The basic physical idea with which this article is concerned is that at elevated temperatures a high-porosity thin-film coating on a solid-phase, virtually nonporous basis can be expected to disintegrate (crack). The process is due to two factors: adhesion of the thin-film coating to the basis and "two-dimensional sintering," when the main dilatation takes place in a plane parallel to the plane of the basis. This idea, although apparently simple, has never been investigated before. Yet there must be considerable interest in the possibility of studying the sintering of "active" porous structures by observing the process of loss of continuity by high-porosity thin coatings.

Our main experiments consisted in isothermal annealing of thin-film powder coatings — nickel coatings (NiC) on nickel bases and copper coatings (CuC) on molybdenum bases. The heating of specimens to isothermal annealing temperatures was performed at a very slow rate (~10^{-1} deg K/sec). Coatings were applied by roll-compacting loosely poured layers of a nickel powder of practically uniform particle size and of a copper powder onto appropriate bases. The linear particle size of the nickel powder was \( r = 7 \cdot 10^{-8} \) m, while that of the copper powder ranged from \( 10^{-8} \) to \( 5 \cdot 10^{-6} \) m. The thickness of the roll-compacted layers, of porosity equal to about 0.55, was varied from \( 3 \cdot 10^{-6} \) to \( 6.5 \cdot 10^{-5} \) m. The bases were nickel (NiB) and molybdenum (MoB) plates produced by high-temperature sintering of coarse powders (\( r = 5 \cdot 10^{-6} \) m). The coatings adhered quite strongly to their bases. Annealing was effected at comparatively low temperatures (180-420°C) in a vacuum corresponding to \( 7 \cdot 10^{-3} \) Pa. Low temperatures were chosen in order to rule out the possibility of any significant atomic bulk mass transfer.

The coating and basis materials of the NiC/NiB specimens were identical, and consequently no thermal stresses were set up when these specimens were heated to temperatures at which disintegration was observed. Because of this, disintegration could only have been due to dilatation brought about by the sintering of the particles in the coatings. During the heating of the CuC/MoB specimens thermal stresses were generated, but according to elementary estimates, the dilatation induced by them (\( \approx 10^{-3} \)) was much less than that caused by the sintering of the particles, which attained some 10%.

The disintegration process was observed and photographed in situ using a long-focus optical microscope. Annealed specimens were examined in a scanning electron microscope. Quantitatively, the disintegration of a NiC/NiB specimen (Fig. 1) was characterized by the duration of isothermal annealing \( t_d \) which resulted in the appearance of cracks in it. Control annealing experiments carried out at 500°C on uncoated NiB and MoB bases revealed no visible changes in their surface structure during 10-h heating.

![Fig. 1. Disintegration of thin-film nickel coatings from ultrafine powders (T_{ann} = 420°C, t_{ann} = 60 sec, and d = 10^{-8} m): a) cracks on free coating surface; b) cross section through same specimen.](image)
One of the most important findings of this study was that the characteristic disintegration time was virtually independent of coating thickness (Fig. 2). Yet in the case of nonporous thin-film coatings [1] these two parameters are clearly related to each other. This leads to the conclusion that under the conditions of our investigation disintegration was in fact due, as expected, to a sintering process taking place in the whole volume of the porous coating.

Experiments conducted in a vacuum at various temperatures demonstrated that, other things being equal, the characteristic time $t_d$ decreased with rise in annealing temperature according to the exponential law $t_d \sim \exp(-Q/kT)$. From the results of our experiments the effective energies of activation for the process responsible for the disintegration were found to be as follows: For the Ni/Cr system $Q_{Ni} = 1.1 \pm 0.1$ and for the Cu/Mo system $Q_{Cu} = 0.9 \pm 0.1$ eV — values close to literature data on the energy of activation for grain-boundary self-diffusion [2].

The anticipated time of disintegration at any given temperature proved to vary markedly as a function of characteristic linear particle size. Coatings from finer powders disintegrated at lower temperatures and in a shorter time. It was found that, to an approximation, $t_d$ was related to $r$ by the expression $t_d \sim r^2$.

It is interesting to note some qualitative relationships established in the course of experiments on the disintegration of coatings from powders of different particle sizes. The intensity of disintegration of thin-film powder coatings grew with decreasing starting particle size (Fig. 3). A characteristic feature of the disintegration of copper powder coatings of smaller particle size ($r \leq 7 \cdot 10^{-8}$ m) was the formation during the time $t_d$ of large agglomerates of sintered particles having the appearance of grains with smooth surfaces on the background of the fine structure of the coatings. This phenomenon was observed even more clearly in [3].

As the coatings investigated were characterized by high porosity and disintegrated at comparatively low temperatures, it is reasonable to assume that their principal densification mechanism involved sliding of particles relative to one another. A formal description of this process will be found in [4-6].