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EPR study of the pressing process of polycrystalline MgO

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In this paper the pressing process of polycrystalline MgO was studied using an EPR method. The EPR data showed that the process for particle deformations starts at a rather low pressing pressure (0.5 GPa). When pressing brittle and semibrittle materials one has to take into account the process of particle fracture.

1. Introduction

The process of powder pressing, one of the main methods in the field of powder metallurgy and ceramics, is interesting especially from the point of view of its accompanying physical phenomena. With regard to up-to-date ideas [1], the densification of powders, depending on the pressure used, is divided into four stages:

1. unstable spatial structures,
2. stable spatial structures,
3. macrodeformations of volume powder particles, and
4. volume flow.

During the deformation of powders (stages 3 and 4), there occurs an increase in the density of dislocations in the green pellets. The process of dislocation multiplication is followed by an increase in the point defect concentration [2]. The high sensitivity of paramagnetic impurities to the changing of the crystal lattice symmetry, makes it possible to use the electron paramagnetic resonance (EPR) method (for accuracy a paramagnetic microprobe is used) for the study of pressing stages 3 and 4.

In this paper we studied stages 3 and 4 of pressed polycrystalline MgO. It was proved that where brittle materials are concerned, a fifth stage exists, as well, during which the process of particle fracture takes place.

2. Experimental procedure

For the study of the pressing process, a powder of magnesium oxide was used, with a specific surface area of about $10\,m^2\,g^{-1}$. A small content of Mn^{2+} ions (0.01%) in the powder permitted the use of the EPR method for the study of regularities in defect formation during the pressing process.

The powders were pressed into pellets in ordinary metal dies in the pressure range 0.1 to 0.3 GPa. In the pressure range 4 to 8 GPa, the pressing was done by an isostatic press (model D 0043) used for the production of synthetic, superhard materials. The powder was preliminary compressed into pellets under a relatively small pressure, and then it was pressed in high pressure chambers of the "anvil-toroid" type. The pressure in the chamber was determined using a chamber pressure – pressing force calibration graph which was constructed using the known phase transitions of bismuth and tantalum [3]. The action of the force on the sample was obtained by the automatic work regime of the press [4] for a given program and with the use of precise installations which assured the maintenance of the pressure. The time required to obtain the necessary pressure could be chosen from an interval of 10 to 300 sec. Measurement of the EPR spectra was carried out on a RE 1306 radiospectrometer at room temperature.

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3. Results and discussion

3.1. Changes in the EPR spectrum of Mn^{2+}

The EPR signal of Mn^{2+} in polycrystalline MgO is a sextet made out of almost equally spaced, hyperfine lines, $-1/2$ to $1/2$ m, with the parameters of the spectrum, $g = 2.0014$, $a = 18.6 \times 10^{-4}\ cm^{-1}$ and $A = -81.0 \times 10^{-4}\ cm^{-1}$ (where g is the spectroscopic splitting factor, a is the splitting parameter in a cubic field, and A is the constant of the isotropic ultra-fine effect) [5]. With an increase of the pressing pressure, starting from 0.5 GPa, the following was observed: (a) a decrease in intensity of the hyperfine (HF) lines without changes in the intensity, (b) a change in the intensity ratio of the HF lines, (c) an increase (especially for HF lines with $m > 0$, where m is the possible quantization of the electron spin) in the asymmetry parameter A/B (B is the constant of the anisotropic ultra-fine effect) of the lines, (Fig. 1), (d) a considerable increase in intensity of hyperfine forbidden transitions (HFT), $-1/2$, $m \leftrightarrow 1/2, m+1$.

For the explanation of the given results we shall consider the influence of lattice defects on central transitions (CT) of Mn^{2+} ion, which is in a cubic crystal field. Generally, a spin-Hamiltonian, for the spectrum of Mn^{2+}, in a deformed cubic field could be written

$$\mathscr{H} = g\beta H \cdot S + \frac{1}{6}a\left[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1) \cdot (3S^2 + 3S - 1)\right] - AS \cdot I + D\left[S_z^2 - \frac{1}{3}S(S+1)\right]. \quad (1)$$

where S is the effective-spin operator, I is the absorption intensity and D is the axial distortion parameter. The last term takes into account the existence of the deformation. It is considered that the deformation axis corresponds to one of the crystallographic axes ⟨0 0 1⟩. If we account for the corrections for second and third orders in the perturbation theory, the angular dependence of CT, $-1/2$ to $1/2$ m, is given by the expression [6–8]

$$g\beta H = g\beta H_0 + \frac{2}{3}\frac{a^2}{g\beta H_0}(2 + 3p - 5p^2) - Am - \frac{A^2}{2g\beta H_0}\left[\frac{35}{4} - m^2\right] + \frac{4D^2 \sin^2 2\theta}{g\beta H_0} - \frac{2D^2 \sin^4\theta}{g\beta H_0} - \frac{5}{2}\frac{aD}{g\beta H_0} \cdot \sin^2 2\theta\,[\sin^2\theta \cdot \cos 4\varphi - 7\cos^2\theta + 3] + \frac{70A^2am}{(g\beta H_0)^2}p - \frac{4A^2Dm}{(g\beta H_0)^2} \cdot (3\cos^2\theta - 1) - \frac{36D^2Am}{(g\beta H_0)^2}\sin^2 2\theta + \frac{2D^2Am}{(g\beta H_0)^2}\sin^4\theta, \quad (2)$$

where

$$p = \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3 + 5\sin^4\theta \cdot \cos 4\varphi)$$

and H is the resonance field, H_0 the resonance field for $I = 0$, φ and θ are the observation conditions of the signal.

According to the statical theory of the non-uniform widening of spectral lines, in the case where the energy shift of a sole centre is defined by terms of a second-order approximation, the width of the resulting signal and its displacement is proportional to the dislocation density [9]. Since there exists a simple relationship between the dislocation density N, and the mean distortion

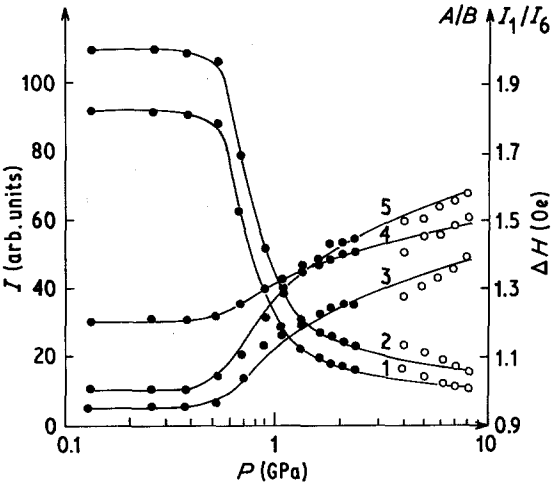

Figure 1 The variation of: 1. the intensity of the central transition from $m = 5/2$, 2. the intensity of the central transition from $m = -5/2$, 3. the line width from $m = -5/2$, 4. the ratio I_1/I_6, 5. the asymmetry parameter A/B of the line from $m = 5/2$, due to the pressing pressure values.

parameter D_m, which is $D_m \simeq N^{1/2}$ [10], we can presume that for each deformation state there is a suitable dislocation density, i.e. its own value of D_m.

From Equation 2, the shift of the resonant signal (and the width of the Gaussian) is equal to

$$H_D - H_{D=0} = \frac{D}{g\beta}\left\{\frac{4D\sin^2 2\theta}{g\beta H_0} - \frac{2D\sin^4\theta}{g\beta H_0} - \frac{5}{2}\frac{a}{g\beta H_0}\sin^2\theta \times [\sin^2\theta\cdot\cos 4\varphi - 7\cos^2\theta + 3] - \frac{4A^2 m}{(g\beta H_0)^2}(3\cos^2\theta - 1) - \frac{36D\cdot Am}{(g\beta H_0)^2}\sin^2 2\theta + \frac{2DAm}{(g\beta H_0)^2}\cdot\sin^4\theta\right\} \quad (3)$$

A nonuniformly widened EPR line caused by the defects of the crystal, can be considered as a composition of Lorentz and Gauss distributions, where Lorentz and Gauss lines characterize an ideal crystal and its defects, respectively. When combined, the width of the resulting signal can be expressed through its component Lorentz and Gauss lines [11]

$$\Delta H = \frac{\Delta H_L}{2} + \left(\frac{\Delta H_L^2}{4} + \Delta H_G^2\right)^{1/2} \quad (4)$$

where H_L is the Lorentz line and H_G is the Gauss line.

Hence, from Equations 3 and 4, the width of the CT in a crystal is angularly dependent. For small values of a and D, when it is rather difficult to measure the shift of CT as well as its widening, the lattice defects can cause a weakening of the amplitude of the signals and an appearance of anisotropy of this signal, which is greater for the high-field CT components.

A resulting spectrum of a polycrystal is formed by a response signal, whose position is determined by the condition $\sin\theta/(dH(\theta)/d\theta) \to \infty$, where $dH(\theta)/d\theta$ is a derivative of Equation 2. For the CT, taking $\varphi = 45°$, response signals are found at $\theta_1 = 90°$ and $\theta_2 = 54°45'$ for $D \ll a$, and at $\theta_1 = 90°$ and $\theta_2 = \arctan\ [(4 - 36Am/g\beta H_0)/(5 - 37Am/g\beta H_0)]^{1/2}$ for $D \gg a$. The splitting of the response signal increases with an increase of D and it depends on m. For θ_1 the width of an individual line differs from its width, ΔH, at θ_2. All this means that the growth of powder defectiveness is accompanied by weakening of the CT signal and by an increase of its width, as well as by an increase of the asymmetry parameter which depends on m. The way the asymmetry of HF components changes indicates that parameter D has a negative value. A simpler way of estimating D_m is by measuring the ratio of the integral intensities of HFT and CT. For a polycrystal [12], this ratio equals

$$I_{HFT}/I_{CT} = \left[\frac{35}{4} - m(m+1)\right] \times \left(\frac{512}{15}D_m^2 + \frac{800}{63}a^2\right)\frac{1}{(g\beta H_0)^2} \quad (5)$$

Variation of D_m due to the pressing pressure is given in Fig. 2. From Equations 3 and 5 it follows that the sensitivity of CT and HFT to lattice defects increases with a decrease of the working frequency of the radiospectrometer.

A study of the line form of the HF components brought a somewhat unexpected result. Instead of an increase in the contribution of the Gauss component occurring in the resulting line, which is typical for nonuniformly widened signals, a growth of the Lorentz component was observed. An identity of saturation curves for initial and deformed samples (at room temperature) eliminates the possibility of determining the dominant role of the mechanism for the uniform widening of individual lines. The Lorentz character of deformation-widened lines was observed in the EPR spectra of Fe^{2+} and in the electron nuclear double resonance (ENDR) spectra of Co^{2+} in MgO [13]. It is possible that such a modification of the line form is caused by a creation of various kinds of

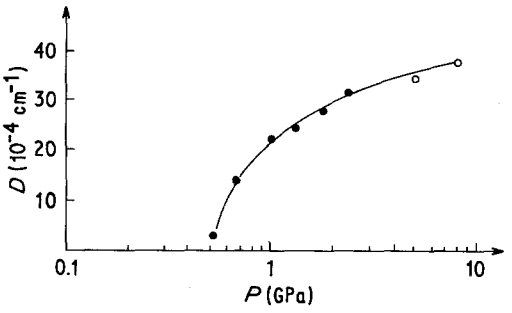

Figure 2 Variation of the distortion parameter D_m depending on the pressing pressure value.

defects (dislocations, vacancies, etc.) in the sample and by their nonuniform volume distribution.

Measurement of the widening of X-ray lines was carried out using a DRON-1 device. The width of the line from (2 2 2) plane in the initial samples was about 0.50°, and in the deformed ones at 8 GPa it was 0.58°, which is within the experimental error range. This allows an estimation of the order of magnitude of the dislocation concentration in the deformed sample to be about 5×10^9 cm^{-2}. The given results confirm that the sensitivity of central transitions of Mn^{2+} EPR spectra in polycrystalline MgO to the existence of lattice defects, is determined by the width of individual lines in the initial samples, and seems to be at least two orders of magnitude greater than when measuring the widening of X-ray lines.

3.2. Initiation of the F-centres

Beside the given changes in the EPR spectra of Mn^{2+}, we detected a rise of a weak signal from F_1-centres (anion vacancies that have captured an electron) especially in samples exposed to high isotropic pressures. Spectrum parameters are $g = 2.0023 \pm 0.0002$, $A_N = (3.71 \pm 0.02) \times 10^{-4}$ cm^{-1}, width of the central line, $\Delta H = (0.08 \pm 0.1)$Oe. The amplitude of the signal was proportional to the value of the pressing pressure (Fig. 3).

It is known that slow plastic deformation of MgO crystals generates anion vacancies, which, when γ-irradiated, turn into F-centres [12]. Impact loading, high speed deformations and grinding of crystals are accompanied by a direct generation of F-centres [12].

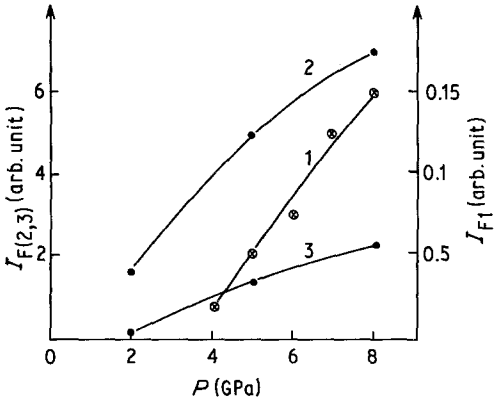

Figure 3 Variation of the signal intensity from F_1-centres depending on the pressing pressure value for the: 1. initial powders, 2. unannealed crystal line particles ($d \simeq 300$ μm), 3. annealed crystalline particles ($d \simeq 300$ μm).

One of the causes of the initiation of F-centres could be the great speed at which the applied pressure is changed. However, the absence of a noticeable dependence of I_F (the integral intensity) on the loading speed, enables one to ascribe the spectrum to the brittle fracture processes of the initial powder particles when pressed. The nature of F-centre formation is explained in the following way. It is known that crystal fracture is preceded by an accumulation of dislocations [2], i.e. by a formation of regions with a high content of vacancies. On the other hand, formation of new surfaces by crack openings is accompanied by an electron emission of various energies, and by ionization, optical, acoustical etc. effects [14]. Because both processes happen practically at the same time, it can be considered, that while a fracture of solids goes on, a formation of vacancies in the fracture zone is accompanied by an intensive irradiation of the zone which stimulates the formation of F-centres.

For a more convincing proof of the assumption of particle fracture while pressing, powders made from milled MgO crystals with a particle size, d about 300 μm (unannealed, and annealed at 1100° C for 2 h), were studied. The intensity of signals from F-centres in those samples after pressing was far greater, the intensity of the unannealed powders being higher than the annealed ones (Fig. 3). We showed before that the intensity of signals from the F-centres, formed by grinding MgO crystals, is proportional to the specific surface of powders, or inversely proportional to the mean particle size [15]. Using this it is possible to estimate the mean particle size of the pellets after pressing, by comparing the signal intensities from F-centres of initial powders and pressed samples. It has to be taken into account that the dispersion in air destroys about 80% of the F-centres [12], and that the pressing is done in a limited volume where the air access is difficult. Calculated mean particle sizes in pressed samples are given in Table I. Note that the grinding of particles with $d = 300$ μm at high pressures is proved with confidence by microscopic analyses.

The signal from the F-centres was somewhat asymmetrical with a non-Lorentz form. Obviously, this was caused by superposition of an intensive line from the F_1-centres and a relatively weak signal from F_2-centres with $g = 2.0007$ and a width, $\Delta H = 1.6$ Oe, which represents electron capturing vacancies connected with cation

TABLE I Mean particle size in the samples ($d \simeq 300\,\mu m$) after pressing from EPR data

Samples	Pressing conditions (μm)		
	2 GPa	5 GPa	8 GPa
Unannealed	100	40	32
Annealed	250	170	100

vacancies. F_2-centres can be formed during the crushing of particles, and by the action of thermal changes in the sample caused by plastic deformations, adiabatic compressing etc. In accordance with Vlasova and Kakazei [12], at the annealing temperatures 300 to 400° C, a decrease in intensity of the signal from F_1-centres and a growth of the signal from F_2-centres was observed.

The differences in the ways of formation of F-centres for different samples indicates the existence of a dependence of fracture processes during the pressing on the particle size of initial powders, as well as on their state of defectiveness.

4. Conclusion

It is known that in the first two stages of densification, energy for compressing the polycrystal is mainly used in elastic deformation of the particles and on overcoming the force of friction, i.e. on rearranging the particles to form a dense packing. Further growth of the pressing pressure helps the formation of plastic deformation zones on places of interparticle contacts.

EPR data show that the process of particle deformation starts at rather low pressing pressures (0.5 GPa). This is natural, for real particles have a developed surface, rich with different kinds of defects. The existence of these defects can become a source for the formation of dislocations at low pressing pressures. The density of formed dislocations, in the experimental error range, is proportional to the value of the pressing pressure.

The observation of the rupture processes of particles during pressing is caused by anisotropic properties of particles which lead to the formation of gradient fields of mechanical strains in the sample, on one side, and by mechanical properties of the MgO on the other. Namely, magnesium oxide at room temperature is a semibrittle material. Although the role of plastic deformation grows with a decrease of the particle size, especially under 100 μm, the factor of brittle fracture at high pressing pressures is of essential importance. That means that when pressing brittle and semibrittle materials one has to take into account the fifth stage of the densification process, i.e. the process of particle fracture.

On the whole, the given results show wide possibilities of utilizing the EPR method for studying the features of pressed polycrystalline structures.

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