

Elsewhere [1] we showed that the interaction of a relativistic electron beam with a powder mixture of ferrite-forming oxides is characterized by the formation of up to  $10^{20}$  radiation defects per second and considerable cation ranges as compared to elementary jumps, thus ensuring that processes of diffusion sintering of powder moldings and solid-phase reactions are accelerated (by two or three orders of magnitude) [2, 3].

Analysis of the experimental data [1-3] and mechanisms of radiation-stimulated diffusion (RSD) [4, 5] including the mechanisms of radiation-stimulated defect formation permits the conclusion that under bombardment with electrons having an energy of 0.3-15 MeV the experimentally observed effects can be attributed to RSD from radiation-generated defects (mechanism of additional defects), which arises as a result of subthreshold mechanisms.

In this paper we estimate the realization of a shock-type subthreshold mechanism by means of an ionization mechanism of defect formation, which ensures accelerated solid-phase reactions and sintering of oxide powder systems under the action of a relativistic electron beam.

One of the main mechanisms of interaction of fast electrons with a material consists in the ionization of atoms of the material [6], with the attendant formation of secondary electrons with energy of up to  $E/2$ . There is also a certain probability [7-9] that the inner electron shells of the atom (K, L, M, ...) will be ionized. The ionization cross section of, e.g., the K shell varies from  $10^{-20}$  to  $10^{-24}$  cm<sup>2</sup> for different atoms.

Ionization of the K and L shells causes the Auger effect to occur [10] in the channels K-LL, L-MM, L<sub>I</sub>-L<sub>III,IV,VM</sub>, etc., resulting in the formation of a multiply charged ion; a "horizontal" cascade of Auger ionization is also possible. The rearrangement of an electron shell takes place in a time of the order of the Auger transition ( $10^{-15}$ - $10^{-14}$  sec). Characteristically, in the case of metal oxides ions of the metals form: Mn, Fe, Ni, Cu, and Zn form with an average charge of +7, Mg with +3, Ba with +9, and oxygen with +2 [10].

Thus,  $10^{-15}$ - $10^{-14}$  sec after ionization of the inner shell of the metal atom the atom is the center of the minimum of two ions with like charges (metal ion and oxygen ion), between which Coulomb repulsive forces arise,

$$F_C = (1/4\pi\epsilon_0\epsilon)(Q_1Q_2/r_a^2),$$

where  $\epsilon_0$  is the electric constant;  $\epsilon$  is the relative dielectric constant;  $Q_1 = 2e$  is the charge of the oxygen ion;  $Q_2$  is the charge of the metal ion; and  $r_a$  is the distance between the oxygen and metal ions. Such a Coulomb interaction with allowance for the time and energy parameters is characterized as a microscopic electrostatic explosion, leading to the formation of defects of various types.

We note that, providing the energy conditions allow, a high-multiplicity ion can cause Auger ("horizontal") ionization of several neighboring atoms in succession, resulting in the formation of an entire complex of ions of like charge in which the Coulomb interaction is stronger.

The probability of a microscopic electrostatic explosion with the formation of defects of various types is found from the expression [4, 11] characterizing the cross of subthreshold defect formation. For ionization of the K shell of the atom we have

$$\sigma_{\text{subthr}} = \sigma_K \alpha_{\text{Auger}}^\eta. \quad (1)$$

Here  $\sigma_K$  is the cross section for the ionization of the K shell of the atom;  $\alpha_{\text{Auger}}$  is the relative probability of an Auger cascade; and  $\eta$  is the probability factor, taking into account the finite lifetime of a localized multiple charge. The probability of multiple

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Leningrad. Translated from *Prikladnaya Mekhanika i Tekhnicheskaya Fizika*, No. 1, pp. 10-15, January-February, 1992. Original article submitted July 10, 1990; revision submitted October 22, 1990.

ionization of an atom  $\alpha_{\text{Auger}}$  for K shells of light atoms and L shells for intermediate and heavy atoms is close to one [12]. The quantity  $\eta$  is determined by the ratio between the lifetime  $\tau_K$  of a multiple positive charge and the time  $\tau_d$  necessary for the ions to acquire a kinetic energy equal to or greater than the energy of displacement of an atom in an interstice ( $\geq E_d$ ).

The lifetime of a multiple positive charge depends mainly on the time of charge neutralization by free conduction electrons. According to the estimates of [4, 13],  $\tau_K \approx 5.5 \cdot 10^{-14}$  sec at  $T = 293$  K; the charge lifetime decreases slightly with rising temperature [4] since  $\tau_K \sim (1/T)^{1/4}$ , and is estimated to be  $\tau_K \approx 3.6 \cdot 10^{-14}$  sec at  $T = 1600$  K.

The Coulomb interaction time  $\tau_d$ , during which ions acquire an energy greater than  $E_d$ , is found from  $\tau_d \geq \sqrt{2ME_d/E_K}$  ( $M$  is the atomic mass). In this case  $\eta = 1$  if  $\tau_d \leq \tau_K$ .

For the oxide systems under consideration  $\tau_d \approx (3-28) \cdot 10^{-15}$  sec, i.e., is smaller than  $\tau_K$ , and Eq. (1) thus takes on the form  $\sigma_{\text{subthr}} \approx \sigma_K$ .

The microscopic electrostatic explosion produces clusters of radius  $r_{\text{exp}}$ , inside of which a high vacancy concentration (up to 20-30%) arises [14] and, hence, the peripheral region of the explosion contains an equivalent number of interstitial atoms.

The cluster size can be estimated on the assumption that the explosion energy released in a microscopic volume melts a region of radius  $r_{\text{exp}}$ , which is determined from [15]

$$(4/3)\pi r_{\text{exp}}^3 N_0 = E/3kT_m,$$

where  $N_0$  is the number of atoms per unit volume;  $E$  is the explosion energy;  $T_m$  is the melting point; and  $k$  is Boltzmann's constant.

The number of defects (vacancies) formed in the cluster is estimated [14] in terms of the parameter

$$\delta = 0,2(4/3)\pi r_{\text{exp}}^3 N_0. \quad (2)$$

The zone of the cluster formed may encompass several hundred unit cells of the lattice structure of metal oxides. Table 1 shows the results of calculations of the kinetic energy  $E_K$  that ions acquire in a time  $\tau_i = 3 \cdot 10^{-14}$  sec as a result of the electrostatic explosion, the cluster radius, and the number of explosion-generated defects, as well as the characteristic of the lattice structure of the metal oxides considered. The complete picture of the subthreshold mechanism of defect formation is determined by the probability of this mechanism arising and the flux of electrons capable of initiating the mechanism.

The total number of clusters formed when oxides of metals are irradiated with an electron beam is found from

$$N_{\text{cl}} = \sigma_K N_0 \Phi t.$$

Here  $t$  is the irradiation time; and  $\Phi$  is the electron flux density:  $\Phi = J n_{\text{sec.K}}^e$ ;  $J$  is the density of the primary electron flux;  $n_{\text{sec.K}}^e$  is the number of secondary electrons capable of ionizing the K shell of atoms. The total number of defects generated per unit time has the form  $N_{\text{tot}}/t = \sigma_K N_0 \Phi \delta$ .

Table 2 shows the values of the binding energy  $I_K$  of K electrons for some metal atoms [16],  $\sigma_K$ ,  $n_{\text{sec.K}}^e$ , which arise as a result of ionization of the respective metal oxides by a primary electron, and the total number of defects formed per unit time in a unit volume under irradiation with an 8-MeV electron beam with a flux density of  $50 \mu\text{A}/\text{cm}^2$ . As we see from Table 2, the theoretical estimate of the number of vacancies formed in iron oxide as a result of the subthreshold mechanism of defect formation is in good agreement with experimental results, according to which the number of vacancies is estimated at  $10^{20} \text{ cm}^{-3} \cdot \text{sec}^{-1}$  [1].

We note that the equilibrium number of thermal defects in the metal oxides studied, apart from nickel oxide, is  $10^{14}-10^{17} \text{ cm}^{-3}$  [17, 18] at 1600 K, which is more than three orders of magnitude smaller than that of the number of radiation-induced defects. For nickel oxide at 1600 K the equilibrium number of thermal defects reaches a value of the order of  $10^{20} \text{ cm}^{-3}$ , which is comparable to radiation effects in the initial period of irradiation. The experimental and theoretical estimates [17] of the diffusion coefficients for radiation defects are almost two orders of magnitude higher than the thermal diffusion coefficients for nickel and more than four to five orders of magnitude higher for other metals, i.e., the equilibrium concentration of thermal defects plays an insignificant role in processes of electron-thermal synthesis. Moreover, the experimental data [1] indicate the existence of zones containing up to

TABLE 1

Oxide	Ions	$E_K, \text{ eV}$	$r_{\text{exp}}, 10^{-10} \text{ m}$	$\delta$	Characteristic of lattice structure	Lattice constant $a, 10^{-10} \text{ m}$	No. of molecules per primitive cell
MgO	O <sup>2+</sup>	46,6	7,5	19	Cubic	4,218	4
	Mg <sup>2+</sup>	30,9					
MnO	O <sup>2+</sup>	454	18	223	»	4,42	4
	Mn <sup>7+</sup>	134					
Fe <sub>2</sub> O <sub>3</sub>	O <sup>2+</sup>	204	16	124	Trigonal	5,43	2
	Fe <sup>7+</sup>	56,2					
NiO	O <sup>2+</sup>	562	17	251	Cubic	4,195	4
	Ni <sup>7+</sup>	154					
ZnO	O <sup>2+</sup>	1589	27	681	Hexagonal	3,25 ( $c = 5,20$ )	2
	Zn <sup>7+</sup>	393					
BaO	O <sup>2+</sup>	244	17	96	Trigonal	5,54	4
	Ba <sup>9+</sup>	28,5					

TABLE 2

Atoms of metals	$I_K, \text{ keV}$	$\sigma_K, \text{ cm}^2$	$n_{\text{sec}}, \text{ K}$	$N_{\text{tot}}/t$
Mg	1,305	$2 \cdot 10^{-20}$	214,5	$1,39 \cdot 10^{20}$
Mn	0,539	$8 \cdot 10^{-22}$	58,14	$1,5 \cdot 10^{20}$
Fe	7,112	$6,8 \cdot 10^{-22}$	53,2	$0,56 \cdot 10^{20}$
Ni	8,332	$4,94 \cdot 10^{-22}$	66,0	$1,5 \cdot 10^{20}$
Zn	9,659	$3,68 \cdot 10^{-22}$	42,64	$1,4 \cdot 10^{20}$
Ba	37,441	$2,47 \cdot 10^{-23}$	9,61	$1,6 \cdot 10^{17}$

30-40% of the iron oxide phase with a deficiency of iron cations, i.e., electron-thermal processes in powdered metal oxides form zones (clusters) deficient in metal cations, which suggests the existence of mechanisms that displace mass over considerable distances.

The most probable mechanism, from the standpoint of both the energy [19, 20] and the structure of the metal oxides, is the formation of dynamic crowdions as a result of an electrostatic explosion with metal cations being displaced by channeling in rows of close packing of oxygen ions. For metal cations this mechanism of channeling displacements is facilitated as compared to oxygen ions since the metal atoms are smaller than the oxygen ion, and the oxygen-ion packing density creates distinctive channels for the motion of focused chains of metal ions. As a result metal ions leave the explosion zone for a distance of the order of  $10^3$ - $10^4$  nm and the explosion zone has a large number of vacancies.

The subthreshold mechanism of defect formation under discussion can be characterized as a shock mechanism, since the time  $\tau_i$  for which the electron excitation acts and the time  $\tau_d$  of atomic displacement from a site into an interstice are shorter than the period  $T^*$  of effective oscillations.

The mechanism of radiation-induced defect formation in powdered moldings is the same for sintering and solid-phase reactions, but the mechanism of radiation-stimulated diffusion of the two processes is different since in the first case it is determined by the diffusion of the vacancies formed in the cluster and in the second case, by the diffusion of metal cations. Pores and the region of contact of powder grains are the principal sinks for radiation defects in the first case and the surface of the powder grains in the second case.

We should point out a distinctive feature of the mechanisms of electron-thermal sintering and electron-thermal homogenization, which is characterized by the nonequilibrium of the system of powdered material. The surface of the powder grains is a region with an enormous number of sinks for various kinds of defects, which is perfectly indispensable for the processes of radiation defect formation to occur and for diffusion to be accelerated.

If the irradiated material contains sinks for defects, then ions ejected from a cluster by an explosion are absorbed by those sinks, leaving vacancies in the cluster. If sinks are not present at all or are present in insignificant number, the medium surrounding the cluster

TABLE 3

Oxide	T, K	$D^*/p^2$ , cm <sup>2</sup> /sec	$D_p^{\text{exp}}$ , cm <sup>2</sup> /sec	$D_T$ , cm <sup>2</sup> /sec
Fe <sub>2</sub> O <sub>3</sub>	1300	1·10 <sup>-8</sup>	5·10 <sup>-9</sup>	2·10 <sup>-14</sup>
MnO	1300	5,8·10 <sup>-9</sup>	5·10 <sup>-9</sup>	6,7·10 <sup>-13</sup>
NiO	1400	7,8·10 <sup>-11</sup>	2·10 <sup>-9</sup>	6,8·10 <sup>-11</sup>

has a strong epitaxial effect on the orientation of the crystallizing region and the initial crystal structure is restored almost completely (irradiation of a powder mixture of oxides and the thermally sintered mixture characterize the given process [1]). The formation of defects, both as vacancies in the cluster and as interstitial atoms far from the cluster, thus is characterized by a parameter  $\delta$  and is determined by the defect structure of the entire crystalline material.

Since the initial metal-oxide powder mixture is a highly nonequilibrium system, i.e., the surface of the powder grains is a region with an enormous number of sinks, the ions ejected by an explosion move toward the surface of the powder grains as a result of focused displacements or channeling, thus producing an excess cation concentration, which creates conditions for solid-state reactions to occur. An excess vacancy concentration arises inside powder grains, thus facilitating sintering of the powder moldings.

The initial stage of the solid-state reactions and the sintering is characterized by the highest degree of nonequilibrium of the powder systems and the parameter  $\delta$  is maximum [determined by Eq. (2)]. As the sintering proceeds the nonequilibrium of the powder system decreased greatly, causing  $\delta$  to decrease gradually because part of the defects formed do not find sinks and return to the cluster.

An estimate of  $\delta$  as well as the parameter  $p$ , characterizing the increase in the length  $\lambda$  of the elementary jump as a result of the mechanism of focused displacements and channeling of metal ions, can be made by comparing the experimental and theoretical diffusion coefficients for metal oxides (Table 3). The diffusion coefficient  $D_p^{\text{exp}}$  pertains to steady-state RSD since the powder molding has already reached the sintering state (irradiation time 5-10 min), i.e., the conditions of nonequilibrium of the powder molding decrease substantially.

The quantity  $D^*/p^2$  characterizes acceleration of the radiation-stimulated diffusion and is determined from

$$D = (p\lambda)^2 v_i \sigma_R \Phi \delta t, \quad D^* = D/t,$$

where  $D$  is the RSD coefficient;  $v_i$  is the frequency of the elementary jump; and  $t$  is the time of irradiation with an electron beam, sec.

For iron, zinc, and nickel oxides  $p = (8-17) \cdot 10^{-9}$  m and  $\delta = 0.016, 0.12, \text{ and } 0.4$ , respectively; which is much less than the values given in Table 1 for the initial stage of RSD.

The estimates and analysis made of the subthreshold mechanism of defect formation, which occurs in powder oxide systems under irradiation with a beam of relativistic electrons, make it possible to explain the experimental data on sintering and homogenization of powder oxide materials.

#### LITERATURE CITED

1. V. V. Grishaev, A. P. Erastova, M. N. Korotkova, et al., "Study of the change in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase in electron-thermal fertilization processes," *Elektron. Tekh. Ser. 6. Materialy*, No. 7(192) (1984).
2. V. V. Grishaev, A. P. Erastova, B. M. Lebed', and I. I. Marchik, "Random homogenization of ferrite powders," *Elektron. Tekh. Ser. 6. Materialy*, No. 10(183) (1983).
3. V. V. Grishaev and B. M. Lebed', *Elektron. Tekh. Ser. 6. Materialy*, No. 1(200) (1985).
4. Sh. A. Vakhidov, *Radiation-Activated Process in Silicon* [in Russian], Fan, Tashkent (1977).
5. V. S. Vavilov, A. E. Kiv, and O. R. Niyazova, *Mechanisms of Defect Formation and Migration in Semiconductors* [in Russian], Nauka, Moscow (1981).
6. A. V. Vorob'ev and B. A. Kononov, *Passage of Electrons through Matter* [in Russian], Tomsk. Gos. Univ., Tomsk (1966).

7. I. B. Borovskii, Physical Fundamentals of X-Ray Spectral Analyses [in Russian], Izd. Mosk. Gos. Univ., Moscow (1956).
8. H. Kolbenstvedt, "Simple theory for K ionization by relativistic electrons," J. Appl. Phys., 38, No. 12 (1967).
9. S. M. Darbinyan and K. M. Ispiryan, K Ionization of Channelized Relativistic Particles [in Russian], Erevan Fiz. Inst., Erevan (1981).
10. E. S. Parilis, The Auger Effect [in Russian], Fan, Tashkent (1969).
11. V. A. Vinetskii and G. T. Kholodar', Radiation Physics of Semiconductors [in Russian], Naukova Dumka, Kiev (1979).
12. J. Durup and R. Z. Plactzman, "Role of the Auger effect in the displacement of atoms in solids by ionizing radiation," Disc. Faraday Soc., 31, No. 3 (1961).
13. S. Dzhumanov, "Ionization mechanism of the formation of point defects in ionic crystals," in: Radiation-Stimulated Phenomena in Oxygen-Containing Crystals and Glasses [in Russian], Fan, Tashkent (1978).
14. R. I. Garber and A. I. Fedorenko, "Focusing of atomic collisions in crystals," Usp. Fiz. Nauk, 83, No. 3 (1964).
15. B. Kelly, Irradiation Damage of Solids, Pergamon, NY (1966).
16. A. A. Botaki, A. A. Vorobe'ev, and V. P. Ul'yanov, Radiation Physics of Ionic Crystals [in Russian], Atomizdat, Moscow (1980).
17. V. V. Grishaev, A. P. Erastova, B. M. Lebed', et al., "Radiation-stimulated diffusion in oxide metals," Izv. Akad. Nauk SSSR, Neorg. Mater., 24, No. 11 (1988).
18. G. V. Samsonov, Handbook of the Physicochemical Properties of Oxides [in Russian], Metallurgiya, Moscow (1978).
19. N. P. Kaashnikov, Coherent Interaction of Charged Particles in Single Crystals [in Russian], Atomizdat, Moscow (1981).
20. I. Linkhard, "Effect of the crystal lattice on the motion of fast charged particles," Usp. Fiz. Nauk, 99, No. 2 (1969).

#### CHANGE IN THE SURFACE TENSION COEFFICIENT OF METALS IN AN ELECTRIC FIELD

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UDC 532.612.4

Because of the development of electrohydrodynamic ion sources the question of change in surface tension coefficient of liquid metals in a strong electric field has taken on practical importance. The present work is an attempt to evaluate this effect. It is shown that in limitingly strong fields the change in  $\gamma$  does not exceed 10-20%.

The question of the change in surface tension coefficient of a liquid metal in a strong electric field is of practical importance in studies of electrohydrodynamic (EHD) ion sources [1, 2]. In such sources field evaporation of ions occurs from the curved surface of a liquid metal located in an electric field of intensity  $E_0 \sim 10^8$  V/cm. Surface equilibrium is insured by equality of the capillary and electrical pressures:

$$E_0^2/8\pi = 2\gamma/r. \quad (1)$$

Knowing  $E_0$  and the surface tension coefficient  $\gamma$ , Eq. (1) can be used to calculate the radius of curvature of the emission zone  $r$  [3], which is an extremely important characteristic determining the parameters of the EHD-emitter.

However it cannot be excluded that in an electric field the value of  $\gamma$  decreases. In the fields usually achieved such changes are obviously small, and the authors have found no study which considers this question. However EHD-emitters produce the highest field intensity which can be applied to a surface (at higher intensities ion emission increases intensely so that the ionic space charge screens the field), so that the change in the surface tension coefficient can in principle be significant.

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Novosibirsk. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, No. 1, pp. 15-17, January-February, 1991. Original article submitted April 25, 1991.