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Powder Processed Aluminium Alloys

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Abstract

The increasing interest in light weight materials coupled to the need for cost-effective processing have combined to create a significant opportunity for aluminium powder metallurgy. Net shape processing of aluminium by the classical press-and-sinter powder metallurgy technique using elemental powder blends is a unique and important metal-forming method which is cost effective in producing complex parts very close to final dimensions. Here we describe alloy developments for press and sinter material. This includes the design of alloys based on the characteristics of ideal liquid phase sintering systems, the optimisation of the concentration of the major alloying elements, the use of microalloying additions and the development of metal matrix composites.

1. Introduction

Powder metallurgy (P/M) is the processing of parts from metal powders. Powders are used to process the reactive and refractory metals, to generate properties not attainable through conventional metal working processes or to manufacture parts to net shape. Aluminium powder metallurgy is used for the latter two reasons. Aluminium P/M is currently used to produce ultra-high strength and creep resistant alloys beyond the levels possible by conventional ingot metallurgy. Coupled with an improved alloying capability which provides new possibilities for alloy design, this has facilitated the development of materials with exceptional mechanical properties. While these alloys have attractive properties, they are expensive to produce, limiting their use to niche applications, mainly in the aerospace industry.

In contrast, there is significant industrial potential for aluminium alloys fabricated via net shape P/M techniques using inexpensive, elemental powder blends. In particular, the automotive industry demands both low weight and low cost materials in order to reduce fuel emissions and improve fuel economy at affordable prices. Additional potential markets for Al P/M parts include hand tools, where moving parts against gravity represents a challenge; and office machinery, where reciprocating forces are important. However, the properties of conventional, press-and-sinter aluminium P/M alloys are generally inadequate for many potential applications in these industry sectors.

The objective of this paper is to review recent work at The University of Queensland which is focussed on improving the sintered properties of aluminium powder alloys.

2. An Alloy Design Strategy

Alloys are generally designed to accommodate the manufacture of goods made from them as much as the properties required of them in service. It is for this reason that sintered steels, for example, often contain copper or phosphorous in addition to carbon and nickel. Similarly, cast aluminium alloys are different to forging alloys which are different again to extrusion alloys. However, this principle has not been widely applied to pressed and sintered P/M aluminium. The compositions of the current commercial alloys are compared to standard wrought material in Table 1. It is noteworthy that the compositions of the P/M alloys are essentially identical to those of the wrought material. It is therefore not surprising that their sintering response is weak and the resultant properties are poor.

Table 1: The composition of commercial aluminium P/M alloys.

Alloy	Manufacturer	Cu	Mg	Si
602	Alcoa	-	0.6	0.4
601	Alcoa	0.25	1.0	0.6
6711	Ampal	0.25	1.0	0.8
321	Eckart	0.2	1.0	0.5
AA6061	wrought	0.25	1.0	0.6
202	Alcoa	4.0	-	-
2712	Ampal	3.8	1.0	0.75
201	Alcoa	4.4	0.5	0.6
2014	Alpoco	4.4	0.5	0.8
13	Eckart	4.5	0.5	0.2
123	Eckart	4.5	0.5	0.7
AA2014	wrought	4.5	0.5	0.8

Instead of sintered alloys which simply mimic existing wrought alloys, it is preferable to have alloys that are specifically designed to be sintered. Here we consider four possible approaches: (1) fundamentally redesigning the composition based on the phase diagram characteristics of ideal liquid phase sintering systems; (2) re-evaluating the base composition of conventional alloys in order to maximise the sintering response and the tensile properties in the as-sintered state; (3) microalloying with selective elemental additions to manipulate the sintering response; and (4) adding a ceramic reinforcement to make a metal matrix composite. We begin, however, with a discussion of the oxide film.

3. The Surface Oxide

Aluminium is always covered by an oxide. The thickness of the oxide is dependant on the temperature at which it formed and the atmosphere in which it is stored, particularly the humidity. The thickness on atomised powder can vary from 5-15 nm [1-4]. The oxide prevents solid state sintering in low melting point metals [5], including aluminium [6]. This has been explained in terms of the relative diffusion rates through the oxide and the metal, for metals with stable oxides [7-9].

The use of liquid phases is an alternative to solid state sintering. An essential requirement for effective liquid phase sintering is a wetting liquid [10]. High melting point, ionocovalent materials such as metal oxides are generally poorly wetted by liquid metals, except at high temperatures [11]. It is therefore apparent that the oxide on aluminium is a sintering barrier and needs to be disrupted or removed. For aluminium at 600°C, a $PO_2 < 10^{-50}$ atmospheres is required to reduce the oxide [12]. This corresponds to a dew point of ≤ -140°C [13]. This is impossible to obtain in conventional atmospheres. Although the oxide cannot be removed, it may be disrupted by sintering in the presence of magnesium. Magnesia has a lower free energy of formation than alumina [14] and magnesium metal can partially reduce alumina to form spinel, $MgAl_2O_4$ [15-21]. During sintering, reaction of Mg with the Al_2O_3 film ruptures the oxide which exposes the underlying metal and facilitates sintering [22]. Less than 0.2% Mg is all that is required. This is shown in Figure 1.

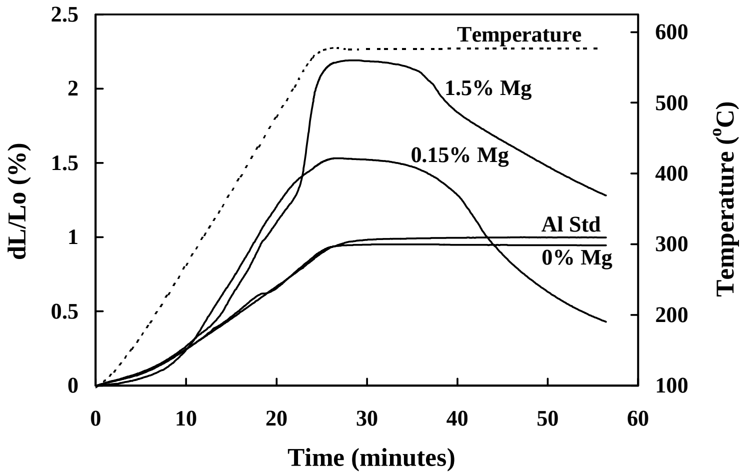

Figure 1: Dilatometry curves for Al-xMg alloys, where x is 0, 0.15 and 1.5 wt % Mg showing the effect of trace additions of magnesium on the sintering response of aluminium [22].

4. An Ideal Liquid Phase Sintering System

Based on an understanding of fundamental liquid phase sintering phenomena, German recognised that it is possible to define certain ideal phase diagram characteristics [23, 24]. The key features of an ideal liquid phase sintering system are:

- The additive should have a lower melting point than the base. The alternative is a low melting point eutectic which is less advantageous because liquid formation does not occur spontaneously on heating.
- The solubility of the additive in the base should be low because this ensures that the additive remains segregated to particle boundaries and maximises the liquid volume.
- While the base should be soluble in the liquid, it is not necessary for the base to be soluble in the solid additive. Completely miscible liquids ensures that mass transport is not constrained.

In addition, the base should also have a high diffusivity in the liquid. This ensures high rates of mass transport and therefore rapid sintering. An examination of the binary aluminium phase diagrams indicates that Al-Sn is perhaps the only system which exhibits almost all of the ideal features. The melting point of tin (232°C) is considerably lower than that of aluminium (660°C) and there are no intermetallic phases. Tin is sparingly soluble in solid aluminium: the maximum solid solubility is <0.15%. Aluminium is completely soluble in liquid tin and no immiscible liquids form. In addition, the diffusivity of Al in liquid Sn is about five times greater than the self diffusivity of liquid Sn [25].

In the presence of magnesium, tin is indeed a very effective sintering aid. This is illustrated in Figure 2, which is a densification contour map for the Al-Sn-Mg system. The densification is a function of the green density, sintered density and theoretical density and is a measure of the sintering response: positive values indicate shrinkage, negative values indicate expansion; full density is achieved at a value of one. The closely spaced, parallel contour lines at low magnesium concentrations indicate that small quantities of magnesium are required to activate the system. The widely spaced, gently sloping contour lines at higher magnesium concentrations indicate that the system is relatively insensitive to Sn concentration and Mg levels greater than the critical concentration. At a tin concentration of 8%, the sintered density approaches 99% of theoretical. The tensile strength of the Al-Sn system, however, is low because the aluminium is essentially unalloyed and the properties are controlled to some extent by the tin, which forms a continuous boundary network at high concentrations.

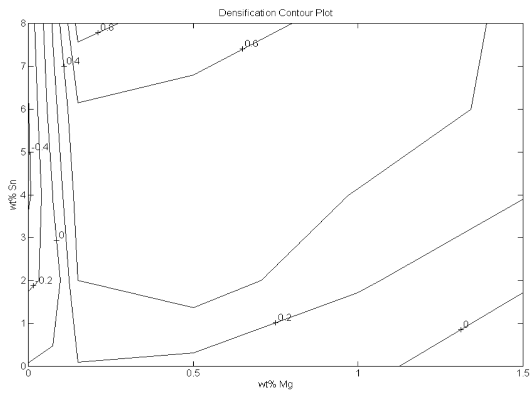

Figure 2: Contour map showing densification as a function of magnesium and tin content. Each contour represents a densification of 0.2. See text for details.

5. Re-Design of Al-Cu-Mg-Si Alloys

The age hardening response of conventional 2xxx series alloys is a major consideration in their design but sintered alloys of the 2xxx type are more widely used in the T1 rather than the T6 condition. The principle design criterion therefore needs to be sintering not ageing. To this end, we have recently re-evaluated the entire composition spectrum in order to maximise the sintering response and the tensile properties in the as-sintered state. Using a statistical design of experiment approach, models were developed for density, yield stress, ultimate tensile strength and elongation of sintered Al-Cu-Mg-Si alloys [26]. Copper has the major influence on the tensile properties of sintered aluminium (Figure 3). Magnesium and silicon do effect some properties, but to a lesser extent. While Mg is necessary to reduce the oxide, an extensive secondary pore network develops from excess magnesium and this severely limits the ductility. Hard intermetallic particles, which are a residue of the sintering liquid, also reduce the tensile ductility. The total alloy content and the sintering temperature therefore need to be adjusted to minimise the sintering liquid volume to just that extent necessary to affect sintering. An optimum combination of properties are achieved in an Al-2.5Cu-0.5Si-0.5Mg alloy. This develops a tensile strength of 267 MPa and a ductility of 6%. This compares favourably with a sintered 2014 type alloy (P/M alloy 201) which develops a tensile strength of 209 MPa and a ductility of 3% in the T1 condition [27].

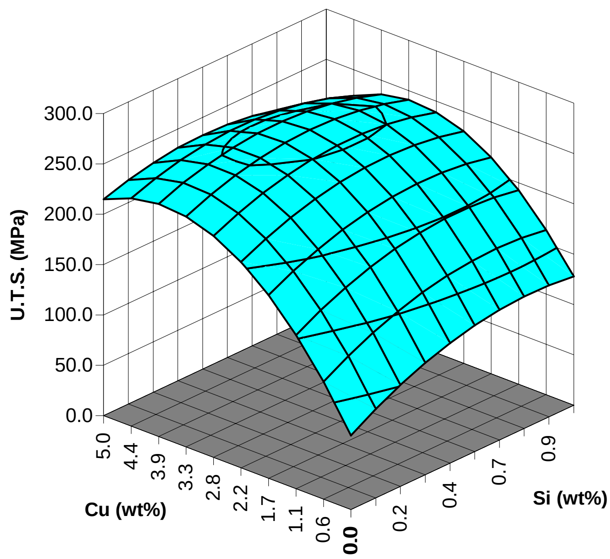

Figure 3: The tensile strength as a function of the copper and silicon concentration for alloys containing 1.1 %Mg and sintered at 570 °C [26].

6. Microalloying

The sintering response of the 2xxx alloys is significantly enhanced by the addition of 100 ppm Sn, Pb, In, Bi or Sb [28]. These elements have both a high diffusivity in aluminium and a high vacancy binding energy. They therefore diffuse into the aluminium ahead of the copper, where they preferentially bind with vacancies. This reduces the rate of copper diffusion into the aluminium, allowing more liquid to persist for longer times. The transient aspect is delayed, liquid phase sintering is enhanced and densification increases.

This improved sintering response can be translated into better tensile properties if the processing conditions are also modified [29]. Increasing the sintering temperature from the standard 590°C to 620°C increases the sintered density but results in the formation of an embrittling phase. This can be removed by incorporating the solution treatment into the sintering cycle (a modified T5 heat treatment). These conditions produce a tensile strength of 375 MPa, an increase of nearly 20% over the unmodified alloy. The ductility is unaffected.

The 7xxx series alloys have the greatest response to age hardening but do not have good sintering characteristics and have not had significant use as conventional P/M materials. Micro-alloying with 100 ppm of Pb substantially improves the sintering response of an Al-Zn-Mg-Cu alloy (Figure 4). Similar amounts of Sn and In also have a beneficial effect, although not as pronounced. These elements have a low surface tension, a low vapour pressure and do not form stable compounds with the other alloying elements at the sintering temperature. The Pb, Sn or In segregates to the liquid-vapour interface during sintering and thereby lowers the surface tension of the liquid, which reduces the wetting angle, enhances wetting, improves liquid spreading and therefore sintering [30]. When the alloy composition and process variables are optimised, tensile strengths > 440 MPa can be obtained in the T6 temper [31].

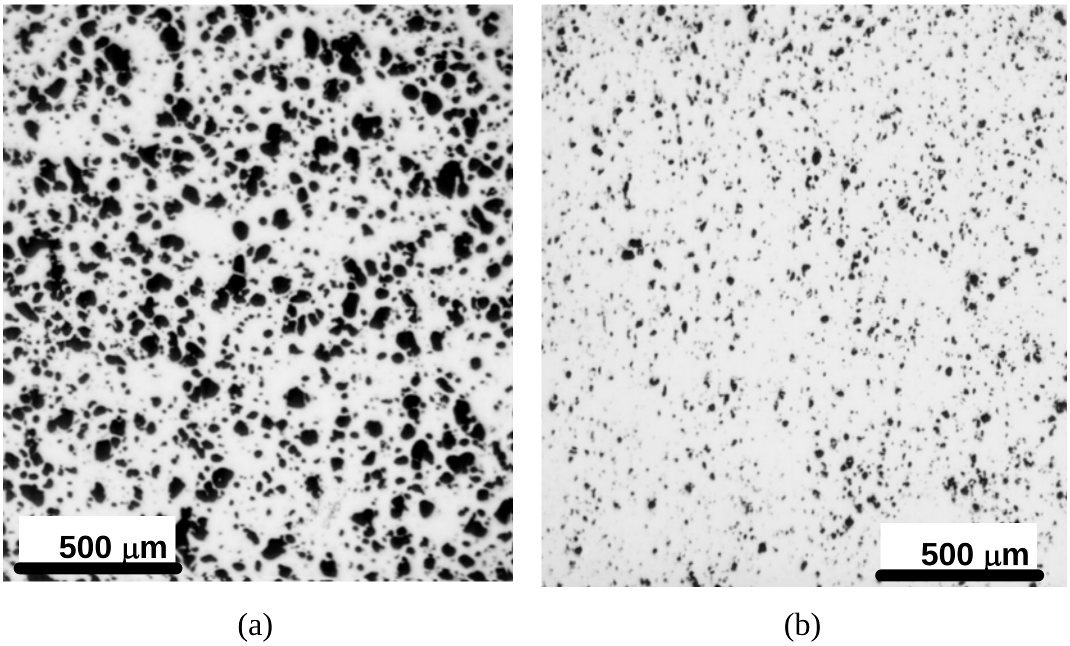

Figure 4: Optical micrographs of unetched sections of sintered (a) Al-8Zn-2.5Mg-1Cu and (b) Al-8Zn-2.5Mg-1Cu-0.07Pb showing the effect of the trace element on porosity [30].

7. Metal Matrix Composites

An alternative to conventional alloys are metal matrix composites (MMCs), which have a high specific modulus, good wear resistance and a tailorable coefficient of thermal expansion. A major drawback to these MMCs is high cost. The reasons are twofold. First, the material itself is expensive because specially synthesised pre-alloyed powders are usually required and many processing steps are needed. The powders are typically cold pressed, then hot pressed or sintered and extruded. Canning and vacuum degassing are common. The second reason that these alloys are expensive is due to the high costs of secondary processing. They are not produced to near net shape and therefore require extensive forging or machining, which can be particularly problematical because of the ceramic component. Spray forming overcomes some of these problems by the direct formation of a near net shape billet [32-34]. However, shapes are limited and processing is difficult.

Conventional P/M processing can overcome both these problems. Only two processing steps are required (pressing and sintering) and the part is formed into its final shape in one operation – it is the quintessential net shape process. Thus there is significant potential for press-and-sinter processed aluminium P/M composites in order to provide high stiffness at low cost. However, adding significant quantities of an inert ceramic reinforcement phase to an aluminium P/M matrix is problematical.

The inert, ceramic particles not only reduce the volume of densifying material, they also create a hydrostatic tensile stress in the matrix which opposes the sintering stress [35, 36]. As a body containing rigid inclusions densifies, the inclusions move towards each other. Each inclusion therefore experiences a force due to the presence of the other inclusions [37, 38]. The closer the particles, the greater the force. The matrix between the inclusions is therefore under compression and faster than average densification occurs between particles which are separated by a gap smaller than the average, i.e. there is a critical separation distance which is equal to the average separation distance. When a summation is carried out over many particles, the composite will densify at a slower rate than an unreinforced matrix. The regions between closely spaced inclusions, which densify at a rate greater than the average, increase in strength relative to the unsintered regions. A tensile stress therefore develops in the remaining porous regions, which are also constrained from sintering by the newly sintered regions. This causes de-sintering and crack-like void formation [39].

For optimum sintering, inclusions need to be equiaxed and uniformly distributed. Clustering of reinforcing particles should be avoided. This can be achieved by matching the particle size of the reinforcement powders to the particle size of the matrix powders [40]. For very fine reinforcement particles, every aluminium particle will be completely surrounded by reinforcement particles and the system will be incompressible and non-sinterable. As the particle size ratio is increased, the volume fraction reinforcement can be increased. At a large particle size ratio, the reinforcement particles have a lower probability of being part of a cluster network and are evenly spaced through the aluminium matrix. Load bearing clusters do not impede compaction and the sintering rate is homogenised throughout the compact.

Desintered zones are less likely to form and sintering cracks are less likely to develop. Improved sintered densities result. Coarse reinforcement particles are therefore preferred.

A second distinct feature that can be clearly correlated with high performance sintered MMC’s is that the reinforcing phase must be fully wet by the liquid phases produced during sintering in order to generate an effective, load bearing interface. In the absence of wetting, sintering is poor and the properties are much-reduced.

When particle clustering is controlled and the ceramic/matrix interface properly engineered, then effective sintering results and very attractive properties can be achieved. At an as-sintered density of 99%, these new experimental alloys have a modulus of 130 GPa and an ultimate tensile strength of 212 MPa in the T4 temper. The ceramic particles also provide a significant improvement in the abrasive wear resistance and to the fatigue life. With 20 vol% ceramic, the fully reversed fatigue life increases by 25% to 100 MPa. The wear resistance of an Al-Mg-Cu-Si alloy with 5% hard phase is equivalent to that of a hypoeutectic Al-Si-Cu die casting alloy. A typical abrasive wear surface is shown in Figure 5.

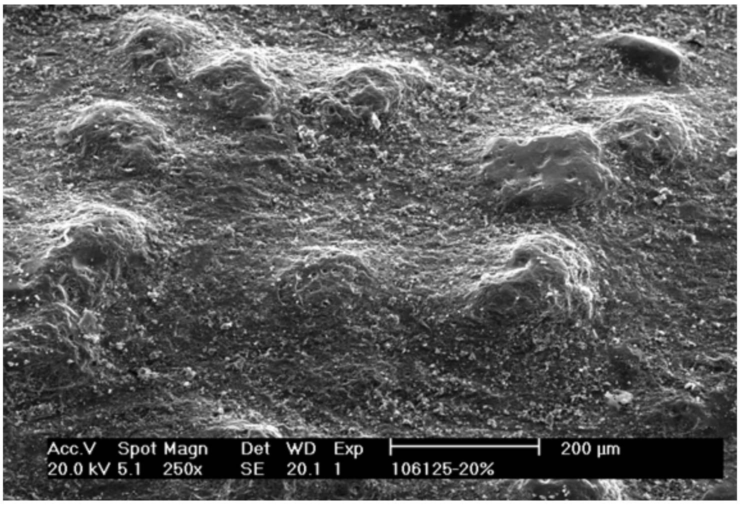

Figure 5: Scanning electron microscopy image of the wear tested surface of a metal matrix composite with 20 vol% ceramic. The reinforcement can be seen protruding from the wear surface.

8. Applications

The major current application for P/M aluminium is the cam shaft bearing cap. This has been in service in the USA with Ford, DaimlerChrysler and General Motors since the early 1990s, without a failure. Potential automotive applications include connecting rods and oil pump gerotors in automatic transmissions where the sintered aluminium part will replace a sintered steel component. The major weight saving comes not from the direct material substitution, which is small for small parts, but through the potential for redesign. In gerotors, the major weight saving comes about by substitution of a cast iron housing with an aluminium die casting. However, a steel gear set inside an aluminium housing increases noise and vibration and decreases efficiency because of the mismatch between the coefficient of thermal expansion of the aluminium and the steel.

An aluminium gear therefore facilitates the use of an aluminium housing. Connecting rods in North American passenger vehicles are currently made via powder forging using an Fe-Cu-C alloy. Because this is a reciprocating part, the inertial loads on other engine components are significant. Substitution of steel by aluminium will allow resizing of the crank shaft and ancillary equipment for substantial weight savings. In non-automotive applications, aluminium P/M parts may replace small aluminium die castings where the better material utilisation and closer tolerances of the P/M process are advantageous. Possible applications include pistons and couplings.

9. Summary

The increasing interest in light weight materials coupled to the need for cost-effective processing have combined to create a significant opportunity for aluminium P/M, particularly in the automotive industry. Aluminium P/M adds light weight, high compressibility, low sintering temperatures, easy machinability and good corrosion resistance to all the advantages of conventional P/M. However, most current commercial alloys are based on standard wrought alloys which were not designed to be sintered and the properties are poor as a consequence. The tensile properties of pressed-and-sintered aluminium alloys are not limited by the oxide film on the surface of the powder particles because trace additions of magnesium react with it to form spinel. This breaks up the oxide, facilitating sintering. Aluminium P/M alloys can be improved without recourse to hot working or master alloy powders if their design is based on an understanding of the underlying sintering processes. Aluminium P/M parts are currently used in low stress applications in marine transport, hand tools and office machinery and have started to penetrate the automotive industry. Further developments in alloy composition and processing technology, including the development of metal matrix composites, will provide many more opportunities in the automotive industry.

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References

[1] I. E. Anderson, J. C. Foley, and J. F. Flumerfelt, "Simplified Aluminum Powder Metallurgy Processing Routes for Automotive Applications," presented at Powder Metallurgy Aluminum and Light Alloys for Automotive Applications, Dearbon, MI, 1998.

[2] A. Ozbilen, A. Unal, and T. Sheppard, "Influence of Oxygen on Morphology and Oxide Content of Gas Atomised Aluminium Powders," presented at Physical Chemistry of Powder Metals - Production and Processing, St Marys, PA, 1989.

[3] P. Nielsen, Y. L. Liu, and N. Hansen, "Manufacturing of Aluminium Composites with High Purity Matrix," presented at 1993 Powder Metallurgy World Congress, Japan, 1993.

[4] Y. Kim, W. M. Griffith, and F. H. Froes, *Journal of Metals*, vol. 37, pp. 27-33, 1985.

[5] R. F. Smart and E. C. Ellwood, *Nature*, vol. 181, pp. 833-834, 1958.

[6] R. Q. Guo, P. K. Rohatgi, and D. Nath, *Journal of Materials Science*, vol. 32, pp. 3971-3974, 1997.

[7] Z. A. Munir, *Journal of Materials Science*, vol. 17, pp. 2733-2740, 1979.

[8] Z. A. Munir, *Powder Metallurgy*, vol. 24, pp. 177-180, 1981.

[9] P. K. Higgins and Z. A. Munir, *Powder Metallurgy International*, vol. 14, pp. 26-29, 1982.

[10] W. Kingery, *Journal of Applied Physics*, vol. 30, pp. 301-306, 1959.

[11] J. V. Naidich, *Progress in Surface and Membrane Science*, vol. 14, pp. 353-484, 1981.

[12] L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*. New York: McGraw Hill, 1953.

[13] C. Lall, *International Journal of Powder Metallurgy*, vol. 27, pp. 315-329, 1991.

[14] M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald, and A. N. Syverud, *Journal of Physical and Chemical Reference Data, Supplement No. 1*, 1985.

[15] G. M. Scamans and E. P. Butler, *Metallurgical Transactions A*, vol. 6A, pp. 2055-2063, 1975.

[16] C. G. Levi, G. J. Abbaschian, and R. Mehrabian, *Metallurgical Transactions A*, vol. 9A, pp. 697-711, 1978.

[17] R. Molins, J. D. Bartout, and Y. Bienvenu, *Materials Science and Engineering*, vol. A135, pp. 111-117, 1991.

[18] J. Homeny and M. M. Buckley, *Materials Letters*, vol. 10, pp. 421-424, 1991.

[19] A. Munitz, M. Metzger, and R. Mehrabian, *Metallurgical Transactions A*, vol. 10A, pp. 1491-1497, 1979.

[20] A. D. McLeod and C. M. Gabryel, *Metallurgical Transactions A*, vol. 23A, pp. 1279-1283, 1992.

[21] D. H. Kim, E. P. Yoon, and J. S. Kim, *Journal of Materials Science Letters*, vol. 15, pp. 1429-1431, 1996.

[22] R. Lumley, T. B. Sercombe, and G. B. Schaffer, *Metallurgical and Materials Transactions A*, vol. 30A, pp. 457-463, 1999.

[23] R. M. German and B. H. Rabin, *Powder Metallurgy*, vol. 28, pp. 7-12, 1985.

[24] R. M. German, *Liquid Phase Sintering*. New York: Plenum Press, 1985.

[25] C. H. Ma and R. A. Swalin, *Acta Metallurgica*, vol. 8, pp. 388-395, 1960.

[26] B. J. Hall and G. B. Schaffer, *Journal of Light Metals*, vol. 2, pp. 229-238, 2002.
[27] ASM Handbook, *Volume 7 Powder Metal Technologies and Applications*. Materials Park, OH: ASM International, 1998.
[28] T. B. Sercombe and G.B.Schaffer, *Acta Materialia*, vol. 47, pp. 689-697, 1999.
[29] T. B. Sercombe and G.B.Schaffer, *Materials Science and Engineering*, vol. A268, pp. 32-39, 1999.
[30] G. B. Schaffer, S. H. Huo, J. Drennan, and G. J. Auchterlonie, *Acta Materialia*, vol. 49, pp. 2671-2678, 2001.
[31] G. B. Schaffer and S. H. Huo, *Powder Metallurgy*, vol. 42, pp. 219-226, 1999.
[32] A. G. Leatham and A. Lawley, *International Journal of Powder Metallurgy*, vol. 29, pp. 321-329, 1993.
[33] E. J. Lavernia and X. Liang, *Reviews in Particulate Materials*, vol. 2, pp. 3-62, 1994.
[34] B. Li and E. J. Lavernia, "Spray Forming," in *Non-equilibrium Processing of Materials*, C. Suryanarayana, Ed. Amsterdam: Pergamon, 1999, pp. 153-193.
[35] G. W. Scherer, *Journal American Ceramic Society*, vol. 70, pp. 719-725, 1987.
[36] R. K. Bordia and G. W. Scherer, *Acta Metallurgica*, vol. 36, pp. 2411-2416, 1988.
[37] S. Sundaresan and I. A. Aksay,*Journal of the American Ceramic Society*, vol. 73, pp. 54-60, 1990.
[38] F. F. Lange, *Journal of Materials Research*, vol. 2, pp. 59-65, 1987.
[39] O. Sudre, G. Bao, B. Fran, F. F. Lange, and A. G. Evans, *Journal of the American Ceramic Society*, vol. 75, pp. 525-531, 1992.
[40] G. B. Schaffer and S. H. Huo, "On the Development of Sintered Aluminium Matrix Composites," presented at Powder Metallurgy Aluminum and Light Alloys for Automotive Applications, Dearborn, Michigan, 2000.