CAPILLARY FORCES IN LIQUID PHASE SINTERED STRUCTURES AND THE ANALOGY WITH FOAMS AND EMULSIONS

Andreas MORTENSEN* and Christopher SAN MARCHI

Laboratory of Mechanical Metallurgy, Department of Materials, Swiss Federal Institute of Technology Lausanne, Switzerland

ABSTRACT

We draw a parallel between the local equilibrium microstructure of liquid phase sintered materials and the structure of foams and emulsions in the limit that the liquid phase sintered material has an isotropic liquid-solid interfacial energy and a mostly zero dihedral angle. Using this direct analogy and experimental data for the osmotic pressure of emulsions, we predict the liquid pressure in liquid phase sintered structures containing more than 64 vol. pct solid. We also use this analogy to estimate the importance of gravity-induced gradients in these liquid phase sintered materials.

INTRODUCTION

Liquid phase sintering poses an interesting problem in high-temperature capillarity: to a large extent and through several parameters, capillarity determines both the feasibility and the rate of the process, as well as the resulting material microstructure. The practical importance and overall complexity of this process have prompted many investigations, principally focused on systems of practical significance, which nearly always feature some solubility of the solid in the liquid. Such systems can densify by grain shape accommodation, as a result of comparatively rapid diffusion of the solid through the liquid. Coarsening of the solid particles during and after sintering is also a necessary characteristic of these materials, as both coarsening and densification are driven by the same process of dissolution, followed by diffusive transport through the liquid and reprecipitation of the solid phase along interfaces with lower curvature.

The structure of the liquid and solid phases after completion of densification is of particular interest in liquid phase sintering. When densification has necessitated grain shape accommodation of the solid particles, there is a natural tendency for the network of solid particles to expand, thus creating what has been termed a "sphering force" [1-4]. The sphering force is caused by the excess interfacial energy that results from deviations in the equilibrium shape of solid particles (a sphere if the liquid-solid interfacial energy is isotropic), caused by grain shape accommodation. The result is a net force towards expansion of the touching solid particle network, which is resisted by a negative pressure in the liquid, itself also capillary in nature. A few theoretical analyses have been proposed to quantify these forces and accommodated shapes [1-4]; in the present article, we propose a somewhat different approach to this end. Our starting point is the parallel that exists between liquid foams (and emulsions) and the simple solid-liquid structures of liquid phase sintered systems that are not faceted and display a dihedral angle of zero.

* Corresponding author - Andreas Mortensen, MX.D. 121, LMM - EPFL, CH-1015, Lausanne, Switzerland, FAX 41 21 693 4664, email: andreas.mortensen@epfl.ch

This document is provided by JAXA.

THE PARALLEL BETWEEN LIQUID PHASE SINTERED STRUCTURES AND FOAMS

A liquid foam is a structure composed of gas-filled bubbles surrounded by liquid. The bubbles in a foam cannot be spherical as the fraction of liquid relative to that of gas is too low. At ambient conditions, the gas pressure within these bubbles equals one atmosphere plus the capillary pressure caused by the curved interfaces, as well as neighboring bubbles. It turns out that in all but the finest of foams, the capillary pressure is significantly less than 10^5 Pa and, for all practical purposes, the bubbles can be considered incompressible [5]; thus their volume does not vary with the fraction liquid.

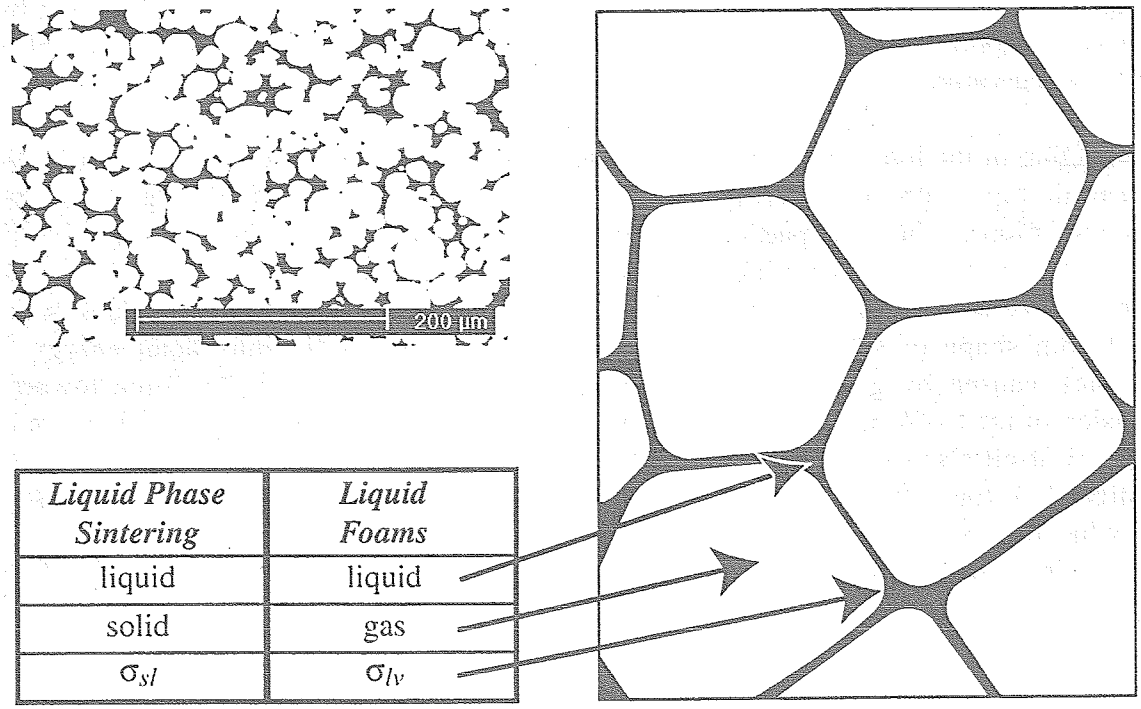
The parallel between such a foam and a liquid phase sintered material at sintering temperatures is quite complete if the liquid phase sintered material displays the following three features:

(i) the solid-liquid interfacial energy σ_{sl} is isotropic, such that a solid particle isolated in the liquid is spherical (*i.e.,* the solid is not faceted);

(ii) the dihedral angle between the solid grain boundaries within the liquid is always zero, such that all solid grains are separated from one another by a film of liquid; and

(iii) the material has reached a state of local equilibrium after completion of densification, such that there are no significant gradients in solid phase free energy (which drive densification by solution-reprecipitation) along the liquid-solid interface that surrounds each particle.

Even in systems such as the tungsten heavy alloys, Fig. 1, which feature an approximately zero dihedral angle and no faceting, these conditions will never be met exactly. First, although these and other systems can feature a zero dihedral angle for the liquid in contact



Liquid Phase Sintering	*Liquid Foams*
liquid	liquid
solid	gas
σ_{sl}	σ_{lv}

Figure 1. Micrograph of a liquid phase sintered tungsten heavy alloy (90W-7Ni-3Fe) and schematic of the analogy with liquid foams.

This document is provided by JAXA.

with a high-angle grain boundary in the solid, low-angle grain boundaries in crystalline solids always have an energy that, for small misorientations, increases linearly with the misorientation angle. Hence, the dihedral angle will always display a range of values between 180° and zero depending on relative grain orientation.

The mechanisms by which the particles change their shape to adopt a configuration of minimum local free energy is a second difference between liquid foams or emulsions on one hand, and liquid phase sintered structures on the other. Gas-filled bubbles in a foam and liquid drops in an emulsion can change their shape nearly instantly by diffusion or flow of the fluid across the particles. Hard solid particles in a liquid phase sintering structure can change shape by diffusion of the solid through the liquid; hence, they, too, are "soft". But it takes more time for local equilibrium to be reached in liquid phase sintered structures, and the transport path towards local capillary equilibrium can differ. There can also be some differences in the coarsening mechanisms. For example, the influence exerted by the crystalline nature of the solid (which allows coalescence by grain rotation towards low misorientation angles) is specific to liquid phase sintering. Despite these differences, capillary equilibrium in liquid phase sintering structures and in foams or emulsions is, when it is reduced to its simplest expression, the same basic geometrical problem: namely, an assembly of equisized three-dimensional particles that (i) are incompressible but can deform to adapt their shapes to local capillary equilibrium, (ii) are separated by pools of liquid, (iii) feature a finite interfacial energy along the liquid-particle interface, (iv) have no discontinuities in the tangent of their limiting surfaces, and (v) have a volume fraction too high for the particles to be spherical. Fig. 1 summarizes this parallel between foams and liquid phase sintering in schematic form.

THE OSMOTIC PRESSURE

Calculating the excess capillary free energy and, hence, the curvature of interfaces between the continuous (liquid) phase and the discrete phase (droplets, bubbles or solid particles) is a difficult problem (see *e.g.,* [3, 6]). Several analyses have been proposed to this end, some of which are simple but approximate (e.g., [1]), while others are more complex and precise but rely on the assumption that particles are packed regularly along bcc or fcc lattices [2-4, 6, 7].

For foams and emulsions, the "osmotic pressure" Π [8] is used to quantify internal forces caused by capillary forces. By definition, Π is the pressure required to maintain the particle-liquid assembly at its (high) volume fraction solid V_s when the liquid is put into contact, through a filter, with a larger pool of liquid at the ambient pressure. It is known from the theory of the deformation of wet porous media [9, 10] that the response of this solid-liquid mixture to an external applied pressure P_{ap} is roughly the same as that of the dry solid phase subjected to an "effective" stress or pressure P_e, and that P_e is equal to the applied pressure P_{ap} minus the pressure in the liquid P_l. In the case of an emulsion where the continuous liquid is exposed to ambient pressure, P_l is the atmospheric pressure and P_{ap} is the atmospheric pressure plus the osmotic pressure Π. Hence, $P_e = \Pi$ and is the pressure required to push the droplets together, so as to squeeze and pack them to the volume fraction V_s. Experimental measurements of Π for emulsions of mono-sized droplets have been performed by Mason et al. [8, 11]: the osmotic pressure normalized with (σ/ r) is plotted in Fig. 2 as a function of the droplet volume fraction V_s in the emulsion where σ is the liquid-liquid interfacial energy in the emulsion and r is the average droplet radius. In this

This document is provided by JAXA.

normalized form, the correlation between Π and V_S is geometrically based and should hold for emulsions, foams and liquid phase sintering structures. It is apparent from the figure that Π undergoes a significant jump (note that the coordinates are logarithmic) around $V_S = 0.64$, the packing density for random dense spheres. This stands to reason, since it is when spherical droplets are randomly packed to their maximum possible volume fraction that the "squeezing" responsible for the osmotic pressure begins. Above this critical V_S the normalized osmotic pressure can be approximated as an exponential in V_S:

$$\Pi \approx 4.5\ 10^{-7}\ \exp(16.05 \cdot V_S)\ \sigma\ r^{-1}. \qquad (1)$$

APPLICATION TO LIQUID PHASE SINTERED STRUCTURES

Based on the above parallel, let us now take the correlation for osmotic pressure derived from experiment on emulsions as giving the corresponding sphering force (in the terminology of the liquid phase sintering literature) for a liquid phase sintering structure with a (mostly) zero dihedral angle and an isotropic solid-liquid interfacial energy. In this case, the effective pressure P_e which deforms the solid particles during liquid phase sintering equals the osmotic pressure measured in emulsions, with σ now replaced by the liquid-solid interfacial energy σ_{ls}.

One implication of this analogy is that existing theories for the "sphering force" are not all that precise: the analysis presented in Ref. [1] is off by a factor of about four, and the analysis presented in Ref. [4] is also in disagreement, since it predicts an osmotic (i.e., effective) pressure of zero for volume fractions solid up to about 75 vol. pct. (as a consequence of the assumption of a fcc distribution of solid particles).

A second implication is that through Eq. (1) the liquid and solid pressures in a liquid phase sintering material are provided with improved precision: if $P_{ap} = 0$ the liquid pressure is equivalent but opposite in sign to the osmotic pressure: $P_l = -\Pi$. This, in turn, yields directly the curvature $C_{l,v}$ of liquid surface menisci wherever the liquid contacts the ambient

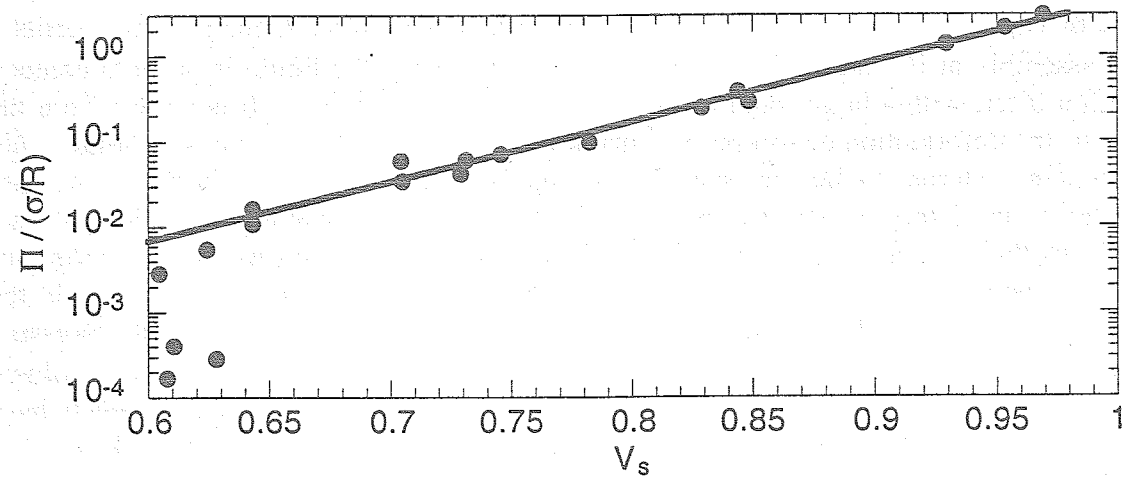


Figure 2. Plot of the osmotic pressure normalized with (σ/ r) in an emulsion of silicon oil in water as a function of the droplet volume fraction V_S in the emulsion; from Ref. [8].

This document is provided by JAXA.

atmosphere:

$$C_{l,v} = 4.5\ 10^{-7}\ \exp(16.05 \cdot V_s)\ s\ r^{-1} \quad (2)$$

where $s = \sigma_{sl}/\sigma_{lv}$ is the ratio of the solid-liquid interfacial energy to the surface tension of the liquid. Since this ratio is significantly lower than unity (for most systems slightly greater than 0.1), the radius of curvature of these menisci is significantly greater than that of the solid spherical particles except when V_s approaches one. The smallest closed pore that can exist in the fully sintered structure at local equilibrium thus has a radius that is larger than the particle size, and which increases as particles coarsen (and hence as r increases). This fact and its consequences are well known, as in the gradual filling of large pores (from small to large pores) as coarsening progresses in liquid phase sintering structures [2].

Consider now the effect of gravity on a liquid phase sintered body of height H. It is easily shown [12] that the solid experiences a gradient of effective pressure P_e, and hence in osmotic pressure Π, equal to:

$$\frac{d\Pi}{d\chi} = V_s(\rho_g - \rho_l)\, gH \quad (3)$$

where $\chi = z/H$ is fractional height measured from the top free surface. A parallel to gravity-induced gradients in liquid phase sintered structures is the classical problem of drainage in liquid foams [13]. Knowing the relation between Π and V_s (Eq. (1) and Fig. 2), this equation can be recast in dimensionless terms as

$$\left(\frac{r\ d\Pi}{\sigma_{sl} dV_s}\right) \frac{1}{V_s} \frac{dV_s}{d\chi} = \frac{N_{BO}}{2} \quad (4)$$

where the Bond number, N_{BO}, represents the ratio of forces due to gravity and forces caused by capillarity:

$$N_{BO} = \frac{2r(\rho_g - \rho_l)\, gH}{\sigma_{sl}} \quad (5)$$

The precise distribution of V_s along the height of a given sintering compact is then calculated by integration of this equation subject to mass conservation [12]. Also, since the left-hand side of Eq. (4) decreases as V_s increases, the highest possible value for $dV_s/d\chi$ in any liquid phase sintered structure of given Bond number is that predicted for $V_s = 0.64$ [12]. Given that for $V_s = 0.64$, $d\Pi/dV_s$ can be approximated as $V_s \cdot \sigma_{sl}/r$ [8], an upper bound for gravity-induced gradients in V_s is

$$\left(\frac{dV_s}{d\chi}\right)_{max} \approx 0.5\ N_{BO} \quad (6)$$

This is higher than the expression in Ref. [12] by a factor of about three (as a consequence of the overestimated curvature, and hence overestimated P_e, in Ref. [1]). Nonetheless, the conclusion reached in that work remains valid: except for combinations of large values of H and r (such as $r \approx 100$ μm and $H \approx 10$ cm), gravity-induced gradients are small in liquid phase sintered tungsten heavy alloys such as 88W-8.4Ni-3.6Fe.

This document is provided by JAXA.

CONCLUSION

Fully densified liquid phase sintered structures contain capillarity-induced internal pressures. In simple liquid phase sintered structures, featuring an isotropic liquid-solid interfacial energy and an average dihedral angle near zero, these pressures can be deduced by direct analogy with emulsions (and liquid foams). The liquid pressure, the smallest stable pore size, the solid phase "sphering force", and the magnitude of gravity-induced density gradients can be calculated for liquid phase sintered materials such as the tungsten heavy alloys, using experimental data gathered on emulsions.

ACKNOWLEDGEMENT

This work was sponsored by core funding of our laboratory at EPFL.

REFERENCES

1. A. Mortensen, Acta Mater. 45, 749 (1997).
2. H.H. Park, S.J. Cho, and D.N. Yoon, Metall. Trans. 15A, 1075 (1984).
3. H.H. Park and D.N. Yoon, Metall. Trans. 16A, 923 (1985).
4. H.H. Park, S.J.L. Kang, and D.N. Yoon, Metall. Trans. 17A, 325 (1986).
5. D. Weaire and M.A. Fortes, Adv. in Phys. 43, 685 (1994).
6. M.D. Lacasse, G.S. Grest, and D. Levine, Phys. Rev. E 54, 5436 (1996).
7. S.A. Koehler, S. Hilgenfeldt, and H.A. Stone, Langmuir 16, 6327 (2000).
8. T.G. Mason, J. Bibette, and D.A. Weitz, Phys. Rev. Lett. 75, 2051 (1995).
9. A. Nur and J.D. Byerlee, J. Geophys. Res. 76, 6414 (1971).
10. J. Bear, Dynamics of Fluids in Porous Media, (American Elsevier, New York, 1972) p.764.
11. T.G. Mason, M.D. Lacasse, G.S. Grest, D. Levine, J. Bibette, and D.A. Weitz, Phys. Rev. E 56, 3150 (1997).
12. C. San Marchi and A. Mortensen, Metall. Mater. Trans. 31A, 397 (2000).
13. G. Verbist, D. Weaire, and A.M. Kraynik, J. Phys.-Condens. Mat. 8, 3751 (1996).

This document is provided by JAXA.