Sintering with Additives*

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Shrinkage, grain growth, dimensional changes and homogenization during liquid phase sintering of ceramics or metallic systems, are influenced by the presence of additives. Additives are intentionally added to control the microstructural and dimensional development during sintering. Additives may be present in solid state only or may form liquid phases. In this paper the effect of additives on sintering will be described using examples which cover some of the essential basic principles of interactions of additives with the host material.

The addition of Ni to the refractory metals W and Mo is used to describe all three stages of solid state sintering as well as postdensification by hot isostatic pressing. It is shown that the densification phenomena during solid state sintering are changed by the presence of additives via simultaneous increase of the grain boundary diffusivity and of the surface diffusivity in this system. From experiments with W-Ni, Mo-Ni and Fe-Cu it is concluded, that in the presence of liquid additives the densification phenomena, rearrangement and center to center approach occur by elementary mechanisms as particle disintegration, coarsening and directional grain growth.

The influence of driving forces provided by chemical reaction on the kinetics of mass transfer is discussed for diffusion induced grain boundary migration and for liquid film migration. These types of interface migration were found to be caused by the interdiffusion of the additives with the host metal. Liquid film migration is thought to be of great importance for the homogenization of Fe-Cu and Fe-Cu-C alloys during liquid phase sintering.

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1 Introduction

Preformed compacts of ceramics or metallic powders are "sintered", i.e. heated to high temperatures where shrinkage, grain growth, annealing recovery, compositional homogenization, and chemical reactions to form new phases or compounds may occur. During cooling, changes such as precipitation hardening or other phase transformations may occur in specific systems.

Most high-tech ceramics and some PM materials are sintered with porosity elimination, as a goal. Hence, compact shrinkage is a necessity. In contrast, many other PM compacts are mainly annealed and for these it is desired that *no* dimensional change takes place. The dies are "sized" to give compacts which result in sintered parts of defined size and shape specifications.

Fine grained segregation-free material is obtained, particularly for materials and phase combinations which cannot be prepared by foundry procedure: melting, casting, and solidification. Examples are refractory metals (W, Mo), hard metals (WC-Co), heavy metal alloys and many high-tech ceramics. These high performance materials must be sintered to complete density, and a small grain size must be maintained. Of major interest for the production of PM materials are the mechanisms and processes that control densification and grain coarsening¹⁾.

Sintered structural parts are usually in economic competition with similar parts manufactured by casting and machining. To avoid machining the size and shape of structural P/M parts after

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sintering must fit the required tolerances after a simple coining operation. The dimensions of structural parts are well controlled if shrinkage or swelling during sintering is negligibly small. Therefore porosity after cold compaction and after sintering should be approximately equal. To keep the dimensional changes during sintering small, coarse powders ($>100\text{ }\mu\text{m}$) were cold compacted to high density into the final shape of the part. A high green density is required for components to obtain satisfying mechanical properties. To obtain a high green density and to avoid rapid degradation of the pressing tools, powders with low yield strength and high plastic deformability are prepared. To obtain alloys, mixtures of different unalloyed powders are usually used, but pre-alloyed powders are also employed. During sintering chemical bonds form between the particles and homogenization of the components occurs. Homogenization of the sintered structural parts is a necessary precondition for reasonable mechanical properties for solid solution hardening or precipitation hardening or formation of martensite. Dimensional control and the required hardenability of sintered structural parts require knowledge of the diffusion processes leading to dimensional changes and homogenization²⁾.

Shrinkage and grain growth of ceramics and metallic materials and dimensional changes and homogenization of metallic structural parts are influenced by the presence of unintentional impurities and intentional additives. Impurities are always present in sintering systems; impurity levels $<300\text{ ppm}$ must be considered as low. The usual impurity level is several thousand ppm¹⁾. In many metal systems, impurities determine shrinkage and the grain growth during sintering.

Additives are intentionally added to systems to control the microstructural and dimensional development during sintering. The amount of additive may vary from 0.1 to 10 wt.%. Some additives are present as solid phases only, as solid solutions with the host metals or as segregates at the interfaces of the host metals. Other additives form liquid phases which often penetrate as thin liquid films between the particles and grains of the host powder³⁾.

In the present paper the effect of additives on sintering will be described using examples which cover some of the essential basic principles of interactions of additives with the host material.

2 The Influence of Nickel Additions to Tungsten and Molybdenum

The similarities of enhanced sintering of different combinations of refractory metals and group VIII metals emphasize that similar processes are responsible for the activated sintering in all combinations⁴⁾. Element combinations, where activated sintering occurs, show a low solubility of the low melting activator element in the refractory metal and a high solubility of the refractory metal in the liquid.

This fact in combination with very low bulk diffusion rates of the activators in the refractory metals guarantees the segregation of the activators at the grain boundaries of the refractory host metal^{5,6)}. Activated sintering of W-Ni and Mo-Ni will be discussed but it is implied that similar processes are essential for activated sintering of other combinations mentioned above.

2.1 Influence of Nickel on Transport Mechanisms in Tungsten and Molybdenum

The bulk self-diffusion of W is very low. The activation energy of 382 kJ/mol and the pre-exponential factor of $10^{-7}\text{ m}^2\text{s}^{-1}$ yield at 1400°C a bulk diffusivity of $1.1\cdot 10^{-19}\text{ m}^2\text{s}^{-1}$ ⁷⁾. The low bulk diffusivity is not measurably increased by the presence of Ni in W-Ni solid solution. This was shown by measuring the Ostwald ripening of fine pores in a single crystal of saturated W (Ni) solid solution⁸⁾. An arrangement of pores was produced by sintering a compact of large single crystal W spheres in a matrix of fine W powder and 0.15 wt%Ni sintered at 1400°C. The large single crystals grew rapid-

ly into the matrix of fine W grains. Behind the rapidly migrating boundaries fine pores and a saturated W (Ni) solid solution were left (compare^{9,10}). After annealing at 1400°C for 120 h no coarsening of the pores could be measured. It is concluded that the bulk diffusion of W (Ni) solid solution far beneath a value which would influence solid state sintering at 1400°C to a measurable degree.

It was already deduced by various investigators^{11~13}) that the transport of W or Mo in their grain boundaries or in thin second phase layers at the particle contacts must be fast if Ni or other activating elements are to be effective. Two independent measurements confirm that the presence of Ni at W or Mo grain boundaries increases the grain boundary self diffusion coefficient of these materials.

In recent experiments the creep of thin W foils coated with Ni by PVD was measured under stresses which were comparable to those which are present during activated sintering of a compact of 1 μm powder. Since all grain boundaries were perpendicular to the surfaces of the foils the plausible creep mechanism which resulted in bending was Coble creep (details are described in¹⁴).

Schintelmeister and Richter reported similar measurements by another method¹⁵). At first Ni was introduced to a polycrystalline W bulk by grain boundary diffusion. The bulk surface was plated with the isotope W 185. The plated W was annealed at temperatures between 1250 and 1500°C. The autoradiographic activity was measured.

Our recent experiments and the earlier experiments of Schintelmeister and Richter of grain boundary diffusion on Ni free and Ni-doped W grain boundaries show that grain boundary self-diffusion of W at 1300°C is increased by a factor 500 to 5000 if Ni is present (Fig. 1). The grain boundary self diffusivity of Mo is increased by a factor of 25 at 1300°C if Ni is present in the grain boundaries¹⁶).

Fig. 1 Grain boundary self-diffusion coefficients of W. Undoped $\circ$ ¹⁵), $\circ$ ¹⁶); Ni-doped $\times$ ¹⁵), $\bullet$ ¹⁶).

Fig. 2 AES analysis of grain boundaries in sintered Mo and Mo-1Ni compacts after heating to temperature at 3 K/min and immediate quenching¹⁴). (a) Mo; (b) Mo-1Ni

These experiments set grain boundary self diffusion as the essential mechanism which causes accelerated shrinkage in activated sintering.

2.2 Segregation of Nickel at Tungsten and Molybdenum Boundaries

The hypothesis of Brophy, Shepard and Wulff¹¹⁾ was to assume a thick layer of activator (host metal solid solution) between the host metal particles. This hypothesis was recently rejuvenated^{4,6)} but experimental evidence shows that fast activated sintering is possible with a conventional grain boundary segregation of Ni at the boundaries of the refractory metals. AES depth profiling was made of fractured sintered specimens of Mo-N. Two different Mo powders¹⁷⁾ were used. The finer Mo powder had a specific surface of 0.8 m²/g. The other Mo powder was much coarser. Compacts of both powders with 1 wt%Ni showed fast shrinkage when heated at 10 K/min. The compacts were quenched after heating to 1000, 1150 and 1300°C and fractured in an AES facility. Figure 2 shows the results of the AES analysis which yielded Ni concentrations of appr. 20 at% restricted to a grain boundary layer of one atom thickness¹⁷⁾. Depth profiling showed the rapid exponential decrease of the Ni intensity with ion bombardment time, which means that Ni was present only as a segregate at the Mo grain boundaries. The concentration of Ni at the boundaries was independent of the specific surface of the Mo powders.

Similar results were obtained from AES of grain boundaries in thin Mo foils which were coated by Ni on the surface, annealed for 2 h at 1200°C, and subsequently fractured. Hofmann and Hofmann¹⁸⁾ also measured Ni and Fe segregations of less than 50 at% in a monolayer at the grain boundaries of Ni and Fe doped W which was sintered at 1470°C.

From these experiments it is concluded that segregation of Ni at grain boundaries of W or Mo enhances the grain boundary self diffusion of these elements by orders of magnitude.

2.3 Influence of Nickel Additions on Final Stage Sintering of Tungsten

Final stage of sintering starts when the break up of interconnected pore channels leads to isolated pores which lie along three or four-grain junctions¹⁹⁾. During the final stage sintering both densification (pore shrinkage) and coarsening (pore coarsening and grain coarsening) occur simul-

Fig. 3 Microstructure showing pore drag and pore/grain boundary separation during final stage sintering of W-0.15 Ni at 1400°C⁸⁾.

Fig. 4 Pore/grain boundary separation during final stage sintering; $2R_0$ is the initial grain size.

Fig. 5 Microstructure of W-0.15Ni after sintering at 1400°C for 3 h²²⁾.

Fig. 6 Microstructure of W-0.15Ni after sintering at 1400°C for 1 h and subsequent HIPping at the same temperature for 60 min at 200 MPa²²⁾.

taneously. Shrinkage occurs by migration of vacancies from the pores along the grain boundaries to vacancy sinks (grain boundaries and free surfaces). In the final stage there are two phenomena by which pores coarsen: by mass transfer between isolated pores and by pore coalescence during grain growth. During grain growth pores either remain at the boundaries or become separated and “trapped” inside the grains. Pores that are trapped usually shrink at much lower rates than pores which are at grain boundaries, since bulk diffusivity is much smaller than grain boundary diffusivity. Pore drag and pore grain boundary separation are shown in Fig. 3.

There are two regimes where pores can remain attached to the grain boundaries (Fig. 4). Pores which are large enough are immobile but retard the motion of the boundary (pore control in Fig. 4)^{19~21)}. Pores which are small enough move along with the grain boundaries without stopping their motion. The mechanisms of pore migration are by surface diffusion, lattice diffusion and evaporation and condensation through the vapor phase. The intersection of the two regimes of poreboundary interaction leads to a pore-boundary separation region with G^* as the smallest grain size where grain boundary pore separation occurs.

From Fig. 4 the problem of manipulating final stage sintering by additives becomes obvious. Fast shrinkage at small grain sizes (yielding trajectories which pass below the separation field) requires a low surface diffusivity, D_{sv} , and a high grain boundary diffusivity, D_{gb} ($D_{gb} + \text{perpendicular to the boundary plane}$ can be shown to be related to the grain boundary self diffusion coefficient D_{gb}). To avoid grain boundary pore separation at medium grain size and smaller pore size the separation field has to be shifted to larger grain sizes which requires the opposite, high surface diffusion and low grain boundary diffusivity.

Final stage sintering of W with Ni shows extensive grain boundary pore separation since both grain boundary and surface diffusion are increased by the presence of Ni at the grain boundaries. Figure 5 shows the microstructure of W-0.15Ni after final stage sintering.

2.4 Final Stage Hipping of Ni-doped Tungsten

One possibility to increase the flow of vacancies to the sinks is by application of an external pressure. When samples are subject to a high hydrostatic pressure as during HIP, the surface and grain boundary diffusion constants essentially remain constant, but the applied pressure gives much steeper gradients of the chemical potential of the vacancies and results in a faster vacancy flow towards the grain boundary sinks. The driving force for diffusional pore coarsening on the other hand

remains unchanged. Figure 5 clearly shows the grain boundary pore separation in a W-0.15wt%Ni compact during sintering⁸⁾. The large pores are too immobile to remain attached to the grain boundaries. As shown in Fig. 6 the application of 200 MPa at 1400°C changes the microstructure dramatically.

In the wake of migrating grain boundaries all pores were eliminated. It can be shown that densification by other mechanisms (e.g. power law creep which is most frequently observed in other systems and which depends on the bulk diffusivity) is small compared to the pore shrinkage by vacancy elimination at the grain boundaries²²⁾. The presence of Ni increased the grain boundary diffusivity considerably, whereas bulk diffusivity is too low to yield any influence even at HIP conditions. The pore grain boundary breakaway diagram can be used for the HIP conditions after some additional kinetic considerations. If pores come into contact with a grain boundary they were subject to separation after a short time. During HIPping, pores which come into contact with a grain boundary shrink in a short time interval to a size at which the attachment due to boundary control becomes dominating. This time interval is shorter than the time which elapsed before the contacting grain boundary migrated into a breakaway condition.

3 Influence of Liquid Phase

3.1 Densification Phenomena

Densification during liquid phase sintering is based on rearrangement and shape change of the solid constituent particles^{2,3,26)}. The liquid regions may originate from low melting point particles or areas which have built low melting point compositions by diffusion during heating. With the condition of 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. In order to distinguish clearly between rearrangement which is essentially rate controlled by the mechanical movement produced by the capillary forces and rearrangement which is rate controlled by dissolution-reprecipitation processes, these particle movements are described as primary and secondary rearrangements.

Fig. 7 Direct observation of skeleton disintegration during early stage of liquid phase sintering of carbonyl Fe (<5 μm) plus 30 wt%Cu (10 μm) at 1150°C in SEM with hot stage device²⁾.

An example of secondary rearrangement is shown in Fig. 7. In many systems a rigid skeleton of small particles forms as a result of *solid state* sintering during heating to the temperature of liquid formation. When, in a Fe-30Cu material the Cu melts it is instantaneously drawn into the small pores between the $2\text{ }\mu\text{m}$ Fe-particles which form a rigid skeleton. No shrinkage or change of particle morphology observed for times up to 2 min. This period ends with the collapse of particle chains as the melt penetrates along the grain boundaries leading to rapid shrinkage of the sample by secondary rearrangement within the specimen²³.

The penetration of melt along the grain boundaries is one of 4 basic solution-precipitation phenomena which were observed or predicted to occur during liquid phase sintering

- grain boundary penetration
- coarsening
- contact flattening
- liquid film migration

3.2 Grain Boundary Penetration

Grain boundary penetration leads to skeleton disintegration as shown above, but also to contact dilatation, particle dilatation and subsequently to particle disintegration.

Early grain boundary attack itself does not necessarily lead to densification. But if grain boundary attack is completed along all grain boundaries of a polycrystalline particle, particle disintegration and densification by secondary rearrangement may occur. This is illustrated in Fig. 8 (a) and (b). In Al_2O_3 -glass mixtures the shrinkage after particle disintegration due to rearrangement

Fig. 8 Microstructural changes and shrinkage during liquid phase sintering of Al_2O_3 -alkali borate glass²³.

Fig. 9 Grain boundary penetration during liquid phase sintering of a Fe-10Cu compact²⁴.

could be separated from shrinkage due to other primary rearrangement or solution-precipitation processes²⁹. Up to 1400°C, the shape and size of the polycrystalline Al₂O₃ spheres were maintained and only primary rearrangement occurred. Above this temperature grain boundary attack and particle disintegration occurred and secondary rearrangement led to considerable additional shrinkage.

The attack of grain boundaries by a melt during sintering is most extensively studied in the Fe-Cu system in which compacts of Fe spheres with 10 vol% Cu spheres (Fig. 9(a)), both of 100 μm diameter were sintered at 1165°C for times up to 60 min²⁴. After annealing for 3 min above the melting point of Cu, all contact regions between the Fe particles were filled with liquid (Fig. 9(b)). After 8 min, grain boundary attack had led to severe changes in the contact area geometry; instead of flat inter-particle contact areas, wavy layers of liquid were present and bumps consisting of Fe(Cu) solid-solution formed opposite each grain boundary. The additional melt in prior contact areas and at prior grain boundaries in the interior of the Fe particles caused contact and particle dilatation leading to macroscopic swelling²⁴.

3.3 Coarsening

During liquid phase sintering of materials grain growth is one of the most obvious microstructural changes. In many systems grain coarsening follows the relation

$$\bar{G}^3 = (\bar{G}_0^3 + kt)^{1/3}$$

which indicates diffusion controlled Ostwald ripening as the rate controlling step^{25,26}. Experiments with Fe-20 wt% Cu and Fe-30 wt% Cu samples also showed that during liquid phase sintering the particle size distribution developed a steady state form which could be described by

$$D(S) = 2.136 S^2 \exp(-0.712 S^3)$$

where $2S$ is the reduced particle size, $G/\bar{G}$, with $\bar{G}$ as the average particle size.

When Price, Smithells and Williams published their famous micrographs of a W-Cu-Ni heavy metal alloy in 1937 they already recognized that grain growth and shape change of the solid constituents had occurred simultaneously²⁷. From recent experiments with mixtures of small tungsten powder (10 μm) and large single crystal W seeds (220 μm) that were liquid phase sintered in the presence of a Ni-rich melt, this idea was rejuvenated. It was emphasized from the microstructural development of these samples that shrinkage is directly related to grain growth and shape accommodation. During liquid phase sintering the initial spherical shape of the single crystal seeds changed towards polyhedral shapes (Fig. 10). Special etching showed the shape change of the spheres to be due only to the precipitated material²⁸, that was supplied by dissolving smaller particles. Calculations of microstructural development to be expected showed similar general features as found in the liquid phase sintering experiments²⁹. The calculations were conducted with the assumptions that the large particles were taking part in the usual Ostwald ripening of the arrangement. No pressure in the flat contact areas was assumed beyond a value which kept the thickness of the thin liquid films in the contact areas between the particles at a constant value. As seen already from the experiments the calculation showed that the deposition of material in the contact areas is extremely small in this system of large and small particles (Fig. 10).

During liquid phase sintering of a system with a steady state particle size distribution, similar shape accommodation was observed. During coarsening many grains rapidly accommodated their shape to a changing vicinity (Fig. 11)³⁰. Even inert obstacles did not hinder further grain growth and were entrapped into growing grains³¹. This extreme of shape accommodation to an adjacent particle shown in Fig. 12 in Mo-Ni-Al₂O₃. The shape development of the Mo grains during an-

(a)

Microstructure after 3 min

(b)

Calculated microstructure
after 1 min

(c)

Calculated microstructure
after 120 min

(d)

Microstructure after 120 min

Fig. 10 Grain growth and shape accommodation during liquid phase sintering of W-Ni at 1670°C²³⁾.

Fig. 11 Microstructure of Mo-4Ni after cyclic liquid phase sintering between 1300 and 1460°C. Held at 1460°C for 30 min in each cycle. Microstructures around a pore obtained by strong etching in a Murakami solution³⁰⁾.

Fig. 12 Etch boundaries around an alumina particle trapped within a growing Mo grain. Mo-4Ni0.6Al₂O₃ specimen sintered in four cycles (4+2+2+2 h)³¹⁾.

nealing is indicated by etching boundaries. During liquid phase sintering with 2 wt%Ni at 1460°C the Mo grains trapped small Al₂O₃ spheres (black). No evidence of contact flattening was found. Contact flattening should have led to etching boundaries joining at larger angles in the vicinity of the contact areas of Mo grains with Al₂O₃ particles.

3.4 Contact Flattening

Contact flattening is a classical approach to explain shape change and shrinkage during liquid phase sintering³²⁾. The contact flattening assumes thin liquid films in contact areas separating the particles. All particles transmit forces caused by the presence of pores. Close to the contact areas and through the thin liquid layers, the forces between the particles are thought to be transmitted whereby the stress is intensified in the contact areas compared to other areas of the particles. Thermodynamically, the increased pressure usually results in an increased solubility of the solid phase in the liquid. The concentration gradient owing to the stress gradient in the liquid film and the adjacent solid areas yields a flow from the contact areas towards other lower stressed areas of the melt or the solid. In most cases the flow is assumed to be diffusion controlled. The continuous flow of dissolved material leaving the contact areas leads to a shape change of the particles and to the center to center approach of the particles.

Although many researchers have tried to find clear microstructural evidence for contact flattening to be a major mechanism during liquid phase sintering, no unambiguous results have been published up to now.

One of the major criticisms against the basic assumptions made for modelling contact flattening

pointed out that grain growth is completely neglected in the classical approach, although grain growth is much faster than the predicted contact flattening rates. A detailed calculation which took over all assumptions of the classical contact flattening theory but included in addition rapid grain growth showed that the contact flattening approach is incorrect²⁶⁾. The results of those calculations which included grain growth were in sharp contradiction to the variety of experimental results for those systems where shrinkage and grain growth during sintering had been measured.

3.5 Shrinkage During Liquid Phase Sintering

It must be concluded that shape accommodation during sintering occurs during grain coarsening and is due to the small reprecipitation rate at particle contacts. Shrinkage may be vaguely described as secondary rearrangement which occurs when small particles are dissolved giving way for the movement of larger particles. The model of contact flattening cannot describe the experimental observations of shape accommodation. If calculations based on the contact flattening concept which include in addition the observed rapid grain growth were performed the results are in sharp contradiction with the experimentally measured shrinkage behavior.

3.6 Diffusion Induced Grain Boundary Migration and Liquid Film Migration Due to Additives

In recent years boundary migration in metals and ceramics, which is associated with a noticeable concentration change in the wake of the moving boundaries, has been investigated intensively. It is known as diffusion induced grain boundary migration (DIGM)³³⁾ and liquid film migration (LFM)^{34,35)}. The migrations are of considerable importance to solid state and liquid phase sintering with additives.

When a well recrystallized Mo foil is annealed at 1380°C essentially no grain growth can be detected, but if a thin (unreacted) Ni film is applied to the surface (or if the sample is exposed to Ni vapour), the grain boundaries develop bulges often looking like worms or snakes³⁶⁾ (Fig. 13). The length of the grain boundary and hence the grain boundary area is increased due to the formation of the bulges. Microprobe measurements show that the Ni concentration is increased in the boundaries. Behind the migrating boundaries, a saturated solid solution is formed (Fig. 14). The Mo crystals in front of the migrating boundaries are completely free of Ni. From those measurements it became obvious that the formation of a solid solution may provide the driving force which allows the increase

Fig. 13 Morphology of a surface of a Mo foil with a thin initially unreacted coating Ni layer after sintering at 1420°C for 10 min³⁶⁾.

Fig. 14 Concentration profile across the migrated boundary shown in Fig. 13³⁶⁾.

of the boundary area. Other measurements showed that this type of boundary migration occurs when the solid solution left in the wake of the boundary has a lower free enthalpy than the material in front of the boundary³⁶⁾. Thus the concentration in the wake of the migrating boundary may be higher or lower in solute concentration than in the front of the boundary. A second prerequisite is that the boundary provides a sink or source for the requested changes of the solute.

The free enthalpy change is necessary but does not yield itself the atomistic kinetics which cause boundary migration. The present atomistic model is based on coherency strains owing to changes in the lattice parameters in the solid in front of the migrating boundaries^{33~35)}.

The solid in front of the migrating boundaries is not in equilibrium with the solute concentration of the boundary and solute will either deplete from or diffuse into this solid. When the boundary migrates at a constant velocity a steady state concentration profile will develop. The concentration gradients in the solid close to the liquid/solid interface will be very steep. If the lattice parameter changes with the concentration of the solute and coherency of the peripheral layers of the solid is maintained, coherency strains will arise. These coherency strains raise the free enthalpy of the solid which is in contact with the boundary. The solid in the wake of the migrating boundaries is thought to lose the coherency with the initial grain rapidly due to the incorporation of misfit dislocations.

This model was first proposed by Hillert³⁷⁾ and recently refined by Cahn and Yoon³⁴⁾. It explains nicely the effects of liquid film migration. Some modifications are required to explain the more complex stress states at grain boundaries during diffusion induced grain boundary migration.

As mentioned above DIGM and LFM are important for many systems sintered with additives. Economically, the most important systems for structural parts are Fe-Cu based alloys. The penetration of melt into contact areas and grain boundaries yields perfect conditions for LFM²⁾. Figure 15 shows an area in an Fe particle after liquid phase sintering in the presence of Cu for 2 min. The thin liquid films have formed the bulges characteristic for LFM. Solid solutions of Fe-Cu have formed in the wake of the migrating boundaries.

It must be emphasized that the bulk diffusivity of Cu in Fe is extremely small, thus no solid

Fig. 15 Liquid film migration in Fe-10Cu during liquid phase sintering at 1120°C³⁸⁾.

Fig. 16 Liquid film migration in Fe-10Cu-0.45C sintered at 1150°C for 20 min²³⁾.

(a)

(b)

Fig. 17 Microstructure (a) and bend strength (b) of Mo-Ni after slow cooling. MSD cooling procedure resulted in bulged interlocking grain boundaries.

solution formation is expected by this mechanism during the sintering times and temperatures applied usually in practice. The rapid homogenization is obtained by LFM, and hence LFM seems to be of great importance for this system.

In the Fe-Cu-C system penetration of melt along grain boundaries is suppressed. Penetration of contact areas is possible however. Figure 16 shows the microstructure of Fe-10Cu-0.4C after liquid phase sintering for 20 min at 1130°C. The thin liquid layers in contact areas are shifted by liquid film migration. In the wake of the moving boundaries a saturated solid solution of Fe-Cu is left, which mainly contains the pearlite which preferentially formed in these areas during cooling due to the fact that the eutectoid of Fe-C forms at a higher temperature than the eutectoid of Fe-Cu-C.

It is well known that W or Mo embrittles if sintered with activators like Ni. The Ni segregates at the grain boundaries. If an appropriate heat treatment is done, LFM and DIGM may produce bulged grain boundaries (Fig. 17(a)) which mechanically interlock the grains. This tailored microstructure improves the mechanical properties considerably. Figure 17(b) shows the bend strength of Mo, Mo sintered as usually with Ni, and Mo sintered with Ni and heat treated obtain LFM and DIGM.

Literature

- 1) E. Klar: "Gas and Water Atomization", in "Metals Handbook, Ninth Edition, 7, Powder Metallurgy", coordinator E. Klar: American Society for Metals, Metals Park, Ohio 44073, (1984), 24.
- 2) G. Petzow and W. A. Kaysser: in "Sintered Metal-Ceramic Composites", G. S. Upadhyaya ed.: Elsevier Science Publishers, Amsterdam, (1984), 51.
- 3) G. Petzow, W. A. Kaysser and M. Amtenbrink, in "Sintering-Theory and Practice", Materials Science Monographs, 14, D. Kolar, S. Pejovnik and M. M. Ristic: (1982), 27.
- 4) R. G. German: Science of Sintering, 16 (1984), 75.
- 5) M. P. Seah: J. Physics. F: Metal Physics, 10 (1980), 1043.
- 6) R. Miodovnik: Powder Metallurgy, 28 (1985), 151.
- 7) N. L. Peterson: in "Solid State Physics", F. Seitz, D. Turnbull and H. Ehrenreich eds. Academic Press, New York (1968).
- 8) W. A. Kaysser, Y. S. Kwon, I. H. Moon and G. Petzow: unpublished.
- 9) W. J. Muster, D. N. Yoon and W. J. Huppmann: J. Less-Com. Met., 65 (1979), 211.

- 10) W. A. Kaysser, S. Pejovnik and G. Petzow: Z. Metallkde. **71** (1980), 649.
- 11) J. H. Brophy, L. A. Shepard and J. Wulff: in "Powder Metallurgy", W. Leszynski: AIME-MPI, Interscience, NY., (1961), 113.
- 12) R. M. German and Z. A. Munir: in "Reviews on Powder Metallurgy and Physical Ceramics", Saint-Saphorin, **2** (1982), 9.
- 13) I. J. Toth and N. A. Lockington: J. Less-Com. Met. **12** (1967), 353.
- 14) W. A. Kaysser, M. Hofmann-Amtenbrink and G. Petzow: Powder Metallurgy, **28** (1985), 199.
- 15) V. W. Schintelman and K. Richter: Planseeberichte für Pulvermetallurgie, **13** (1970), 3.
- 16) W. A. Kaysser, M. Hofmann-Amtenbrink and G. Petzow: Proc. "1984 Powder Metallurgy Group Conference", 29-31 Oct., Harrogate (1984).
- 17) M. Amtenbrink: Doktorarbeit Universität Stuttgart (1985).
- 18) H. Hofmann und S. Hofmann: Scripta Metall., **18** (1984), 77.
- 19) K. Uematsu, R. M. Cannon, R. D. Bagley, M. F. Yan, U. Chowdry and H. K. Bowen: Int. Symp. of Factors in Densification of Oxide Non-Oxide Ceramics, Hakone, Japan (1978), 190.
- 20) R. J. Brook: J. Am. Cer. Soc., **52** (1969), 56.
- 21) C. H. Hsueh, A. G. Evans and R. L. Coble: Acta Metall., **30** (1982), 1269.
- 22) W. A. Kaysser, M. Mitkov and G. Petzow: Proceedings "Colloquium on Unconventional Forming Processes in Powder Metallurgy", 19-20. Sept., Paris (1984).
- 23) W. A. Kaysser and G. Petzow: Powder Metallurgy, **28** (1985), 145.
- 24) W. A. Kaysser, W. J. Huppmann and G. Petzow: Powder Metallurgy **23** (1980), 86.
- 25) W. A. Kaysser, S. Takajo and G. Petzow: Acta Metall. **32** (1984), 115.
- 26) W. A. Kaysser and G. Petzow: Z. Metallkde., **76** (1985), 687.
- 27) H. S. Price, C. J. Smithells and S. V. Williams: J. Int. Met. **62** (1938), 239.
- 28) D. N. Yoon and W. J. Huppmann: Acta Metall. **27** (1979), 693.
- 29) W. A. Kaysser, M. Zivkovic, M. M. Ristic and G. Petzow: in "Contemporary Inorganic Materials: Progress in Ceramics, Metals and Composites", G. Ondracek and O. Vöhringer eds., Bilateral Seminars of the International Bureau KFA-Jülich CIM, (1986), 217.
- 30) S.-J. L. Kang, W. A. Kaysser, G. Petzow and D. N. Yoon: in "Modern Developments in Powder Metallurgy", E. N. Aqua and C. M. Whitman: MPIF-APMI, Princeton, N.J., **15** (1985), 477.
- 31) S.-J. L. Kang, W. A. Kaysser, G. Petzow and D. N. Yoon: Acta Metall., **33** (1985), 1919.
- 32) W. D. Kingery: J. Appl. Phys., **30** (1959), 301.
- 33) M. Hillert and G. Purdy: Acta Metall., **26** (1978), 333.
- 34) D. N. Yoon, J. W. Cahn, C. A. Handwerker, J. E. Blendell and Y. J. Baik: to be published in "Interface Migration and Control of Microstructure", NBS, Washington.
- 35) C. A. Handwerker, J. W. Cahn, D. N. Yoon and J. E. Blendell: to be published in "Atomic Transport in Alloys: Recent Developments", G. E. Murch, M. A. Dayananda, TMS/AIME Publications (1985).
- 36) M. Hofmann-Amtenbrink, W. A. Kaysser and G. Petzow: J. Physique, **C4** (1985), 545.
- 37) M. Hillert: Scripta Metall., **17** (1985), 237.
- 38) W. A. Kaysser and G. Petzow, unpublished.

会 告

第4回ビギナーズ・セミナー

——新しいセラミックス開発の鍵——

主 催: (社)窯業協会

協 賛: (社)粉体粉末冶金協会他

日 時: 昭和62年11月9日(月)～12日(木) 3泊4日

場 所: (財)アジアセンター

小田原市城山4-14-1 TEL0465(22)6131

プログラム:

1. セラミックス原料	大津賀 望
2. セラミックスの成形	荒川 正文
3. セラミックスの焼結	木島 式倫
4. 開発とは何か?	山本 登
5. セラミックスの微構造	浜野 健也

6. セラミックスの熱的性質とその測定法 高橋 洋一

7. セラミックスと生産技術 戸田 堯三

8. セラミックスの電磁氣的性質とその測定法
河本 邦仁

9. セラミックスの機械的性質と測定法 松尾陽太郎

参加費: 主催・協賛学会会員 1名 10万円

非会員 1名 12万円

(宿泊費, 食費, テキスト代を含む)

定 員: 60名 (定員になり次第締め切ります)

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