Advanced Materials by Powder Metallurgy

Ceramics/Intermetallics
Hot Isostatic Pressing
Dispersion Hardening
Rapid Solidification

By Wolfgang A. Kaysser* and Günter Petzow

1. Introduction

One of the techniques which have an inherent potential to produce some of the future's tailored, high-tech materials is powder metallurgy (PM). The efficient use of powder metallurgy depends both on a scientific understanding of the complex physical and chemical problems of powder production, handling, forming and consolidation and on highly developed complex engineering capabilities. The interaction between materials science and engineering is a characteristic feature of the new powder metallurgy.

From the ancient powder forged pillar of Delhi to the present, powder metallurgy has shown itself to be a potent method for forming special, artificial materials when no other techniques are available due to high melting points or bad machinability of the materials or microstructures not obtainable by other techniques. PM high-tech materials must be fine grained and completely free of pores. Mechanisms of powder densification and simultaneous microstructural changes are therefore of major technical and scientific interest.

The basic steps of conventional powder metallurgy are powder preparation, handling, shaping, and consolidation.[1] Powders may be produced by chemical reactions from precursors or by disintegrating solid or liquid bulks. The powders are shaped in dies under uniaxial load or put into thin-walled capsules and isostatically pressed. The shaped compacts contain pores between the individual particles which amount to porosities between 60 and 10 vol-%. One of the purposes of the subsequent sintering, a heat treatment below the melting temperature of the major constituents, is to eliminate the pores; the process is driven by a reduction in solid–vapor interface area. Porosity reduction requires an increasing fraction of solid material in each unit volume cell by rearrangement or by shape change of the particles (Fig. 1 top).

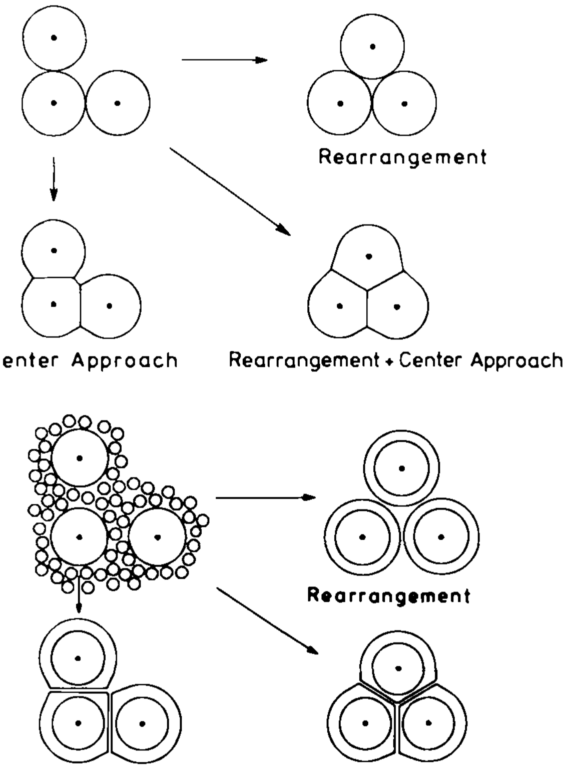

Fig. 1. Shrinkage by rearrangement and center approach (shape change) during sintering. Top: Monosized grains without coarsening. Bottom: Grains with broad size distribution and coarsening.

2. Advanced PM Materials by Pressureless Sintering

Shape change or center to center approach during solid state sintering occurs in a quantified way when vacancies diffuse from pores into the grain boundaries where they are subsequently eliminated. Unfortunately, the transport of vacancies to the grain boundary sinks by bulk diffusion or by grain boundary diffusion does not provide complete densification in metal powders of sizes between 1 and 100 μm. In the final stage of sintering, when the porosity is below 6%, the continuous pore channels transform into isolated pores which lie at grain boundaries. If the pores are too small to hold the grain boundaries, but too large, and therefore too immobile, to move along with the grain boundaries, grain boundaries and pores separate during regular grain growth (Fig. 2). Pores that are trapped inside the grains shrink at much lower rates than pores at grain boundaries, and they are therefore deleterious for densification. Powders can be sintered to full density if the diffusion mechanism controlling the vacancy transport from the

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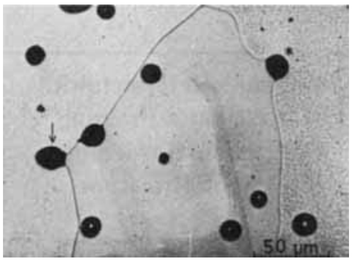

Fig. 2. Microstructure showing pore drag (asterisk) and pore/grain boundary separation (arrow) after final stage sintering of W – 0.15 wt.-% Ni at 1400 °C for 3 h.

pores to the grain boundaries is enhanced and if the grain boundary mobility is decreased by additives. These basic principles were successfully applied to obtain translucent ceramic materials for sodium vapor pressure lamps. The dense alumina (Lucalox) can be produced by pressureless sintering when the bulk diffusivity is enhanced and the grain boundary mobility is reduced by doping the powder with less than 1000 ppm magnesia.[2]

The bulk diffusivity of metals, which controls a major transport path for vacancies from the pore to the grain boundary via diffusion through the bulk, can only be moderately increased by doping with small amounts of an alloying metal additive. The enhancement of the grain boundary self-diffusion, which controls a second major transport path for vacancies, as in W doped with Ni,[3] however, also increases the grain growth rate leading to increased pore/grain boundary separation.

The metallic materials produced by pressureless sintering, such as hard metals, heavy metal alloys and permanent magnets, are all sintered in the presence of a liquid phase, which reflects the problems of sintering to a pore-free material in the solid state, but also indicates the ability to obtain dense materials by liquid phase sintering. The microstructural development and the shrinkage during sintering in the presence of a liquid phase are governed by a number of basic principles.[4] At sintering temperatures in all materials one or more phases are solid and at least one phase is liquid. After processing the microstructure consists often of two solid (sometimes interpenetrating) networks. Densification during liquid phase sintering is also based on rearrangement and shape change of the solid constituent particles (Fig. 1 bottom). The driving force for both phenomena results from a decrease in energy caused by changes in the areas of the liquid/vapor, liquid/solid and solid/vapor interfaces during rearrangement and/or shape change. Melt may originate from low melting point particles or areas which have built low melting point compositions by diffusion during heating. With good wetting, the liquid phase is pulled by capillary forces into particle necks and small pores. As a reaction to the capillary forces, particles are rearranged if their mobility allows it. This rearrangement of the solid particles is a necessary prerequisite for effective densification throughout the sintering process even during later sintering stages, when, for example, the rates of particle shape change also limit the rearrangement rate. Shrinkage due to the shape change of the solid constituents always involves solution-reprecipitation processes, e.g., when during coarsening by diffusion controlled Ostwald ripening the grains accommodate their shape to a changing environment.[5] This is shown in Figure 3 for liquid phase sintering of Mo–Ni by internal etching boundaries. A major part of the shrinkage results from rearrangement when small particles are dissolved making way for the movement of larger particles (see also Fig. 1 bottom).

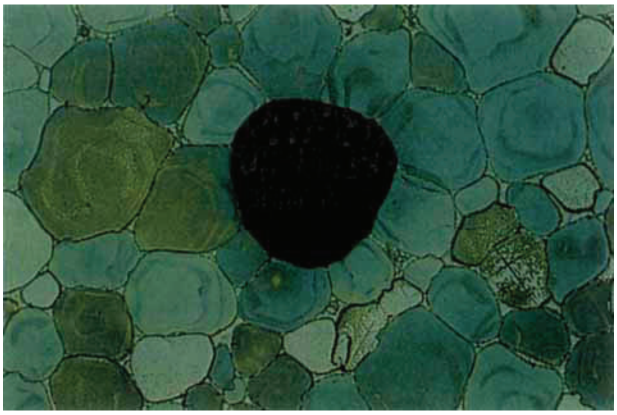

Fig. 3. Microstructure of Mo-4wt.-% Ni after cyclic liquid phase sintering between 1300 and 1460 °C (Held at 1460 °C for 30 min in each cycle). Etched with *Murakami's* solution. [5] The bulk material is densely packed; the center is a pore. Scale: 24 mm equal 10 µm.

Due to the effective shrinkage mechanisms liquid phase sintering yields dense PM materials. As shown above, densification requires grain growth and rearrangement. Complete elimination of pores is thus limited to systems where either powders are fine initially or where large amounts of a suitable liquid phase are available. Typical examples of liquid phase sintered high performance materials are hard metals (e.g. WC-Co cutting tools) or hard magnets (e.g. Fe-Nd-B shown in Figure 4[6]).

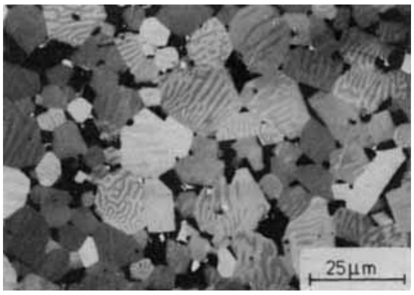

Fig. 4. Pore free microstructure of liquid phase sintered Fe-18.5Nd-6.5B. The magnetic grains are indicated by line patterns (Kerr effect). The black areas are solidified eutectic melt.

3. Advanced PM Materials by Pressure Assisted Consolidation

For most of the complex alloy systems fine powders and suitable melt phases are not available. The powder metal lurgical production of these advanced materials of great commercial interest only became possible when, mainly in the early eighties, modern engineering provided production facilities for powder consolidation where heat (as during sintering) and pressure (as during compaction) could be applied simultaneously. The simultaneous application of pressure and heat allows the use of comparatively coarse, prealloyed powders with complex microstructures and high yield strength. Densification is readily attained without solid state sintering additives and without the presence of a liquid phase. The processes most frequently used are hot isostatic pressing and hot extrusion.

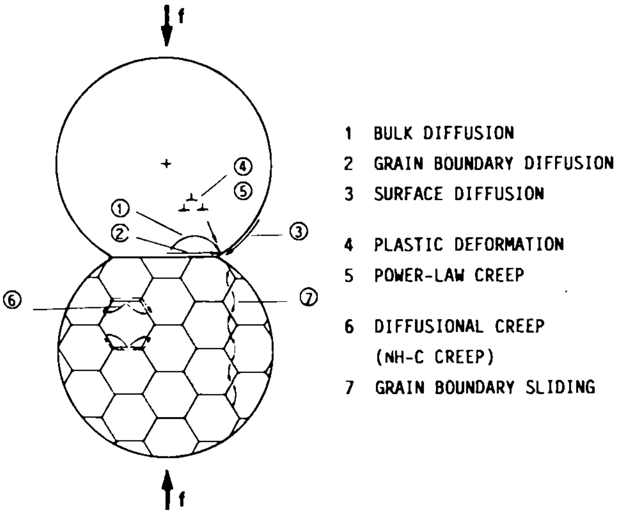

Fig. 5. Transport mechanisms during hot isostatic pressing. f = force.

During *hot isostatic pressing* (HIPing) plastic flow and a number of creep mechanisms contribute to densification (Fig. 5).[7,8] Which one of these mechanisms dominates shrinkage and neck growth rate depends on a number of powder parameters (size, grain size, current geometry, bulk material properties, interface properties) and processing parameters (pressure, temperature, time). The neck growth and center approach rates are described by analytical equations but can also be predicted from the deformation of single powder particles under a well controlled load in a dilatometer.[8] These experiments indicate power-law creep as the dominant densification mechanism for most metal alloys.

During normal HIPing the powders must be encapsulated in closed thin-walled preforms, a tedious and costly operation. In 1985 a new method, sinter-HIPing, started to come into use.[9] The development became possible through the construction of improved HIP equipment with pressure vessels which allow dewaxing of binders, often added to the initial powder mixtures for superior handling, vacuum sintering and subsequent HIPing in one cycle. The vacuum sintering is performed to closed porosity (porosity below 6%), i.e. to a state where all pores are separated from each other and completely enclosed in a dense material matrix. The sources for the closed pores are not limited to the usual porosity remaining from the starting porosity in dense randomly packed powder arrangements, but may also stem from undestroyed initial powder agglomerates, inhomogeneous flow of powder particles during mould filling or inhomogeneous drying in slip cast greens. The elimination of these larger pores, which constitute critical defects in the final material, during HIPing or sinter-HIPing makes the PM materials often superior to cast materials which frequently contain casting porosity. Figure 6 shows the collapse of a large pore during HIPing of presintered Al_2O_3-anorthite by a combined flow of Al_2O_3 grains and the anorthite glass.[9]

Fig. 6. Closing artificial pore in presintered Al_2O_3-10 vol-% anorthite after HIPing at 10 MPa for 30 min. The arrows indicate the formation of special boundaries by coalescence of the Al_2O_3 grains.

As mentioned above, the use of HIPing or hot extrusion provides dense materials also from unsinterable particulate combinations, such as short-fiber reinforced composites and oxide dispersion strengthened high-temperature alloys. Mixtures of fibers of high strength and high stiffness with fine powders are consolidated at temperatures low enough to avoid fiber decomposition by chemical reactions with the matrix, but sufficient to allow adequate bonding of the fibers to the matrix. Whereas reinforcement of metals and ceramics with long fibers was found economically unviable, *short-fiber reinforcement*, particularly with SiC whiskers, is seen to offer a more favorable cost property-improvement ratio.[10] At present the most frequently investigated systems are SiC-whisker reinforced Al_2O_3, Si_3N_4, and Al alloys.[10] A number of technical and economic problems are, however, still unsolved. The SiC whiskers are too expensive. The distribution of the whiskers in the fine powder matrix and sintering to closed porosity as well as chemical reactions between the whiskers and the matrix require further research.

Oxide dispersion hardened Al alloys or superalloys are produced by reaction milling in an attritor. During milling, surface oxides on the powder are destroyed and finely distributed in the interior of the powders together with other intentionally added fine oxide powders due to a continuing fracture and rejoining sequence.[11] A modification of this method is the reaction milling of a mixture of Al and graphite powder which provides an extremely homogeneous distribution of fine graphite inclusions in the Al matrix.[12] During tempering of the hot extruded milled blends, fine Al_4C dispersoids form at the sites of the fine graphite inclusions (Fig. 7). The tensile strength of this material at 400°C is 50% of the room temperature tensile strength.

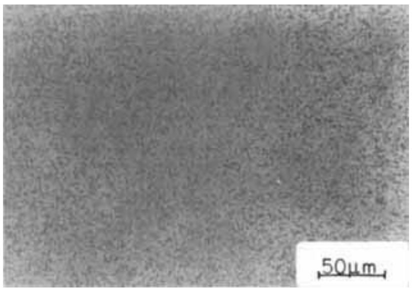

Fig. 7. Microstructure of a dispersion hardened Al alloy (DISPAL 1 Si 12 transv.).

HIPing and other new consolidation methods such as hot extrusion also allow fast densification and defect healing of coarse, unsinterable powders with unusual microstructures. Such powders are produced by *rapid solidification*; high cooling rates and high undercooling result in refined microstructures, decreased segregation, metastable and new phases, as well as in increased solid-solubility ranges. Gas or water atomization are valuable methods for producing rapidly solidified powders for high-performance materials in large quantities. With these methods a thin falling stream of the molten alloy is disintegrated into fine droplets by the impact of high pressure gas or water jets.[1]

An important aspect of the *microstructural refinement* is the cooling rate of the droplets which determines the velocity of the solidification front. The cooling rate is governed by the convective heat transfer from the droplet to the surrounding flowing gas. The cooling rates range from 10^4 to 10^7 K s^{-1} for droplets of 50 μm (argon) to 5 μm (helium) in diameter, respectively. For a special group of advanced PM materials fine microstructures are not sufficient, but *segregation-free microstructures* are required. They allow the formation of highly supersaturated solid solutions yielding a large amount of extremely fine precipitates during ageing. These are often stable against further coarsening due to a low equilibrium solid solubility of the alloying elements in the solvent at service temperatures. Segregation-free solidification is only possible if the growth velocity of the solidification front is larger than the diffusion speed of the solute atoms.[13] In Cu-7wt.-%Sn a solidification-front velocity of about 4 m s^{-1} is required for segregation-free solidification, which is high compared to the velocity of 0.02 m s^{-1} obtained during cooling of an atomized 5 μm droplet. To attain a sufficiently fast solidification-front movement in fine melt droplets, considerable undercooling of the liquid is necessary. Undercooling is possible if potent heterogeneous nuclei are absent. The probability of a potent heterogeneous nucleus being present in a droplet decreases rapidly with decreasing droplet volume. The percentage of powder particles which have solidified after considerable undercooling increases rapidly with decreasing particle size. Due to extensive engineering efforts and the application of advanced principles of fluid mechanics, facilities are now available for producing the required fine powders in large quantities.

From the abundance of recent developments of materials from rapidly solidified powders, three examples are presented. The first example, the aluminides, illustrates the beneficial use of high cooling rates to obtain finer microstructures. The other two examples, a dispersion strengthened Cu-Sn alloy and a Cu-Ti-B alloy, are indicative of the advantages of high undercooling.

Iron aluminide and nickel aluminide *intermetallics* have recently been the object of considerable interest as potential structural materials for high temperature applications. The cubic DO_3 (Fe_3Al), $L1_2$ (Ni_3Al), and B2 (FeAl, NiAl) lattice structures yield special properties such as a low density (compared to the superalloys), high strength and high elastic moduli which make them interesting for lightweight applications in the aerospace industry. Excellent corrosion resistance up to 800°C with high yield strength at elevated temperatures open a wide field in coatings, especially in oxygen-rich hot gases, with an optimum relation of price to performance. A major problem of coarse-grained intermetallics is their extreme brittleness, whereas single crystals and polycrystals with grain sizes smaller than 20 μm display considerable ductility at room temperature.[14] The reasons for the failure of coarse-grained materials are the weak grain boundary structures and the sensitivity of grain boundaries to segregation of impurity atoms. Several remedies exist to improve the unfavorable properties, the most promising one being the use of rapid solidification to obtain fine-grained materials. Figure 8 top shows Ni_3Al powder with an average grain size below 15 μm which was obtained by Ar atomization.[15]

A homogeneous distribution of fine oxides, giving a *dispersion strengthened material*, can be obtained directly from rapidly solidified melts. The Ar-atomized Cu-7Sn particle shown in Figure 8 bottom has an area where segregation-free solidification occurred. Undercooling was increased by minimizing the number of potent nuclei. With the addition of Al, the metal oxides which were the initial potent nuclei of the melt were transformed into fine, dispersed Al_2O_3 particles of low potency. A homogeneous distribution of Al_2O_3 particles was obtained in areas which

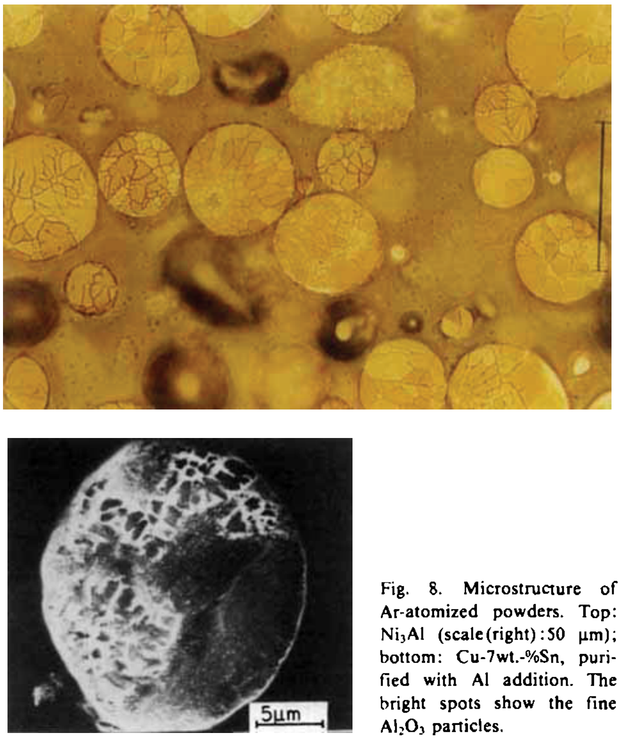

Fig. 8. Microstructure of Ar-atomized powders. Top: Ni_3Al (scale(right): 50 µm); bottom: Cu-7wt.-%Sn, purified with Al addition. The bright spots show the fine Al_2O_3 particles.

solidified segregation-free[16] (small bright spots in Fig. 8 bottom).

Cu-Ti alloys are mainly used as electric conductors and contact materials with increased microhardness and only slightly reduced electrical conductivity compared to unalloyed Cu.[17] The mechanical and electrical properties of Cu-Ti can be further improved by the addition of boron resulting in *dispersion hardened copper alloys* for welding machines, where a high microhardness is obtained by additional dispersion strengthening. If suitable amounts of B and Ti are added to Cu, extremely stable TiB_2 precipitates form during ageing with a negligible amount of Ti and B remaining in the solid solution, providing an increased hardness at high electrical conductivity. However, during cooling of ternary Cu-Ti-B melts at rates below 10^4 K s^{-1} the primary solidification of TiB_2 yields precipitates, which are too coarse for effective precipitation hardening. In atomized powders the primary precipitation of TiB_2 during solidification is suppressed due to undercooling and a high cooling rate. Ti and B remain in a supersaturated Cu solid solution, which provides a hardness of more than 500 $HV_{0.1}$ after ageing the powders at moderate temperatures.[18]

4. Outlook

Powder metallurgy (PM) is now recognized by most of the governments of the industrial nations to be key technology in the development of advanced materials. For example, in 1987, the Bundesministerium für Forschung und Technologie invested no less than 60 million DM in support of the German PM research and development program. Faith in the potential of powder metallurgy rests on two factors:

- PM can satisfy the demands of specific material requirements. The inherent flexibility of PM materials, as compared to cast materials, results from an almost unlimited number of workable phase combinations, which include ceramics, polymers and metals. PM is one of the most promising techniques for the production of complex composites.
- PM enables the production of refined, homogeneous and highly supersaturated materials. New classes of materials can be used, which require small grain sizes, such as the intermetallic phases.

Powders are increasingly being used for the production of thin layers and layered structures. The plasma spraying of powders has already established itself as one of the most important methods for the production of high quality surface coatings. The spray deposition of atomized liquid droplets onto substrates is increasingly serving the same purpose. Fine droplets form a rapidly solidifying thin liquid layer on a substrate. The latter method smoothly bridges the gap between PM and casting technology.

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