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Electronic paramagnetic resonance investigation of the evolution of defects in zinc oxide during tribophysical activation

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Zinc oxide powder was tribophysically activated by grinding in a vibromill in a continual regime in air. Investigations based on the application of the electronic paramagnetic resonance (EPR) method were performed, with the purpose of establishing laws for defect formation from the viewpoint of the evolution of the fine defect structure of dispersed systems. The main focus was on the influence of the duration of tribophysical activation (TA) on the process of defect formation. Six signals were seen on the EPR spectra obtained. These signals were identified, which enabled definition of the evolution scheme of the defect structure in polycrystalline samples of zinc oxide during tribophysical activation by grinding, based on the established dependence of the formation of different centres from the grinding time.

1. Introduction

Tribophysical activation is used as a method for modification of physico-chemical properties of dispersed systems in technologies for obtaining powders and ceramics [1, 2]. However, the nature of this modification, due to the specific multiparameter object of investigation, i.e. the dispersed system, is still not explained in many cases. In [3] it was suggested that this problem could be determined from the evolution of the fine defect structure (FDS) of the disperse system under investigation. The term FDS includes complete information on the type of defect (i.e. the crystallographic lattice, individual particles and agglomerates), its concentration and space localization. To be able to obtain such universal information it is necessary to apply a great number of classical and advanced methods of investigation adapted for polycrystalline samples.

In this paper the application of EPR to determine the nature and order of formation of defects in powders during TA in zinc oxide is given. Some new EPR results connected with tribophysically activated zinc oxide are given and compared with existing ones [4–12].

In [9–12], EPR signals were also investigated of zinc oxide powders activated in different ways, e.g. mechanical, thermal, etc. It should be emphasized that conclusions were not obtained for monocrystalline powders. Besides this, detailed data on parameters that characterized the experimental conditions were not always given in these papers.

On the other hand, the existence of a large number of varied paramagnetic centres and the fact that they have been well investigated in monocrystalline zinc oxide, enable it to be used as a suitable material to investigate the evolution of defect structures under different external influences by EPR. In this paper special attention was paid to the influence of the duration of tribophysical activation by grinding on the process of defect formation.

2. Experimental procedure

A zinc oxide powder (99.99% ZnO) whose specific surface area was 3.6 $\mathrm{m^2\,g^{-1}}$ was used. Tribophysical activation was performed by grinding in a continual regime in a vibromill in air, and the grinding time t_{ml}, varied from 3 to 300 min. Recording of EPR spectra was performed at room te^{G}mperature on a radio spectrometer SE/ × 2547 with a computer program for spectrum's analysis.

3. Results and discussion

The starting zinc oxide powder had no EPR signals. EPR signals appear (Fig. 1) with increasing grinding time t_{ml}, and the intensities of the signals do not uniquely depend on the t_{ml} value. Signals appear after grinding starts, while the fields are lower ($g > 2.0023$, g is the spectroscopic splitting factor in the case of a free electron), gradual intensity, and then disappear, to be exchanged for signals with $g < 2.0023$.

We used literature data from EPR investigations of zinc oxide defects [13–16], which are given in Table I,

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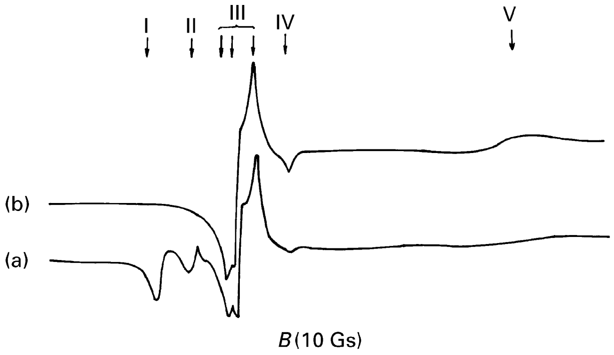

Figure 1 EPR signals obtained during TA for zinc oxide powder: (a) $t_{ml} = 30$ min, and (b) $t_{ml} = 300$ min.

TABLE I EPR signal parameters in TA zinc oxide powder and defect signal parameters from monocrystals investigated

Signal	g-factors obtained	Centre	Parameters of Second-rank Symmetric tensor g in the spin Hamiltonian for monocrystal	References
I	$g_\perp = 2.0190$ $g_\parallel < g_\perp$	$V_{Zn}^-:Zn_i^o$	$g_{xx} = 2.0185$ $g_{yy} = 2.0188$ $g_{zz} = 2.0040$	[13]
II	$g_\perp = 2.0130$ $g_\parallel = 2.0140$	V_{Zn}^-	$g_\perp = 2.0128$ $g_\parallel = 2.0142$	[14]
III	$g_1 = 2.0075$ $g_2 = 2.0060$ $g_3 = 2.0015$	$(V_{Zn}^-)_2^-$	$g_{xx} = 2.0077$ $g_{yy} = 2.0010$ $g_{zz} = 2.0059$	[13]
IV	$g_\perp = 1.9965$ $g_\parallel = 1.9950$	F^+	$g_\perp = 1.9963$ $g_\parallel = 1.9948$	[15]
V	$g = 1.9640$	SDC	$g \approx 1.96$	[16]

to identify paramagnetic centres that formed during TA. We can see that the nature of the paramagnetic centres in these papers was determined from an analysis of the angular dependence of the position of the EPR lines in the magnetic field, the shapes and intensities of the lines of the superfine structure, and in some cases (spin $S > 1/2$) the lines of the fine structure. In EPR spectra of polycrystalline samples the shape and size of singularities (sharp peaks) are the result of calculation of mean values of spectra in monocrystalline samples [17]

$$J \text{ polycrystal } (B) = N/8\pi^2 \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\varphi \times \int_0^{2\pi} d\Psi \Phi[B - B_0(\theta, \varphi, \Psi)] \cdot V(\theta, \varphi, \Psi)$$

where N is concentration of paramagnetic centre, B magnetic field, Φ and V are the line form and intensity of the absorption of the paramagnetic centre, and θ, φ, and Ψ are Euler angles, respectively. For centres with $S = 1/2$, which appear in our case, the positions of singularities in spectra of polycrystalline samples correspond to the values of the g-factors of resonant lines at critical points in the monocrystalline samples ($g_\perp$ and $g_\parallel$ or g_1, g_2 and g_3). In our case the following signals were obtained and identified.

3.1. Signal I: $g_\perp = 2.0190 \pm 0.0005$, $g_\parallel < g_\perp$

As can be seen in Table I, such a signal (to the greatest degree) corresponds to the complex: zinc vacancy with a hole that is localized on one of the four oxygen ions, V_{Zn}^-, and an internode neutral zinc atom, $Zn_i^0 - V_{Zn}^-:Zn_i^0$. Singularity in high fields of such a centre ($g = 2.0040$) was not noted due to its low intensity and to superimposition of more intensive lines from other centres.

3.2. Signal II: $g_\perp = 2.0130 \pm 0.0005$, $g_\parallel = 2.0140 \pm 0.0005$

This signal completely originates from the V_{Zn}^- centre and it can form from centre I if the internode zinc atom moves away from the vacancy at a distance larger than the third co-ordination sphere. Let us note that when temperature, $T < 170$ K there are two spectra characteristic of the V_{Zn}^- centres, which are connected with the oxygen ions in different states that surround the zinc vacancy: (i) axial, with a low intensity, caused by the hole, localized on the axial oxygen ion; and (ii) rhombic, which is caused by the localization of the hole on one of the three basic oxygen ions O^{2-}, from the oxygen tetrahedron that surrounds the vacancy. When $T > 170$ K, due to thermally activated hole mobility around the vacancy, a spectre (with parameters of the spin Hamiltonian given in Table I) is formed.

3.3. Signal III: $g_1 = 2.0075 \pm 0.0005$, $g_2 = 2.0060 \pm 0.0005$ and $g_3 = 2.0015 \pm 0.0005$

This signal is in accordance with the data from Table I and caused the complex that consists of two mutually close zinc vacancies on the (0 0 1) plane and that encompass one hole, i.e. $(V_{Zn}^-)_2^-$. In accordance with [13] the x-axis of the g-tensor complex lies in the plane (1 2 1 0) and forms an angle of 70° with the c axis, while the angle between the z- and c-axes is 54.6°.

3.4. Signal IV: $g_\perp = 1.9965 \pm 0.0005$ and $g_\parallel = 1.9950 \pm 0.0005$

This signal is connected to the oxygen vacancy V_O^{2+}, which includes one electron (V_O^+), i.e. the F^+ centre [15].

3.5. Signal V: $g = 1.9640 \pm 0.0005$

This signal is related to small donor centres (SDC) (Table I) and correlation of its intensity with sample electroconductivity is known [16]. When $T = 77$ K the intensity of this signal increases more than 50 times.

3.6. Signal VI: a wide anisotropy line (Fig. 2)

This line is related to the oxidation products of the ground material from which the mill is made and its

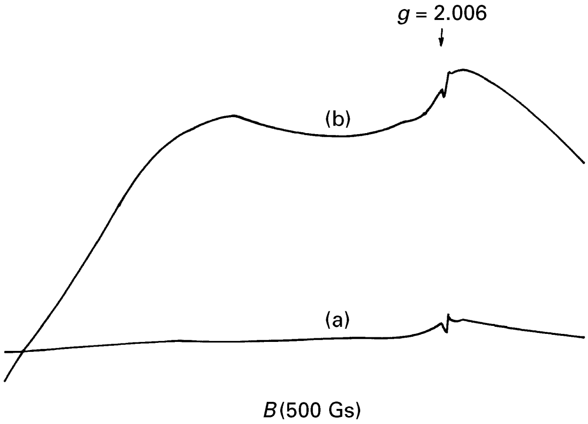

Figure 2 EPR spectra obtained during TA of zinc oxide powder showing the products of the oxidation of ground mill-material and its interaction with ZnO for: (a) $t_{\mathrm{ml}} = 30$ min, and (b) $t_{\mathrm{ml}} = 300$ min.

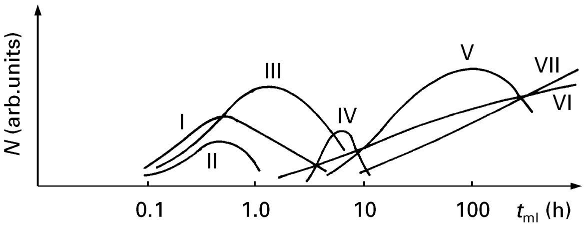

Figure 3 A descriptive scheme of the change of the defect structure of zinc oxide with the duration of TA (curve VII is connected to the defect states that form as result of the interaction of zinc oxide with molecules from the gas environment.

interaction with zinc oxide. Note that a similar signal also appears after intensive TA grinding of Al_2O_3 [18], only in this case its intensity is a lot lower, this is understandable having in mind the low abrasiveness of zinc oxide compared to Al_2O_3.

The quantitative change in the signal obtained with grinding time requires special attention. Thus, signals I and II are characterized by linear growth of their amplitudes until $t_{\mathrm{ml}} = 30$ min, then the amplitudes decrease in such a way that in samples with $t_{\mathrm{ml}} = 300$ min only traces of signal I remain (when this sample is X-rayed this signal does not increase significantly). An increase of the amplitude of signal III is noticed until $t_{\mathrm{ml}} = 120$ min, and then it gradually decreases. Signals IV and V appear only in samples with $t_{\mathrm{ml}} = 300$ min. As the maximum grinding time in our experiments was 300 min, we used data from [6] to estimate the amplitude at higher grinding times. In [6] EPR data are given for zinc oxide ground for 10–300 h. The absence of signal IV in these samples indicates that defects appear, grow and disappear in the grinding time interval from 5 to 10 h. According to [6] the intensity of signal V increases to $t_{\mathrm{ml}} \approx 100$ h and then decreases, and is accompanied by the growth of a signal with $g = 2.003$, which is attributed [6] to chemo-absorbed molecular O_2^- ions. Signal IV, connected with the products of the ground mill-material, its oxidation and interaction with zinc oxide, becomes significant in samples with t_{ml} higher than 30 min, when its intensity becomes proportional to the grinding time. In this paper we did not investigate the nature of signal VI separately.

These investigations enable us to suggest the following evolution scheme for the formation of defect states in zinc oxide during tribophysical activation (Fig. 3). During the initial zinc oxide grinding period, monovacancies in the zinc sublattice are formed, i.e. the $V_{\mathrm{Zn}}^-{:}\mathrm{Zn}_i^0$ and V_{Zn}^- centres. With increasing grinding time the metal sublattice of the defect structure becomes more complex and formation of the divacancy complex $(V_{\mathrm{Zn}}^-)_2^-$ occurs. Further increase of the grinding time leads to the formation of a monovacancy defect structure and F^+ centres in the oxygen sublattice. Further grinding causes union of the cation and anion defect structure, and thus the formation of traps for electrons and contributes to: (i) the increase of electroconductivity in the samples; (ii) chemo-absorption of gases (note that at certain grinding stages this process can lead to decreasing electroconductivity in the samples and (iii) interaction of the ground mill-material with the zinc oxide.

Thus it is shown that evolution of the defect structure in polycrystalline zinc oxide can be followed by EPR investigation during TA; which records the gradual transformation of a conditionally ideal lattice in starting samples, the formation and concentration of elementary defects, the formation of various complexes, interaction of formed defects with the ground mill-material and the gas environment, and a dispersed system with modified chemical activity.

4. Conclusions

Six EPR signals were recorded and identified in zinc oxide samples that were tribophysically activated by grinding on a vibromill. It has been shown that the signals were caused by the formation of defects in the zinc oxide lattice I, $V_{\mathrm{Zn}}^-{:}\mathrm{Zn}_i^0$; II, V_{Zn}^-; III, $(V_{\mathrm{Zn}}^-)_2^-$; IV, F^+; V, SDC; and VI the product of the interaction of the ground mill-material and zinc oxide. The dependency of the formation of different centres with grinding time suggests the following scheme for the evolution of defect structures in polycrystalline zinc oxide samples during tribophysical activation by grinding:

$$\begin{tikzcd}
\mathrm{Zn}^{2+}_{\mathrm{lattice}} \arrow[r] & V_{\mathrm{Zn}}^-{:}\mathrm{Zn}_i^+ \arrow[r] & V_{\mathrm{Zn}}^-{:}\mathrm{Zn}_i^0 \arrow[r] & V_{\mathrm{Zn}}^- + V_{\mathrm{Zn}}^- \arrow[r] & (V_{\mathrm{Zn}}^-)_2^- \arrow[dr] & \\
 & & & & & \mathrm{SMD} \\
 & & \arrow[r] & \mathrm{O}^{2+}_{\mathrm{lattice}} \arrow[r] & V_{\mathrm{O}}^+ + \mathrm{O}^- \arrow[ur] &
\end{tikzcd}$$

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