LOW-TEMPERATURE FORMATION OF SOLID SOLUTIONS IN
SUBSURFACE LAYERS OF CRYSTALS IN CONDITIONS OF
SINTERING DISPERSED PARTICLES

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The problem of formation of contacts is one of the classic problems of the physics of sintering. Formation of contacts between dissimilar powder particles in sintering at high temperatures and the role of mutual diffusion in this process have been studied in detail and examined by Ya. E. Geguzin [1].

In subsequent stages, in experimental examination of the process of sintering two-component mixtures of high-dispersion powders from virtually soluble compounds it was detected that solid solutions also form at low temperatures (of the order of (0.3-0.4) $T_m$, where $T_m$ is the melting point of the component with the higher melting point) where diffusion in the volume of the powder particles is almost completely ‘frozen’ [2-4]. It was shown that the mechanism of diffusion-induced boundary migration (DIBM) is one of the effectively acting mechanisms of low-temperature homogenizing of the mixtures. A solid solution based on one of the components of the mixture forms as a result of mutual diffusion in the components along intergranular boundaries of the base crystal and subsequent migration of these boundaries [5].

General considerations show that mutual surface diffusion like diffusion along intergranular boundaries may be accompanied by displacement of the surface in the direction of the normal as a result of build-up of atoms of both types on this surface. Since surface diffusion is quite fast already at temperatures of the order of (0.3-0.4) $T_m$, it may lead to the process of formation of solid solutions in the subsurface layers of powder particles without volume diffusion taking place.

The aim of our experiments was to examine this mechanism of formation of solid solutions and analyze kinetic relationships of the process.

The process of subsurface formation of the solid solution was examined in the conditions of sintering dispersed powder particles of the one of the components of a mutually soluble binary system to the single crystal surface of another component. We selected KCl—KBr, Cu—Ni and Au—Ni systems. KBr powder particles with a size of 0.5-15 μm were sintered to freshly cleaved surfaces of KCl with the (001) orientation or to vicinal surfaces close to (001) which were polished and annealed at temperatures just below the melting point. After annealing macrosteps formed on the vicinal surfaces, their density and geometry depended on the orientation of the surface and the annealing conditions.

Sintering was carried out in air in a ‘house’ made of KCl under isothermal conditions at 200 and 250°C which corresponds to (0.45-0.50) $T_m$. KCl particles were sintered to the cleaved surfaces of KBr in the ‘house’ made of KBr under the same conditions. The dispersed particles of copper or iron 0.5-2 μm in size were sintered to the surfaces of nickel with the orientation to (111) at 500-600°C i.e., (0.45-0.50) $T_m$, in a flow of dry hydrogen. Nickel specimens were polished mechanically and chemically and were then annealed in hydrogen for 4 hours at 1000°C. After specific periods of time annealing was interrupted and fixed sintered particles were photographed in a MIM-10 optical microscope. The composition of the subsurface layer was examined in a JSM-820 scanning electron microscope equipped with a LINK AN-10000 microanalysis system. The composition was measured by x-ray microanalysis and microanalysis in back scattered electrons.

The results show that crystals of a regular form (close to square) form and grow with time around dispersed particles of BKr during the sintering to the cleaved surface of KCl. These crystals decorate cleavage steps (Fig. 1). The maximum size of the crystals was approximately 150 μm, the maximum height according to electron microscopic data was around 1 μm.

The investigations carried out using SEM showed the zone in the vicinity of the particle and the resultant crystals consist of a KCl—KBr solid solution whose concentration depends on the distance of the given crystallite from the initial particle. For example, the KBr concentration decreases with an increase from the distance from the center of a KBr particle,
Fig. 1. Consecutive stages of sintering a KBr particle to the (100) surface of KCl at temperatures of 200 (a, b) and 250°C (c, d) for 0.5 (a), 6 (b), 3 (c), and 23 min (d).

whereas the KCl concentration increases (Fig. 2a, b). The smooth distribution of the concentration of the solution is disrupted if the diffusion zone contains cleavage steps containing active centers of nucleation of crystallite.

Quantitative estimates of the concentration of the solid solution in the crystallites were obtained by computer processing, using a standard program, the distribution of brightness on micrographs obtained in the compo regime (Fig. 2c) in which the brightness of the image is proportional to mean atomic number. The results show that the KBr concentration in the resultant crystallites varies from 5 to 20% and that the mean concentration increases with an increase of the size of these crystallites. In addition to relatively large crystallites, visible in the optical microscope, the surface contains very small nuclei (0.1-0.01 μm) of the solid solution with a two-dimensional density of the order of 10^{12} m^{-2}.

It should be mentioned here that the image contrast in the compo regime depends, generally speaking, not only on the condition but also on the surface relief of the specimen. Therefore, in evaluating the concentration we also analyze the topography contrast (Fig. 2d). Comparison of the micrographs shows (Fig. 2c, d) that the contrast in the compo regime is linked with the difference of the composition of the crystallites in comparison with the substrate composition and not with the surface topography.

It is important to stress that the coefficients of volume diffusion of chlorine in KBr and bromine in KCl at the examined temperatures are of the order of 10^{-20} m^2/sec [6], since the length of the diffusion zone \( (D_t)^{1/2} \) during the maximum experiment time (of the order of 10^3 sec) does not exceed several tens of atomic spacings. This means that the crystallites of the solid solution could not form by diffusion mixing of the components and form by another mechanism with no volume diffusion.

In sintering dispersed particles of KBr to the vicinal surfaces of KCl, containing macrosteps, the crystallites of the solid solution nucleate and growth preferentially on steps (Fig. 1), and the density of the crystallites is so high that they merge on the steps. Consequently, layer growth of the solid solution takes place on the stepped surfaces.

A similar pattern of formation of the solid solution in the subsurface layer of the substrate was detected in experiments with sintering dispersed particles of copper and gold to the vicinal surfaces of nickel. Electron micrographs, obtained in x-ray beams (Fig. 3), under distribution of the concentration around the particles, measured by x-ray microanalysis show that a region several particle radii in size is characterized by a smooth reduction of the surface concentration of copper or gold (and, correspondingly, by an increase of the nickel concentration). It is natural to link this region with the zone of surface diffusion.