Since the works of Vacek and Agte [1, 2], in which the first attempts were made to discover the physical causes of the pronounced accelerating effect that minor additions of nickel have on the shrinkage kinetics of tungsten powder compacts, many other investigations devoted to this subject have been reported in the literature. With all the information available, however, it is still not possible to build up a complete picture, free from internal contradictions, of the processes and structures thanks to which mass transport within tungsten wires is markedly accelerated in the presence of a solid-phase nickel coating.

Our own experiments were carried out with the aim of examining the activating influence of a solid-phase nickel coating on the sintering of tungsten in the case of objects of extremely simple geometry, where mass transport can be quantitatively characterized by geometric parameters that are easy to measure with high accuracy. Such objects were provided by wire models similar to those that have been used on many occasions in various physical studies of the sintering process. In our earlier investigations into the role of solid-phase coatings, too, use was made of modeling with wires [3].

Possible Mechanism of the Influence of a Solid-Phase Coating on Shrinkage

There is a great deal of evidence, obtained both in production and special experiments, to show that this so-called activity remains high as long as dislocations are preserved within the particles, but decreases when the number of dislocations falls. The following methods of introducing dislocations into powder particles have been suggested: plastic deformation, use of anomalously high current densities in the electrolytic manufacture of powders, and instantaneous quenching from the liquid phase in the production of powders by the atomization technique.

The experimentally observed activating influence of a coating on shrinkage can, in a general case, be the result of dislocations being generated at the interfaces between the particles and the activating coating and subsequently introduced into the particles. Such a hypothesis has already been put forward by one of the authors [4]. Let us now consider it in greater detail.

Fig. 1. Typical distributions of dislocations across depth of diffusion zone in system Ni–W after annealing for 80 h at 1450°C, × 600.
The mechanism through which a solid-phase coating can affect shrinkage kinetics is as follows. At the particle/coating interface, the difference between the lattice parameters of the two materials leads to the formation of so-called misfit dislocations, whose density per unit length of the contact surface may be approximately evaluated with the formula 
\[ \rho_m \approx \Delta a / \bar{a}^2 \]
where \( \bar{a} = (a_1 + a_2) / 2 \) and \( a_1 \) and \( a_2 \) are the lattice parameters of the particle and the coating, respectively. The dislocations can escape into the particle, as a result of which a high volume density of dislocations is obtained in the latter. On 1 cm² of the contact surface, \( \rho_S = 2 \rho_m \); it follows, therefore, that the number of dislocations appearing on the whole surface of the particle, which is assumed for simplicity to be spherical, is \( N_S = 2 \cdot 2 \pi \rho_m R \). On passing into the particle, these dislocations give rise to a mean volume density of dislocations of
\[ \rho_v = N_v / \pi R^2 = \frac{4 \Delta a}{R} \frac{\bar{a}}{a} \sim \frac{1}{R} \]

At reasonable values of the magnitudes determining \( \rho_v (\Delta a / a = 10^{-4}, a = 3 \cdot 10^{-8} \text{ cm}, R \approx 10^{-4}-10^{-3} \text{ cm}) \), the resultant density is found to be approximately equal to \( 10^{15}-10^{14} \text{ cm}^{-2} \), which is several orders higher than the starting density of dislocations in particles having no nickel coating. Such a high density of dislocations can generally ensure that particles exhibit a high level of "activity" toward their solid-phase activating coatings.

As has been demonstrated by numerous experiments, the process of diffusional homogenization is responsible for the migration of misfit dislocations into the specimen. Here experience shows that the migration of dislocations is much faster than the propagation of the diffusion front, or, to be more precise, that dislocations are found in that part of the diffusion zone in which the concentration of the diffusing component is very low.

To confirm that this phenomenon is observed also in the system Ni–W under examination, special experiments were carried out. A layer of nickel was applied to the surface of a tungsten single crystal by vacuum vaporization. The specimen prepared in this manner was subjected to diffusional annealing, after which, using the technique of serial grinding, a study was made of the dislocation structure in a plane perpendicular to the surface coated with nickel. A typical distribution of dislocations across the depth of the diffusion zone and the variation of the width of the dislocation-containing zone with time are illustrated in Figs. 1 and 2, respectively. From the results of these experiments it follows that, at 1450°C, powder particles \( \sim 10 \mu \text{m} \) in linear size will be fully pierced by dislocations generated at the particle/coating interface in a time of the order of a few minutes.

The activating effect of such dislocations upon the mechanism of sintering may manifest itself in two ways.

Firstly, the dislocations may lead to a growth in the diffusional permeability of the particles, i.e., to an increase in the effective volume coefficient of diffusion \( \bar{D} \), which, according to Hart's model [6], is given by the expression:
\[
\bar{D} = D_0 \left( 1 + \frac{D_1}{D_0} \rho S \right),
\]
where \( D_0 \) is the coefficient of diffusion in a defect-free single crystal, \( D_1 \) the coefficient of diffusion along dislocations, \( \rho \) the density of dislocations, and \( S \) the cross-sectional area of a dislocation tube along which diffusion takes place in accordance with the coefficient \( D_1 \). At \( \rho \gg D_0 / D_1 \cdot 1 / S \), mass transport within the particles will be controlled by the coefficient \( \bar{D} = D_1 \rho S \) and, consequently, the activation energy of the process will be equal (assuming the possible temperature dependence of \( \rho \) to be negligible) to the activation energy of the diffusion process along dislocations. At \( D_0 / D_1 \approx 10^{-5} \) and \( S \approx 10^{-15}-10^{-14} \text{ cm}^2 \), \( \rho \) would be expected to be greater than \( 10^9-10^{10} \text{ cm}^{-2} \). From a phenomenological aspect, the sintering process in these circumstances will be described by the equations applicable to defect-free powder particles, the only difference being that mass transport is now determined by \( D_1 \) and not \( D_0 \).

Secondly, dislocations within the particles may act as sources and sinks in the mechanism of diffusion-viscous flow at a viscosity coefficient \( \eta = kT / D_0 \rho \) [5]. For such a situation to arise, it is nec-