
Lecture

SINTERING OF COVALENT SOLIDS

SVANTE PROCHÁZKA

Ceramics Laboratory, General Electric Research and Development Center, Schenectady, N. Y., USA

Sintering is the most versatile process of making inorganic materials from substances which cannot be melt, cast, and plastically worked. All materials which can be melt-cast can also be prepared by powder metallurgical processes but not vice versa. With ceramics sintering is, of course, the most popular fabrication process.

In sintering, powders are compacted into desired shapes and heated. The surface tension acts as a flexible membrane stretched over the surface of the compact. It puts every contact point between the particles under pressure and induces matter transport from the loaded contact points into the interparticle void (pores). The consequence is that the particles approach each other and the object shrinks until the voids become filled. This process is called densification and is the desired objective in materials fabrication. If the process is conducted correctly, a pore-free body may be obtained.

There are a great many substances which decompose or evaporate below their melting point, that can be consolidated into dense bodies by sintering, because it can be conducted at two-thirds of the melting point. Compounds made up from elements in the upper right hand corner of the periodic table, such as SiC, B₄C, Si₃N₄, diamond, SiB₃, BN, etc, which we can denote as covalently bonded, are the hardest, the strongest, the most refractory, and the most resistant to creep. They have high moduli and thermal conductivities and possess very attractive engineering properties. They are, however, also the most difficult to process into materials. Until relatively recently there were not any practical processes for making covalent materials without compromising the good engineering properties. The reason was that they refused to densify by sintering; that is, their powder compacts when heated remained porous and weak until they evaporated.

In crystalline solids the matter transport, which brings about densification, occurs by diffusion along several different paths, among which transport along

grain boundaries is the most important. Low self-diffusivity in covalent solids was blamed in the past for the absence of densification on sintering. However, as data for self-diffusion in Si, Ge, SiC, and B became available, it turned out that the reason is more complicated and that both kinetic and thermodynamic factors are responsible.

Meanwhile observations have been made that small amounts of specific additives (dopants) to some very fine powders of covalent materials will induce, under certain circumstances, densification. One of the first of such observations was made here at GE CRD in 1973 when we demonstrated that as little as 0.3% boron and 1% carbon made SiC densify to near theoretical density on heating to 2000° C. Development of processes for fabrication of dense SiC, Si₃N₄, AlN, and B₄C materials followed these observations shortly and rapidly expanded into a new field of “non-oxide ceramics.” This field has since grown into a respectable industry.

Information about the progress of sintering is usually obtained from shrinkage, i.e. the dimensional changes the bodies undergo on heating. These may be interpreted in terms of rate processes according to several models that have been proposed. With the exception of sintering of glasses, agreement is rarely very good. The origins of the discrepancies are many and are still not well understood. Non-ideal particle packing because of particle size and shape distribution, a multiplicity of transport mechanism, anisotropy of surface energy, grain boundary sliding, and the effects of impurities are frequently cited to make the predictive power of sintering models limited. One may observe that whenever a new sintering model is proposed new data are usually generated to support it; the existing data would not fit.

Sintering of crystalline materials frequently defies the rate process intuition of chemists. More heating will not drive the process closer to completion. This statement is particularly true with covalent materials and can be illustrated by Figures 1 and 2. In these

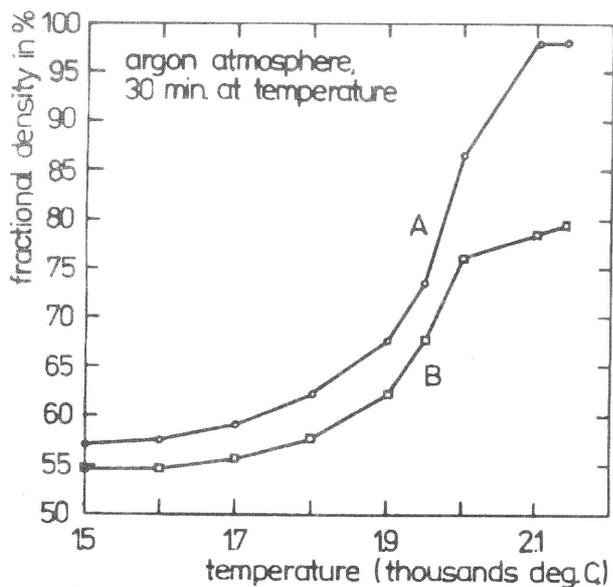


Fig. 1. Densification response of compacts of two silicon carbide powders with addition of boron and carbon sintered in argon

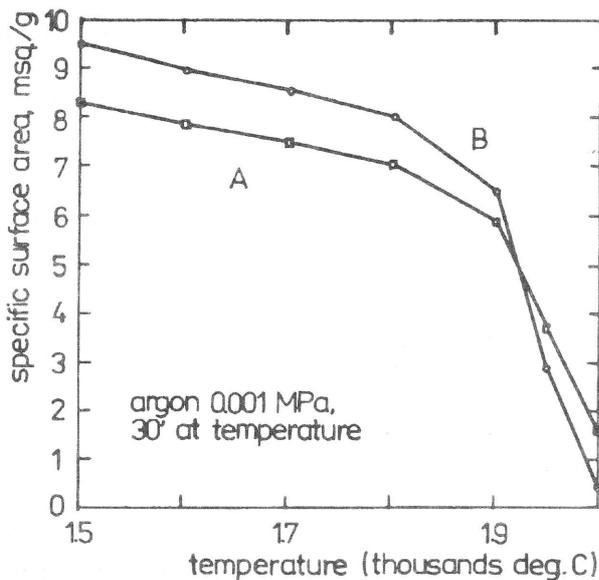


Fig. 2. Specific surface area of SiC powder compacts sintered in argon at different temperatures

graphs we plot relative density (essentially the degree of densification) and specific surface area for two different silicon carbide powder compacts, A and B, as a function of temperature. One can observe that the two SiC powders, chemically hardly distinguishable and identically doped, show a substantially different response. Powder A could be brought to full density by heating to 2100 °C, while powder B stopped den-

sifying when it reached about 80% of relative density.

In Figure 2 we plotted specific surface areas of the same powders as a function of temperature. The surface is the origin of surface energy of the system which, as we already mentioned, is the driving force of densification. We can see that the surface areas are reduced as sintering progresses, i.e. the energy is consumed. One way it is consumed is by frictional forces in the transport process which brings about densification. The important point is that while powder B densified less, its surface area, and with it the available energy, was reduced more than in powder A; the process in powder B was more energy wasteful.

We may replot the data as specific surface area (which we have now normalized to bring the starting surface areas for both specimens at the same level) as a function of relative density. This we have done in Figure 3. The plot shows that the process in specimen A proceeds along a line connecting A and O; i.e. it tends toward full density. In specimen B the trajectory is steeper, falls well below A-O, and terminates at B'. The system reached its finite density at this point. It has left very little surface area, ran out of energy, and the transport processes ceased. It can never get to O from B'. In this case we end up with a porous body.

The failure to densify is the most common difficulty in making materials by sintering of covalent substances; it is poorly understood and cannot be corrected by heating the system more or longer or by other simple means. In order to find out what has

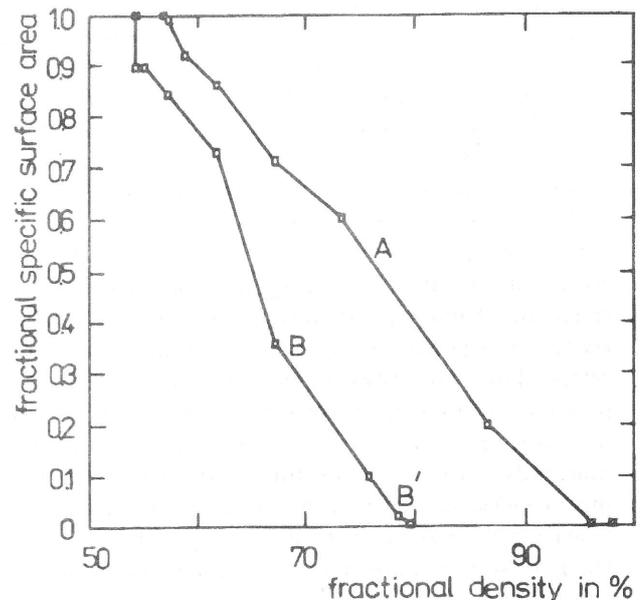


Fig. 3. Specific surface area vs. fractional density for two SiC powders. The specific surface area was expressed as a fraction of initial value.

gone wrong with B one needs deep insight into the mechanism of the process. We can only give a simplified picture of what complicates sintering in covalent solids.

There are two additional processes that proceed along with densification in sintering and compete for the source of energy, the surface energy. They are coarsening and grain boundary formation.

When matter can be transported from the surface of one particle to another, the larger particles will grow and the smaller disappear, as in Ostwald ripening. This process is coarsening, and it may occur, for instance, by evaporation and condensation. In the diagram in Figure 3 it corresponds to moving vertically down along the ordinate. This reduces the surface area (and thus the driving force for densification) but does not produce any densification. With respect to sintering it is, therefore, an undesirable process that wastes energy.

Formation of a polycrystalline solid from a powder aggregate by densification (or any other consolidation process) is accompanied by formation of new interfaces: grain boundaries (or phase boundaries if more than one phase is present). When an interface is formed, the grain boundary energy γ_{gb} (or phase boundary energy) is expended. This energy is stored in strained atomic bonds at the interface. In densification two surfaces merge to form one grain boundary. In theory then, as long as $2\gamma_{sv} > \gamma_{gb}$ or $\gamma_{gb}/\gamma_{sv} < 2$, the process may proceed. (A more rigorous analysis shows that the condition is $\gamma_{gb}/\gamma_{sv} < 1.71$). In most materials such as metals and oxides, the ratio of γ_{gb}/γ_{sv} is anywhere between 0.3 and 1.0, and thus there is always enough energy to form the grain boundaries and, hence, to densify. Sintering is therefore not inhibited, in this case, by energetics.

In covalent materials grain boundary energies are believed to be high as a result of high stiffness and directionality of chemical bonds. Calculations seem to support this expectation, although good data are still scarce. Consequently, the energy balance in the sintering of covalent materials may not be favorable. There may not be enough energy in the surface to form the grain boundaries. This happens when $\gamma_{gb}/\gamma_{sv} > 1.71$. Under these conditions densification does not proceed at all and all that is observed on heating of a powder compact is coarsening.

The situation is further complicated because of the high absolute values of in covalent solids. The average surface energy of SiC, for instance, has been calculated at 3.5 J/m^2 , a huge value compared to other solids. (An experimental value is 1.9 J/m^2 , also very high.) Systems with high surface energies tend to reduce it by adsorption. Oxygen, for instance, can reduce γ_{sv} in SiC to a mere 0.3 J/m^2 and Si to 0.6 J/m^2 . In other words, capillary phenomena such as sintering in covalent solids will be strongly affected by certain impurities. This effect is indeed observed. The presence of oxygen or condensed Si inhibit densification in SiC because by reducing it increased the ratio of γ_{gb}/γ_{sv} .

On the other hand, segregation of impurities, that is migration of atoms dissolved in the solids to grain boundaries, may affect the above ratio favorably. Segregation is driven by lattice strain energy and may reduce γ_{gb} because the presence of solute atoms in the grain boundaries may improve accommodation. In such a case, it will reduce the above energy ratio and promote densification in sintering. It is very probable that this is the mechanism by which sintering activation by some dopants such as B, Be, and Al in SiC or B in Si takes place.

It is the energy trail that helps understand sintering in covalent materials. As long as we deal with substances that have high enough surface energy with respect to grain boundary energy, such as most metals, oxides, silicates, etc., and are therefore dealing with systems far from equilibrium, the process of densification usually proceeds smoothly, unperturbed by other, simultaneously proceeding, energy consuming processes. Such processes can be ignored in the first approximation. Moving into the domain of covalent solids, which have larger grain boundary-to surface energy ratios, the systems are closer to equilibrium, energy is tight, and relatively small perturbations may upset the densification process. This is, of course, common in physics; close to equilibrium we find new phenomena, elsewhere unobservable or unimportant.

On the occasion of my retirement from the Ceramic Laboratory of GE R&D my colleagues asked me to give a seminar discussing my most important contribution to ceramic science. The above is an abbreviated form of my presentation.

Submitted in English by the author