Evolution of Surface and Pore Volume in Compacted Metal Powders

O. Blaschko, R. Glas, G. Krexner, and P. Weinzierl

Institut für Experimentalphysik, Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria

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Sintering of compacted metal powders is investigated by small-angle neutron-scattering techniques. The results evaluated in terms of the total pore surface area F and the total pore volume V give evidence for a universal relation between F and V thus indicating that both coarsening and pore elimination contribute to the surface reduction during the sintering process.

The physics of nonequilibrium phenomena is currently the subject of numerous experimental and theoretical studies. One part of these efforts deals with the investigation of decomposition processes where the order parameter is a conserved quantity [1]. Another part of these studies investigates ordering phenomena where the evolution occurs by domain-wall migration and curvature-driven growth [2,3]. In the latter case the order parameter is not conserved but the integral volume remains constant during the evolution.

By way of contrast, the porosity shrinkage during sintering of metal powders is a nonequilibrium phenomenon in which no conserved quantity exists but, beyond that, even the macroscopic sample volume changes during the evolution of the system. During sintering a sample represents an open system from which voids are eliminated.

Generally, the evolution of metastable states towards equilibrium is driven by the interplay of different thermodynamical quantities, i.e., volume, surface, and distortion energies. In the case of sintering the porosity shrinkage is nearly entirely governed by the gain in surface energy.

The densification behavior of compacted metal powders during sintering comprises several stages [4]. First the powder particles form zones of contact between each other. This process occurs early during the heating phase and induces only a minor decrease in pore volume. Then a marked reduction of the void volume follows, resulting in density changes and macroscopic shrinkage of the sintered material. Finally, at late times, the porosity decrease is very low. Both bulk and surface diffusion contribute to the complex atomic rearrangements during the different stages. Furthermore, defects and lattice distortions influence the sintering behavior especially at early times.

Most investigations in the literature deal with the time evolution of density and macroscopic shrinkage but despite its fundamental importance little is known on the behavior of the total surface of the system during sintering.

In this Letter we present the first results of a series of small-angle neutron-scattering (SANS) experiments on sintering in metals giving insight into the relation between surface evolution and densification behavior during sintering. The results show that both coarsening and cav-

ity elimination characterize the system evolution towards equilibrium. The present investigations cover a wide time and temperature range. SANS experiments allow the observation of the total pore surface F which can be obtained by applying the Porod [5] law $I \propto F/Q^4$ to the
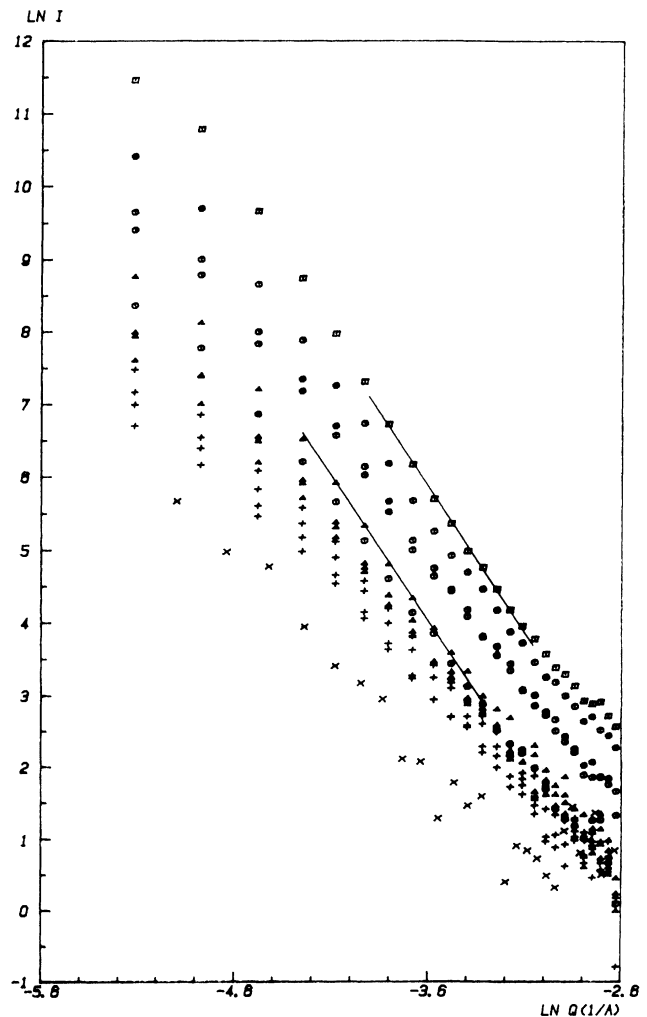

FIG. 1. Neutron small-angle scattering data for molybdenum samples sintered under time and temperature conditions given in the inset of Fig. 2. The range of validity of the Porod law is marked for two samples by straight lines showing a slope of -4 in this doubly logarithmic plot.

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measured scattering intensity distribution [I is the measured neutron intensity, $Q = 2k\sin(\Theta/2)$, where k is the neutron wave vector and Θ is the scattering angle]. SANS is therefore a unique tool for the investigation of porous systems, in particular, when the porosity is closed.

Pure powders of niobium and molybdenum were used as starting material for the sintering process. The powders were mechanically compacted yielding an initial porosity of 20–40 vol% and then sintered for various times and temperatures by Metallwerke Plansee (Austria). The average size of the initial powder grains was 5 and 20 μm for Mo and Nb, respectively. The measured neutron-scattering intensities were normalized using the incoherent scattering of water. This normalization procedure allowed us to evaluate the total porosity surface in absolute units of cm^2/g.

Neutron small-angle scattering data for molybdenum corresponding to different stages of sintering are shown in Fig. 1. The Porod dependence ($I \propto F/Q^4$) of the intensity curves is clearly distinguishable as indicated by the straight lines in the doubly logarithmic plot. The integral porosity surface F is plotted versus the total porosity volume V in Fig. 2 (coarse-grained powder data; for the fine-grained powder see below). V is obtained from the macroscopic density of the samples. The inset gives the time evolution of the density for the three sintering temperatures investigated, i.e., 1500, 2000, and 2500°C. Despite the fact that the density evolution takes a clearly different course depending on temperature the ensemble

of molybdenum samples seems to be represented by a single curve in the (F vs V) plot of Fig. 2 (solid line).

Similar measurements were done on niobium and the results are shown in Fig. 3. Here again samples showing an obviously different dependence of density on time as a function of temperature can be represented by a single curve in the (F vs V) plot.

The experimental results show that a unique relation between F and V exists over a wide range of densification of the sintered material. This relation does not depend on temperature and sintering time. The data points of both molybdenum and niobium can be described to a good approximation by the equation $F = aV^2$. The constant a, however, is somewhat different for the two materials and turns out to depend on the initial (F, V) characteristics of the powder compact.

The dependence of the observed relation on the initial powder characteristics was further investigated by choosing molybdenum powder with a smaller initial grain size (2 μm) as starting material for the sintering process. The results obtained are displayed in Fig. 2 (fine-grained powder data). Initially the sintering system composed of the finer powder shows a smaller total cavity volume but a similar pore surface in comparison with the powder consisting of coarser grains. The further (F, V) evolution during sintering is consequently much steeper but can likewise be represented by the functional relationship $F = aV^2$ (Fig. 2, dashed line).

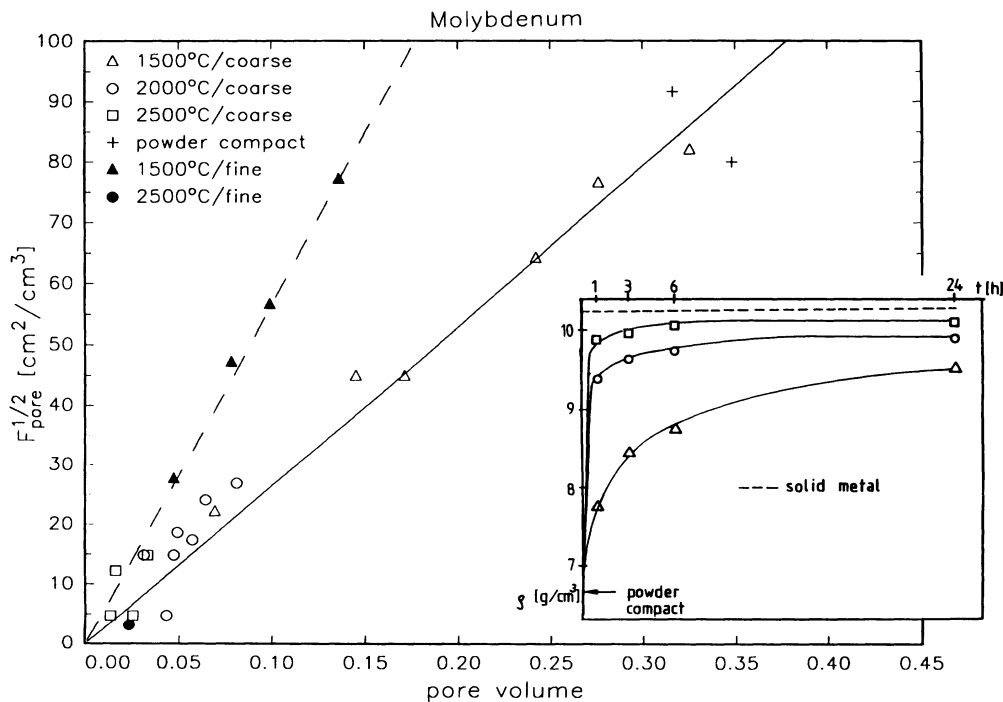The quadratic dependence of F on V obtained during

FIG. 2. The sintering process in molybdenum: Evolution of the square root of the total pore surface area F as a function of the total pore volume V. V is given as the sample volume fraction occupied by voids. Sintering times cover a range from 10 min to 24 h. The straight lines are guides to the eye (solid line, coarse-grained powder; dashed line, fine-grained powder). Inset: Three curves giving the time dependence of the density for three different sintering temperatures. The melting point of molybdenum is 2617°C.
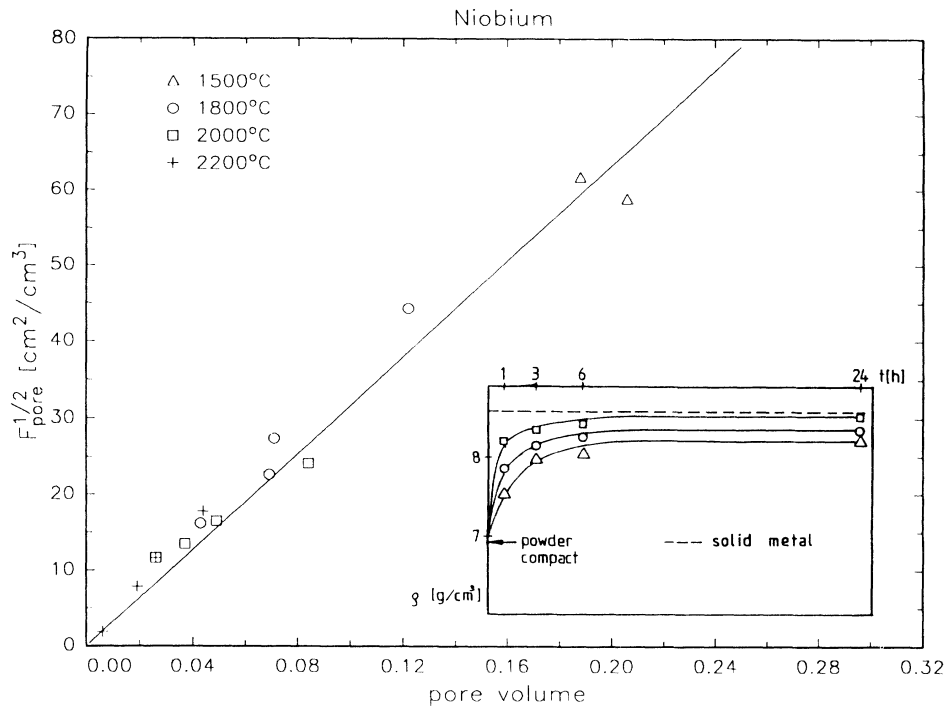
FIG. 3. The sintering process in niobium using the same representation as in Fig. 2. The melting point of niobium is 2468 °C.

different sintering processes shows that the pore surface is more strongly reduced than the total cavity volume, especially during the early stages of sintering where the pore surface is large. This means that coarsening of the cavities occurs during the entire sintering process: Indeed, if the pore structure is characterized by a mean pore radius

R then F can be written $F = V/R$. In the case of a constant mean radius (i.e., no coarsening) this would result in a linear relation between F and V in contradiction to the experimental results.

It follows that the surface reduction during sintering is governed by two processes: (a) pore elimination at the
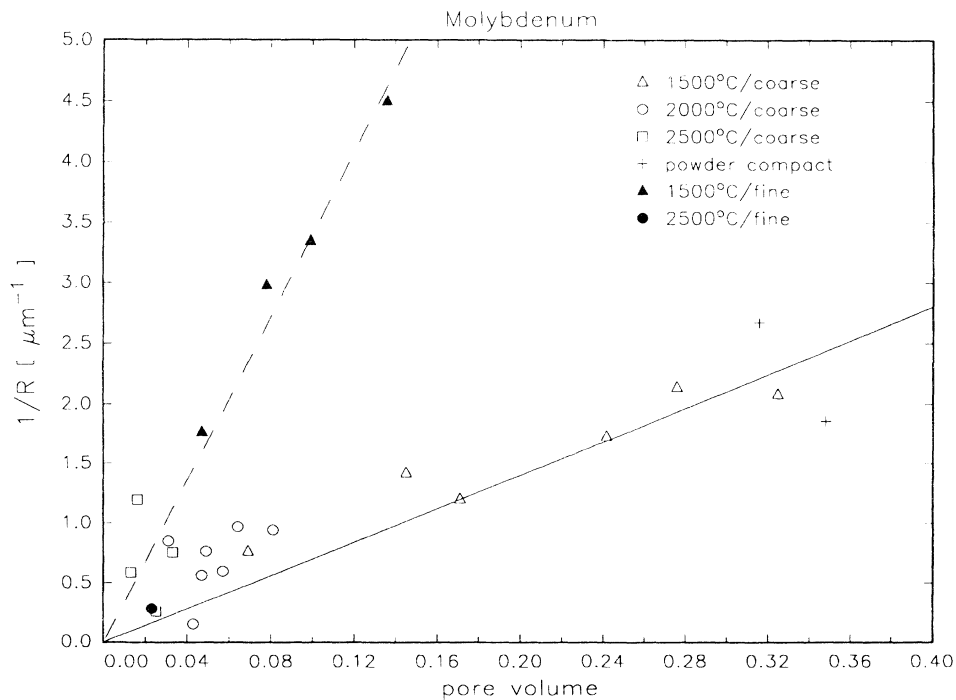

FIG. 4. Sintering process in molybdenum in a $1/R$ vs V representation (solid line, coarse-grained powder; dashed line, fine-grained powder).

outer surface of the system inducing a surface decrease $dF = dV/R$ and (b) pore coarsening causing likewise a reduction of the pore surface $dF = -(V/R^2)dR$. The two mechanisms are not independent as both V and R evolve during sintering.

It is difficult to relate the present findings directly to theories of sintering which deal essentially with the time evolution of macroscopic density as a function of temperature. Yet in their seminal work on alloy decomposition Lifshitz and Slyozov [6] devoted a section to the sintering behavior of the inner part of a sample volume on the assumption that the total cavity volume V remains constant. They characterized the sinter cavities in terms of a local droplet equilibrium of a sinter pore of radius R and its surrounding vacancy supersaturation Δ. They found that coarsening takes place and that on assuming V to be constant the vacancy supersaturation varies as $\Delta \sim F$.

The present experiment supplies information on a real system where the sinter process is inherently connected with a porosity volume decrease. Analyzing the observed relation $F = aV^2$ one obtains by differentiation $dF = 2aV\,dV$. It follows then from the experiment that

$$\left[\frac{dF}{F}\right] = 2\left[\frac{dV}{V}\right] . \tag{1}$$

On the other hand, from the general relation $F = V/R$, where R denotes the mean cavity radius, one obtains

$$\left[\frac{dF}{F}\right] = \left[\frac{dV}{V}\right] - \left[\frac{dR}{R}\right] . \tag{2}$$

Equating now expressions (1) and (2) one gets

$$\left[\frac{dV}{V}\right] = -\left[\frac{dR}{R}\right] . \tag{3}$$

This means that the two variables determining F (i.e., V and $1/R$) both contribute to the sintering process and show an identical relative variation. The evolution of the sintering system is represented in a $(V, 1/R)$ space in Fig. 4. The figure shows that the system evolves from its initial nonequilibrium $(V, 1/R)$ position, essentially determined by the (F, V) characteristics of the early sintered compact, most directly—i.e., on a straight line—towards an absolute minimum, namely, the origin of the $(V, 1/R)$ plot. During this evolution the surface energy decreases as $\sim V^2$.

The above analysis describes the sintering process by using the quantity V/F which has the dimension of a characteristic length. For a monodisperse distribution of spherical voids this length obviously has to be considered the mean pore radius. This straightforward interpretation is possibly no longer applicable to the very first stages of sintering when the porosity is open and the network of interconnecting channels contributes significantly to the inner surface of the sample. In the present case, however, it is known from electron microscopy [7] that after sintering 30 min at 1500°C (the lowest sintering

temperature investigated) the pore morphology nearly exclusively consists of spherical voids which predominantly can be found at the boundary surfaces of the sinter grains.

The description of a population of spherical pores through a characteristic radius has proved to be a useful approach in both theoretical and experimental studies. It is in accordance with results of numerical simulations (see, e.g., [8]) which demonstrate that the long-term evolution of a system containing spherical voids does not critically depend on the details of the pore size distribution as long as the distribution is not extremely irregular. The SANS spectra, however, give no indication that such conditions apply in our experiment.

To conclude, the present neutron small-angle scattering investigation relates the evolution of the pore surface to the densification behavior of the sintered material. The results indicate a strong contribution of coarsening to the elimination of pore surface in contradiction to current understanding of the sintering process. The observed relation between F and V does not depend on sintering temperature and sintering time.

Compacted metal powders are complex nonequilibrium systems. However, as experiment shows they exhibit remarkably simple behavior with regard to the fundamental thermodynamic variables driving the evolution of the system. In the present case the system disposed to reduce its free energy in two ways (pore elimination and coarsening) both of which actually are made use of. The evolution of the system can be predicted proceeding from the (F, V) characteristics of the initial metal powder compact without detailed knowledge of the thermal treatment of the sample.

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