COMPUTER SIMULATION OF MICROSTRUCTURE FORMATION IN A PIEZOELECTRIC CERAMIC

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1. The microstructure of real samples of a piezoelectric ceramic (PEC) is an ensemble of randomly oriented crystallites, pores, and a thin film of glass phase between them, subject to microcracking at some places [1, 2]. Intercrystallite (intergrain) microcracks are formed during the preparation of the samples and have a considerable effect on the strength of the PEC. The choice of the optimum technological conditions makes it possible to obtain piezoelectric components that contain a minimum number of microcracks and are thus stronger.

The technology for a piezoelectric ceramic based on gradient sintering of a pressed ferroelectric powder produces conglomerates (clusters) of crystallites [3, 4]. During sintering the PEC sample shrinks as the grain structure is formed. The shrinkage is evidently caused by the temperature gradients that arise when the sample is heated. The formation of the microstructure of the piezoelectric ceramic during sintering passes through several stages. In the first stage, individual grains that are nuclei of conglomerates of grains, are formed in the pressed powder. The structure formation process encompasses the range of temperatures from 800 to 1300 K. In the next stage, new grains around the nuclei, i.e., conglomerates become larger (up to 100 grains per conglomerate). In our experiment we observed preferential growth of conglomerates perpendicular to the direction of the temperature gradient at the given point of the sample. When the temperature in the given microvolume reaches 1300-1500 K a glass phase, evidently consisting of impurity atoms initially distributed inside the grains, is formed at the boundaries of the conglomerates. This film acts as a lubricant which enables the conglomerates to slip, going over into a closer packing. A characteristic feature of this stage is a considerable shrinkage of the sample, consisting in the expulsion of the gaseous component and formation of a closed porosity because the grain conglomerates shift. Finally, in the final stage the conglomerates "cake together." As a result of these processes two types of grain boundaries exist in the piezoelectric ceramic at the same time: inside grain conglomerates and between conglomerates. Boundaries of the second kind contain a solidified glass phase. The PEC sintering processes described above are responsible for the growth of the heating rate of the intermediate product and have been studied most fully during the sintering of a piezoelectric ceramic with the TsTS composition in a temperature gradient [3]. The study of microstructures at different stages of sintering requires much work: accordingly, once the laws governing microstructure formation have been determined experimentally, it is desirable to use computer simulation to analyze the process.

2. Let us consider a flat sample of pressed powder PEC in a gradient furnace. The problem of sintering a piezoelectric, with the assumption that the temperature gradient is constant on a small portion of the front, is given in [5]. Obviously, however, this problem must be solved in the rigorous formulation. We assume that the distribution of the temperature T in the furnace depends on only one coordinate x and consists of segments of constant temperature and a linear dependence on x. A rectangular sample of size [a, b] is introduced into the furnace along the x axis at a velocity v. We consider the first fundamental problem of heat conduction for a quasilinear heat equation with variable $u = T - T_0$ (T_0 is the ambient temperature)

$$\frac{\partial u}{\partial t} = \frac{\partial}{\partial x}\left(k(u, c)\frac{\partial u}{\partial x}\right) + \frac{\partial}{\partial y}\left(k(u, c)\frac{\partial u}{\partial y}\right), \tag{2.1}$$

the initial condition $u(0, x, y) = 0$, and the boundary conditions

$$u(t, 0, y) = u_1(t),\ u(t, a, y) = u_2(t),\ u(t, x, 0) = u(t, x, b) = u_3(x, t)$$

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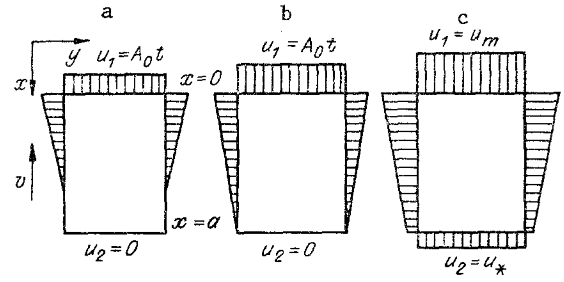

Fig. 1

[k(u, c) is the thermal diffusivity and c is the porosity]. The boundary conditions at different times t are shown schematically in Fig. 1a-c for $u_3(x, t)$, respectively:

$$u_3 = \begin{cases} 0, & x > vt, \\ A_0 (vt - x)/v, & x \leqslant vt, \end{cases}$$

$$u_3 = A_0 t (a - x)/a, \quad u_3 = u_* + (u_m - u_*)(a - x)/a$$

(A_0 is a given constant). We note that for the values of the problem parameters the heat front was convex so that the temperature u at the trailing end of the sample introduced into the furnace begins to rise after a time $\Delta t = a/v$. The calculation was stopped when the temperature $u(x, y) \geqslant u_*$ (u_* is the sintering temperature) is reached in the entire region.

The solution of the problem (2.1) is constructed by the method of sum approximation [6], using a purely implicit locally one-dimensional scheme. The finite-difference analog of Eq. (2.1) and the initial-value conditions are written. The difference equation is solved by the difference factorization method. The temperature field u(x, y) is obtained by solving the quasilinear equation by the iteration method at each step with respect to time.

The choice of the thermal diffusivity k(u, c) should be considered separately. This choice is determined by the shrinkage of the PEC. In the calculation we assume that in the initial (unsintered) sample the pores are distributed uniformly and their concentration c^0 is given. Given the sintering temperature $u_* < u_m$ and the velocity v at which the sample enters the furnace, we can define k(u, c) as

$$k(u, c) = \lambda/(c_V \rho),$$

where c_V is the heat capacity; ρ is the density of the sintered material; and λ is the effective thermal conductivity of the grain mixture. Methods of calculating λ for a porous medium with allowance for the molecular and radiant components of the heat transfer are given in [7, 8]. It was shown there that the main contribution to λ at fairly high temperatures comes from the radiant component and, importantly, a monotonic increase in λ of the porous material is observed as the temperature rises, although the thermal conductivity of the solid component decreases.

In the given case λ depends on the thermal conductivity of the sintered and unsintered components. The thermal conductivity of the first part coincides with the thermal conductivity of the ready material. The thermal conductivity for the unsintered region is found with allowance for the porosity in the region by means of the principle of generalized conductivity [7, 8]. Then in the entire region under consideration λ depends on the concentration and thermal conductivity of both components. The sought component of λ is found from the rule of interpenetrating components [7].

Let us refine the details of the calculation of k(u, c). In accordance with the concepts of Sec. 1 we assume that in part of the sample, where $u \geqslant u_*$, the PEC pressed powder recrystallizes and the forming microstructure shrinks. A structural fragment of the sample is simulated in the calculation. For this purpose we choose the neighborhood of the thermal front in the form of a rectangle, one side of which is the same order at the width of the front (250 μm) and the other is 400 μm long. The rectangular region is divided by a square net with 10 μm cells. Each cell is assigned to a powder particles or a pore. We assume that the nucleation of a crystallite in the powdery material of the initial sample is thermally activated; accordingly, each cell (not occupied by a pore) is assigned a random number (time of nucleation of an individual crystallite) by means of a random-number generator from the exponential distribution [9]

$$P_{ij}(t) = 1 - \exp(-t/\tau_{ij}).$$

Here $\tau_{ij} \sim \exp(U/k_BT)$ is the average waiting time for the formation of a conglomerate nucleus at the node of the i-th row and the j-th column; U is the activation energy; k_B is Boltzmann's constant; and T is the temperature at the net node with coordinates {i, j}. We assume that the grain with the minimum random waiting time t^0_{ij} is the first to form and its immediate neighbors with coordinates $\{k, \ell\}$ get priority, whereupon the corresponding $t_{k\ell}$ decrease. In the next step of the calculation we find the minimum grain nucleation time t^0_{ij} among all the competing net nodes; the node nearest to an already nucleated crystallite, i.e., conglomerate nucleus, may be such a node. In this case we speak of the growth of a conglomerate of grains. In the general case the nucleation time $t^0_{k\ell}$ for a crystallite along with a previously formed conglomerate is found from

$$t^0_{kl} = t_{kl} + \frac{t^0_{ij} - t_{kl}}{S\exp(1-S)} \tag{2.2}$$

(S is the area occupied by the conglomerate along with which a grain may be nucleated). We note that (2.2) takes into account the nucleation time of neighboring grains. When S is still fairly small, crystallites neighboring on the given conglomerate have priority in the crystallization processes. As S grows the nucleation of a new conglomerate gains priority. The model does not take secondary recrystallization processes into account.

The phenomenon of macroscopic shrinkage of the sample is simulated when the formation of the system of conglomerates has been completed in a region of the order of the width of the sintering front. A fragment of the formed PEC microstructure is shown in Fig. 2 (a – before shrinkage, b – after shrinkage). The porosity is shaded here and the smaller number of conglomerates indicates that they were nucleated earlier. The computational algorithm for shrinkage provides for the successively alternating shift of clusters in the directions indicated by arrows in Fig. 2b, until all possibilities of their moving has been exhausted. They do not change volume, shape, and spatial orientation as the conglomerates move, because the grain boundaries of the second kind are rigid [4]. It is assumed in the calculation that the shrinkage takes place instantaneously.

The given model, therefore, considers PEC sintering in three successive main stages: first, the motion of the thermal front [solution of problem (2.1) with appropriate thermal diffusivity] and subsequent determination of the sintering region $(u \geqslant u_*)$, second, recrystallization and shrinkage of the formed structure in that region, and, finally, calculation of a new value of k(u, c) followed by the solution of Eq. (2.1). The recrystallization and shrinkage of the model fragment of the microstructure were averaged over the results of 100 realizations to obtain statistically reliable data.

Briefly we discuss the effect of the kind of crystallite packing. We note that in this paper we have studied the microstructural processes on a square net. One can expect that models of different packings lead to similar results. We confine the discussion to the secondary recrystallization. Anderson et al. [10] showed that for sufficiently high temperatures the kinetics of grain growth and the morphology of the microstructure on triangular and square nets do not have visible differences. Such data were also obtained for the hexagonal structure. Since these models show roughly the same results, simulation on square nets is justified. As for the choice of the number of nodes of the computational net, during their analysis they calculated versions with twice as many nets nodes as in this paper. The results of the calculations indicate slight changes in the microstructure of the sample.

3. Having constructed a numerical model of the PEC structure after sintering we go on to simulate the cooling of the sample. This is accompanied by the formation of microcracks on part of the cluster boundaries because of the formation of temperature gradients, which cause thermal stresses. These stresses have their maximum in the neighborhood of the thermal front. It is known [1, 2] that at a temperature T above the Curie temperature T_C the piezoelectric material is in a paraelectric phase with a cubic lattice, so that microcracking in this temperature range ($T > T_C$) is due to the temperature gradients. In the ferroelectric phase internal stresses are also caused by phase transformations and the anisotropy of the thermal expansion coefficient. Bearing in mind the gradient sintering method, which envisages the gradual withdrawal of the sintered PEC sample, we confine the calculations to thermal stresses that arise when $T > T_C$.

A uniform temperature $T = T_m$ is established in the entire sample after sintering. Suppose that the PEC microstructure does not change during cooling and the thermal conductivity k(u, c) of the sintered material is determined only by the solid component of the piezoelectric

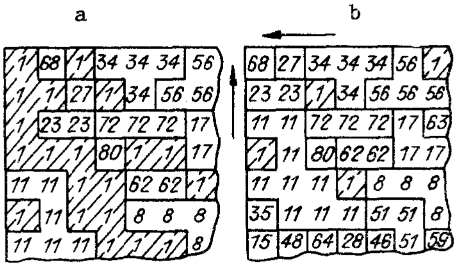

Fig. 2

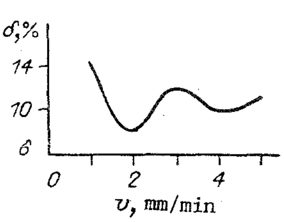

Fig. 3

ceramic (without allowance for porosity). The simulation of the motion of the thermal front is continued until the temperature reaches T_c at one boundary of the sample.

Simulation of the microcracking of boundaries in the given case consists in considering the following stages in succession: finding the distribution of the temperature field u(t, x, y) from (2.1) with the initial condition $u(0, x, y) = u_m$ and the boundary condition, similar to those in Sec. 2, but with v replaced by −v, and at nodes of the net of normal stresses isolating rectilinear segments of the cluster boundaries and determining the mean normal stresses $\langle\sigma\rangle$, and, finally, verifying the conditions for the formation of microcracks on the pertinent boundary.

The thermal stresses are found from the given field u(t, x, y) by means of a finite-difference implementation [6] of the method of [11] and the mean stress along a given boundary of length ℓ causes cracking upon satisfaction of the inequality

$$\langle\sigma\rangle\sqrt{\pi l} \geqslant K^* \tag{3.1}$$

(K^* is the fracture toughness of the PEC [4]). From (3.1) we see that the longest and most stressed segments of the cluster boundary are subject to cracking.

4. Let us discuss the results of computer simulation, in accordance with Secs. 2 and 3. As the model we chose a PEC with the composition TsTS-83G, for which $T_* = 870$ K, $T_m = 1500$ K, $T_c = 600$ K, $c^0 = 40\%$, and $K^* = 0.9$ MPa·m$^{1/2}$ [3, 4]. Calculations show that the microstructure of the sintered material depends essentially on the initial density c^0. In particular, as the porosity increases the mean conglomerate radius $\langle R\rangle$ and the shrinkage coefficient k_Δ decrease. This is evidently explained by the fact that when the porosity is high the crystallite phase is enclosed by pores, thus preventing further growth of the conglomerates. The predominance of smaller conglomerates, in turn, results in a closer packing of the structure. Moreover, the conglomerates are elongated along the temperature front and the shape anisotropy coefficient is ≈1.2 (at $c^0 = 40\%$), which accords with the data of the experiments in [3,4].

Figure 3 shows the dependence of the fracture of cracked boundaries on the velocity v of the PEC sample. This range of v was used in the gradient sintering of a PEC with the composition TsTS-83G [3, 4]. As follows from Fig. 3, an increase in the velocity does not significantly affect the fraction of boundaries subject to microcracking. At the given parameters of the material this quantity is stabilized after a value of ≈10%. The number of cluster boundaries formed during sintering in the model region as well as the number of microcracks at those boundaries behave in a similar way. Considerably more microcracking is observed, however, at substantially higher v.

In summary, the previously found dependence of the cracking resistance K_{Ic} of a material on the porosity c^0 [12-14] is a more important factor in determining the strength of a piezoelectric ceramic than is the velocity of the PEC sample in a chosen range of v.

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CHANGE IN VOLUME OF REAL ELASTOMERS UNDER UNIAXIAL TENSION

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The characteristic of transverse compression ν, generalizing Poisson's ratio to the case of moderately large elongations, has been introduced for elastomers. It has been found that for 10 rubbers used in the footwear industry ν is constant up to a breaking strain of the order of 150%.

The relative change in the volume of the rubber is calculated from the formula [1]

$$\theta = (dV - dV^0)/dV^0 = \lambda_1\lambda_2\lambda_3 - 1$$

(λ_i are the principal multiplicities of the elongations). Under uniaxial tension

$$\lambda_1 = \lambda > 1,\ \lambda_2 = \lambda_3 = \lambda^{-1/2}\sqrt{1+\theta}.$$

By S^0 and S we denote the cross-sectional areas of the sample before and after deformation, related by

$$S^0/S = 1/\lambda_2\lambda_3 = \lambda/(1+\theta). \tag{1}$$

We introduce the characteristic ν as follows

$$S^0/S = 1 + (\lambda - 1)2\nu. \tag{2}$$

From (1) and (2) we have

$$\theta = (1 - 2\nu)(\lambda - 1)/[1 + (\lambda - 1)2\nu]. \tag{3}$$

For small strains

$$\lambda - 1 = e_1,\ e_2 = e_3 = -\bar{\nu}e_1,$$

where e_i are the principal relative elongations; and $\bar{\nu}$ is Poisson's ratio. Since the relative elongations are small (e_1, $e_2 \ll 1$) we have

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