћење ЕПР за ту сврху базирано је на познатој чињеници да током механичког третмана неких материјала долази до стварања бројних парамагнетних центара. Такви центри могу да се користе као ЕПР-сонде за различите термијске процесе који се јављају током механичког третмана система који садрже ZnO.

Кључне речи: *цинк-оксид; механички третман; тачкасти дефекти; загревање; електронска парамагнетна резонанција.*