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STUDY OF ELEMENTARY MECHANISMS DURING SINTERING OF MgO WITH Mn₂O₃, MnO₂ AND NiO ADDITIVES

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Résumé. — L'étude a porté sur l'influence des additifs d'oxydes de manganèse (Mn₂O₃ et MnO₂) et d'oxyde de nickel (NiO) sur les processus élémentaires qui ont lieu pendant le frittage de MgO dans l'intervalle de températures de 600 °C à 1 200 °C. Les concentrations des additifs étaient respectivement de 0,01, 0,1, 1,0 et 3,0 moles %. Sur la base des spectres EPR des systèmes étudiés, on a suggéré un mécanisme de réaction à l'état solide qui consiste en peu d'étapes : à la fois en décomposition et en dissociation des oxydes du groupe fer. Dans un bon nombre de cas, la diffusion des ions métalliques dans le réseau de MgO s'effectue par le mécanisme de surcharge. Il se produit de plus une interaction directe du MgO avec les produits oxydés (par exemple la formation de spinelle de MgMn₂O₄). La contribution de chacun de ces processus au mécanisme général d'interaction est déterminée par la concentration des additifs insérés et par les conditions de frittage.

Abstract. — The influence of manganese oxides (Mn₂O₃ and MnO₂) and nickel oxide (NiO) additives on elementary processes occurring during MgO sintering, in temperature range 600-1 200 °C, was investigated. The concentration of additives were 0.01, 0.1, 1.0 and 3.0 mol %. On the basis of EPR spectra of investigated systems was suggested the mechanism of the solid state reaction which consists of few stages : both of decomposition and dissociation of oxides of the iron group. In quite a number of cases the diffusion of metal ions into MgO lattice proceeds by the overcharging mechanism. Further, a direct interaction of MgO and oxide products (for example formation of MgMn₂O₄ spinel) takes place as well. The contribution of each of these processes to the general interaction mechanism is determined by the concentration of inserted additives and by sintering conditions.

1. Introduction. — The explanation of mechanisms of various processes in solids, which occurs in the bulk or on the solid surface, is a very important task in the field of the science of sintering. It requires both the *chemical* and the *physical* approach to the solution of this problem. It is established that *diffusional alloying* is of the important influence on the course of elementary processes occurring during sintering. In every specific case the intensity of the densification process depends on the choice of starting components as well as on conditions of thermal treatment. Knowledge of interaction mechanism in such composite systems is necessary for the optimal choice of the quantity and kind of alloying component [1].

In the range of a large investigation program of the influence of small additives quantities on elementary processes occurring during MgO sintering, in this work such processes in MgO-Mn₂O₃, MgO-MnO₂

and MgO-NiO systems were studied on the basis of EPR signals. The investigation was done using EPR method because of the high sensitivity of this technique and fast response to qualitative and quantitative changes occurring in the systems even in those stages of the process when other experimental methods could not be applied.

2. Experiments. — The investigated samples were obtained from MgO-Mn₂O₃, MgO-MnO₂ and MgO-NiO mixtures by pressing into the form of pallets. Green compacts were sintered in air in the temperature range 600-1 200 °C during 1 min, 10 min, 30 min, 90 min and 240 min. In table I mixtures with different concentration of additives used in this work are marked.

The measurement of EPR was performed with a 3-centimetre radiospectrometer with double modulation of the magnetic field, mostly at room tempera-

TABLE I

The investigated systems

Mol. %	Mixtures mark		
	MgO-MnO ₂	MgO-NiO	MgO-Mn ₂ O ₃
3	1	5	9
1	2	6	10
0.1	3	7	11
0.01	4	8	12

ture. The width of EPR (ΔH) lines was determined between the end points of the differential absorption curve. In the case of the approximately equal values of ΔH and the value of hyperfine structure constant, for the determination of the width and shape of the individual component line was applied the method suggested in paper [2] in which is included the ratio of the intensity of the hyperfine component peaks, difference between the extremes of the hyperfine components with end positions and their relation.

For measurement of the area under the absorption spectra curve, the reference signal was also determined. Diphenylpicrylhydrazyl and Cr³⁺ in Al₂O₃

EPR signals were used as a reference standard. It made the determination of the relative value of the intensity of peaks EPR signal possible. Then the signals were registered in the regimes suitable for the graphic integration. The area under the absorption curve is proportional to the quantity of the paramagnetic ions, and according to the method of odd moments is equal to [3]:

$$S = (H_J - H_{J-1}) \sum_{j=1}^m (H_J - H_0) y'_j$$

where y'_j is the ordinate of the line in field H_j in relative units, H_0 —the line centre position. In the case of the Lorentzian form of the EPR line we used the expression [3]:

$$S = \frac{2\pi}{\sqrt{3}} y'_m (\Delta H)^2$$

where y'_m is peak intensity in relative units. The error in the determination of the area is $\sim 30\%$.

The saturation of the hyperfine component Mn²⁺ in MgO in the function of the intensity of the high frequency modulation in the radiospectrometer reso-

TABLE II

The influence of sintering conditions on width (ΔH , Oe) and intensities (I , rel. int.) of EPR signals Mn²⁺ in MgO

t (min)	T (°C)	1		10		30		90		240		
		No.	ΔH	I	ΔH	I	ΔH	I	ΔH	I	ΔH	I
600		1						2.3	8	3.3	17	
		3						1.4	0.5	1.4	0.7	
		4								1.3	0.3	
		9					2	30	2	80	2	250
		10					1.3	6	1.3	7	1.3	16
		11									1.3	0.8
800		1			2.3	1 000	2.3	2 000	2.3	4 000	2.3	10 000
		3	1.3	2	1.3	16	1.3	20	1.4	60	1.6	80
		4	1.3	1	1.3	5	1.3	10	1.3	10	1.3	12
		9	2.9	1 200	2.5	10 000	2.0	14 000	2.0	16 000	2.0	20 000
		10	3.1	500	1.6	1 000	1.6	1 000	1.3	1 000	1.3	1 000
		11	3.4	60	1.6	80	1.4	100	1.3	100	1.3	100
1 000		12			1.3	5	1.3	7	1.3	8	1.3	10
		1	2.4	6 000	3.9	19 000	30	10 ⁵	50	5 × 10 ⁵	56	10 ⁵
		3	1.8	150	1.8	300	1.8	700	1.8	1 100	1.8	4 500
		4	1.3	15	1.3	30	1.3	50	1.3	100	1.3	800
		9	4.1	14 500	5.2	60 000	6.2	1.5 × 10 ⁵	13	6 × 10 ⁵	29	2 × 10 ⁶
		10	1.8	4 400	1.8	5 200	1.7	8 000	1.7	14 000	4.0	44 000
1 200		11	1.3	320	1.3	120	1.3	160	1.3	200	1.3	300
		12	1.3	40	1.3	40	1.3	40				
		1	30	2.4 × 10 ⁵	52	4 × 10 ⁵	65	7 × 10 ⁵	70	10 ⁶		
		3	2.0	2 000	2.0	3 600	2.0	4 400	2.0	7 600	2.0	10 ⁴
		4	1.6	300	1.6	360	1.6	460	1.6	600		
		9	16.3	7 × 10 ⁵	20	9 × 10 ⁵	34	1.3 × 10 ⁶	44	1.7 × 10 ⁵		
	10	2.6	28 000	4.2	1.4 × 10 ⁵	6.2	2.5 × 10 ⁵	15	5 × 10 ⁵	17	8 × 10 ⁵	
	11	1.3	280	1.7	10 ⁴	2.0	2.5 × 10 ⁴	2.3	4 × 10 ⁴	2.6	8 × 10 ⁴	
	12					1.3	500	1.3	2 000	1.3	5 000	

nator was measured by the comparison of the given signal with the unsaturated DFG signal at the given intensity.

2.1 EPR SPECTRA IN SYSTEMS MgO-MnO₂ AND MgO-Mn₂O₃. — 2.1.1 Mn²⁺ in MgO. — In mixtures 1-4, 9-12, sintered in the temperature range of 600-1 200 °C, is observed the sextet of lines, whose intensity, width and shape vary in dependence of the conditions of the preparation (table II). The given spectrum is described by the spin Hamiltonian :

$$\mathcal{H} = g\beta H + ASI \quad (1)$$

where g is the factor of the spectroscopic splitting, β -Bohr magneton, S -effective electronic spin, I -the nuclear spin, A -constant of the hyperfine interaction, H -intensity of the magnetic field. The measured spin Hamiltonian constants amount :

$$g = 2.0015 \pm 0.0003 ;$$

$$A = 0.0081 \pm 0.00005 \text{ cm}^{-1},$$

and this enabled the identification of the noticed specter as the specter of Mn²⁺ in MgO [4]. In some samples in vicinity of the intensive hyperfine lines, belonging to the central transition-1/2 → 1/2, one can observe a number of slight lines conditioned by the appearance of the fine structure lines in the polycrystal [5]. The constant of the fine structure a is $0.0019 \pm 0.0001 \text{ cm}^{-1}$, and this is in agreement with the data obtained for monocrystals [4].

In mixtures 1, 9 and 10 with the increasing sintering temperature and time occurred both broadening of the hyperfine component and the formation of wide tails round them. Their formation might be the result of the transformation of the wide line into several narrow ones, which in numerous cases flow into one (Fig. 1). The wide line may be conditioned both by the appearance of the fine structure lines and by the existence of areas with the increased concentration of Mn²⁺ ion in the samples.

It is interesting to notice the dependence character of the lines of the hyperfine structure Mn²⁺ on the sintering time in mixtures 10 and 11 at 800 °C (table II). In order to explain the nature of the line narrowness with the increasing time of the sintering, the curves of the saturation were photographed. From the course of the saturation curves (Fig. 2) it is possible to conclude that the basic mechanism of the line broadening in the initial stage of sintering is the reduction in the spin-lattice relaxation time, which may be the consequence of the existence of the Mn²⁺ complex with some additional impurity characterized by a short relaxation time (for example Mn³⁺ or O₂⁻). The non-existence of the similar effect in mixtures 3 and 4 indicates some differences in the insertion of Mn²⁺ ions into MgO from MnO₂ and Mn₂O₃ at 800 °C.

2.1.2 Mn⁴⁺ in MgO. — Spectrum Mn⁴⁺ in the cubic field of MgO [6] was observed only in mixtures with a small concentration of additives : 3, 4, 11 and 12. The spectrum is described by the spin Hamiltonian (1) with constants $g = 1.9939 \pm 0.0003$ and $A = 0.0071 \pm 0.0005 \text{ cm}^{-1}$. The width of the line ($\sim 1.9 \text{ Oe}$) and the shape of the lines (almost Lorentzian) keep practically unchanged with temperature and sintering time. In figure 3 is given the dependence of the relative intensity of Mn⁴⁺ signal on the conditions of the sintering. Let's also stress that the signal of Mn⁴⁺ ion in the cubic field of MgO is also registered in the MgO-NiO system, during time when the signal of Mn²⁺ ion was not observed.

2.1.3 MgMn₂O₄ signal. — In mixtures 9 and 10, sintered at 600 °C, besides the spectrum Mn²⁺ in MgO, there is also a unit line with $g = 1.996 \pm 0.002$ and the width $\sim 160 \text{ Oe}$. The intensity of this line is increased with sintering time. In these samples, heated at 800 °C in the initial stage ($t = 1 \text{ min}$) is observed a line of the Lorentzian shape with the same g -factor but of different width $\sim 100 \text{ Oe}$. With the increasing time of sintering, the line disappears. The line with $g = 1.996$ and $\Delta H = 40 \text{ Oe}$ was registered in mixture 1, sintered at 800 °C. The dependence of the signal relative intensity on sintering time is shown in figure 4. In samples sintered at 1 000 and 1 200 °C, such a line was not observed.

The observed lines were conditioned by the formation of MgMn₂O₄ phase [7]. During that, the wide line $\sim 160 \text{ Oe}$ corresponds to the amorphous spinel phase, and the narrow $\sim 40 \text{ Oe}$ — to the crystal phase. The line of width $\sim 100 \text{ Oe}$ belongs to the transient state — from the amorphous to the crystal state. Due to the greater quantity of defects in the amorphous phase, weakening of the internal bonds between Mg ions occurs, and this conditions the broadening of the resonance line.

Finally, in mixture 1, sintered at 1 200 °C, on the spectrum Mn²⁺ in MgO there is a wide symmetrical line nearly of the Lorentzian shape with

$$g = 2.006 \pm 0.002 \quad \text{and} \quad \Delta H \sim 170 \text{ Oe} .$$

It was observed that no considerable changes occurred in the temperature range of 77-800 K. In paper [7] a similar line was attributed to the Mn₂O₃ phase. However, it is more probable that this line is the result of the interaction of MgO and MnO₂, because such a line was not observed in MgO-Mn₂O₃ samples.

2.2 EPR SPECTRA IN SYSTEM MgO-NiO. — A spectrum of Ni²⁺ and Ni³⁺ ions [8, 9] in samples of the MgO-NiO system, was noticed ; this spectrum is described by the simple spin Hamiltonian in the form :

$$\mathcal{H} = g\beta HS \quad (2)$$

with

$$g = 2.215 \pm 0.001 \text{ for Ni}^{2+}$$

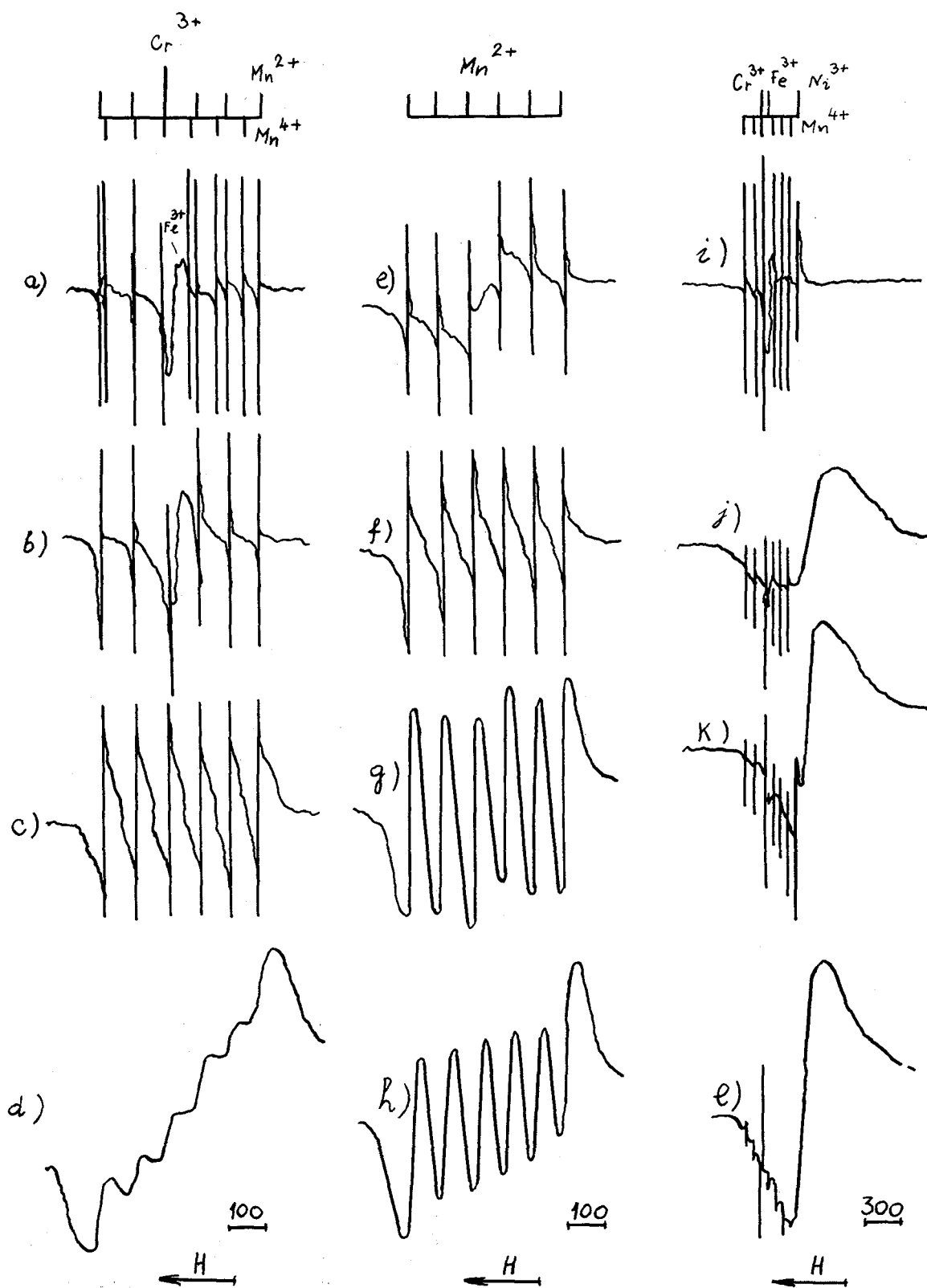


FIG. 1. — EPR spectra in systems MgO-MnO₂ (a, b, c, d), MgO-Mn₂O₃ (e, f, g, h) and MgO-NiO (i, j, k, l): a) No. 4, $T = 800^\circ\text{C}$, $t = 240$ min; b) No. 1, $T = 800^\circ\text{C}$, $t = 240$ min; c) No. 1, $T = 1000^\circ\text{C}$, $t = 10$ min; d) No. 1, $T = 1200^\circ\text{C}$, $t = 90$ min; e) No. 9, $T = 800^\circ\text{C}$, $t = 1$ min; f) No. 10, $T = 1200^\circ\text{C}$, $t = 30$ min; g) No. 9, $T = 1200^\circ\text{C}$, $t = 10$ min; h) No. 9, $T = 1200^\circ\text{C}$, $t = 90$ min; i) No. 8, $T = 1000^\circ\text{C}$, $t = 30$ min; j) No. 5, $T = 800^\circ\text{C}$, $t = 30$ min; k) No. 6, $T = 1000^\circ\text{C}$, $t = 30$ min; l) No. 5, $T = 1000^\circ\text{C}$, $t = 90$ min.

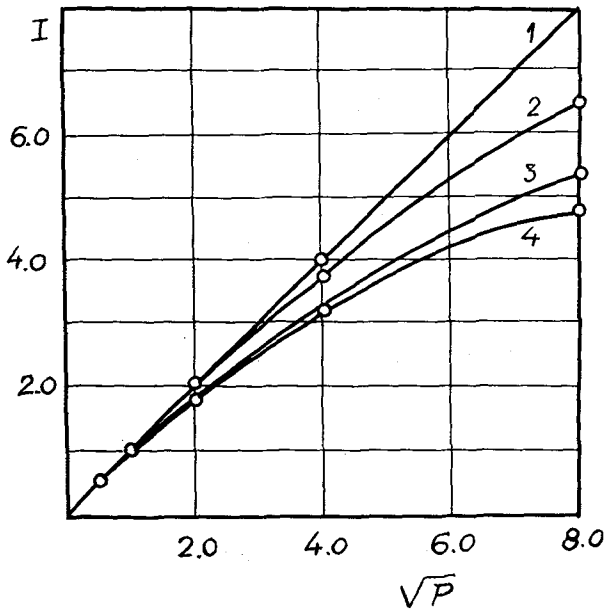


FIG. 2. — The change of the signal intensity of Mn²⁺ spectrum in MgO in the function of the intensity of high-frequency modulation: 1) without saturation; 2) in the sample No. 10, $T = 800^\circ\text{C}$, $t = 1$ min; 3) in the sample No. 11, $T = 1200^\circ\text{C}$, $t = 240$ min; 4) in the sample No. 10, $T = 800^\circ\text{C}$, $t = 30$ min.

and

$$g = 2.1700 \pm 0.0005 \text{ for Ni}^{3+}.$$

Widths and shapes of the lines for Ni²⁺ ions a certain degree depend on temperature and time of sintering. For example, in mixture No. 5 at 1000 °C ΔH varies from 400 to 220 Oe with the increasing time of sintering. The shape of the lines is neither of Gaussian nor Lorentzian shapes nor the combination of these two, and this confirms the assumption [9] of the superposition of the following mechanisms of EPR line broadening: the spin-lattice relaxation, the angular dependence of the fine structure transition, dipole-dipole and volume interaction. In dependence of temperature and time of sintering one of the said mechanisms is dominant. The relative intensity change in Ni²⁺ spectrum in MgO is shown in figure 5. The width of the line for Ni³⁺ ions in MgO is ~ 6 Oe and is not dependent on the conditions of sintering. The behaviour of the relative intensity of lines Ni³⁺ in MgO is shown in figure 6.

2.3 THE ACCOMPANYING EPR SPECTRA. — In all examined mixtures from 1-12 the signals of the impurity Fe³⁺ and Cr³⁺ ions were noticed. The absence of the concentration dependence of the formation of Fe³⁺ and Cr³⁺ on MnO₂, Mn₂O₃ and NiO additives allows the assumption that the existence of the signals is conditioned by Fe and Cr impurities existing in the starting MgO.

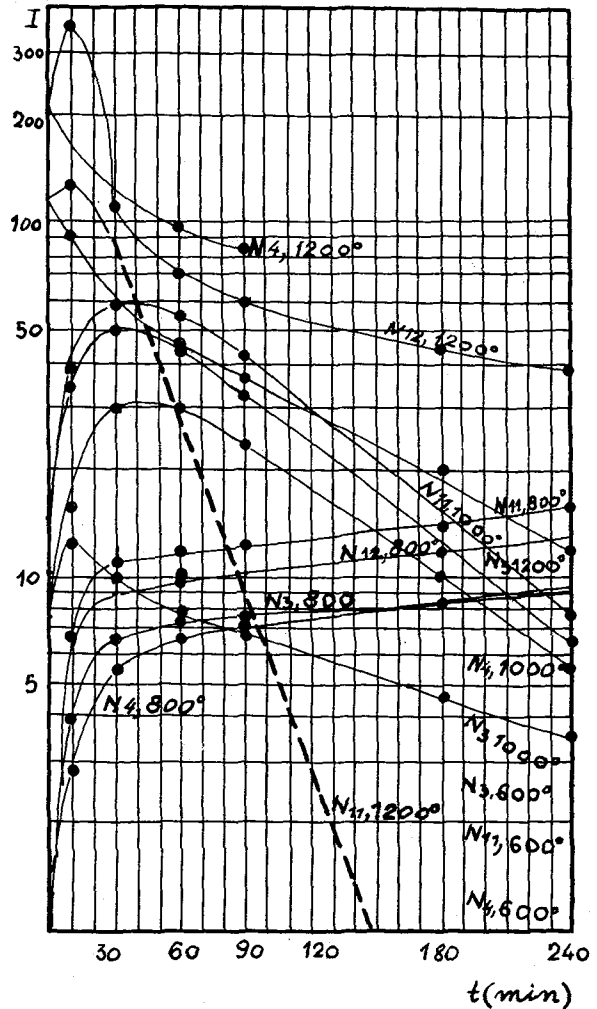


FIG. 3. — The relative intensities of EPR signals of Mn⁴⁺ in MgO in the function of sintering conditions.

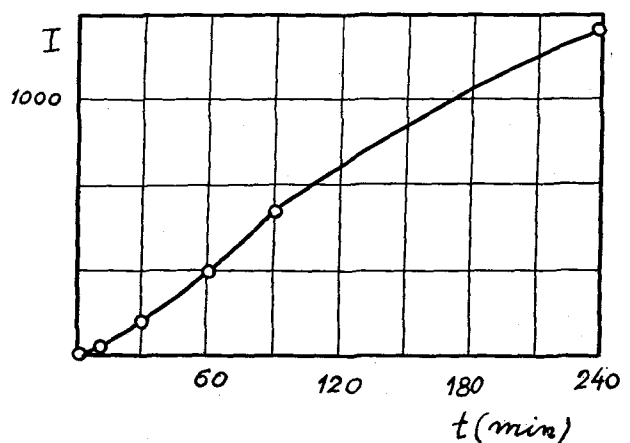


FIG. 4. — The relationship between intensities of EPR signals of the spinel phase in the mixture No. 1 at 800 °C and sintering time.

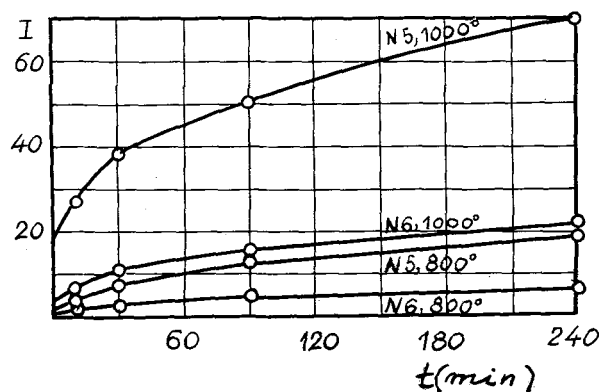


FIG. 5. — The relative intensities of EPR signals of Ni^{2+} in MgO in the function of sintering conditions.

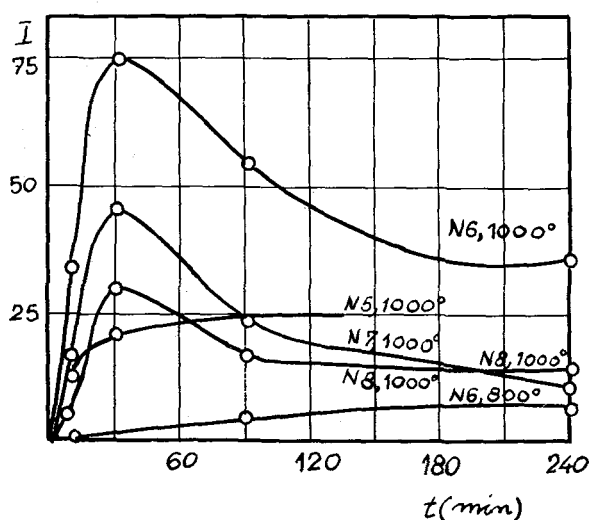


FIG. 6. — The relationship between intensities of EPR signals of Ni^{3+} in MgO and sintering conditions.

3. Discussion of the results. — 3.1 Mn^{2+} IN MgO.

— Without dwelling upon the general description of EPR spectrum Mn in MgO, which have been considered in literature in detail [4, 10, 11], let's consider the specificities occurring during sintering of the systems MgO- MnO_2 and MgO- Mn_2O_3 , and which can contribute to the interpretation of the interaction mechanism in the examined system. As can be seen in table II the increase in temperature and time of sintering leads to the increasing intensity of Mn^{2+} signal in MgO. The absence of the proportionality between the total intensity of Mn^{2+} signal and MnO_2 or Mn_2O_3 concentration at temperatures lower than 1 200 °C may be conditioned both by the concentration dependence of the diffusion coefficient of Mn^{2+} ions in MgO and by the interaction of variously valent diffusing ions with the lattice defects, impurities and oxygen from air which leads to the formation of Mn^{3+} ions. The role of the latter mechanism becomes more important during the approximately equal

defect concentrations and the manganese ions. The increase in temperature and time of sintering leads to the recovery of defects as well as to a more uniform distribution of additives in the system, and this can especially be observed in the samples sintered at 1 200 °C. In mixtures 1 and 9 sintered at 1 000 and 1 200 °C 240 min, the concentration of Mn^{2+} ions in MgO is approximately proportional to the total content of manganese in the system. Hence, the change of the total quantity of Mn^{2+} ions cannot be described by any concrete simple relation with one or two values of diffusion coefficient or activation energy.

In mixtures 1, 9 and 10 considerable broadening of lines of Mn^{2+} in MgO with the increasing temperature and sintering time can be noticed (table II). In the examined range of concentrations, the change in the line widths submits to the dipole-dipole broadening mechanism, while the contribution of the dipole-dipole interaction to the lines broadening is equal to [12]:

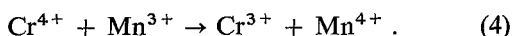
$$H = 2.3(g\beta\rho) [S(S+1)]^{1/2} \quad (3)$$

where ρ is the density of spins (Mn^{2+} ions) in cm^{-3} . In this way the line width is proportional to the concentration of paramagnetic ions. Such a character of broadening corresponds to the conditions when a uniform distribution of impurities in the whole system is concerned. While comparing changes of ΔH on time of sintering at 1 000 and 1 200 °C some differences between the line width and the quantity of the inserted additives were observed in mixtures 1 and 9. Thus, in sample of the series 1 ΔH increases faster than in the samples No. 9, where the quantity of Mn^{2+} additive is less, almost two times. Similar character of the change of the line widths may be conditioned by the formation of a new phase in MgO- MnO_2 system at given temperature. This phase retards the uniform distribution of Mn^{2+} ions in the system. The registered signal with $g = 2.006$ in the mixture 1, sintered at 1 200°, is probably some reflection of the existence of such a phase. In MgO- Mn_2O_3 system a similar signal was not perceived.

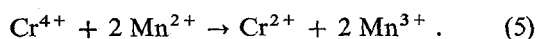
The narrowness of lines in the mixtures No. 9-11 at 800 °C with the increasing time of sintering, is conditioned by the existence of Mn^{3+} ions in the examined system. The distribution of Mn^{3+} ions occurs mainly in the surface layers of MgO particles, because the volume diffusion of these ions is hindered by the absence of the overcharging compensator. The Mn^{2+} ions, which are also located in the surface layer, in the beginning, produce the broadening of EPR line, due to their interaction with Mn^{3+} ions. With the increasing time of sintering the quantity of Mn^{2+} ions diffuses into the bulk of MgO particles, and do not react with Mn^{3+} ions, rapidly increases, and this results in the increased intensity of the signal and its narrowness. The observations presented in paper [13] have indicated the surface distribution Mn^{3+} ions in MgO where was noticed the effect of

the linear reduction in vacancy concentration from the surface to the crystal centre, conditioned by Mn³⁺ ions, which had replaced Mg²⁺ ions. The absence of a similar broadening effect in the mixtures 1-4 is the result of the lower concentration of ratio Mn³⁺/Mn²⁺ in the surface area in the initial moment of sintering ($t = 1$ min), and this was conditioned by some other reaction mechanism in the system MgO-MnO₂.

3.2 Mn⁴⁺ IN MgO. — During high-temperature treatments both the decomposition of MnO₂ and Mn₂O₃ and the dissociation of the products of the decomposition into Mn²⁺, Mn³⁺ and Mn⁴⁺ ions occurs. Some approximately equal concentration of Mn⁴⁺ ions in samples with MnO₂ and Mn₂O₃ (Fig. 3) indicates the absence of the direct insertion of Mn⁴⁺ into MgO lattice. Let's also stress the fact that the concentration of the formed Mn⁴⁺ ions nearly always corresponded to the concentration of Cr³⁺ ion that existed as an impurity in MgO, and in the cases where the additive content was greater (No. 1 and 9), neither of these two spectra was observed. It is possible to presume one of the potential mechanisms of Mn⁴⁺ ion formation in MgO cubic field for the case of lower additive concentrations:



In the case of higher additive concentrations the following mechanism of valency change is more probable:



The conditions of the non-local compensation of the overcharging of Cr³⁺ and Mn⁴⁺ ions in MgO, which cause the existence of the cubic crystal fields round these ions, are more suitable in the surface disordered particle layers of MgO. During the high-temperature treatment, when the crystallization of the disordered amorphous layers takes place, the condition of the overcharging compensation are deranged and the weakening of the signal from the high-valency additives (especially of Mn⁴⁺) in the cubic field was observed. Such a crystallization process starts proceeding intensively at 1.000 °C.

3.3 MgMn₂O₄. — From the analysis of EPR spectra of MgO samples with some higher contents of Mn₂O₃ (No. 9 and 10) follows that the formation process of spinels starts proceeding at 600 °C. In this case the surface interaction between MgO and Mn₂O₃ particles takes place, and this interaction results in the formation of the spinel amorphous phase. The increase of the temperature up to 800 °C leads both to the crystallization process of the spinel amorphous phase and to its dissolution in MgO. As the dissolution rate is high, the narrow line of the spinel phase is noticed only in the initial moments of sintering, due to the small additive concentration.

In the case of equimolar MgO-Mn₂O₃ mixtures, the formation process of spinels is very expressed at 800 °C [7].

In the mixtures MgO-MnO₂ the formation of spinels starts proceeding at higher temperatures (~ 800 °C), which is conditioned by the decomposition of MnO₂ to Mn₂O₃ at this temperature [14]. Due to the catalytic properties of MgO surface, the decomposition of Mn₂O₃ and the spinel phase formation dominates over the process of its dissolution, and this results in broadening of EPR signal from MgMn₂O₄ (Fig. 4).

On the basis of the said results, the reaction sintering process in the systems MgO-MnO₂ and MgO-Mn₂O₃ may be presented in the following way. Within the whole temperature range from 600-1 200 °C the insertion of Mn²⁺ ions into MgO is proceeding. This is a proof of the decomposition of Mn oxides up to MnO. Simultaneously with this, the interaction of MgO with manganese oxides as well as with the products of the decomposition is taking place. In favour of this conclusion is the evidence of the appearance of spinels at 600-800 °C as well as the formation of the phase with $g = 2.006$ at 1 200 °C in the system MgO-MnO₂. The interaction of manganese ions with oxygen from air, MgO lattice defects and impurities of different valency leads to the formation and stabilization of Mn⁴⁺ ions in MgO cubic field.

3.4 Ni²⁺ AND Ni³⁺ IN MgO. — The formation of EPR spectrum of Ni³⁺ in MgO is conditioned both by the existence of oxygen from air in the contact areas of NiO and MgO particles and by the lattice defects and impurities existing in MgO [15]. During the first stage of the isothermal sintering such a surface process is more intensive in comparison with the processes of diminishing of the system effective surface area, and this leads to increased intensity of the signal in the first 30 min, and after that to its diminishing to the optimum value (Fig. 6, $T = 1\ 000$ °C). The formation of Ni³⁺ ions on the surface requires, for the maintenance of the electro-neutrality, the replacement of three neighbouring Mg²⁺ ions with two Ni³⁺ ions and the formation of one cation vacancy. As the diffusion of such a complex system into the bulk is rather difficult at lower temperatures, the role of the given surface complexes is manifested in easier insertion of Ni²⁺ ions into MgO lattice, from the starting NiO, owing to the existence of vacancies in MgO. However, one cannot exclude the possibility that the insertion of Ni²⁺ ions into MgO lattice may proceed due to the overcharging of Ni³⁺ ions up to Ni²⁺ together with accepting electrons by the Ni²⁺ subsurface ions. As a confirmation of the given assumption may be taken the differences in the diffusion coefficients, registered for Ni²⁺ ions in MgO [15] in air

$$(\sim 8 \times 10^{-12} \text{ cm}^2/\text{s})$$

and in the vacuum

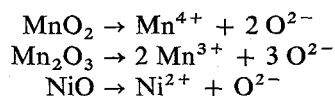
$$(\sim 4.8 \times 10^{-12} \text{ cm}^2/\text{s}),$$

as well as the absence of Ni^{3+} ions during the diffusion in vacuum. The existence of Ni^{2+} wide line in MgO in different concentrations of NiO indicates the formation of the piled Ni^{2+} ions in the subsurface layer. The character of the change in the intensity of EPR spectra Ni^{2+} in MgO submits to the parabolic law [9]. Although such a character of the dependence is typical for bulk diffusion processes, judging from the value of the process activation energy which amounts 1.1×10^5 kJ/kmol [9], the dominant mechanism in the examined temperature range must be surface diffusion. Ni^{2+} ions, piled on the surface and possessing strong Ni-Ni bonds (the bond energy is 30-35 kcal/g atom) [16] may have an important influence on shrinkage in MgO-NiO system.

In this way the interaction process in the system MgO-NiO is reduced to the following: dissociation of NiO into Ni^{2+} and O^{2-} ions; transition of Ni^{2+} ions into Ni^{3+} ions due to the reaction with the oxygen from air, lattice defects and impurities, and its arrangement in the surface layer; diffusion of Ni^{2+} ions into MgO lattice.

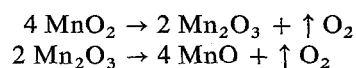
4. Conclusion. — The interaction process in MgO-MnO₂, MgO-Mn₂O₃ and MgO-NiO systems is

proceeding by complex mechanisms. The first of them is the dissociation of components:



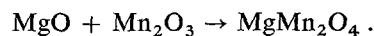
with subsequent diffusion of metal ions into MgO lattice. It is in most cases followed by ions overcharging which depends on surrounding atmosphere, defect concentration in MgO and the existence of impurities.

The second process occurring during sintering is the decomposition of manganese oxides:



with subsequent dissociation and diffusion of manganese ions into MgO. In spite of that the possibility of formation of surface MnO₂ or Mn₂O₃ complexes is not excluded (for example, solid solution of Mn₂O₃ in MnO₂).

The third mechanism is the direct interaction of MgO and oxide products, for example:



The contribution of each of those processes to the general interaction mechanism depends on the concentration of inserted additives and sintering conditions.

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