

PHYSICAL FOUNDATIONS FOR HIGH-TEMPERATURE ELECTRON-BEAM MODIFICATION OF CERAMICS

Yu. M. Annenkov

UDC 535.372

We consider the phenomenon of radiation-accelerated high-temperature mass transfer (RAHTMT) in heterogeneous ion structures under the influence of powerful electron beams. We present a theoretical basis for a surface-recombination mechanism for RAHTMT. The basis for the mechanism is the notion of volume-inhomogeneous dissipation of radiation energy in heterogeneous structures and thermal-diffusion stimulation of mass transfer. We show that high-temperature radiation annealing is an efficient technological method for obtaining ceramics with different and unique properties. Methods of radiation modification have been used to obtain corundum–zircon ceramics with world-class properties.

INTRODUCTION

Ceramics are heterogeneous materials with a highly developed hierarchy of structural inhomogeneities. Among the major problems of ceramic technology is solution of the problem of eliminating metastable excited states and forcing systems as close as possible to thermodynamic equilibrium. One of the most effective methods for "normalization" of ceramic structures is the use of powerful fluxes of ionizing radiation.

Research has been conducted at Tomsk Polytechnic University over the past ten years on the processes that take place in ionic structures under the influence of intense electron beams that can raise the temperature of a target to 2300 K under stationary conditions.

The result of this research has been to establish the existence of the following phenomena, which reflect the specific properties of the effects of powerful radiation on solid bodies:

- realization of energetic mechanisms for the decay of electron-excitation Frankel defects in ionic crystals [1, 2];
- generation of acoustic waves in crystals that stimulate migration of point defects [3];
- the phenomenon of gigantic acceleration of high-temperature diffusion processes in ionic structures [4, 5];
- the effect of solution of parasitic phases and pores during radiation modification of ceramics [6].

The results listed above and the data of [7] permit us to state confidently that we have definitely established the existence of radiation accelerated high-temperature mass transfer in heterogeneous ionic structures, and we even have examples of practical application for this effect [8]. However, current thinking about the source and mechanism of radiation accelerated high-temperature mass transfer remains sketchy and hypothetical in nature.

One of the basic problems considered in this paper is increasing the depth and expanding the theoretical explanation of this important phenomenon. From the most common positions, the increase in diffusion activity in a solid body during irradiation is the result of either a change in the coefficient of self diffusion, or the influence of physical fields: electrical, thermal, and stress fields. The current theory of radiation accelerated diffusion considers primarily the behavior of the coefficient of self diffusion at relatively low temperatures.

At temperatures approximating the pre-fusion state of the material, a high concentration of stable defects causes the role of diffusion due to physical fields to be predominant. However, there has been little theoretical development of this idea, and it has been limited primarily to consideration of metals [9, 10].

We have estimated the effectiveness of currently known mechanisms for radiation accelerated diffusion in ionic structures as they apply to high-temperature ($T \geq 800$ K) and powerful [$W_1 \approx 10^7$ Gy/sec] radiation by electrons. The Deans –

Damask mechanism, which is due to excess defects and those that appear during elastic interactions, is not effective under the given conditions. Indeed, even at $T \approx 800$ K, the coefficient of radiation accelerated diffusion in KBr and MgO is 3-4 orders of magnitude less than the natural coefficient of diffusion. We have obtained results that eliminate the mechanisms of θ -bursts (Lenchenko) and A-effect ionization (Klinger). Detailed analysis of the mechanisms for diffusion of defects resulting from nonradiative recombination of electron excitations on diffusants has been performed (Abakumov, Rashba, Vinetskii, Chaika, Kimmerling, et al.). The processes considered by these authors do not assure radiation acceleration of mass transfer at elevated temperatures. Indeed, at high temperatures with uniform absorption of radiation, the rate of nonradiative recombination at a diffusant is 2-3 orders of magnitude less than that of thermally stimulated defect jumps.

We are thus led to conclude that the mechanism of high-temperature radiation stimulated mass transfer in ionic structures is, first of all, associated with the appearance of gradients in physical fields. Analysis of this issue demonstrates the great importance of gradients at the microscopic level for high-temperature radiation accelerated diffusion. This situation is associated at inner or outer surfaces of ceramic or sintered material with rapid recombination of electron excitations.

The above considerations led the author, as early as the Tomsk Conference on the Physics of Dielectrics in 1988, to propose a new approach to high-temperature radiation accelerated diffusion in heterogeneous structures, an approach that is called the surface recombination (SR) mechanism. We will present the fundamentals of the SR mechanism, taking into account current knowledge concerning the problem. The inner and outer surfaces of heterogeneous structures (ceramics), because of the high frequency of defects, are powerful sources of electronic disturbance. In connect with this, the domains of structural disturbance are characterized by an elevated (in comparison with the interior rate) rate of electron-hole and exciton recombinations, which leads to the appearance of local temperature gradients, defects, and stresses. This process intensifies mass transfer at the boundaries of different phases, leads to homogenization of structures, and results in other solid-phase reactions.

Construction of a theoretical basis for the SR mechanism requires answers to three major problems that reflect the physical essence of the description we propose:

1. What is the relationship between the rates of electron-hole recombination in the interior and at the surfaces of an object?
2. What are the values and lifetimes of the local temperature gradients that appear during recombination of electron excitations at perturbed structures?
3. Is the thermal diffusion flux sufficient to assure experimentally observable phenomena?

These problems determine the structure of the present article. In addition, we will consider new materials for creation of ceramics with outstanding mechanical properties with radiation technology. Our theoretical analysis of radiation stimulated phenomena in ceramics will be conducted for high-temperature (1000-2000 K) irradiation of materials by pulsed electron fluxes with the following parameters: pulse duration $\tau_i = 5 \cdot 10^{-4}$ sec, dose absorption per pulse $W_i = (10^6 - 10^7)$ Gy/sec, electron energy 2 MeV.

1. ELECTRON-HOLE RECOMBINATION PROCESSES IN CERAMIC STRUCTURES SUBJECT TO HIGH-TEMPERATURE PULSED IRRADIATION BY ELECTRONS

Realization of the surface recombination mechanism requires, first of all, predominance of electron-hole recombination in the plasma in regions between grains over recombination in the interior. This requirement leads to two new conditions: 1) the recombination must occur at trap centers, and 2) the lifetimes of free electrons and holes in the interior of a grain (τ_0) must be larger than the time required for an electron disturbance to migrate from the interior of a ceramic grain to the intergrain region (τ_d).

We state satisfaction of condition 1 as $R_t \gg R_{tt}$, where R_t is the rate of recombination at trap centers, and R_{tt} is the zone-zone rate. At high temperatures and disturbance densities, satisfaction of the condition $R_t \gg R_{tt}$ is not obvious and requires special consideration.

The quasistationary equation for electron-hole recombination is of the form

$$\Gamma - n/\tau - \gamma n^2 - Cn^3 = 0, \quad (1)$$

where Γ is the rate of generation of charge carriers; n is the quasistationary concentration of charge carriers; τ is the lifetime of charge carriers in the interstitial regions; γ is the coefficient of zone-zone radiative recombination; C is the coefficient of the zone-zone A-effect recombination.

There are three forms of electron disturbance recombination: linear, $R_t = n/\tau$, quadratic, $R_{tt} = \gamma n^2$, and cubic, $R_o = Cn^3$. Usually, $R_{tt} \gg R_o$, so we must establish a relationship between R_t and R_{tt} . This problem is solved during analysis of quasistationary radiation conductivity under conditions of pulsed irradiation of microsecond duration. This has been done for ceramics by a number of authors [11, 12]. A linear law relationship has been established between radiation conductivity and radiation dosage:

$$\sigma_p (\Omega \cdot \text{cm})^{-1} = A \cdot W_u = (10^{-13} - 10^{-14}) W_u (\text{Gy/sec}). \quad (2)$$

The activation energy (u) for radiation conductivity in the 300-700 K temperature interval for different types of electronic ceramics is (0.1-0.3) eV. Other authors have observed even smaller radiation conductivity at higher temperatures. In the computations below, we adopt the worst-case assumption of $u = (0.1-0.2)\text{eV}$.

The results we have presented make it possible to compute an averaged estimate for the quasistationary density of an electron-hole plasma in ceramic structures under the influence of high-temperature pulsed irradiation. Analysis of the data and its extrapolation to higher temperatures made it possible to obtain an expression for the quasistationary density of an electron-hole plasma in ceramic structures under the influence of high-temperature pulsed irradiation:

$$n = A \cdot W_1 / (\mu e) \cdot \exp[u/\kappa \cdot (1/T_0 - 1/T)]. \quad (3)$$

Here A is the coefficient of proportionality between σ_p and W_1 (see formula (2)); T_0 is the ambient temperature; μ is the effective mobility of charge carriers at the temperature T . In expression (3) the parameters A and u are reliable, since they were obtained by averaging a large amount of experimental data. The value of μ for high temperatures was obtained by extrapolation of the results of low-temperature measurements for oxide compounds comprising the basis of ceramics [13].

Formula (3) can be used for pulses of length above the microsecond range with $W_1 = (10^5-10^8)$ Gy/sec. Computations with (3) for ceramic materials with $W_1 = 2 \cdot 10^7$ Gy/sec, $\tau_u = 5 \cdot 10^{-4}$ sec, and $T = 1800$ K yield densities for electron-hole plasmas of the order of $n = 10^{13} \text{ cm}^{-3}$. The dispersion of the values of n for different types of oxide ceramics is no greater than an order of magnitude. The values obtained for n are not inconsistent with the behavior of electron-hole plasmas in ionic compounds under the influence of electron irradiation [14].

To determine the effectiveness of different paths for electron-hole recombination in oxide structures, we used the value of the coefficients of interzone radiation and A-effect recombination for semiconductors [15]. In particular, we took $\gamma = 10^{-12} \text{ cm}^3/\text{sec}$ and $C = 10^{-32} \text{ cm}^6/\text{sec}$. In accordance with Eq. (1), for our case we have $r_{tt} = \tau n^2 = 10^{14} \text{ 1}/(\text{cm}^3 \cdot \text{sec})$, $R_o = Cn^3 = 10^7 \text{ 1}/(\text{cm}^3 \cdot \text{sec})$.

For $W_1 = 2 \cdot 10^7$ Gy/sec, the generation rate for electron-hole pairs in the ceramic is $\Gamma = 2 \cdot 10^{-22} \text{ 1}/(\text{cm}^3 \cdot \text{sec})$. Thus, we have a difference between Γ and R_{tt} of 8 orders of magnitude, which is more than enough to preclude computational inaccuracy and makes it possible to draw a key conclusion.

In the presence of high-temperature pulsed irradiation with $W_1 < 10^8$ Gy/sec, the primary channel for dissipation of the energy of thermalized electron-hole plasmas in ceramics and materials with similar defect structures is nonradiative recombination at trap centers.

Good experimental confirmation of our assertion is provided by the linear relationship (2) between radiation conductivity and dosage. In accordance with Rouse's theory [16], such a law holds only when there is a linear law for recombination of carriers and there is a uniform distribution of trap centers in the forbidden zone.

The next problem is to determine the lifetime of charge carriers: $\tau = 1/(NSV)$, where N and S are the concentration and cross section of acceptor centers in the forbidden zone, and V is the speed of the carriers. It is clear that for ceramics, τ is considerably higher in the interior than in the interstitial region because of the difference in N .

In connection with this, we introduce the following notation: τ_0 , S_0 , and N_0 are the bulk parameters of a ceramic grain; τ_M , S_M , and N_M are the parameters of interstitial regions. Within metallic oxides, the traps are multiply charged, so each defect is capable of trapping several charge carriers, which become centers of recombination. At high temperatures, the centers of recombination become partially ionized and a repulsive force appears. In connection with this, we take $S_0 = S_M \sim 10^{-17} \text{ cm}^2$.

At low temperatures, the number of centers of recombination corresponds to the concentration of defects, so we take $N_0 = 10^{18} \text{ cm}^{-3}$, $N_M = 10^{20} \text{ cm}^{-3}$. At high temperatures, we have, for the lifetime of centers of recombination (τ_p),

$$\tau_p = 1/v^* \cdot \exp(E/\kappa T), \quad (4)$$

where v^* is a frequency factor, and E is the ionization energy of the center of recombination.

Under the influence of radiation, we assume a center to be stable if $\tau_p > \tau_1$. Calculations show that for $T = 2,000 \text{ K}$ and $\tau_1 = 5 \cdot 10^{-4}$, this condition is associated with centers of recombination having $E > 1.5 \text{ eV}$, and in this case, their concentration is no more than an order of magnitude less than the concentration of recombination centers at lower temperatures. Accordingly, for the temperature region (1500-2000) K, we take $N_0 = 10^{17} \text{ cm}^{-3}$, $N_m = 10^{19} \text{ cm}^{-3}$. As a result, the lifetimes of free charge carriers in ceramic structures are determined by their lifetimes in interstitial regions:

$$\tau = (\tau_M \cdot \tau_0) / (\tau_M + \tau_0) = \tau_M. \quad (5)$$

In this section we have obtained the following characteristics (necessary for subsequent analysis) for electron-hole processes:

$T, \text{ K}$	$\tau_1, \text{ sec}$	$W_1, \text{ Gy/sec}$	$\Gamma, \text{ cm}^{-3} \cdot \text{sec}^{-1}$	$\tau_M, \text{ sec}$	$\tau_0, \text{ sec}$	$n, \text{ cm}^{-3}$
2000	$5 \cdot 10^{-4}$	$3 \cdot 10^7$	$3 \cdot 10^{22}$	10^{-9}	10^{-7}	10^{13}

Here τ_1 is the duration of electron pulses, W_1 is the total dosage, Γ is the rate of generation of electron-hole pairs, τ_0 is the lifetime of electron-hole pairs inside a grain, τ_M is the lifetime of an electron-hole pair in interstitial regions, and n is the density of electron-hole pairs.

Thus, we can summarize the above analysis in a simple relation:

$$\Gamma = n/\tau_M = R_t. \quad (6)$$

As a result, for ceramics with grains that are small on average, electron-hole recombination proceeds primarily in interstitial regions. However, this conclusion is valid only if the migration time of electrons and holes into the interstitial regions (τ_d) is smaller than their lifetime in the interior of a grain (τ_0).

In the next section we consider the reliability of the condition $\tau_0 > \tau_d$.

2. DIFFUSION TIME FOR MIGRATION OF ELECTRONIC DISTURBANCES IN CERAMIC GRAINS

We model a ceramic grain by a sphere of radius R that is surrounded by an interstitial region of thickness δ . Suppose that at the initial time the concentration of electron-hole pairs in a grain is C_0 , and in the interstitial region $C_p = 0.1C_0$, and assume that the interstitial region is a sink of infinite capacity. Let us determine the time required to balance the concentrations of electron-hole pairs in the system under consideration (τ_d).

Under our assumptions, the diffusion equation takes the form

$$\frac{\partial C}{\partial t} = D_e \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (7)$$

with the following boundary conditions: $C(r, 0) = C_0$ is the initial concentration of electron-hole pairs in a grain; $C(T, t) = C_p = \text{const}$ is the concentration of electron-hole pairs in the interstitial region; $C(0, t) \neq \infty$; $\partial C(0, t)/\partial t = 0$ is a symmetry condition. Here D_e is the effective coefficient of diffusion for electron-hole pairs; C , r , and t are the current values for the concentration of electron-hole pairs, the radius of the sphere, and time.

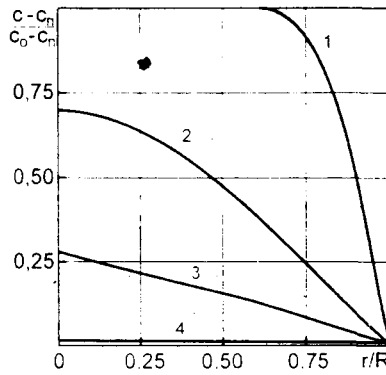


Fig. 1. Distribution of the concentration of electron-hole pairs relative to the radius of a ceramic grain in relative units for different relaxation times: t , sec. 1) $1.7 \cdot 10^{-10}$, 2) $1.7 \cdot 10^{-9}$, 3) $3.5 \cdot 10^{-9}$, 4) $7 \cdot 10^{-9}$; $R = 3 \cdot 10^{-4}$ cm, $D_l = 5$ cm²/sec.

The solution of (1) is given by the expression [17]

$$\theta = \frac{C(r, t) - C_p}{C_0 - C_p} = \sum_{n=1}^{\infty} \frac{2(-1)^{n+1} R}{\pi \cdot n} \frac{R}{r} \sin \frac{\pi n r}{R} \exp(-\pi^2 n^2 F_0). \quad (8)$$

For realistic values of the parameters in Eq. (8), the value of the dimensionless time $F_0 = D_e/R^2 \approx 1$, so in (8) we neglect all terms in the series except the first:

$$\theta = \frac{C(r, t) - C_p}{C_0 - C_p} = \frac{2 R}{\pi r} \sin \frac{\pi r}{R} \exp(-\pi^2 F_0). \quad (9)$$

Final results of computation of the space-time distribution of the electron-hole plasma in a "grain-interstitial regions" system are shown in Fig. 1. Analysis of the computational data makes it possible for us to conclude that complete equilibrium in the concentrations of diffusing particles in the system occurs at $F_0 = 0.5$. Then we have the following expression for the diffusion time:

$$\tau_d = 0,5 R^2/D_e. \quad (10)$$

The expression $D_e = \kappa T \mu_e/e$ was used in [13] to determine the quantity D_e from experimental data for the mobility of electrons (μ_e) in oxide compounds. For $R = 3 \mu\text{m}$ and $D_e = 5$ cm²/sec, the time to drain electrons and holes from a grain into the interstitial region was $\tau_d = 10^{-8}$ sec.

Thus, for a grain with an effective size no less than $10 \mu\text{m}$, $\tau_d < \tau_0$. As a result, within the lifetime of electron disturbances within a grain, they successfully migrate to the interstitial regional and participate there in recombination. We are thus led to conclude that the relation $\tau_0 > \tau_d$ is satisfied.

The notion of a high efficiency for neutralization of electron disturbances at the inner and outer surfaces of solid bodies is consistent with the most common theoretical positions. The boundaries between grains and phases have an irregular structure with a high concentration of trap centers (Tamma levels, natural and impurity defects, dislocations), reduced matter density, and are areas in which elastic stresses are present. These factors provide stimuli for neutralization of electron disturbances in the interstitial space.

We now consider one channel for spatial redistribution of an electron-hole plasma that is due to the gradient in the concentration of trap centers in heterogeneous systems. This phenomenon causes the interstitial region to become hotter than crystalline grains and causes mechanical stress. The electron-hole plasma tends to become redistributed so as to compensate for the stressed state of the material. In other words, the presence of elastic mechanical stress is a second powerful stimulus for movement of electrons and holes into the interstitial region.

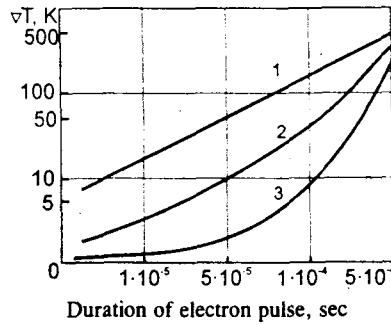


Fig. 2. Space-time distribution of temperature in model of ceramic grains with pulsed electron irradiation. Adiabatic regime: 1) $r/R = 1$ (grain surface), 2) $r/R = 0.5$, 3) $r/R = 0$ (center of grain; $\nabla T = T - T_0$, where T_0 is the initial temperature; τ is the duration of the electron pulse; $W_I = 2 \cdot 10^7$ Gy/sec, $R = 3 \cdot 10^{-6}$ m, $a = 2 \cdot 10^{-8}$ m²/sec.

Finally, we must also consider the effect of "free space." The fact is that when recombination of a thermalized electron-hole plasma occur with radiation, we see the birth of radiation defects or lattice heating. These processes require the presence of "free space," so the process proceeds efficiently only in the regions of a solid body with reduced substance density. Such structures are provided by the interstitial phases.

Thus, in heterogeneous systems with highly developed internal surfaces, electron disturbance (including excitons) decay through nonradiative recombination occurs preferentially at surface regions.

Under the influence of pulsed electron excitation of ceramic structures or sintered materials with durations of $\tau_I = 5 \cdot 10^{-4}$ sec, there is a quasistationary flux of electron disturbances in the interstitial regions. Here the flux is close to the rate of generation of electron-hole pairs. In our case, $\Gamma = 5 \cdot 10^{22}$ cm⁻³·sec⁻¹.

Since electrons and holes preferentially recombine in the interstitial regions within about 10^{-9} sec with generation of heat, the flux of electron-hole pairs into the interstitial region is equivalent to heating and the appearance of a thermal flux within the grains (q_c). We are led to conclude that temperature gradients appear between the interstitial regions and the grains when heterogeneous material are subjected to pulsed high-temperature irradiation.

The next problem is determination of the size of the local temperature gradients and their lifetime (τ_T).

3. LOCAL TEMPERATURE GRADIENTS IN CERAMIC MATERIALS SUBJECTED TO PULSED ELECTRON IRRADIATION

As we have already noted, in structures with high developed internal surfaces, absorption of the energy from an electron flux occurs preferentially at interstitial boundaries, causing them to heat rapidly. To compute the thermal gradients in boundary zones, we will assume that the rate of generation of electron disturbances does not substantially exceed the rate of nonradiative extinction in interstitial regions.

We model the process under discussion in the following way.

1. A crystalline grain is modelled by a sphere of radius R surrounded by interstitial matter with thickness δ .
2. The energy of the electron-hole plasma created by the electron beam in the spherical body of radius $R + \delta$ is precipitated by nonradiative recombination at trap centers with a preferred location within the layer of thickness δ .

Our model corresponds best to the thermophysical problem of heating of a sphere when the temperature of the surface is a linear function of time, $T_p(t) = T_0 + bt$.

In this case, the differential equation of thermal conductivity takes the form

$$\frac{\partial T(r, t)}{\partial t} = a \left[\frac{\partial^2 T(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial T(r, t)}{\partial r} \right]. \quad (11)$$

TABLE 1. Phenomena Characteristic of Thermal and Radiation Annealing in Ionic Structures

Thermal annealing	Radiation annealing
Segregation	Structural homogenization [6]
Coalescence of pores	Decomposition of pores [7]
Precipitation of impure phases	Decomposition of impure phases [6]
Growth of grains	Recrystallization
Partial phase transition T → M in ZrO ₂ -Y ₂ O ₃	[present article]
	Activation of phase transition M → T in ZrO ₂ -Y ₂ O ₃ [present article]

Here $T(r, t)$, t , and r are the instantaneous values of temperature, time, and the radius of the sphere, and a is the coefficient of thermal conductivity. The boundary conditions of the problem are $T(r, 0) = T_0 = \text{const}$, $\partial T(0, t)/\partial r = 0$, $T(0, t) \neq \infty$, $T_p(R, t) = T_0 + bt$. We obtain the following solutions from classical work [18]:

$$T = bt - bR^2/6a \cdot (1 - r^2/R^2), \quad (12)$$

$$T = 4bt \frac{R}{r} i^2 \operatorname{erfc} \frac{1 - r/R}{2\sqrt{at/R^2}}. \quad (13)$$

Expression (12) holds for Fourier numbers $F_0 = at/R^2 > 0.2$, while for smaller, we use formula (13).

According to the model, the rate at which the surface of the sphere heats (b) is equal to rate of heating in the interstitial region and is determined by the amount of radiation:

$$b = 2W_1^i R/3C_0\delta, \quad (14)$$

where C_0 is the specific heat of the material. The term $2R/3\delta$ accounts for preferential emission of energy through nonradiative recombination in the interstitial region.

A key problem in computing temperature gradients in solid bodies is proper choice of the coefficients of thermal conductivity and diffusivity. For all practical purposes, no data is available for ceramic materials in the 1000-2000 K range. At room temperature the thermal conductivity (λ) of ionic compounds is 3-15 W/m-deg. Heating an object causes the thermal conductivity to drop, and for $T \gg \Theta_D$ it has been observed that $\lambda \sim T^{-2}$ [19]. This effect is caused by anharmonic processes and can cause λ to be reduced by more than a factor of ten when the temperature of a material is raised from 300 to 2000 K.

We will consider thermal transfer in the microregions close to the intergrain boundaries. In this case it would hardly be correct to use the averaged values of λ obtained from macroscopic measurements. This position is supported by the extremely high density of defects at substance boundaries, which must result in a considerable increase in thermal resistivity. In our case, it is relevant to consider even the barrier layers that appear at phase boundaries because of dilaton effects [20]. An example of the strong influence of structural irregularity on thermal transfer is the fact that for amorphous materials, thermal resistivity is several orders of magnitude lower than in crystals of the same composition. In view of the preceding, we used the following values for thermal characteristics in our computation of temperature gradients: $\lambda = (0.1-0.3) \text{ W/(m-deg)}$, $a = (1.5) \cdot 10^{-8} \text{ m}^2 \cdot \text{sec}$.

We used the method discussed above to compute the space-time distribution of temperature in our model of a ceramic grain during a powerful electron pulse of duration $5 \cdot 10^{-4} \text{ sec}$. We used broad limits for variation in the size of grains, the power and duration of irradiation, and the thermophysical characteristics of the material. The ultimate conclusion of our work was that our model maintains temperature gradients at a level of $10^6-5 \cdot 10^7 \text{ deg/m}$ for almost all of τ_1 .

As an example, Fig. 2 shows some of our calculation results. As we can see, the temperature at the edge of the grain is considerably higher than in the center. The greatest effect, which exceeds 100° , occurs in a radiation-time interval of $5 \cdot 10^{-5}-10^{-4} \text{ sec}$. When the duration is longer, the process enters a stable mode with constant temperature gradient.

TABLE 2. Results of Radiation Annealing of Ceramics

Ceramic	σ_{bend} , MPa	K_{1C} , MPa $m^{1/2}$	T-phase content, %	M-phase content, %	Porosity, %
$ZrO_2-3M\% Y_2O_3$	<u>520</u>	<u>20.5</u>	<u>86</u>	<u>14</u>	<u>2.1</u>
	333	15.2	64	36	4.5
80% ($ZrO_2-Y_2O_3$) 20% Al_2O_3	<u>1044</u>	<u>12.8</u>	—	—	<u>2.2</u>
	580	7.9	—	—	5.0

Note. σ_{bend} is the resistance to bending, K_{1C} is the coefficient of fracture resistance. Underscores indicate the initial properties of ceramics fired at 2000 K. The radiation regimen was $T = 1850$ K, $t = 60$ min.

Differentiation of expressions (12) and (13) with respect to r yields an analytic formula for the temperature gradient in our model of a grain under the influence of pulsed irradiation:

$$\nabla T = 2W_1 Rr / 9C_0 a \delta. \quad (15)$$

As the spherical coordinate r changes, the temperature gradient in the sphere increases from 0 to its maximum value, which appears at $r = R$.

That ∇T is independent of t follows from the regularity of the process of heating a sphere with a surface by a constant thermal flux, which corresponds to the conditions of pulsed irradiation. As formula (15) implies, the radiation stimulated gradient in ceramic grains is determined by the dosage, thermophysical properties of the material, and geometric factors. It is to be emphasized that the size of the grain has a strong influence on ∇T . When $R \approx 10 \mu\text{m}$, the temperature gradients close to the intergrain boundaries may reach $5 \cdot 10^7$ deg/m. This result is consistent with the view of the theory of relaxation processes in thermophysical systems. Indeed, the time required for achievement of temperature equilibrium in different structures under stationary conditions is $\tau_b \sim R^2/a$, where R expresses the effective size of the system. When we consider dimensions of the order of microns, we obtain $\tau_b \sim 10^{-4}-10^{-3}$ sec, which corresponds to the duration of electron-pulse duration used in the present paper.

Thus, the computations we have performed make it possible to draw a scientifically and practically important conclusion. In rigid structures with highly developed inner surfaces, pulsed irradiation is associated with the appearance of "scintillating" temperature gradients of $10^6-5 \cdot 10^7$ deg/m with lifetimes determined by the duration of the pulse.

4. FEATURES OF HIGH-TEMPERATURE RADIATION ANNEALING

By radiation annealing we mean optimization and improvement of the properties of materials by subjecting them to intense radiation fluxes that lead to heating of the surface. This technology is also known as radiation modification.

As the result of study of radiation annealing in ionic crystals and ceramic structures, many researchers have observed specific properties of annealing phenomena that occur in temperature-radiation fields (see Table 1). The data of Table 1 clearly indicate that the evolution of defect structures in materials proceeds, under the indicated influences, in opposite directions. It is clear that radiation annealing assures positive effects, from the viewpoint of practical application.

Thermal annealing of materials in the absence of external motive forces leads to diffusion processes that reduce the chemical-potential gradient of the system. In the case of radiation annealing, only an increase in the coefficients of diffusion for the atoms can either accelerate the process of thermal mass transfer, or leave it unchanged; there is no reversal of the direction. As a result, the source of the characteristic properties of radiation annealing is related most closely to the appearance of diffusion-causing motive forces that result from physical fields.

It is most likely that such a stimulus is the result of local temperature gradients due to the spatially inhomogeneous recombination of electron excitations. Under certain conditions, temperature gradients may cause motion of atoms in directions determined by the classical diffusion laws. In our case, the diffusion that occurs leads to effects and phenomena that are anomalous for ordinary thermal annealing.

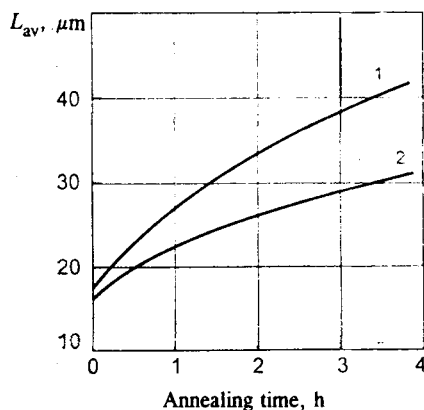


Fig. 3. Kinetics of grain growth in sintered KBr under conditions of thermal(1) and radiation(2) annealing at 820 K.

We can write a general expression for the flux of diffusion particles of the i -th type in a solid body in the form

$$J_i = -D_i (\nabla n_i + n_i F / \kappa T), \quad (16)$$

where D_i and n_i are the partial coefficient of diffusion and the concentration of diffusing particles, and F is the motive force of diffusion, which is determined by a combination of mechanical, thermal, and electrical stresses.

The thermal diffusion component of substance flux is described the expression

$$J_T = -D_i n_i Q \nabla T / \kappa T^2. \quad (17)$$

Here $K_T = n_i Q / \kappa T$ is the thermal diffusion relationship, and Q is the transport heat of the diffusant. The treatment of Q is still under discussion. In particular, the following formulas are assumed for estimating the transfer heat: $Q = E_{\text{form}} - E_m$ [21], $Q = (0.1-0.5) E_m$ [22]. In these relations, E_{form} and E_m are the energies of formation and migration of the diffusant. For ionic compounds, we can tentatively take $Q \approx 1$ eV. It follows from expression (17) that

$$D_T = Q n_i / (\kappa T) \cdot D_i. \quad (18)$$

Since $Q > \kappa T$, the coefficient of thermal diffusion D_T may be substantially greater than D_i .

5. RADIATION MODIFICATION OF ZIRCONIUM DIOXIDE CERAMICS

During the past several years, workers at Tomsk Polytechnic University, in cooperation with the IFPM of the Russian Academy of Sciences and the SKhK have developed high-strength ductile zirconium dioxide ceramics [28-30]. In large part, the prospects for this material are determined by its unique capability to resist rupture resulting from changes in Martensite phases.

High strength ceramics must have a fine grained homogeneous structure and low porosity. At the same time, meeting these requirements presents a major difficulty, since their physical nature makes them antagonistic to each other. Indeed, high density in ceramics is achieved under strict temperature conditions, but these conditions promote growth of grains by recrystallization, which leads to a reduction in mechanical strength.

On the other hand, a central point in the design of high strength ceramics is the problem of optimizing the interstitial regions. It follows from theoretical considerations that the boundaries between grains must behave as thin sheets whose chemical composition is close to that of the crystallite. However, these conditions, are usually not satisfied. Conventional ceramic technology does not use effective methods for controlling the structure of the boundaries between grains. In contrast to the work of others [23, 24], we solved the indicated problems in our work by using an electron beam providing fluxes of up to 10^7 Gy/sec.

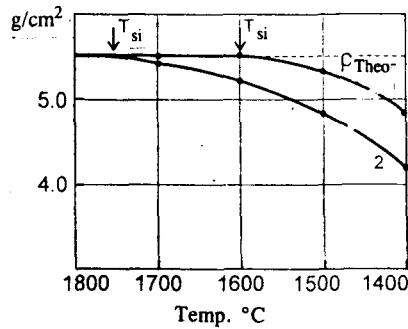


Fig. 4. Relationship between ceramics with composition 80% $ZrO_2-Y_2O_3$ and 20% Al_2O_3 and temperature for radiation (1) and thermal (2) annealing; T_{si} is the temperature of complete annealing. The annealing time was 60 min, and the average dose was $W_{av} = 10^4-10^5$ Gy/sec.

We performed radiation modification of zirconium and corundum-zirconium ceramics with electron accelerators at the Institute for Nuclear Physics of the Siberian Division of the Russian Academy of Sciences at temperatures of 1300-2000 K.

The results of our experiments are shown in Table 2, which shows an almost two-fold increase in the strength of ceramics, and a sharp improvement in ductility. The value of $K_{IC} = 20.5 \text{ MPa}\cdot\text{m}^{1/2}$ obtained for fracture resistance of zirconium ceramics is the best achieved anywhere to date.

There are two basic effects of radiation modification: reduction of porosity and stimulation of a phase transition from monoclinic zirconium dioxide to tetragonal.

The results we have obtained can be used to provide a consistent explanation, from the viewpoint of the above discussion, of a surface recombination mechanism for homogenization of ceramic structures.

The phenomenon of radiation dissolution of parasitic phases that are located in interstitial regions has been observed in radiation annealing of yttrium-barium cuprates [6]. The x-ray phase method was used to establish that nonsuperconducting phases localized in interstitial regions and causing deterioration of Josephson junctions are eliminated by radiation modification at 900 K. This effect has been used to obtain ceramic superconductors with record critical currents of $2 \cdot 10^4 \text{ A/cm}^2$.

This phenomenon, call radiation homogenization, can be observed in other materials, including corundum-zirconium ceramics.

In view of the above discussion, we can present a mechanism for radiative dissolution of interstitial regions in the following way.

Under the influence of the temperature gradient that appears in the presence of electron-hole recombination, the effective coefficient of diffusion and concentration of atoms in interstitial regions become greater than within grains. This leads to a situation similar to that prevailing under conditions required for appearance of the Kirkendahl effect. Thus, thermal diffusion effects cause interstitial regions to become smaller, decaying into the basic phase of the grains. The degree of homogenization in the ceramic structure is considerably increased when there is radiation generation of Frankel pairs in the interstitial region because of the decay of electronic excitation.

Using (17) and allowing for the parameters of the pulsed beam of electrons, the author obtained the following expression for the rate of homogenization in the interstitial region:

$$V_{\Gamma} = D_i \cdot Q_{\tau_1} f \nabla T / \kappa T^2. \quad (19)$$

Substituting the formula (15) for the temperature gradient into (17), we obtain

$$V_{\Gamma} = 2W_1 R^2 D_i \cdot Q_{\tau_1} f / 9C_0 a \delta \kappa T^2. \quad (20)$$

As we can see the rate of homogenization of defects in interstitial regions is determined by the total radiation W_1 , the pulse duration τ_1 , and the pulse frequency f , as well as the characteristics of the diffusion zone.

Computations with formula (20) for zirconium ceramics yield a time for 45 minutes for radiation homogenization. The following parameters were used in the computations: $W_i = 2 \cdot 10^7$ Gr/sec, $R = 3 \cdot 10^{-6}$ m, $D_i = 10^{-12}$ m²/sec, $Q = 1$ eV, $\tau_1 = 5 \cdot 10^{-4}$ sec, $f = 20$ Hz, $C_0 = 700$ J/(kg·deg), $a = 5 \cdot 10^{-8}$ m²/sec, $\delta = 10^{-7}$ m, $T = 1873$ K.

Allowing for some arbitrariness in the choice of parameters like D_i and a , we find that the result obtained is in satisfactory agreement with time required for maximum strengthening of zirconium ceramics by radiation annealing.

From the viewpoint of radiation dissolution of interstitial regions, the radiation-stimulated phase transition that occurs in zirconium dioxide from the monoclinic to the tetragonal configuration at 1873 K is understandable. In our work we investigated ceramics with composition $ZrO_2 + 3M\% Y_2O_3$. Sintering leads to some destabilization of zirconium dioxide as the result of dissociation of the solid solution and formation of the Y_2O_3 phase in the interstitial space. Under the influence of radiation modification, thermal diffusion into the grain causes enrichment of ytterbium oxide, which stabilizes the ZrO_2 in the tetragonal phase. As we can see, in our case we have a situation similar to radiation decomposition of parasitic phases in high-temperature ceramic superconductors [6].

6. RADIATION DECELERATION OF AGGREGATE RECRYSTALLIZATION

In solving problems on obtaining crystals that are simultaneously dense and fine grained, a major difficulty is presented by preventing growth of grains during sintering.

According to Turnbull [25], the motive force for migration of grain boundaries is the difference between the free energy of growing and decaying grains. A major component of this energy is the Laplacian component, which reduces the surface area of the system. In developing technology for slowing recrystallization, we must ensure that during sintering, we create forces that prevent propagation of Laplacian diffusion fluxes through grain boundaries. Such conditions are created by radiation annealing. T. S. Frangul'yan and the author of the present article have observed the effect of deceleration of recrystallization in polycrystalline metal haloid compounds subjected to high-temperature radiation annealing. Our research was performed on pressure formed KBr obtained by hot sintering. Radiation annealing with an ÉLU-4 accelerator generating an electron beam with an energy of 3.5 MeV provided an average absorbed dose of $W_{av} = 10^{-4} - 10^5$ Gy/sec.

Experimental results, as shown in Fig. 3, indicate significant suppression of the recrystallization process in ionic polycrystals when subjected to electron-beam annealing.

The temperature–time relationship for the growth of the effective size of grains (L_{av}) is described by the empirical expression

$$L_{av} = [A \cdot \exp(-u/\kappa T)] t^n, \quad (21)$$

where u is the activation energy of the process, t is the annealing time, and A and n are coefficients. We obtained the following values for the parameters of Eq. (21): for radiation annealing $n_p = 0.22$, $u_p = 0.65$ eV. For thermal annealing, $n_T = 0.35$, $u_T = 0.30$ eV. There is no single explanation for this effect at the present time. However, authors are inclined to accept the following approach.

As we demonstrated above, in the presence of excitation, highly efficient recombination occurs in interstitial regions, which results in temperature gradients and generation of radiation defects. The intense thermal diffusion and concentration fluxes of atoms within adjacent grains may exceed the Laplacian flux of particles, reducing the migration capability of intergrain boundaries. The effect of radiation retardation of recrystallization provides prospects for obtaining fine-grained ceramic structures with electron-beam sintering.

7. RADIATION SINTERING OF CERAMICS

At the end of the 1980s, researchers at Tomsk Polytechnic University performed research on radiation sintering of ceramic structures. The primary sources of radiation in our experiments were type ILU-7 accelerators at the Institute for Nuclear Physics of the Siberian Division of the Russian Academy of Sciences; these machines generate powerful pulsed beams of electrons with energies of 1.7-2 MeV. The output power of the electron beam made it possible to conduct experiments with radiation heating to temperatures of 2300 K.

Earlier research performed with A. P. Surzhikov and A. M. Pritulov established the effects of multifold acceleration of the sintering process of ferrite and high-temperature super-conducting ceramics in a powerful electron flux [6, 26]. In recent years the author and his coworkers have studied radiation accelerated sintering in corundum – zirconium ceramics. In this case, the chemical composition of the stock and the technological parameters were varied within broad limits.

The basic achievement of the indicated group of experiments was observation of a reduction in the sintering temperature in a radiation field to 150-200 K.

The data shown in Fig. 4 illustrate our conclusion and are of great value in applications, since they suggest an effective method for combating recrystallization phenomena.

The major advantage of radiation sintering over thermal sintering is the considerable improvement in the strength of the ceramic structures. In particular, the radiation method made it possible for us to obtain ceramics of 80% $ZrO_2-Ti_2O_3$ and 20% Al_2O_3 that had bending resistances of 1000 MPa, and a rupture resistance of 15-16 $MPa \cdot m^{1/2}$. This is 1.5-2 times greater than in similar materials sintered with conventional techniques.

Practically all of our results on sintering of oxide ceramics can be consistently explained from the viewpoint of surface recombination mechanisms. Confirmation of this conclusion is provided by the results of analysis of radiation and thermal sintering of model structures.

As a model we use the classical system of two spherical objects of diameter $d_{II} = 2-5 \mu m$ that are in contact at one point. The speed of radiation sintering is computed by analyzing the thermal diffusion flux that appears in the diffusion zone as the result of heating due to electron – hole recombination. We modelled a situation similar to sintering of corundum – zirconium ceramics at 1900 K.

The computation of the time required for radiation sintering of grains was performed with a formula obtained within the framework of the surface recombination mechanism:

$$t_p = 0,3 d_n \cdot \kappa T^2 / D_i \cdot Q \tau_1 \cdot f \cdot \nabla T. \quad (22)$$

Here d_{II} is the diameter of particles being sintered, and the remaining parameters are clear from the preceding text.

The time required for thermal sintering was estimated with Geguzin's theory [27]:

$$t_T = d_n^3 \cdot \kappa T / 20 \alpha \Omega D_i, \quad (23)$$

where α is the specific surface energy and Ω is the volume of one particle.

In both cases we took the time for complete sintering to be the time required to solidify the contact neck. Comparison of (22) and (23) yields

$$t_T / t_p = d_n^2 Q \tau_1 f \cdot \nabla T / 6 \Omega \alpha T. \quad (24)$$

Computations with formula (24) show that radiation sintering of the model structure is 10-50 times more efficient than thermal sintering.

The result we have obtained is obvious from the viewpoint of the surface recombination mechanism. Indeed, the radiation energy absorbed by the heterogeneous material is transferred preferentially to the atoms of the inner and outer surfaces, and subsequently dissipated into the volume of the particles.

Thus, radiation sintering leads to a unique situation: the reaction region (the region where the objects are in contact) is not only heated considerably more than the grains themselves, but an excess concentration of radiation defects is created there. These factors greatly stimulate not only sintering, but the process of thermal synthesis of multicomponent structures. In the latter case the efficiency of the surface recombination mechanism is substantially enhanced by the growth of radiation stimulated temperature gradients in the powder systems.

Indeed, the A.P. Surzhikov and the author of the present paper have observed an almost hundredfold increase in the rate of radiation synthesis of ferrites and high-temperature superconducting structures in comparison with purely thermal reactions [6].

Returning to our data on radiation sintering of corundum – zirconium ceramics, we must emphasize that the reduction of the sintering temperature to 150 K is in satisfactory agreement with the results of computation of the excess radiation heating of surface regions in heterogeneous structures. The strengthening of corundum – zirconium due to electron beam sintering can

be explained by positive effects of the technological approach: optimization of intergrain regions, elimination of excess porosity, stabilization of the tetragonal phase of zirconium dioxide, and suppression of recrystallization.

CONCLUSIONS

Ceramic materials constructed with conventional technology have excess internal energy due to residual porosity, heterogeneous structure, parasitic phases, and a high defect density at intergrain boundaries.

In order to transfer the system to a quasiequilibrium state, we subject ceramics to powerful pulsed radiation under conditions of thermal instability of radiation defects. This operation is called high-temperature radiation annealing. In this case, in contrast to the low-power situation, the material does not sustain structural damage, and the effectiveness of the method is increased by the intensity of the reaction.

The radiation accelerated mechanism we have proposed for high-temperature mass transfer does not pretend to universality, and there are a number of results that do not fall within the framework of our scheme. However, the surface recombination mechanism does provide a consistent explanation of the basic effects of radiation sintering and modification of ionic structures.

In addition, the philosophy of volume-inhomogeneous dissipation of radiation in heterogeneous structures and the method given in the present paper for allowing for such effects shows promise for both science and practical applications.

The homogenization effect is a monopole property of high-intensity radiation and can be used as the basis for a radiation technology for obtaining ceramics with unique properties. Production tests indicate that samples of radiation modified corundum–zirconium ceramics may be highly cost effective in comparison with solid solutions.

The author would like to express his deep gratitude to R. S. Frangul'yan, A. P. Surzhikov, A. M. Pritulov, A. V. Vosnyak, V. F. Stolyarenko, and other coworkers at the Tomsk Polytechnic University for their active assistance in developing the approach presented above.

REFERENCES

1. Yu. M. Annenkov and A. P. Surzhikov, *Zh. Tekh. Fiz.*, **55**, No. 4, 735-737 (1985).
2. Yu. M. Annenkov and A. M. Olovyanishnikova, *Fiz. Tverd. Tela*, **27**, No. 10, 3090-3092 (1985).
3. Y. M. Annenkov, V. F. Stolarenko, and T. S. Frangulian, *Phys. Stat. Soc.*, **156**, No. 1, 48-50 (1921).
4. Yu. M. Annenkov, T. S. Frangul'yan, and A. V. Voznyak, *Porosh. Metall.*, No. 8, 15-17 (1991).
5. A. M. Pritulov, A. P. Surzhikov, Yu. M. Annenkov, et al., *Pis'ma v Zh. Tekh. Fiz.*, **15**, No. 12, 82-34 (1989).
6. Yu. M. Annenkov, A. P. Surzhikov, and A. M. Pritulov, et al., Report No. 704-B91, Dep. in VINITI.
7. V. V. Grishaev and B. M. Lebed', *Élektron. Tekh.*, Series 6, No. 1, 18-24 (1985).
8. Author's Certificate No. 1246483–SSSR, N01F1/34, granted to Yu. M. Annenkov, K. P. Aref'ev, V. M. Auslender, et al., *Byull. Izobret.*, (1986).
9. F. V. Nolfi (ed.), *Radiation Induced Phase Changes [in Russian]*, Metallurgiya, Chelyabinsk (1989).
10. V. P. Krivobokov, O. V. Pashchenko, and G. A. Sapul'skaya, *Zh. Tekh. Fiz.*, **64**, No. 5, 37-42 (1989).
11. A. P. Tyutnev, A. A. Ponomarev, and V. P. Zaitsev, *Spectroscopy of Dielectrics and Transfer Processes [in Russian]*, Leningrad (1973), pp. 189-190.
12. S. G. Boev and V. Ya. Ushakov, *Radiation Induced Charge in Solid Dielectrics and Diagnostic Methods [in Russian]*, Énergoatomizdat, Moscow (1991).
13. V. L. Bonch-Bruevich and S. G. Kalashnikov, *The Physics of Semiconductors [in Russian]*, Nauka, Moscow (1977).
14. D. I. Vaisburd (ed.), *High-Energy Electronics in Solid Bodies [in Russian]*, Nauka, Novosibirsk (1982).
15. G. N. Galkin, *Recombination Processes in Highly Excited Semiconductors [in Russian]*, Nauka, Novosibirsk (1981).
16. A. Raus, *Fundamentals of the Theory of Photoconduction [Russian translation]*, Mir, Moscow (1966).
17. Ya. E. Geguzin, *The Diffusion Zone [in Russian]*, Nauka, Moscow (1979).
18. A. V. Lykov, *The Theory of Thermal Conduction [in Russian]*, Vysshaya Shkola., Moscow (1967).
19. A. D. Stuckes, *Phil. Mag.*, **5**, 84-87 (1960).
20. A. A. Kusov, *Fiz. Tverd. Tela*, **21**, No. 10, 3095-3099 (1979).

21. A. Miotello, *Appl. Phys. Lett.*, **40**, 135-127 (1982).
22. M. Uz, D. K. Rehbein, and O. N. Carlson, *Metallurgical Transactions A*, **17A**, 1955-1966 (1986).
23. P. Ramaswamu and D. C. Agrawal, *J. Mater. Sci.*, **22**, 1243-1248 (1987).
24. M. Torana, *J. Am. Ceram. Soc.*, **72**, No. 4, 662-664 (1989).
25. B. S. Bokshstein, *Diffusion in Metals* [in Russian], Metallurgiya, Moscow (1978).
26. Author's Certificate No. 17521154 – SSSR, H01L39/24, awarded to Yu. M. Annenkov, A. P. Surzhikov, A. S. Sigov, et al., *Byull. Izobret.* 1992.
27. Ya. E. Geguzin, *The Physics of Sintering* [in Russian], Nauka, Moscow (1967).
28. Yu. M. Annenkov, T. S. Frangul'yan, N. N. Aparov, and A. M. Pritulov, *Ogneupory.*, No. 5, 12-16 (1995).
29. Y. M. Annenkov, N. N. Aparov, T. S. Frangulian, et al., *Abstracts of International Conference on Radiation Effects in Insulators*, Vol. 1, Nagaya (1993).
30. Yu. M. Annenkov, N. N. Aparov, A. I. Ryabchikov, et al., *Fiz. Khim. Obrab. Mater.*, No. 4, 75-79 (1995).