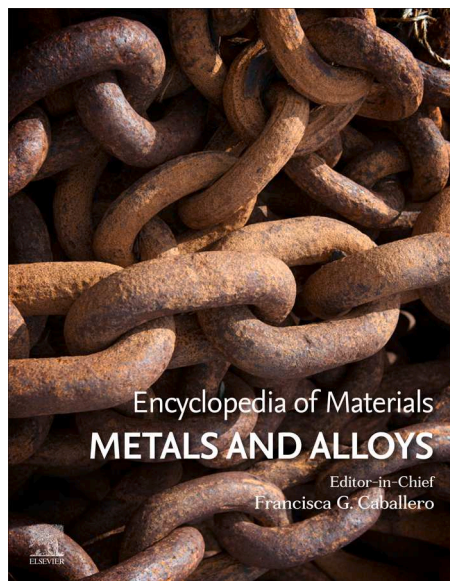


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de Oro Calderon, Raquel, Gierl-Mayer, Christian and Danninger, Herbert. (2022) Fundamentals of Sintering: Liquid Phase Sintering. In: Francisca G. Caballero (ed.), *Encyclopedia of Materials: Metals and Alloys*. vol. 3, pp. 481–492. Oxford: Elsevier.

<http://dx.doi.org/10.1016/B978-0-12-819726-4.00127-7>

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Fundamentals of Sintering: Liquid Phase Sintering

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Variants of the Liquid Phase Sintering Process

Liquid phase sintering occurs when a liquid phase is formed during the sintering process that coexists with the solid particles at high temperature for a certain period. In the presence of a liquid phase, sintering mechanisms are significantly enhanced because the diffusion and mass transfer mechanisms are much faster in the liquid than in the solid state (German, 1985).

The process requires the presence of, at minimum, two chemical elements. In most cases, a mix of powders of different chemical compositions is used, having a major component (that remains solid) and one or several minor ones (these minor ones being the additives that promote liquid formation). The liquid can be formed either through melting of the additive (the melting point/range of which should then be below the sintering temperature) or through the formation of a low-melting eutectic between the solid phase and the additive at the contact points between them.

As an alternative to the powder mix, a single pre-alloyed powder can be used. In this case, the alloying elements are homogeneously distributed in the powder particles, i.e., all powder particles have the same chemical composition. During sintering, the powder compact is heated to an intermediate temperature between solidus and liquidus, giving rise to a spontaneous liquid phase formation at the particle contacts and within the powder particles (Fig. 1-I). In this variant of liquid phase sintering the amount of liquid phase formed can be controlled through the sintering temperature, i.e. solid and liquid phases are in chemical equilibrium, and the ratio solid-liquid is fixed if the temperature is constant. This process is called “supersolidus liquid phase sintering” (German, 1991; Liu *et al.*, 1999) and is used for instance for tool steels and Cu alloys (Mohammadzadeh *et al.*, 2015).

The liquid phase can be present during the whole sintering stage (Persistent Liquid Phase, PLP-Fig. 1-II) or only for a certain period of time (Transient Liquid Phase, TLP-Fig. 1-III), depending on the solubility ratios between liquid and solid phases (Kieffer *et al.*, 1975; Cannon and Lenel, 1953; Kingery, 1959).

When a thermodynamic equilibrium between liquid and solid phase is reached at the sintering temperature, the system can be sintered via persistent liquid phase sintering (Fig. 1-II). The typical precondition for having an equilibrium between solid and liquid phases at a certain temperature is a low solubility of the liquid-forming component in the solid phase. Obviously, the solubility of the solid phase-forming component in the liquid is also relevant for achieving a solid-liquid equilibrium, but this is not an issue in liquid phase sintering because the liquid is always the minor phase (i.e., the solid cannot be completely dissolved in the liquid). Supersolidus liquid phase sintering (as described above) is a special variant of persistent liquid phase sintering. Persistent liquid phases are mostly used for obtaining fully dense products, as it is the case for W heavy alloys and hardmetals WC-Co (Liu *et al.*, 1999; Petzow and Huppmann, 1976). For a given combination of elements, in PLP sintering the amount of liquid phase present during the process is determined by the sintering temperature.

If a thermodynamic equilibrium between solid and liquid phase is not possible, the liquid-forming component will be fully dissolved in the solid particles at high temperature (Fig. 1-III). This means that the liquid phase formed during heating will disappear as thermodynamic equilibrium is reached. This type of process is called transient liquid phase sintering, because the liquid is only present during the early stage of the sintering process (Danninger, 1988; Kieback and Schatt, 1980). Characteristic of this sintering variant is the pronounced chemical inequilibrium in the initial stage (i.e., in the initial powder mix). This is achieved for instance in elemental powder mixes containing constituents with significant mutual miscibility. Also other variants are possible

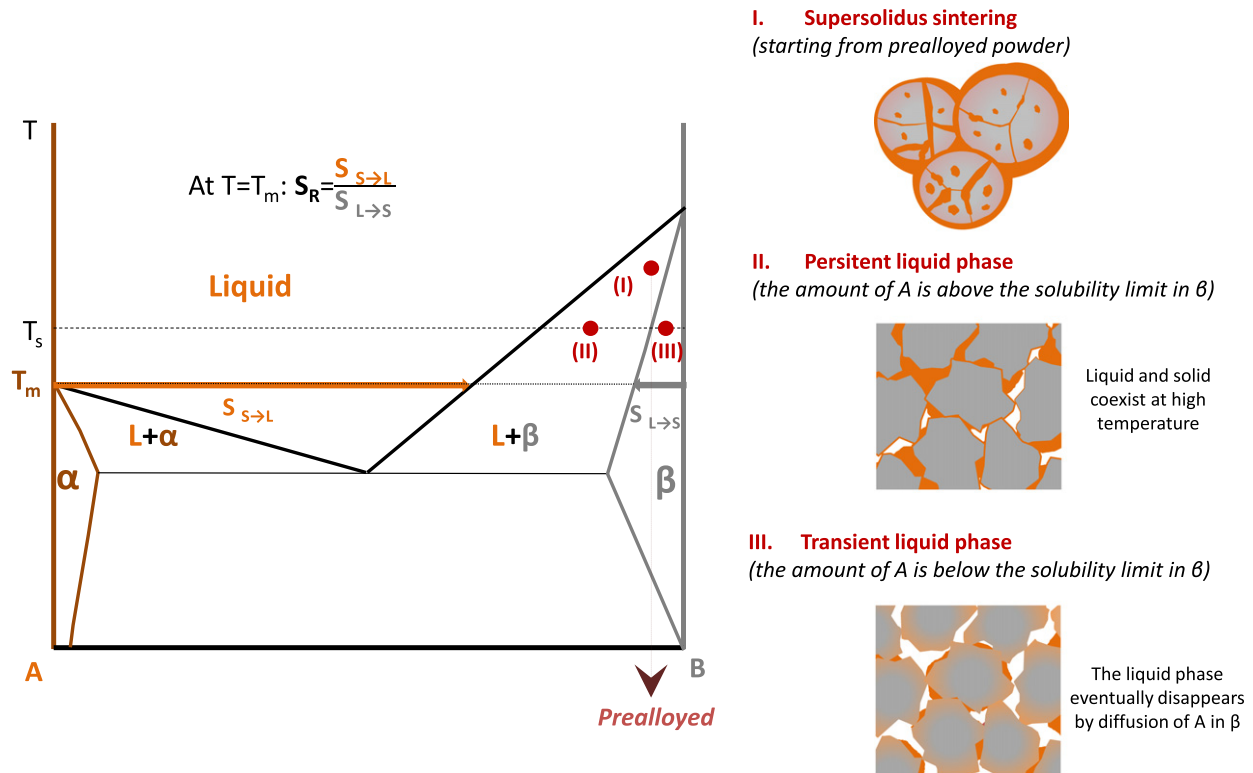


Fig. 1 Variants of the liquid phase sintering process. “A” is the main element forming the liquid forming additive “ α ”, “B” is the main element forming “ β ” (the solid solution phase). Supersolidus sintering (I) would require a prealloyed powder with homogeneous composition. Admixed additions of the liquid former “A” to the solid phase former “B” could give two scenarios: If the amount of α is such that the maximum solubility of “A” in “ β ” is exceeded, then a Persistent liquid phase would form (II). If the solubility is not exceeded (III) then the liquid phase would be of a transient character. In this latter case, at equilibrium conditions, only the solid phase is stable, so the liquid formed would completely solidify by dissolution of A in the solid solution phase “ β ”.

where several elemental additives are used, or where additives with complex compositions are used: the so called masteralloys (i.e., powders that contain several alloying elements combined) (Danninger *et al.*, 2021).

In contrast to persistent liquid phase sintering where, for a certain composition, the amount of liquid phase is determined by the sintering temperature, transient phase liquid phase sintering is a much more complex process. The heating rate is in this case a very critical parameter, as (together with the temperature and the chemical composition) it will determine the amount of liquid phase and the time that it is present. The heating rate has to be sufficiently fast to avoid homogenization of the alloying elements in the base powder in the early stages of sintering. Slow heating rates could even lead to the absence of a liquid phase, if chemical equilibrium or near-to-equilibrium conditions are attained before the minimum temperature required for liquid phase formation is reached. It must also be considered that the composition of a transient liquid phase varies during the sintering process, and the variation in composition is dependent on the heating rates applied.

Sometimes a combination of persistent and transient liquid phases is used, as e.g., in Al-Cu systems (Wantanabe and Yamada, 1968; Kehl and Fischmeister, 1980). In this case, a transient liquid phase is formed in the first place. The TLP cracks the oxide layers covering the Al particles by spreading between metal and oxide, giving rise to the formation of stable metallic contacts. Afterwards a persistent liquid phase is formed by increasing the temperature. Shrinkage promoted by the persistent liquid compensates the initial swelling produced by the transient liquid.

Physical, Chemical and Thermodynamic/Kinetic Aspects Important for Liquid Phase Sintering

Complexity of Powder Metallurgical Systems

The success of a liquid phase sintering process depends on the possibility of providing the necessary conditions for taking advantage of the use of such liquid phase for the particular goals pursued (Danninger *et al.*, 2021). If full density is required, then a system is needed where the solubility ratios favor densification and which presents excellent wetting properties. In other cases, obtaining high levels of density is not the main purpose, but instead a very well controlled dimensional stability or the production

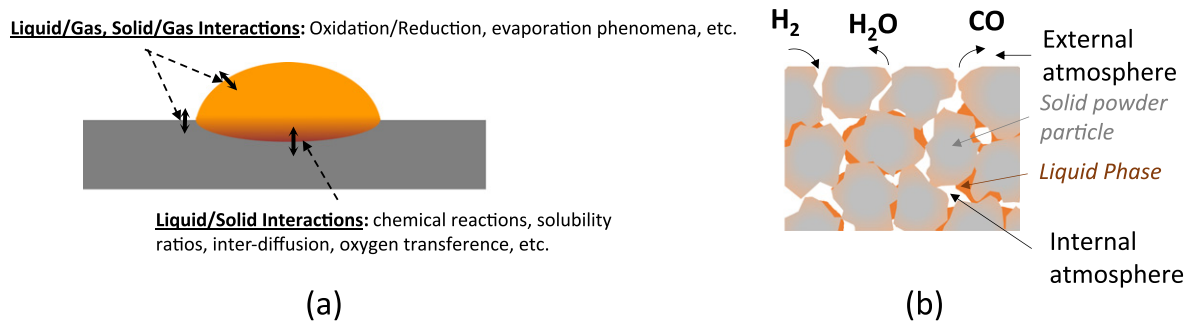


Fig. 2 Complexity of the phenomena affecting the behavior of liquid-solid-gas interacting systems at high temperature, particularly in the case of powder-based compacts. (a) Liquid-Solid-Gas interactions. (b) Situation in a porous compact.

of materials with tailored microstructures might the objective. In general, it should be stressed here that the goal of sintering is not necessarily densification, and many highly successful powder metallurgy products are sintered without significant densification, which holds also for liquid phase sintering. The proper selection of processing conditions and chemical compositions requires then a good understanding of the main aspects that affect the liquid phase sintering process.

Interfacial energies between solid-liquid-gas are a key aspect for liquid phase sintering (German, 1985). Gaseous species and liquid/solid metals (and their oxides) interact at high temperature, involving a rather complex combination of phenomena occurring at the different interfaces (Fig. 2(a)) (Campos *et al.*, 2021). The type of interaction between liquid and solid, as well as their respective reactions with the atmosphere, modify the chemical species present on the different surfaces. Due to the large specific surface area of the powder particles, such surface phenomena play a much more dominant role in powder metallurgy as compared to e.g., ingot metallurgy, especially when the use of liquid phases is considered. Besides, it must be taken into account that the situation in a PM component entails some extra complexity due to heterogeneous conditions in different regions of the component (e.g., closed pores versus pores connected to the surface). Different conditions are to be expected for the “internal” and at the “external” atmospheres (Fig. 2(b)) (Gierl-Mayer, 2020). While the external atmosphere can be well controlled by appropriate setting of the furnace conditions, the internal one is determined by local chemical equilibria that can only be “estimated” based on thermodynamic evaluations. The atmosphere in contact with the liquid/solid surfaces is determined by the capacity of the gaseous species to enter/leave the pore channels. If, for instance, the pore channels are somehow closed (e.g., if very high levels of density are reached before formation of the liquid phase) the more tricky “internal phenomena” become significantly more relevant. Also for an interconnected pore network, however, the mobility of such species, e.g., the ability of reaction products to leave the pore network, are of crucial importance.

This section will describe three aspects that are relevant for the behavior of the liquid and therefore the evolution of the microstructure during liquid phase sintering:

- (1) Mutual solubility between solid and liquid
- (2) Wetting, spreading and distribution of the liquid
- (3) Interactions with the atmosphere

All three aspects are linked with each other by the solid-liquid-gas interactions. The understanding and control of these three parameters is critical for the control of the microstructure and therefore the final properties.

Mutual Solubility

Mutual solubility of the components present in the liquid and solid phases determines the nature of the liquid phase as persistent or transient. This idea is commonly described using the solubility ratio (S_R in Fig. 1), where $S_{S \rightarrow L}$ is the solubility of the solid-phase forming component (typically the main component) in the liquid and $S_{L \rightarrow S}$ is the solubility of the liquid forming component/s in the solid. S_R is valid for a certain isothermal temperature. Apart from the persistent/transient character of the liquid, the solubility ratio affects important factors such as the rearrangement of solid particles, densification and solution-precipitation phenomena. In case of transient liquids, it also affects the volume of liquid formed, the time that the liquid can be present during sintering, and the potential of the liquid phase to provide homogeneous or heterogeneous microstructures.

A so-called unipolar solubility ($S_R \gg 1$ usually achieved with low $S_{L \rightarrow S}$ and high $S_{S \rightarrow L}$) is the most beneficial scenario for reaching high levels of densification. This is the case with hardmetals (WC-Co) and tungsten heavy alloys (e.g., W-Ni-Fe). These systems present low solubility of the liquid-forming component(s) in the solid and high solubility of the solid-forming component(s) in the liquid phase. In such situation, a persistent liquid phase is formed that enhances densification by rearrangement of particles and solution-re-precipitation mechanisms. As the condition is reversed, the ability of the system to densify decreases. Systems like W-Cu and Mo-Cu, with a low solubility of the liquid-forming component in the solid but also a low solubility of the solid-forming component in the liquid, are much less prone to densification. In some cases it is possible to incorporate additives to these systems in order to enhance sintering (namely activated liquid phase sintering (Tandon and Johnson, 1998)). For instance

in the case of W-Cu, where W is practically insoluble in liquid Cu, additions of Ni to the liquid phase can be made to increase the solubility of the solid particles in the liquid and thus promote densification by solution re-precipitation mechanisms. Other possible additives are cobalt, iron and palladium as they all present a high solubility for W (Tandon and Johnson, 1998).

In the case of systems with transient liquid phases the situation is usually inverted ($S_R < 1$). In these systems, the liquid is consumed by the solid particles as a consequence of the high solubility of the liquid-forming component(s) in the solid phase. Nevertheless, the reverse solubility (solubility of the solid-forming component(s) in the liquid) plays also an important role. Two types of liquid phases have been described in ferrous systems depending on this factor: "dissolutive" and "non-dissolutive" (de Oro Calderon *et al.*, 2016a,b,c). "Non-dissolutive" liquids present high solubility of the liquid-forming component(s) in the solid but relatively low solubility of the solid-forming component(s) in the liquid. In this situation, the liquid can quickly penetrate through the pore network, serving as a vehicle for long-distance distribution of the alloying elements present in the liquid phase. This facilitates the homogenization of the microstructure. Characteristic of these liquids is the so-called "copper swelling" observed upon formation of the liquid phase. On the other hand, "dissolutive" transient liquid phases can dissolve significant amounts of the solid-forming component(s). If this leads to an increase of the solidus temperature above the sintering temperature, the liquid phase will solidify and will not be able to penetrate the pore network and be distributed there, which in turn inhibits long distance homogenization. In this situation, the alloying elements tend to remain concentrated in the vicinity or the prior additive particles, leading to heterogeneous microstructures. On the other hand, such liquid phases can be useful for reactive sinter brazing of porous components (Danninger *et al.*, 2021), as described in more detail in Section 3b.

Wetting, Spreading and Distribution of the Liquid Phase

Wetting of a liquid phase on a solid surface is described by the so-called wetting angle or contact angle (θ) which depends on the equilibrium between three surface energies (solid-liquid σ_{SL} , liquid-vapor σ_{LV} and vapor-solid σ_{VS}), as indicated by Young's equation in Fig. 3(a). The lower the resulting contact angle, the larger the contact surface between the solid and the liquid. The liquid is considered to wet the solid phase when the contact angle is less than 90° (Eustathopoulos *et al.*, 1999).

In most solid-liquid systems at high temperature the wetting and spreading of the liquid is affected by the interaction between these two phases at the interface (dissolution, reaction, precipitation, etc.) (Eustathopoulos *et al.*, 1999; Saiz *et al.*, 1998; Saiz and Tomsia, 2005; Dezellus and Eustathopoulos, 2010; Saiz *et al.*, 2010), which typically involve much higher energies than just physical wetting effects. Such interaction modifies the geometrical and compositional characteristics of the solid-liquid interface, and the assumptions of Young's equation are not applicable. Then Smith's equation (Fig. 3(b)) is used to represent the balance of interfacial energies taking into account vertical components and deformation in the solid as a result of the formation of a crater. The situation presented in Fig. 3(b) shows the close dependence between the wetting angle and the reactions that take place at the interface. During a real wetting process, the spreading kinetics of the liquid on the solid surface varies in relation to the degree of interaction between the phases. In inert systems (where there is no interaction between phases) the evolution of wetting is radically different from that observed in reactive systems, where kinetics are conditioned by the phenomena of dissolution and reaction at the interface (Eustathopoulos *et al.*, 1999; Saiz *et al.*, 1998; Saiz and Tomsia, 2005; Dezellus and Eustathopoulos, 2010; Saiz *et al.*, 2010).

In inert systems, the extension of the drop on the substrate is normally rapid, causing the stabilization of the contact angle in the first few seconds after the liquid has formed (Saiz and Tomsia, 2005). On the contrary, when a dissolution process takes place, the extension of the drop on the surface of the substrate is slower and can last from a few seconds to several minutes. On the other hand, dissolution phenomena can generally improve the wetting behavior by increasing the contact surface between the solid and the liquid. In many cases, wettability will improve in presence of a dissolution process as a result of the elimination of interfacial

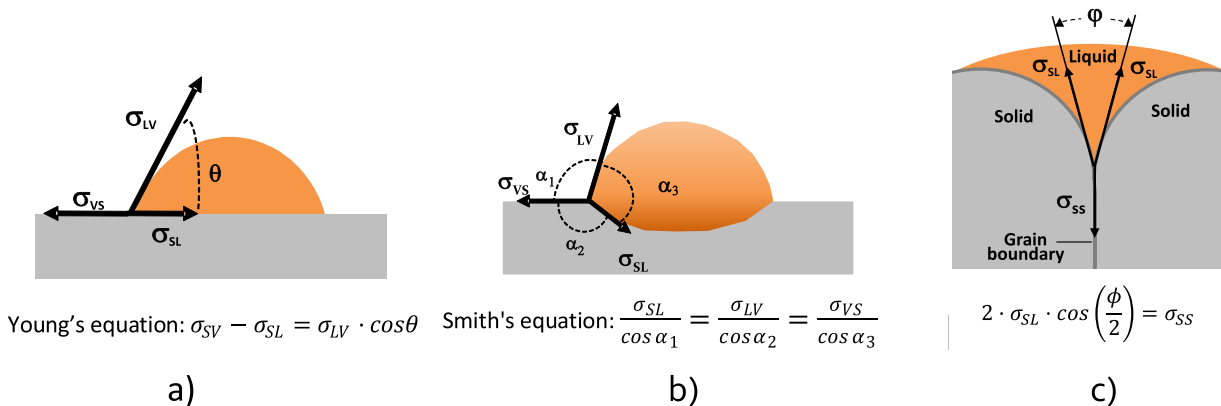


Fig. 3 Relevant parameters for liquid phase sintering which are determined by the relationship between interfacial energies. (a) Wetting in the absence of interaction between liquid/solid phases. (b) Wetting in the presence of interaction between liquid/solid phases. (c) Dihedral Angle.

barriers, which will generally be oxides present on the surface of the substrate (Eustathopoulos *et al.*, 1999; Saiz *et al.*, 1998; Saiz and Tomsia, 2005; Dezellus and Eustathopoulos, 2010; Saiz *et al.*, 2010; Saiz and Tomsia, 2005). Furthermore, the wetting is also strongly enhanced by solubility effects and the resulting gain in entropy, as indicated in sintering of aluminum alloys (see details in Section "Variants of the Liquid Phase Sintering Process") where spreading of a melt between metal and oxide is enabled by formation of solid solution.

The behavior of the liquid during sintering is strongly affected by the wetting conditions (German, 1985, 1996, 2014). When the wettability is good, the liquid wets and spreads over the surface of the solid particles. Capillary forces inside the liquid induce the penetration of the liquid preferentially in the smaller pores and can favor the piling up of the solid particles and with this the densification. On the contrary, a liquid that does not wet will tend to separate from the solid, causing an expansion of the green compact (Petzow and Huppmann, 1976), and eventually the exudation of the liquid phase out of the compact.

Surface energies also determine another important concept for liquid phase sintering, the dihedral angle (ϕ in Fig. 3(c)) which forms at the contact between the grain boundaries of the solid phase and the liquid. The dihedral angle determines the ability of the liquid phase to form furrows in the solid along the grain boundaries or even penetrate inside the solid powder particle through the grain boundaries.

Assuming that the two grains in Fig. 3(c) correspond to the same solid, both solid-liquid energies (σ_{SL}) will be equal and opposite to the grain boundary energy (σ_{SS}), and the vertical equilibrium of forces provides an expression for the dihedral angle, as shown in Fig. 3(c). If the ratio σ_{SS}/σ_{SL} is high (>2), the dihedral angle will be very close to zero and the liquid will be able to penetrate the grain boundary ("grain boundary attack").

Although they derive from different expressions, it is generally assumed that the contact angle and the dihedral angle vary in the same direction, which implies that in most cases they are mainly affected by the solid-liquid surface energy. Dissolution phenomena modify the composition of the liquid and the solid phase, and thus the surface energies. Consequently, the value of both the wetting and the dihedral angle may undergo an evolution during the sintering process (German, 1985; German *et al.*, 2009). Low values of the contact angle and the dihedral angle facilitate the spreading of the liquid over the surface of the solid and the penetration into the interior of the solid particles through the grain boundaries. All these phenomena favor a good distribution of the liquid phase and maximize the contact surface between the phases.

Macroscopic wetting angle studies provide an interesting possibility for understanding and predicting the behavior of liquid phases during sintering. Different studies have been carried out in this direction during the last years, both for ferrous systems and for cemented carbides (Campos *et al.*, 2021; Bernardo *et al.*, 2014a,b, 2016; Oro *et al.* 2012a,b; Alvaredo *et al.*, 2019, 2017; de Nicolás *et al.*, 2020). In ferrous systems, these experiments have revealed the important influence of the presence of reducing agents that can eliminate the oxide barriers. In general, wetting and distribution of the liquid was considerably improved under reducing conditions, and also in presence of dissolutive liquid-solid interactions (Campos *et al.*, 2021; Bernardo *et al.*, 2014a,b, 2016; Oro *et al.*, 2012a,b). This, in turn, had an influence on the final microstructure and dimensional behavior of ferrous sintered materials. In the case of cemented carbides, different macroscopic studies have been made on composites based on TiC, Ti(C,N) or WC hard phases (Alvaredo *et al.*, 2019, 2017; de Nicolás *et al.*, 2020). It has been experimentally proved that in order to use Fe-based binders combined with TiC or Ti(C,N), the addition of other secondary carbides (as WC, TaC, NbC, Cr₂C₃, VC and Mo₂C) is needed. These carbides enhance sinterability by improving the wettability of the solid particles by the liquid phase (Alvaredo *et al.*, 2019, 2017). Modifications of the binder chemistry such as the addition of 15 wt% Ni to an Fe binder have also proved effective in improving the wettability of the binder on Ti(C, N), without the need of adding secondary carbides, because of the increased solubility of Ti (C, N) in the Fe-15Ni liquid phase (Alvaredo *et al.*, 2019).

Oxide Reduction

Oxide layers cover all metallic powders that have ever been exposed to air. Such oxide layers are usually unwelcome since they represent a barrier for diffusion and, in most cases, also for wetting and spreading of liquid phases on the surface of solid particles. Reduction of the oxides covering metallic powders takes place by reaction with reducing agents present in the sintering atmosphere (e.g., H₂, CO) or with elements present in the specimen (typically C). At low temperatures, H₂ is the strongest reducing agent as compared to C or CO, while at high temperatures direct carbothermal reduction is the most efficient mechanism. Therefore, in any system containing both H₂ and C the reduction of the less stable oxides will take place by reaction with H₂, while the most stable oxides will always be reduced at higher temperatures through the carbothermal reactions (Gierl-Mayer, 2020; Danninger and Gierl, 2001, 2007, 2008; Danninger *et al.*, 2002). In an inert atmosphere (i.e., where no reducing agents like H₂ are present) oxides would be reduced only carbothermally (or by a metallic constituent forming more stable oxides). Thus, the reduction of the less stable oxides would be shifted to higher temperatures (e.g., reduction of Fe oxides occurs at approximately 400°C by reaction with H₂, while it occurs at approximately 700°C through the carbothermal mechanism) (Gierl-Mayer, 2020; Danninger and Gierl, 2001, 2007, 2008; Danninger *et al.*, 2002). In case of vacuum sintering, it must be considered that the reduction temperatures by carbothermal reaction will be lowered as the pressure decreases. It is also worth mentioning that, when oxygen-sensitive elements are present, a special care must be taken during sintering particularly due to the "internal-gettering-effects", i.e., oxygen transference from less stable oxides (which are reduced) to oxygen-sensitive elements (which will be oxidized) (Gierl-Mayer, 2020; de Oro Calderon *et al.*, 2016d, 2017a,b; Gierl-Mayer *et al.*, 2016; de Oro Calderon *et al.*, 2015), the net reaction in fact being a metallothermic reduction process.

Carbothermal reduction is always accompanied by a carbon loss. It is therefore not surprising that the first studies on oxide reduction during sintering were made on hardmetals WC-Co (Gestrich, 2004; Leitner *et al.*, 1995, 1997). The reason is that these

materials are especially sensitive to the carbon content. A proper carbon control must ensure that the final carbon content falls within the so-called “carbon window”, where only two phases are present in the final microstructure (i.e., the hexagonal monocarbide WC and Co). It must also be considered that reduction of the oxides entails the elimination of oxygen in the form of gaseous species (e.g., H₂O, CO, CO₂). When full densification of the material is to be achieved through liquid phase formation (as it is the case with hardmetals) the oxides should be ideally reduced before the liquid phase is formed and, even more critical, before significant densification is achieved that results in closed pores. Otherwise, there is a risk of trapping of the gaseous reduction products, resulting in stable porosity and, esp. in case of liquid phase sintering, even blistering. This is not a problem in a system in which the oxides present have a relatively low stability, and if the stability of the oxides present in the system is similar (as is the case of WC-Co). However, when elements with a higher oxygen affinity are considered (like e.g., Cr or V), care must be taken to avoid overlapping between the reduction processes and the densification mechanisms occurring due to liquid phase formation (Gestrich, 2004).

Reduction of oxides is a critical factor for the interaction between solid and liquid phases. Elimination of surface oxides is a necessary pre-requisite for a wetting condition, as has been proved from experiments in the Fe-Cu system. Liquid Cu does not wet an iron substrate under an inert atmosphere, because the substrate surface is fully covered by an oxide. The presence of reducing agents either in the atmosphere, in the solid substrate or in the liquid phase, proved to be very efficient for providing a remarkable improvement of the wetting conditions. In the latter case, adding elements with a high oxygen affinity (e.g., Si) is very efficient for improving the wetting behavior of liquid phases (de Oro Calderon *et al.*, 2016a,b,c, 2012).

Microstructural Evolution

Systems With Persistent Liquid Phase

When the solubility of the liquid-forming component(s) in the solid phase is sufficiently low, a persistent liquid phase can be formed. Persistent liquid phase sintering is typically employed to obtain high levels of density, and therefore the evolution of the microstructure is often discussed in terms of densification and porosity elimination. Fig. 4 shows typical microstructures of materials sintered with PLP. Here, however, it has to be considered that density alone is not a sufficient criterion for liquid phase sintered materials, but also the proper microstructure is required (e.g., not each material containing W, C and Co is already a hardmetal).

If there is a good wetting of the liquid on the solid particles, two typical stages can be defined that describe very well the evolution of the microstructure in these systems (German, 1985; Cannon and Lenel, 1953; Kingery, 1959; German, 1996, 2014; German *et al.*, 2009; Kang, 2005):

Stage I - rearrangement

When the liquid phase forms, it will wet and spread over the surface of the solid particles. Capillary forces inside the liquid will induce a rapid repacking of the solid powders (rearrangement) giving rise to a fast and pronounced densification, the more, the lower the green density was and the smaller the solid particles are. The rate and the degree of densification increase as the solubility of the rearrangement solid-forming component(s) in the liquid increases, because the dissolution of contacts between solid particles and the smoothing of the solid surfaces by dissolution of surface peaks and ridges favor the process. Initially, rearrangement is very rapid and depends mostly on the melt spreading rate. An initially uneven distribution of the liquid phase and/or of the solid particles leads to the formation of clusters of solid particles (Fig. 5(a)), which may enhance already existing heterogeneities. The liquid released from the repacking of particles in the clusters will induce rearrangement in other regions of the microstructure. As the clusters grow in mass, the repacking process becomes slower. After a first very quick rearrangement, a second stage occurs that involves rearrangement of clusters or particle fragments (instead of individual powder particles). In case of

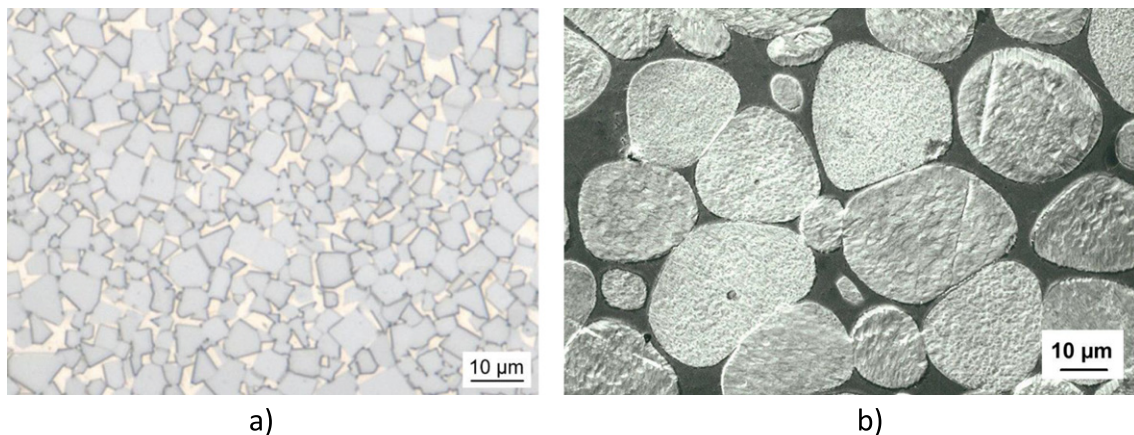


Fig. 4 Typical microstructures of materials sintered with persistent liquid phase. (a) WC-Co hardmetal. (b) W-Ni-Fe heavy alloy.

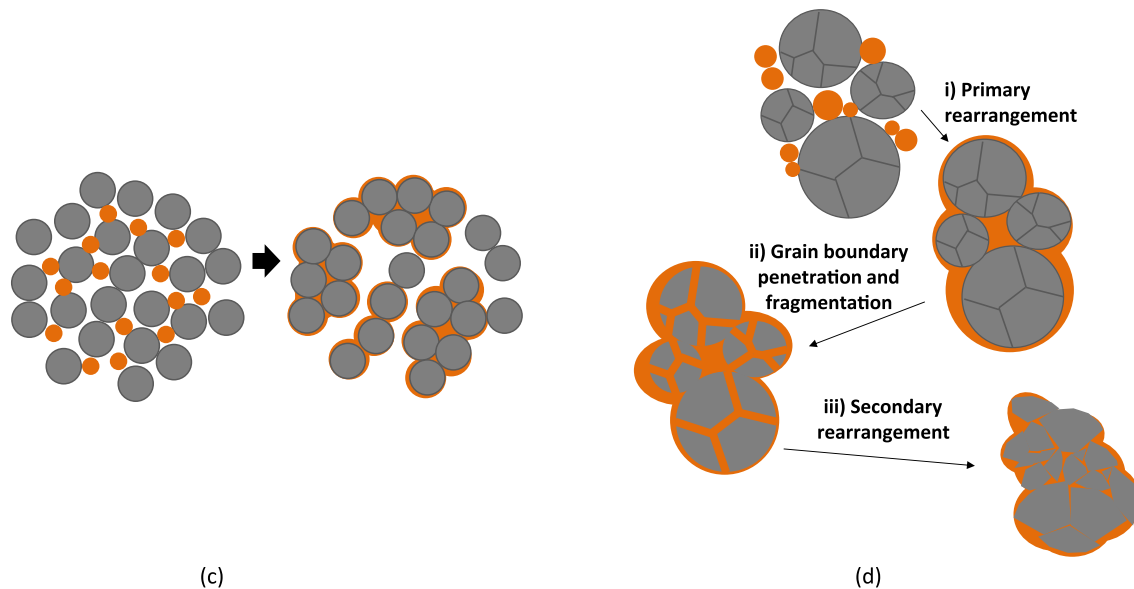


Fig. 5 Processes occurring during the rearrangement stage. (c) Clustering. (d) Grain boundary penetration and fragmentation process. After German, R.M., 1985. *Liquid Phase Sintering*. New York: London Plenum Press.

polycrystalline solid particles, low dihedral angles can favor the penetration of the liquid phase into the grain boundaries of the solid, disintegrating the solid into fragments that will subsequently rearrange further, as “secondary rearrangement” (Fig. 5(b)).

Particle rearrangement frequently provides the most significant contribution to densification during the whole liquid phase sintering process. However, there are several factors that affect the extent of the rearrangement process and therefore its potential to affect densification. The first one is the rigidity of the solid skeleton. Large solid particles with irregular shapes provide solid skeletons with a high rigidity and therefore limited possibilities for rearrangement, in particular with small amounts of liquid. The same effect is to be expected with high initial (green) densities or high densities attained by solid state sintering before liquid phase is formed (Kang, 2005). A high solubility of the solid-forming component(s) in the liquid favors the smoothening of the solid surfaces and the dissolution of the solid-solid contacts, decreasing the rigidity of the system. In the case of insoluble systems, densification is totally by rearrangement, and therefore the final density will be very sensitive to the green density (or to the density achieved by solid-state diffusion). Another very important parameter is the volume of liquid. As the amount of liquid decreases, the solid-solid contacts and thus the rigidity of the systems increase, hampering the rearrangement process. The amount of liquid necessary to trigger rearrangement depends on the particle size and the morphology of the solid particles, small and rounded particles requiring lower volumes of liquid (German, 1985).

Stage II - solution-precipitation and microstructural coarsening

Solution-precipitation occurs already during the rearrangement phase. However, at the early stages after liquid formation, rearrangement is the dominant process for densification because it is the fastest one. When rearrangement ends (or becomes very slow) because the potential of the system for this mechanism is exhausted, solution-precipitation processes become dominant. Solubility of the solid-forming component(s) in the liquid is required for solution-precipitation. Simultaneously to solution-precipitation, grain growth also takes place, both phenomena contributing to the elimination of the residual porosity.

At this stage of the process, accommodation of the particle shapes become relevant. Three processes have been described for particle shape accommodation (Fig. 6(a)): (i)-contact flattening, (ii)-dissolution-precipitation and (iii)-neck formation by solid-state diffusion. Contact flattening (Fig. 6(a-i)) originates from the stress induced by the liquid capillary forces at the contact points between the solid particles (Kingery, 1959). This causes preferential dissolution in these regions, with subsequent re-precipitation of solute in regions far from the contact point (“Kingery mechanism”). As a consequence of this process, the solid surfaces flatten at the contact areas and the particles move (re-accommodate) closer to each other, promoting densification. Dissolution-precipitation processes (Fig. 6(a-ii)) occur because the smaller grains dissolve preferentially in the liquid phase, and bigger particles grow at the expense of the smaller ones (Ostwald ripening effect). Large grains grow and their shapes accommodate to occupy the space left by the smaller ones, which leads to densification phenomena. This process does not necessarily imply center-to-center movements of the large particles, but the re-accommodation of shapes releases liquid that can fill the pores nearby. Another possible mechanism is neck growth by solid-state diffusion (Fig. 6(a-iii)). This process involves both a re-shape and a center-to-center movement of the large particles, but not necessarily a grain growth. As the diffusion processes are much faster in the liquid than in the solid phase, neck growth by solid-state diffusion is usually of minor relevance, except for insoluble systems like W-Cu. In general, densification is enhanced through all these three re-accommodation mechanisms because they provide liquid that can fill the remaining porosity. Capillarity forces favor the filling of small pores, while large pores (e.g., secondary porosity left when the additive particles melt) usually remain stable.

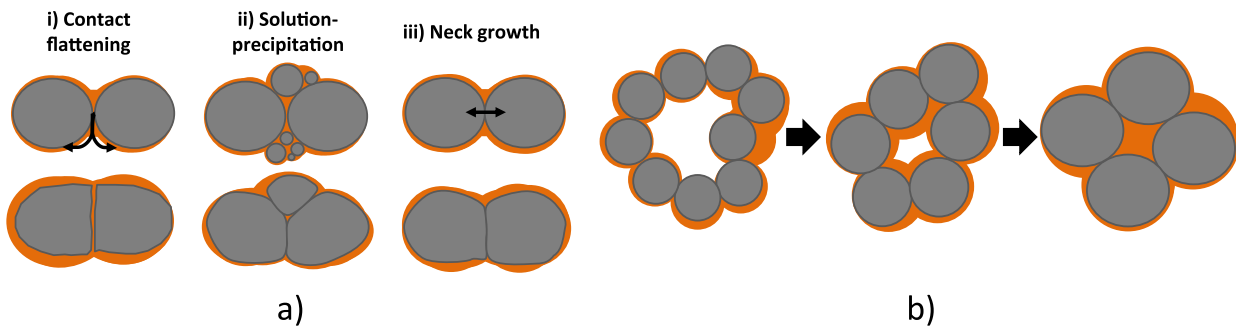


Fig. 6 Processes occurring during the solution-precipitation and microstructural coarsening stage. (a) Accommodation processes. (b) Grain growth. After German, R.M., 1985. *Liquid Phase Sintering*. New York: London Plenum Press.

Accommodation phenomena occur simultaneously with grain growth (Fig. 6(b)). Grain growth can contribute to the closure of larger pores by inducing liquid penetration in the pores. Around a large pore the capillary forces retain the liquid in the surrounding intergrain cavities. When the grains around the pore grow due to prolonged sintering, the liquid reaches a favorable condition for refilling the pore (Kang, 2005). The better the wetting of the liquid (i.e., the lower the contact angle), the more favorable is the removal of residual porosity. Microstructural coarsening occurs both due to solution-precipitation processes and also due to solid-state diffusion, this latter one being predominant in insoluble systems. However, it must be considered that even though full density is beneficial for the material properties, microstructural coarsening can degrade the properties. The presence of remaining porosity in the final microstructure also depends on the sintering atmosphere. Evacuation of the gas present in the pores -prior to the formation of the liquid phase- by using a vacuum atmosphere is the most favorable scenario. Gas enclosed in the microstructure will give rise to the formation of pores. Depending on whether this gas is soluble in the material or not, it might be possible to decrease the level of porosity with increasing sintering times.

Systems With Transient Liquid Phase

Compared with persistent liquid phase sintering, transient liquid phase sintering is a much more complicated process. Due to the high solubility of the liquid-forming components in the solid phase, the liquid will only be stable during a limited time, and afterwards it will disappear by full dissolution of the melt-forming component in the solid. Consequently, kinetic effects gain in importance and, with it, parameters such as the heating rate. There are two main reasons why the stages of microstructural development described for persistent liquid phase sintering are often not useful for describing the evolution of the microstructure during transient liquid phase sintering. One reason is that with TLP the liquid phase activation of the sintering mechanisms is only possible during a limited period of time, which is determined by the dissolution kinetics of the liquid-forming components in the solid phase. Furthermore, an important number of systems processed with transient liquid phase (e.g., systems for PM precision parts such as Fe-Cu-C with Cu content <9 wt %) are prepared using large solid particles and high green densities (typically around 10% porosity, compared to e.g., 45% for hardmetals). Therefore, the rigidity of the system is very high, and densification through rearrangement processes is inhibited.

As a consequence of the unfavorable solubility ratios and in part also the rigidity of the starting solid skeleton, systems such as e.g., Fe-Cu, Fe-Mo-C, etc. (de Oro Calderon *et al.*, 2016a,b; Castro *et al.*, 2012; Berner *et al.*, 1974; Danninger, 1988, 1992; Danninger *et al.*, 2005; Dautzenberg and Dorweiler, 1985; Kaysser *et al.*, 1980) present a swelling phenomenon upon liquid phase formation. This so-called "copper swelling-effect" is associated with the penetration of the transient liquid into the interparticle contacts and grain boundaries, and also with diffusion of its components into the solid particles. In the case of ferrous precision parts, this swelling effect is in many cases welcome because it helps to counteract the natural contraction of Fe during the sintering cycle and thus ensures a final dimensional change close to zero. In fact, in ferrous components for which dimensional accuracy is important, the final density should be rather close to the green density, the main difference being in the size and shape of the porosity.

From the discussion above it is clear that in most systems sintered with transient liquid phases, densification is not the main objective for using liquid phase sintering. Instead, in this case the major benefit of using liquid phase sintering is the dramatic acceleration of the formation of strong interparticle contacts as well as the enhanced homogenization of alloying elements in the microstructure. Microstructural evolution in TLP systems is therefore in many cases described in terms of homogenization of the alloying elements (in contrast with PLP systems in which densification is the most relevant aspect). For TLP systems with a good wettability of the solid by the liquid phase – which is the usual case since wetting is enhanced by formation of solid solution – , two main scenarios can be described depending on the mechanisms of formation of the liquid phase: eutectic reaction or spontaneous melting (Danninger, 1988) (see Fig. 7).

In systems like Fe-Mo-C, the liquid is formed by the eutectic reaction between the solid and the additive particles (see Fig. 7(a)). In such a situation the diffusion processes do not only control the consumption of the liquid phase, but also its formation. As a consequence, the amount of liquid phase at any moment of sintering is always lower than in systems in which the liquid is formed by the spontaneous melting of the additive particles. The liquid formed is then rapidly consumed by solid solution in the Fe particles nearby, without having the possibility to distribute through the pore network. This favors an enrichment of the alloying elements in the regions close to the place where the liquid phase is formed, which may lead to low degrees of homogenization in the microstructure. In

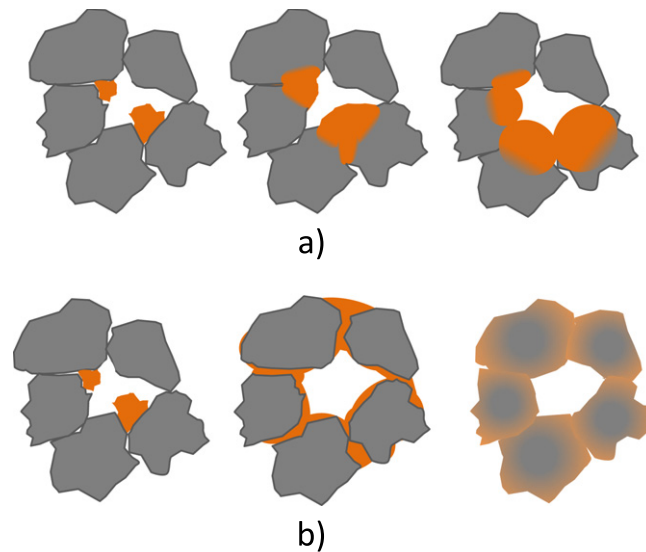


Fig. 7 Microstructural evolution with transient liquid phases depending on the mechanisms of formation of the liquid phase. (a) eutectic reaction with the base powder. (b) spontaneous melting of the additive particles.

these systems it is therefore particularly important to provide homogeneous distribution of the alloying element particles in the powder mix and, if possible, small particle sizes of the additive. If such small additive particles are homogeneously distributed in the mix then the final mechanical properties can be dramatically improved by the formation of the liquid phase (Danninger, 1988, 1992).

Another possibility is to use an additive that melts spontaneously below the sintering temperature (Danninger, 1988). In this case the formation of the liquid is not limited to the contact points, and therefore higher volumes of liquid can be simultaneously formed (particularly by congruent melting or in additives with narrow melting windows). Assuming that wetting conditions are favorable, the liquid phase can be distributed through the pore network, the inter-particle contacts and even in the grain boundaries if the dihedral angle is favorable (see Fig. 7(b)). The infiltration of the pore network by the liquid can be very fast, and thus it can be completed before the liquid is consumed by diffusion in the solid. In this situation, the alloying elements are transported to long distances using the liquid phase as “vehicle”, and the distances that need to be covered by solid state (bulk) diffusion are considerably reduced. With such behavior of the liquid phase, homogenization of the microstructure is very much favored. The situation just described is typical for liquid phase formers recently defined as “infiltrating”-“non-dissolutive” The opposite situation would be found in the so-called “non-infiltrating”- “dissolutive” systems. This differentiation between systems has been recently presented in the context of the study of masteralloys as a vehicle for introducing alloying elements in low alloyed steels (de Oro Calderon *et al.*, 2016a,b) (see Fig. 8). “Non-infiltrating”- “dissolutive” liquids are those transient liquids that present a high solubility of the solid in the liquid phase. In this situation, the liquid phase is not only consumed by dissolution of its component(s) in the solid, but it is also possible to consume it as a consequence of the dissolution of solid-forming component(s) in the liquid phase. In certain systems, it is observed that, as the liquid dissolves Fe in it, the solidus temperature of the melt increases above the sintering temperature and the liquid phase “freezes”. In terms of microstructural changes, the situation for these systems is rather similar to that observed in systems with eutectic reaction (in fact, particularly in complex alloying systems, the contribution of eutectic reactions during melting cannot be discarded). The penetration of melt in the pore network is inhibited, because the pore channels are choked by the liquid solidification (see Fig. 8). Therefore, long-distance homogenization is not possible. The alloying elements remain concentrated in the vicinity of the additives, giving rise to heterogeneous microstructures. Rather characteristic of these systems is also the limited swelling observed upon liquid phase formation, as compared to the so-called “infiltrating”-“non-dissolutive” liquids (as e.g., Cu). It must be remarked here that a critical parameter determining the behavior of a “dissolutive” liquid is the evolution of the solidus temperature of the liquid phase when the solid particles are dissolved. If the solidus temperature would decrease by the dissolution of the solid main component, e.g., Fe (or Fe + C), then the effects of the dissolution process would be inverted. In such situation, the amount of liquid phase would increase as more Fe is dissolved, and this could entail an improvement in the infiltration properties of the liquid. This can explain the situation in which “dissolutive” alloys also present excellent infiltration behavior (Geroldinger *et al.*, 2021). Of course, in this situation, large secondary porosity can be expected (larger than the size of the additives).

The fast development of thermodynamic software tools during the last years has provided the possibility of predicting the behavior of complex alloying systems (Campos *et al.*, 2021; de Oro Calderon *et al.*, 2016a,b,c; Geroldinger *et al.*, 2021). This can be used to select the composition of the melting additive (so-called masteralloys) such as to promote a particular behavior. A liquid with a high infiltration ability can be used as a vehicle for long distance distribution of alloying elements, thus providing rather homogeneous microstructures. In such systems the so-called “Cu-swelling” behavior upon liquid formation is to be expected. On the other hand, “poorly infiltrating” liquids can bring the possibility of obtaining microstructures with tailored inhomogeneity (a unique characteristic

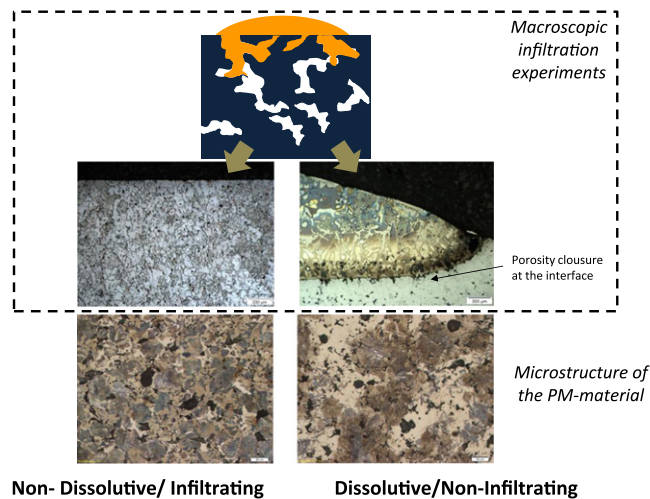


Fig. 8 Microstructures obtained with transient liquid phases depending on the type of solid-liquid interaction. Dissolutive/Non-infiltrating vs. Non-dissolutive/Infiltrating behavior: Macroscopic experiments and microstructural features in ferrous sintered components.

of PM materials). In the latter case, the dimensional changes observed upon liquid phase formation would be significantly lower than in the former case. In brief, in the future, a proper design of the liquid phase and the liquid/solid interaction might give the possibility to tailor the final microstructure and the dimensional behavior of sintered components processed by liquid phase sintering.

Rather characteristic of many systems sintered with transient liquid phases is the presence of secondary porosity, i.e., a pore remains stable in the place where the liquid former additive was located (Danninger, 1988; Kieback and Schatt, 1980; Danninger and Gierl, 2001; Danninger, 1987a,b). The ductile properties of the materials are mostly influenced by secondary porosity. Especially the large pores (that might act as crack-initiating defects) can be very detrimental in case of cyclic loading, these pores initiating fatigue cracks (Weiss and Danninger, 2000). Therefore, the use of fine additive powders properly distributed (to avoid agglomerations that may form large pores) is usually preferred. The size of these secondary pores also depends on the solid-liquid interaction. If the solid surrounding the additive is consumed either by a eutectic reaction (e.g., in Fe-Mo-C systems) or by dissolution in the liquid and subsequent infiltration of the liquid in the solid skeleton (this would be the case of “dissolutive” but “infiltrating” liquids), then the secondary pore can be considerably larger than the original size of the additive. In the case of spontaneous melting and “non dissolutive” (i.e., infiltrating) liquids (such as Cu), the size of the porosity can be very well controlled by controlling the size of the additive. In fact, in the case of Fe-Cu-C it has been determined that by adding Cu particles with sizes below 40 μm (and usually dendritic shape) there is no significant detrimental effect on the properties (Danninger, 1987a,b). The last scenario is that of “dissolutive” liquids with a poor infiltration capacity. As stated before, these systems are much less prone to swell, and also to form secondary pores, and can provide microstructures with tailored heterogeneity.

Another relevant aspect of this last family of systems is their suitability to be used as brazers for PM components. In this latter case, the pores present in the parts to be brazed are significantly smaller than the gap, and the capillary forces pull the liquid into the pores network leaving the gap in the joint empty. Here, a “dissolutive”-“non-infiltrating” behavior of the transient liquid phase is highly welcome. Commercial developments in this direction are the so-called “reactive” fillers, typically Cu-Mn-Si-Fe-B alloys designated as “Sinterbraze” (Knopp, 1996). These last advances in the field of transient liquid phases point out the possibility of performing a microstructural design by carefully analyzing and tailoring the behavior of liquid phases as well as the interaction with the solid phase.

Fig. 8 Microstructures obtained with transient liquid phases depending on the type of solid-liquid interaction. Dissolutive/Non-infiltrating vs. Non-dissolutive/Infiltrating behavior: Macroscopic experiments and microstructural features in ferrous sintered components.

Summary

The presence of a liquid phase during the sintering stage enhances the sintering process by accelerating the diffusion and mass transport mechanisms. The liquid phase can be formed by congruent melting of a minor component –additive – in the powder mix (either an elemental powder or a master alloy powder), or through the formation of a low-melting eutectic between the main component and the additive. Alternatively, a prealloyed powder can be used, in which case the liquid phase is formed by heating to an intermediate temperature between solidus and liquidus (super-solidus sintering).

Two main variants of the liquid phase sintering process can be defined, depending on whether the liquid is present during the whole stage at sintering temperature (Persistent Liquid Phase-PLP) or only for a certain period of time in the early stage of sintering (Transient Liquid Phase-TLP). The persistent or transient character of the liquid phase is determined by the possibility of reaching a solid-liquid equilibrium at the sintering temperature. In PLP sintering, solid and liquid phases are in thermodynamic equilibrium and therefore the amount of liquid phase is determined by the sintering temperature, remaining constant under isothermal

conditions. In the case of TLP, a solid-liquid equilibrium is not possible at the sintering temperature, and therefore the liquid will be fully absorbed by the solid phase at the sintering temperature through formation of solid solution. TLP sintering is a more complex process in which kinetic parameters such as the heating rate play a very important role in e.g. the determination of the amount of liquid phase and the time that it is present.

The interaction between solid, liquid and gas phases at high temperature are a key aspect for liquid phase sintering. Such interactions affect important processes such as reduction/oxidation phenomena, wetting, spreading and distribution of the liquid and dissolution-precipitation, thus being critical for the control of the final microstructure and the properties of the sintered material.

Depending on the particular requirements of the final product, the characteristics of the liquid and its interaction with the solid phase can be adjusted to obtain the most suitable microstructures. When full density products are required (e.g., hardmetals and heavy alloys), typically a persistent liquid phase will be used. In this case, the liquid phase should enhance densification by promoting material redistribution phenomena such as particle rearrangement and solution-precipitation processes. In contrast, some very important PM products (e.g., PM precision parts) are sintered without significant densification, in order to maintain tight dimensional tolerances. Transient liquid phases are very often used for this purpose, and the short-term character of the liquid together with the high rigidity of the systems (often presenting large solid particles and high green densities) inhibit any densification through rearrangement. In this latter case, the major benefit of using a liquid phase is the dramatic acceleration of the formation of strong interparticle contacts, as well as the possibility to obtain materials with tailored microstructures, by e.g., modifying the infiltrating character of the liquid. "Infiltrating" liquids can be used as a vehicle for long-distance transport of alloying elements. As the distances to be covered by solid state (bulk) diffusion are in this case much lower (in fact just the radius of the particles forming the solid skeleton) microstructural homogenization is strongly favored. In contrast, in some systems the interaction between liquid and solid phase will give rise to a concentration of alloying elements in the vicinity of the additive particles. This is the case of systems in which the liquid phase is formed by eutectic reaction, and also in systems in which the liquid phase has a "non-infiltrating" character, thus rapidly solidifying on contact with the solid matrix. The infiltrating or non-infiltrating character of the liquid phase is determined by the dissolution phenomena at the interface. Liquids with a non-infiltrating character can be used to obtain microstructures with tailored heterogeneity, and are also excellent candidates to be used as fillers for brazing of porous PM components.

Liquid phase sintering can thus be used as a very versatile tool in powder metallurgy that can be adapted to provide the required microstructures and properties for different families of PM products.

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