By activated sintering is meant the use of chemical or physical agents to accelerate the processes that occur in sintering.

Methods of activation can be classed into two groups:

1. Activation by external means, such as sintering in special media containing halogens, cyclic oxidation, and reduction during sintering, use of a powdered hydride in the surrounding material, cyclic temperature variation, use of external pressure, etc.

2. Activation by the use of materials having a special initial state. Examples are previously oxidized powders or samples, powders of highly defective structure (unannealed powders of small grain size), addition of materials that give rise to a liquid phase, etc.

Activated sintering is of interest in that it can provide rational technological processes; moreover, it provides material for a better theoretical understanding of sintering.

It has been demonstrated that diffusion is responsible for the increase in density during sintering, and that lattice defects have a pronounced effect on the shrinkage. These defects result from the conditions of production (low temperatures of reduction or decomposition, severe conditions during electrolysis, etc.).

It has been shown that lattice defects accelerate diffusion and creep in cast metals; the greater the deviation from equilibrium, the higher the proportion of defects, and so the greater the shrinkage. A thoroughly annealed powder gives very little change in density. This effect is one important proof that diffusion controls sintering, for the defects would retard the process if plastic deformation were responsible for the shrinkage.

We have demonstrated that the state of the surface layers plays a vital part in bringing about shrinkage; the mere presence of defects is not sufficient to ensure rapid shrinking, but an active state in the surface layers is a sufficient condition. For example, chromium powder made by reduction has a highly defective structure, but it sinters very poorly on heating on account of the resistant oxide films on the particles; no shrinkage occurs. The shrinkage is located mainly at the contacts between particles, so its extent is dependent on the state of the contacts.

There is much evidence in support of this. Very large effects are to be expected if the particles contain many defects and pores and also have active surfaces, for defects facilitate diffusive creep.

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That is, powders having defect surface structures should be used to activate sintering; such structures might be produced in the process. External pressure and the presence of a liquid phase also facilitate coalescence of particles.

However, change of density is not the only factor that governs the properties of the product; other important ones are smoothing of the surfaces of pores, recrystallization, removal of impurities, and homogenization (in initially heterogeneous systems). The conditions may be such as to produce rounded pores, to eliminate impurities, or to produce a highly homogeneous system. Methods of activated sintering should be designed to meet the special requirements of each particular powder product.

The mechanism of the activation process must be elucidated, and this varies with the method of activation. A fairly reliable conception of the mechanism is now available for some processes, but the evidence is still insufficient in most cases.

**Activation by Reduction of Oxides**

It has long been known that a certain amount of oxide has a favorable effect; preliminary oxidation of briquettes is sometimes used in practical work with iron powder, the activation here leading to improved density and strength. Metals such as Fe, Ni, W, Mo, and Cu show the same effect, for their oxides are readily reduced during sintering.

Figure 1 (from [1]) shows the effect of oxygen content on the density of sintered iron powder as made by vortex grinding and by reduction. Here, the oxygen was introduced by heating the pressed briquettes in air.

Both curves show that there is a best oxygen content, though this is different for the two, evidently on account of oxygen present in the initial materials, and of differences in the surface geometry. The strength shows a trend similar to that shown by the density.

The most probable cause is that reduction of the oxide gives rise to numerous mobile atoms in the surface layers of the particles. It is quite clear that the density and strength of the product are directly controlled by surface processes, for low-temperature oxidation produces only surface films of oxide. This is confirmed by the effects of oxygen pressure on the linear shrinkage of briquettes of copper oxide (Fig. 2) [2].

There is a sharp maximum in the shrinkage, at a pressure dependent on the temperature: 0.5-1 mm Hg for 800°, and 10-20 mm Hg at 850°.

The dissociation $2\text{CuO} \rightarrow \text{Cu}_2\text{O} + 0.5\text{O}_2$ produces a pressure of the above order at these temperatures; the maximum shrinkage corresponds to a pressure equal to the dissociation pressure, when the acts of dissociation and combination are most numerous. The activated atoms in the transitional state have increased diffusion mobilities, which are responsible for activating the shrinkage.

A proper understanding of the activation mechanism enables us to choose the proper conditions in each case; here, the main need is to produce conditions such that the surface layers contain an adequate amount of oxide, which must be completely reduced during sintering.

It has been incorrectly claimed [3,4] that moisture in the sintering atmosphere activates shrinkage via repeated oxidation and reduction at a fixed temperature on account of local supersaturation with water vapor. Our experiments (jointly with R. A. Andrievski, G. G. Gnesin, and V. V. Skorokhod) on reduced iron powder, have shown that the strength, plasticity, and magnetic properties are not affected by the use of moist hydrogen (2, 10, 15, and 20% H$_2$O) instead of dry [5,6], nor was there any effect on the density and specific surface. (The specimens were brought to temperature and cooled in dry hydrogen in every case.)

This is only to be expected, for the oxides of iron are unstable under the above conditions, reduction being the only process.