

## Review

# Aluminium powder metallurgy technology for high-strength applications

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A literature survey of aluminium powder metallurgy (PM) for high-strength applications was undertaken. Improvements in aluminium-base alloys made via ingot metallurgy (IM) are reaching the point of diminishing returns. PM offers an alternative technology, capable of producing alloys having improved fatigue, corrosion, and stress-corrosion resistance, as well as improved strength and toughness at room or elevated temperatures. The steps involved in powder metallurgy: powder manufacture, powder processing, de-gassing, and consolidation, are described. The merits and deficiencies of the various processes for each step are compared. The key to successful application of Al powder metallurgy alloys appears to be the de-gassing and consolidation of the powder. The properties of several new PM alloys are compared, with particular emphasis on high-strength, corrosion-resistant alloys and alloys developed for use at elevated temperatures.

### 1. Introduction

Powder metallurgy (PM) is the manufacture, processing, and consolidation of fine metallic particles to produce a metal which often has superior properties resulting from a refined and uniform microstructure.

PM actually predated ingot metallurgy (IM) because of early man's inability to achieve the temperatures capable of melting metals [1]. For example, the Egyptians fabricated iron tools and weapons by hammering iron-rich particles that were heated to temperatures below their melting point. This technique is an example of man's early use of pressing and sintering. Advances in furnace technology pushed PM aside for centuries until the 1800's when platinum and tungsten, because of their high melting-points, could be made only by PM. Today, cemented carbides [2] and tungsten filaments [3] are made exclusively by PM.

Air-frame manufacturers are seriously evaluating the use of aluminium PM alloys because sophisticated air-frame designs require materials having increased specific modulus (Young's

modulus  $\div$  density) [4], higher strength at room and elevated temperatures, and greater resistance to fatigue, corrosion, and stress corrosion [5, 6] than are currently available with conventional aluminium alloys. Interest in PM is evidenced by the considerable government contract activity in the field and by the discussion of this work at a recent conference [7]. For example, research was recently funded by NASA and AFML to develop PM alloys having superior room-temperature or high temperature properties [4, 5, 8-18]. Moreover, supersonic cruise aircraft research (SCAR) has been seeking PM materials having superior properties at intermediate temperatures (135°C). In addition, numerous technology review papers and reports [4-6, 9, 10, 19-25] reflect the keen interest of the aircraft industry and, to a lesser extent, the automotive industry [26] in PM.

At present, high-strength Al-PM alloys are being used on a trial basis in a few commercial applications. It appears that potential manufacturers and users are waiting to see how well the alloys succeed before selecting Al-PM alloys for other applications.

The state-of-the-art of PM technology will be reviewed. First, the metallurgical reasons for interest in PM will be discussed and then it will be shown that improvements in IM are reaching the point of diminishing returns. These topics are followed by a detailed description of PM technology that introduces the advantages of PM techniques. The subsequent three sections compare the properties of various PM alloys with each other and with their IM counterparts. Finally, technical conclusions will be drawn concerning aluminium PM alloys.

## 2. Why powder metallurgy?

Powder metallurgy enables the fabrication of material having superior properties because *small* particles of material can be processed. Thus, PM allows:

- (a) the realization of rapid cooling rates;
- (b) the introduction of strengthening features\*

from the powder surfaces.

It is a general rule of metallurgy that the finer the scale of strengthening features, the better the mechanical properties of the resulting alloy. This rule-of-thumb arises because the degree of strengthening obtained by impeding the motion of dislocations with obstacles is inversely proportional to the mean-free-path between the obstacles [27, 28]. In addition, smaller dispersed particles [29] are less apt to serve as fracture-initiating flaws than larger particles. Also, refinements in grain size [30] and precipitate size [31, 32] often increase corrosion resistance.

The rapid cooling-rates made possible by PM can refine features and improve properties in several ways. For example, grain size can be reduced [33] because of the short time available for nuclei to grow during solidification. In addition, rapid cooling can increase the alloying limits in aluminium [34, 35] by enhancing supersaturation enabling greater precipitation-hardening without the harmful segregation effects that occur when IM alloys are over-alloyed [36]. Moreover, elements that are essentially insoluble in the solid state are often soluble in the liquid state and may be uniformly dispersed in the powder particles during rapid solidification [16, 33, 34]. Non-equilibrium metastable phases [37] or atom "clusters" [38] that do not exist in more slowly cooled ingots can be created by the rapid solidifi-

cation-rate and these phases often increase strength. Finally, precipitation of equilibrium phases that are deleterious to mechanical or corrosion properties can be suppressed by rapid cooling [10].

The introduction of strengthening features from powder surfaces can be accomplished on a fine scale because of the large surface-to-volume ratio of the powder particles. Oxides can easily be introduced on a fine scale from powder surfaces by mechanical attrition, thereby producing oxide dispersion strengthening (ODS) [39]. Carbides [40] and essentially insoluble dispersoids [11] can be introduced in a similar way. Cold-working each powder particle by ball-milling results in increased dislocation strengthening and, upon consolidation, a finer grain (and sub-grain) size than that obtained by working a larger ingot.

Thus, by its very nature PM technology has advantages for improving the properties of alloys.

## 3. Improvements in ingot metallurgy technology

Efforts to improve ingot metallurgy technology were undertaken in the 1970's [6, 21, 22, 41–46, 49, 50], some of which are still being pursued.

For example, Staley [46], of Alcoa, studied the effects of constituent particles and impurity levels on the mechanical properties of 7xxx alloys. He found that their toughness could be improved by decreasing the volume-fraction of constituent particles. This is most readily achieved by increasing base alloy purity. Others [47, 48] have also noted the adverse effect of large particles on the toughness of 7xxx IM alloys. Staley also found that the size of soluble, constituent particles can be refined by thermomechanical treatments. Both of these improvements increase alloy costs. He recommended decreasing the Mg-content and increasing the Cu-content in order to improve toughness. Staley's work led to the development of alloys 7050 and 7475 [49, 50].

Hyatt [51] and Hyatt and Quist [52] (of Boeing Corporation) have been working to improve properties of 7xxx and 2xxx IM alloys for use in Boeing's new airliners (the 757 and 767). They found [21] that increasing the Zn/Mg ratio to 3.5 and raising the copper-content to between 1.7 wt% and 2.3 wt% in 7xxx alloys enhanced resistance to fatigue-crack growth. Their

\*Strengthening features are microstructural obstacles to dislocation motion, for example, solute atoms, GP-zones, precipitates, dispersed oxides, other dislocations, etc.

modifications in alloy composition, along with increases in base-metal purity and their development of thermomechanical treatments (TMTs), led to new IM alloys: 2324 T39 and 7150 T651 plate, and 2224 T3511 and 7150 T6511 extrusions. The TMTs that were developed improved the strength, toughness, and fatigue resistance of the 2xxx alloys. However, simultaneous improvements in strength and toughness of the 7xxx alloys could not be achieved. The combinations of yield strength ( $Y$ ) and fracture toughness ( $K_{Ic}$ ) of the new 7xxx alloys are similar to those of Alcoa's new PM alloys. However, the new IM alloys do not have the corrosion and stress-corrosion cracking (SCC) resistance of the PM alloys. Despite Hyatt's successes in Al-IM alloy development, he believes that little more strength can be obtained from IM alloys of conventional composition without sacrificing toughness. He does, however, see promise for lithium-containing aluminium base IM alloys.

Alcan Corporation [44] undertook a similar programme to improve the properties of 7xxx alloys and developed alloy DTD 5120, which is equivalent to alloy 7010 and similar in composition to alloy 7050. Exfoliation corrosion resistance was increased with respect to existing alloys; however, the alloy has a tensile strength of only 538 MPa, which is lower than the level of about 600 MPa presently sought by the aerospace industry [53, 54].

Wanhill [43] and Wanhill and Van Gestel [41] have improved the fatigue properties of 7xxx alloys by thermomechanical treatment but caution that the methods they have developed are costly. In a survey on TMT of Al-alloys [55] they conclude that only one type of TMT – a treatment for 2xxx alloy sheet – seems commercially practical at present.

Improvements in IM alloys are reaching the point of diminishing returns because the small improvements that may result from enhanced purity or additional TMT increase costs. Moreover, as will be discussed in detail later, the overall improvements in properties are not as great as those obtainable by using PM technology and, for this reason, PM alloys very well may replace IM alloys for many applications requiring high strength and corrosion resistance.

#### 4. Review of powder metallurgy technology

Aluminium powder metallurgy comprises three general steps:

- (a) powder production;
- (b) powder processing (optional);
- (c) de-gassing and consolidation.

First the powder is made [39]. It may then be mechanically processed (e.g., ball-milled) to produce powder of the desired microstructure. Aluminium powder has a high affinity for moisture [56, 57] and the elevated temperature necessary for the subsequent consolidation of Al-powder causes the water of hydration to react and form hydrogen, presenting a safety hazard and causing porosity in the formed product. Hence, powder exposed to ambient air often must be de-gassed prior to complete consolidation. After thorough de-gassing, the individual particles are consolidated to bulk metal by the application of heat and pressure. It is most cost-effective to consolidate immediately after de-gassing in order to avoid re-heating the powder. This consolidation step may be to form a billet, which can receive other forming operations. Alternatively, the powder can be directly consolidated into final-product form, i.e., extrusions, forgings, rolled sheet, etc.

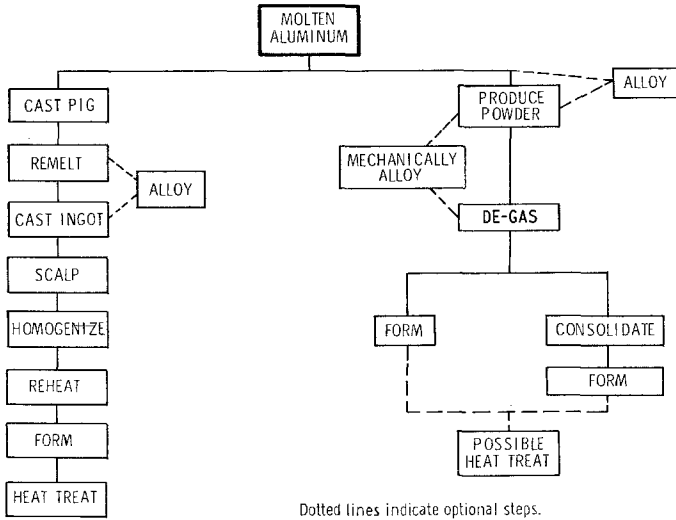
Fig. 1 compares the processing steps required to produce material by IM with those needed for PM. Various PM consolidation procedures are included in Fig. 2. It is evident from these figures that PM offers a reduction in the number of steps necessary to produce a formed metal product. The steps in aluminium PM will now be discussed in greater detail.

##### 4.1. Powder production

Atomization [12, 58–60] is the process most widely used to produce aluminium powder. Liquid metal is sprayed through a nozzle, and the very fine droplets of metal that form are rapidly cooled, usually by a cooler fluid (gas or liquid). The rapid cooling rates obtained ( $10^3$  to  $10^6$  K sec<sup>-1</sup>) [58, 60] are a direct consequence of the fine droplet size and are obviously much greater than the cooling rates obtainable by conventional casting. Numerous variations of the atomization process have been made and are described in two reviews by Grant [58, 59].

Splat-cooling is a process in which cooling rates even greater than those obtained in gas-atomization can be achieved [58]. Liquid metal is either dropped, sprayed, shot [33] or spun [61] against a chilled surface of high thermal conductivity. A copper plate or wheel [62, 63] which is

Figure 1 Comparison of ingot and powder metallurgy.



usually grit-blasted [64, 65] is often used. Cooling rates of  $10^5 \text{ K sec}^{-1}$  are commonly achieved [10, 38] and even higher rates have been reported. For instance, Lebo and Grant shot atomized molten Al-droplets against a grit-blasted copper plate and attained a cooling rate of  $10^8 \text{ K sec}^{-1}$  [64]. In addition, Franetovic *et al.* [66] used Grant's curves [67], relating grain and dendrite size to cooling rate, to estimate a mean cooling rate of  $10^7 \text{ K sec}^{-1}$  and a maximum rate of  $10^9 \text{ K sec}^{-1}$  on the thinnest areas of their splat-cooled powder particles.

Powder may also be made by grinding or milling consolidated metal [39]. This method suggests the possibility of consolidating aluminium

machining chips by PM techniques and avoiding scrap-melting costs. Electrochemical precipitation also is used to produce aluminium powder [68].

These processes are the most important ones for producing powder. The numerous variations [12, 58, 59, 61, 69] in these powder production methods will not be discussed in this review.

#### 4.2. Mechanical powder processing

Mechanical powder processing is an optional procedure undertaken to control powder size and to introduce strengthening features into the powder microstructure. For example, powder made by atomization can be mechanically pro-

#### POWDER CONSOLIDATION

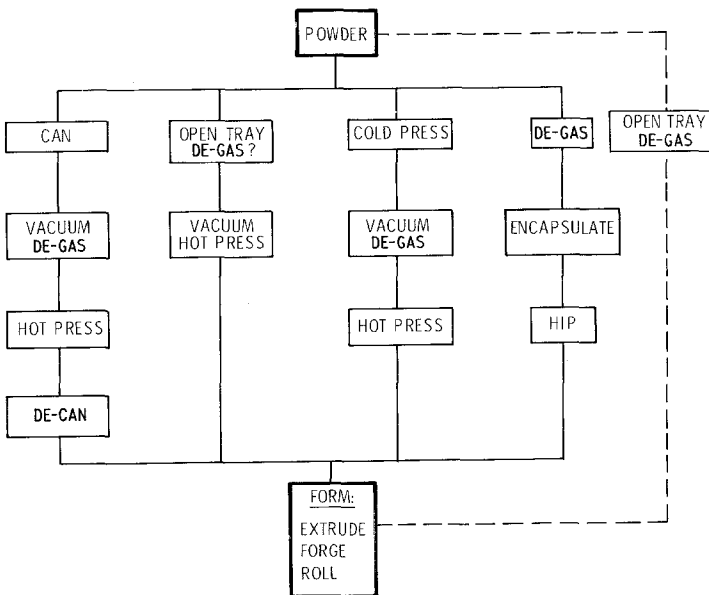


Figure 2 Powder consolidation.

cessed to disperse phases that improve the mechanical properties of the final product.

#### 4.2.1. Sintered aluminium powder

Irmann [70, 71] found that ball-milling aluminium powder in an 8% oxygen atmosphere caused the surface oxide-layer of the powder to be crushed and dispersed in the Al-matrix upon consolidation; he called the material sintered aluminium powder (SAP). The ball-milling can be performed in oil [72], or with ~ 3% stearic acid [39], to prevent excessive welding of powder particles. The oxide dispersion strengthening (ODS) produces high room-temperature strength in consolidated product (350 to 410 MPa tensile strength) and also excellent elevated temperature properties [71, 73]. Ansell [74] attributes the attractive mechanical properties of SAP to the de-activation of normal dislocation sources which occurs during hot-deformation. Mobile dislocations move into the vicinity of the oxide particles and are anchored in place, forming a three-dimensional dislocation network. In order for deformation to take place, dislocations must nucleate from sources other than normal, such as grain boundaries, which require large stresses even at elevated temperatures. Two papers by Goetzel [75, 76] review the early SAP research.

Numerous investigators have superimposed other strengthening mechanisms onto the ODS of SAP. For example, Jangg and Kutner [40] found that ball-milling aluminium with carbon black caused the carbon to become dispersed on the powder surfaces and formed finely dispersed  $Al_4C_3$  upon consolidation. The resulting alloy is thereby strengthened by both oxide and carbide dispersions. Bufferd and Grant [77] and Reynolds *et al.* [78] have successfully superimposed solid-solution strengthening on SAP. Park and Park [79] have superimposed intermetallic dispersion strengthening on SAP. Finally, Cevesara and Fiorini [80] have combined precipitation-strengthening and ODS in their SAP alloys.

Numerous investigators [81–84] have studied the effect of TMT on the properties of SAP and have found that the alloy properties can be greatly altered by changes in extrusion [82, 84] and drawing [83] parameters.

#### 4.2.2. Mechanical alloying

The mechanical alloying process is a high-energy, ball-milling operation and represents an improve-

ment over SAP processing. The milling often is performed in a stirred ball-mill, called an attritor. As in SAP, a dynamic balance is created between welding and fracture of the powder particles during milling [85]. This balance is controlled by small amounts of organic surfactants, which inhibit welding and also introduce dispersoids into the alloy. Dispersoids are also introduced from the oxide initially on the powder surfaces, in a manner similar to SAP, but the resulting dispersion is more uniform [86]. The process also disperses carbon in the aluminium matrix, which may form aluminium carbide upon consolidation [11]. Insoluble alloying elements may also be beaten into a fine dispersion by mechanical alloying [11, 85]. Moreover, the severe working of the powders produces a very fine grain-size and suggests that substructural strengthening [87–89] (high dislocation density and fine sub-grain size) may exist. These strengthening mechanisms can be superimposed on solid-solution strengthening. Hence, a great advantage of mechanical alloying is that all the following strengthening mechanisms can be superimposed:

- (a) oxide dispersion strengthening;
- (b) carbide dispersion strengthening;
- (c) fine grain-size strengthening;
- (d) high dislocation density and sub-structural strengthening;
- (e) solid-solution strengthening.

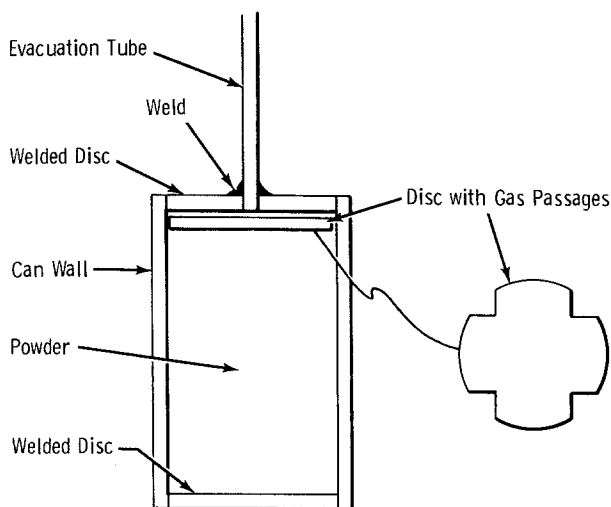
Note that strengthening by precipitation, the primary means of strengthening in high-strength IM alloys, need not be present. Thus, high strength in the consolidated product is achieved without the sacrifice of corrosion resistance which often accompanies the presence of precipitates [31, 32, 90–92]. The aforementioned strengthening mechanisms can also be superimposed on precipitation-strengthening when ultra-high strength is essential but corrosion resistance is of secondary importance.

### 4.3. Powder de-gassing and consolidation

#### 4.3.1. De-gassing

As mentioned earlier, the reaction between aluminium and water at the elevated temperatures necessary for consolidation results in the evolution of hydrogen. The reaction is extremely dangerous if the powder is confined during consolidation because the rapidly evolving gases can cause a pressure build-up and may even cause an explosion. Therefore, it is essential in aluminium PM that the powder contains only minimal amounts of water-of-hydration prior to consolidation.

Figure 3 De-gassing can.



Powder should be de-gassed at a temperature equal to, or greater than, any temperature reached during either consolidation, forming, or service. Consolidated products that experience a greater temperature than the de-gassing temperature can be damaged by gas evolution, producing porosity and/or surface blistering [11]. Unfortunately, very high de-gassing temperatures or prolonged de-gassing times anneal strength from the powder [93–95]. Consequently, the time–temperature sequence of de-gassing is often the key to producing a PM product with excellent properties.

Soviet researchers [96] found that aluminium powder that is de-gassed at elevated temperatures under an argon stream does not re-hydrate when exposed to air until after about five days. They attribute this effect to the slow rate of argon desorption. This result suggests that Al powder can be de-gassed in an atmosphere of argon in an unconfined, open tray and then transferred to a compaction apparatus without re-hydrating upon exposure to air; removing a small volume of argon is easier than removing hydrogen formed by re-hydration. This method is promising because it reduces the de-gassing time and therefore increases throughput and lessens powder annealing. However, more recent Soviet work shows superior properties for material de-gassed in a vacuum [97].

Roberts [94] is keenly aware of the ill effects of a prolonged de-gassing time at elevated temperature. He has performed experiments to delineate the lowest de-gassing temperatures and shortest de-gassing times which will still enable a pore-free material to be produced. He found [94] that de-gassing at about 310°C until achieving a pressure of  $\leq 4 \times 10^{-4}$  torr was sufficient to

produce blister-free consolidated product. De-gassing at 340°C until a pressure of  $3 \times 10^{-4}$  torr was achieved leaves the powder with H<sub>2</sub>O levels undetectable by his analysis.

#### 4.3.2. Consolidation methods

**4.3.2.1. Direct powder forming.** If the powder has been properly de-gassed, it may be directly consolidated to final product form [98]. Lyle and Cebulak [8] pointed out that, for extrusion at high extrusion ratios, a separate compaction step is not necessary, and Naeser [98] has demonstrated this using a conventional extrusion press. Net shape powder-forging is possible [99–101] and saves machining costs. However, hot isostatic pressing (HIPing) [2, 102], which is discussed later, appears to be the most attractive method for net shape forming, provided that the powder surfaces do not have a particularly thick oxide layer. For sheet products, Naeser reported [98] that the equipment needed for direct powder-rolling is very similar to that used for conventional rolling. Soviet scientists have reported that lubrication can be used to improve powder-rolling [103]. Johnson [104] pointed out the low-cost potential of direct powder-rolling. The Reynolds Aluminum Co. is presently operating a commercial, direct powder-rolling mill [105].

**4.3.2.2. Can vacuum de-gassing.** A commonly used means of de-gas–consolidation involves placing the powder in a metal can fitted with an evacuation tube (Fig. 3). The can is then vacuum-de-gassed while being heated to the consolidation temperature. When a suitable vacuum is reached at this temperature, the tube is mechanically crimped or

sealed by welding, and the billet is hot-pressed to full density. An extrusion press with a blind die is commonly used [11, 106]. The advantages of this method are:

(a) consolidation can be performed using readily available equipment, for example, an extrusion press fitted with a blind die;

(b) a fully-dense, thoroughly out-gassed product results.

The disadvantages of this method are:

(a) canning and de-canning add to costs;

(b) a blocked evacuation tube may cause the can to explode;

(c) the time needed for the powder in the centre of the can to reach the de-gassing temperature is often long and can result in excessive powder-annealing.

Roberts [107] suggested evacuating a can containing Al powder to low pressure levels at intermediate temperatures (310–430°C) to remove water-of-hydration while reducing the extent of powder annealing. He recently developed [95] a patented procedure of vacuum de-gassing at intermediate temperatures (about 370°C), back-filling with a depurative gas (very-dry nitrogen), and re-evacuating the depurative gas. Repeating this procedure several times enables the production of a blister-free consolidated product having excellent strength and ductility properties.

**4.3.2.3. Vacuum hot-pressing.** Vacuum hot-pressing in a re-usable chamber eliminates the cost of canning and de-canning. The powder is introduced into a compaction chamber and heated under vacuum to the compaction temperature. When the desired temperature and vacuum are reached, the powder is hot-pressed to 100% density. Although vacuum hot-pressing equipment is expensive, possible advantages may be obtained through its use. It is believed that if the method is preceded by a short-duration, open-tray de-gassing operation at a temperature greater than any the alloy will experience during forming or service, then compaction can proceed at a lower temperature, thereby avoiding unnecessary powder annealing and producing, finally, blister-free material.

**4.3.2.4. Alcoa's cold-press-de-gas-hot-press method.** In order to eliminate canning, Alcoa [108, 109] has:

(a) cold-pressed powder to 70–80% density;

(b) vacuum de-gassed;

(c) hot-pressed to 100% density.

This method has worked well, but, occasionally, canning was still necessary after Step a. In a variation of this method [18, 109], cold isostatic pressing (CIP) to 70% density was substituted for the first step. In this variation, powder is put into a re-usable rubber bag and placed in a fluid (often argon) under high pressure, thereby partially consolidating the powder. Alcoa experienced leakage using this method [18] and has for the present returned to cold-pressing. Van Cleave [110] foresees an optimistic future for CIP.

**4.3.2.5. Hot isostatic pressing (HIPing).** This consolidation technique [2, 3, 102, 110, 111] involves the following steps. First, the powder is placed in a container made of a material that plastically deforms at the consolidation temperature, for example, a polymeric material, a soft metal, or glass. Then, the container may be pre-heated in a conventional furnace and transferred to the hot isostatic press, or may be heated in the HIP chamber itself. The powder is then brought up to temperature under fluid pressure (often argon), resulting in a 100% dense billet.

The obvious questions arise as to when and how the powder should be de-gassed. If a metal can is used, the powder can be vacuum de-gassed in the pre-heat furnace, thereby adding both canning and de-canning costs and presenting the problem of a long exposure at an elevated-temperature. With open-tray de-gassing, one can use less expensive glass or polymeric containers that are designed to pop off by thermal contraction when the billet is cooled after HIPing. This latter approach seems to be the more attractive alternative, and when it is combined with pre-heating outside the HIP, the cycle-time is reduced. One possible cost-effective procedure sequence is:

(a) open-tray de-gas at high temperature for a short time;

(b) cool the powder and transfer it to a polymeric container;

(c) pre-heat at a HIPing temperature lower than the de-gassing temperature;

(d) transfer while hot to HIP;

(e) hot isostatically press the container;

(f) remove from HIP, cool, container pops off.

The only disturbing inefficiency of this method is the cooling and re-heating that follows open-tray de-gassing. These steps are necessary to avoid the

TABLE I Comparison of tensile properties of IM and PM extrusions of alloys of commercial composition

Alloy	Method of formation	Atomized (A) or splat-cooled (S)	Condition	Ultimate tensile strength, UTS (MPa)	Yield stress, YS (MPa)	Elongation (%)	Reference number
3003	PM	(A)	As-extruded	207	145	24	[34]
3003	IM		As-extruded	131	83	32	[34]
5083	PM	(A)	As-extruded	400	262	14	[34]
5083	IM		As-extruded	303	138	28	[34]
2024	PM	(A)	T-4	558	393	16	[34]
2024	IM		T-4	558	393	16	[34]
7075	PM	(A)	T-6	662	614	15	[34]
7075	IM		T-6	648	593	11	[34]
2024	PM	(S)	T-4	543	326	24	[64]
2024	IM		T-4	464	277	22	[64]
3003	PM	(A)	Cold-drawn 80 %	NA*	255	NA	[34]
3003	IM		Cold-drawn 80 %	NA	255	NA	[34]
7075	PM	(A)	T-6510	671	622	14.0	[115]
7075	IM		T-6510	679	627	12.6	[115]

\* Not available

re-hydration of the hot powder that would occur upon exposure to ambient temperatures during encapsulation. Re-hydration can be avoided if encapsulation occurs in a heated, controlled-atmosphere chamber. The method outlined in a-f above has numerous advantages, namely:

- (i) the extent of powder annealing is greatly reduced;
- (ii) net shape compacts having 100% density are produced;
- (iii) canning and de-canning costs are reduced;
- (iv) large billets and/or many pre-forms of various shapes can be made in one production cycle.

**4.3.2.6. The hot-pressing technique of IIT Research Institute.** IIT Research Institute has developed a hot-compression process which consolidates metal into net shape parts or forging stock within a very short pressing time (0 to 2 sec) [112, 113]. The method was developed to consolidate relatively coarse particles of scrap metal or “needles” made by perforated-cup spinning of molten scrap. In either case, since the particles being consolidated are coarser than powder, particle flow is facilitated and the safety problems related to most PM techniques are greatly reduced. This process may even obviate de-gassing. This method offers substantial cost reduction possibilities because, for example, the machining chips can be consolidated into a useful form without melting the scrap.

**4.3.3. Concluding remarks on powder de-gassing and consolidation**

At present, when a consideration is made of

capital costs, productivity, safety, and the resulting material properties, it is unclear which de-gas-consolidation process is the superior method. However, the open-tray de-gassing step appears to be extremely desirable in any optimum procedure because in this way powder can be de-gassed quickly with reduced safety hazards.

In a possible future development, powder manufacture could perhaps be performed so that air and moisture could never contact the powder. Vacuum interlocking chambers could be installed to transfer powder from the manufacturing apparatus to the consolidation chamber, thereby eliminating de-gassing. This approach presents costly engineering problems, but ultimately may be commercially feasible.

**5. Alloys of conventional composition made by powder metallurgy**

Several investigators have made alloys of conventional composition by powder metallurgy [34, 63, 64, 69, 114-117]. In general, the technique leads to an improvement in mechanical properties (see Table I).

For example, Voss [115, 116] has investigated alloys 2024 and 7075 made both by PM and IM in order to assess the effect of PM processing on the performance of these alloys under fatigue-limiting conditions. He found that PM reduced the grain size by an order of magnitude. In addition, constituent particle size was decreased. Voss found that PM also improved resistance to recrystallization and found that powder metallurgy formed alloy 7075 had increased strength-isotropy. Great improvements in fatigue resistance were also



TABLE II Fatigue life to strength ratio from Voss, [115]

Alloy	Method of formation	$S_N^*/UTS$	$S_N^*/YS^\dagger$
7075 T6510	PM	0.212	0.230
	IM	0.156	0.169
2024 T3510	PM	0.239	0.304
	IM	0.214	0.285

\*  $S_N$  = stress for  $10^7$  cycle life.

† 0.2 % off-set yield strength.

obtainable by PM. For instance, in notched fatigue, PM 2024 T3510 alloy had [116] a 46 % increase in stress for 50 % probability of failure and a 23 % increase in stress for 10 % probability of failure compared with IM 2024 alloy. PM 7075 T6510 alloy showed a 20 % increase in stress for 50 % probability of failure and a 52 % increase in stress for 10 % probability of failure compared with IM 7075 alloy. Table II compares fatigue data from the PM alloys investigated by Voss with those of equivalent IM alloys.

Voss did find PM 7075 alloy to be inferior to IM 7075 alloy in two disturbing areas. The fracture toughness of PM 7075 alloy was less than that of IM 7075 alloy. Voss attributed this finding to an increased volume-fraction of constituent particles in the PM alloys. More alarmingly, he found PM 7075 alloy to have an increased fatigue-crack growth rate (FCGR) compared with IM 7075 alloy, at stress intensity levels, ( $\Delta K$ ), less than  $9 \text{ MNm}^{-3/2}$ . Holloway [118] found similar behaviour in MA87 alloy, a more advanced PM alloy. This disturbing increase in FCGR, seen only at low  $\Delta K$  levels, has caused air-frame manufacturers to view PM alloy commercialization with caution.

With respect to IM equivalents, some investigators [64] found that conventional alloys made by PM had superior strength properties, whereas others [34, 115] found similar strength properties (see Table I). In some cases, the increased strength is attained at the expense of ductility. In general, however, corrosion and fatigue resistance are improved by PM technology.

It should be emphasized that alloys of conventional composition made by PM do *not* represent optimized PM alloys [116, 119]. These ‘conventional PM alloys’ often are made because substantial IM data exist and comparison between PM and IM can be more easily made. However, as good as the improvements in properties are for conven-

tional PM alloys, even greater gains can be realized by modifying alloy composition to take advantage of the full potential of PM technology (see Section 2).

## 6. High-strength aluminium base alloys formed using powder metallurgy techniques

Several high-strength aluminium alloys formed using powder metallurgy, exist in both the experimental and developmental stages and the data available on them will now be compared. The reader should consider the difficulty of making comparisons when different test methods were used by various investigators; this difficulty is especially troublesome for corrosion data. In addition, note that most tensile strength data are from extrusions and it is generally easier to obtain ultra-high strength levels on extruded rod than on plate or forgings.

### 6.1. Alloys in the developmental stage

#### 6.1.1. MA67 and MA87 alloys\*

Alcoa has developed several melt-atomized alloys, mostly through government contract funding [8, 18, 108, 109, 120–123]. Cobalt, an insoluble element, has been introduced into the two superior alloys, MA67 and MA87, by the rapid solidification of the atomization process. The basic composition of the alloys is an empirically modified 7xxx alloy plus cobalt [108, 124]. (Compositions of key alloys are included in Table III.) The cobalt reportedly refines grain size and provides elevated- and room-temperature strength while maintaining corrosion and stress-corrosion resistance. However, a higher cobalt content lowers toughness and fatigue-crack growth resistance [124]. Of the two alloys, MA87 has greater corrosion resistance and MA67 has greater strength. On a commercial scale, Alcoa’s alloys have shown combinations of properties superior to those of equivalent IM alloys. For example, at the same strength level above 450 MPa, MA67/87 alloys have much better SCC resistance (Fig. 4 and Table IV) than 7075-T6 alloy. Alternatively, the strengths of MA87/67 alloys are superior to that of 7075 alloy in the corrosion resistant temper (T73). MA87 has between 30 and 80 % better notched fatigue strength over existing IM alloys at the 550 MPa tensile strength level [6]. Table V [121] illustrates the superior

\*These alloys are the experimental precursors of commercial alloys CT90 and CT91, respectively. These alloys are also called X7090 and X7091, respectively.

TABLE III Composition (wt %) of high-strength PM and IM alloys

Alloy	IM or PM	IM	Mg (wt %)	Zn (wt %)	Cu (wt %)	O (wt %)	C (wt %)	Co (wt %)	Fe (wt %)	Si (wt %)	Mn (wt %)	Cr (wt %)	Ti (wt %)	Zr (wt %)	Reference number
IN 9051 (published)	PM	3.2-4.0				0.9-1.8	0.3-1.1		0.8 (max)	0.8 (max)					[147]
IN 9051 (typical)	PM	4		1.4	0.7				0.05	0.1					
MA87	PM	2.5	6.5	1.5				0.4	0.05	0.06					[121]
MA67	PM	2.5	8.0	1.0				1.5	0.07	0.06					[121]
MR61	PM	2.5	8.5	1.5	< 0.5			0.6	< 0.2	< 0.15				0.2	[54]
7075	IM	2.5	5.6	1.6					0.7	0.50	0.30	0.3	0.2		
7178	IM	2.8	6.8	2.0					0.7	0.50	0.30	0.26	0.2		
7049	IM	2.5	7.7	1.6					0.7	0.50		0.15		0.12	
7050	IM	2.2	6.2	2.3											
7475	IM	2.2	5.7	1.6											0.22

TABLE IV Comparative longitudinal properties of die forgings of PM alloys MA67 and MA87 with the equivalent IM 7075 alloy (after [121]).

Alloy	Time* at final ageing temperature (163° C) for PM alloys (h)	Ultimate tensile stress (UTS) (MPa)	Yield strength (YS) (MPa)	Elongation (%)	Ratio of notched tensile strength to tensile yield strength	Fracture toughness, $K_{Ic}$ MN m <sup>-3/2</sup>	SCC - Days to fail at stress (MPa)	SCC - Days to fail at stress (MPa)	SCC - Days to fail at stress (MPa)
MA67	1	641	600	10	0.9	23.2	29, 46, 47	NA	3 > 84 <sup>a</sup>
MA67	12	586	538	12	1.14	NA†	84, 2 > 84 <sup>a</sup>	NA	3 > 84 <sup>a</sup>
MA87	4	607	558	12	1.25	36.1‡	71, 78, 84	NA	3 > 84 <sup>a</sup>
MA87	18	565	510	14	1.34	NA	2 > 84 <sup>a</sup>	3 > 84 <sup>a</sup>	2 > 84 <sup>a</sup>
7075-T6		641	572	12	1.34	NA	1, 2, 2	NA	2, 3, 3
7075-T73		503	434	13	1.45	NA	NA	NA	No failures anticipated

\* Prior heat-treated at 488° C for 2 h, cold water quenched, then heat-treated at 96° C for 24 h.

† Not available.

‡  $K_{Ic}$  because specimen was too thin for ASTM E399.

a The number to the left of the inequality denotes the number of specimens surviving after 84 days.

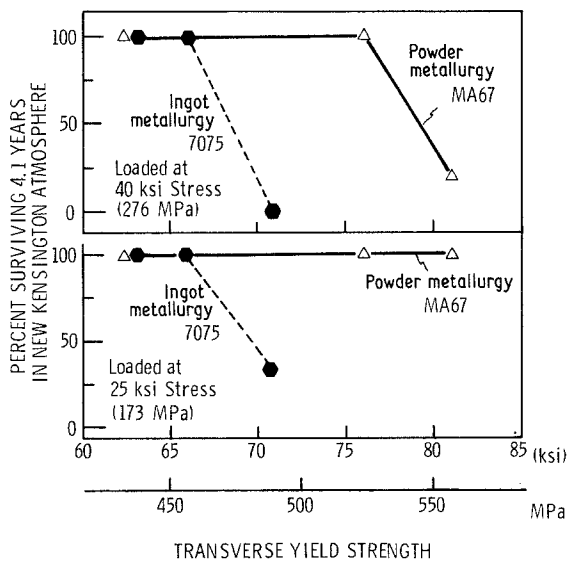


Figure 4 Comparison of stress corrosion resistance of MA67 with that of IM 7075 (after [121]).

toughness of MA87 compared with equivalent IM alloys, some of which have improved base purity. Otto [124] found that MA87 has a 35 to 48 MPa higher strength, equal ductility, and substantially higher toughness than the “improved” IM alloy, 7050. Fig. 5 demonstrates that MA67 has better *S-N* fatigue behaviour than 7075. On the other hand, recent data have revealed that MA87 has a higher fatigue-crack growth rate than 7075 at low stress intensity levels [6, 118]. However, the alloys tested were not compared at the same yield strength level and, therefore, the tests are currently being repeated by Alcoa.

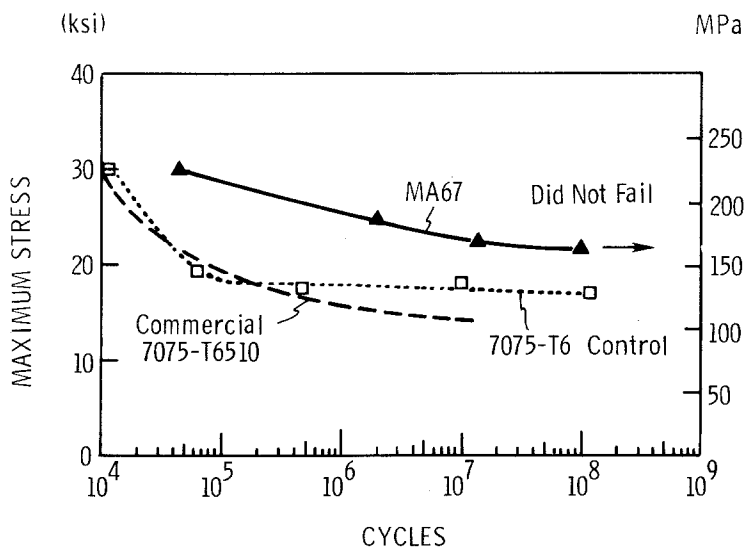


Figure 5 Notched axial fatigue performance of MA67 compared with that of IM 7075 (after [121]).

TABLE V Plane-strength fracture toughness,  $K_{IC}$ , of PM alloy MA87 plate and plate of various IM alloys (after [121]).

Alloy	PM or IM	Fracture toughness, $K_{IC}$ (MN m <sup>-3/2</sup> )	Yield stress YS (MPa)
MA87-A	PM	36*	490
MA87-B	PM	29	503
7475-T651	IM	30	448
7475-T7351	IM	36	372
7050-T3651	IM	29	434
7075-T651	IM	20	448
7075-T7351	IM	22	372
2124-T851	IM	24	421

\*  $K_{IQ}$  because specimen was too thin for ASTM E399.

The Alcoa alloys clearly are further developed than other Al PM alloys. Under Army Manufacturing Technology (MAN-TECH) sponsorship, Cebulak [18] scaled up MA87 and MA67 production to “plant-scale” (1545 kg) billets. Forgings, extrusions, and plates were made from the billets, which were fabricated according to the procedure in Fig. 6. Table VI illustrates that the tensile strength of extrusions made from experimental-scale (probably about 80 kg)\* billets is lower than that of plant-scale billets. This finding has revealed a limitation of the melt-atomized approach (and most probably of the splat-cooling approach), that is, alloys must be heat-treated to attain high strength and, for thick sections, much of the strength potential caused by the rapid solidification rate of the powder is lost during heat-treating. However, the scale-up did produce formed parts that had properties superior to those

\*It should be noted that Alcoa’s experimental scale is really a small commercial scale.

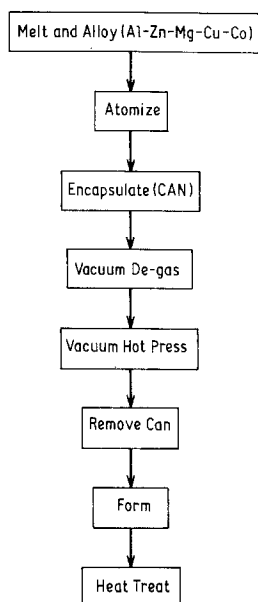


Figure 6 The consolidation procedure used by Alcoa to make 1545 kg billets.

of IM alloys [118], thereby demonstrating that PM alloys can indeed be manufactured on a “plant”-scale.

### 6.1.2. MR61 alloy

Kaiser has developed the melt-atomized alloy, MR61, which is similar in composition to the Alcoa alloys MA67 and MA87 (see Table III), but which additionally contains Zr, presumably for grain refinement. The strength and ductility properties of MR61, as determined from a limited scale pilot run, are excellent [54] (see Table VII) and are comparable with those of MA67.

### 6.1.3. IN 9051 alloy

INCO’s mechanically alloyed Al–4 wt % Mg material, IN 9051, derives its high strength from several superimposed strengthening mechanisms (see Section 4.2.2.). Precipitation strengthening is not necessary, so the corrosion and SCC resistance of the alloy greatly exceed those of 7xxx alloys having comparable strength. Corrosion data (Table VIII) [125] show that IN 9051 is superior to the competitive IM alloy, 7075. A patent application is pending for IN 9051 [93].

Unfortunately, the alloy is susceptible to work-softening during hot-working. For instance, in limited experiments, Pickens [93, 106] found that tensile strength decreases either with increases in extrusion ratio or increases in extrusion temperatures (above  $\sim 400^{\circ}\text{C}$ ). This work-softening is in addition to the softening experienced during elevated temperature de-gassing and has been attributed to dynamic recovery (annihilation of dislocations and sub-structure) or grain growth. For IN 9051 to be a commercially viable alloy, this phenomenon needs to be understood and controlled.

### 6.2. Comparison by Boeing of MA67, MR61, and IN 9051 alloys

Boeing purchased commercial-scale seat tracks, utilizing PM alloys, from Alcoa (MA67 and MA87), Kaiser (MR61), and Novamet<sup>†</sup> (IN 9051) and compared them for tensile properties, corrosion and SCC resistance, and fatigue resistance. At the time of this writing, no publications referring to this comparison were available and only some of the Boeing data could be obtained through private

TABLE VI Comparison of properties of Alcoa MA67 and MA87 extrusions made from experimental\* [121] and plant-scale [18] (1545 kg) PM compacts

Alloy	Scale	Final ageing time (h)	Ultimate tensile strength (UTS) (MPa)	Yield stress (YS) (MPa)	Elongation (%)	Estimated stress corrosion cracking (SCC) threshold (MPa)
MA67	Experimental	2	669	641	11	172
MA67	Plant	1	587	549	9	276
MA67	Experimental	6	621	593	10	$\geq 240$
MA67	Plant	6	544	494	11	310
MA87	Experimental	6	614	586	12	$\geq 310$
MA87	Plant	4	563	515	10.5	310
MA87	Experimental	14	565	524	16	310
MA87	Plant	14	541	492	11.5	310

\* Alcoa’s experimental scale is often on 80 kg billets which is large enough for many commercial applications.

<sup>†</sup> An INCO subsidiary.

T A B L E V I I Longitudinal properties obtained from commercial scale PM alloy extrusions

Alloy	Company	PM approach	UTS (MPa)	YS (MPa)	Elongation (%)	Reduction in area (%)	SCC threshold (MPa)	Reference number	Comments
MR61	Kaiser	Atomized	669	627	9.5			[54]	Data from Boeing seat tracks from limited scale pilot run.
			645	586	10			[54]	
MA67	Alcoa	Atomized	645	641	11		172	[121]	Data not from seat tracks, from 2" diameter extrusions.
			621	593	10		241	[121]	
MA87	Alcoa	Atomized	621	586	12		290	[121]	Data not from seat tracks, from 2" diameter extrusions.
			565	524	16		310	[121]	
IN 9051	INCO	Mechanically alloyed	586	545	5	20	545	[147]	Data from Boeing seat tracks. Excellent corrosion resistance, no SCC up to the YS.
			496	427	6	30	427	[147]	

TABLE VIII Corrosion rates in alternate immersion in 3.5% NaCl aqueous solution [125]

Alloy	Heat treatment	Duration (days)	Corrosion rate (mg day dm <sup>-1</sup> )
7075	T-651	30	1.93
7050	T-651	30	4.06
5083	H 112	30	0.143
5083	H 112	90	0.223
5083	H 112	250	0.341
IN 9051		90	0.096
IN 9051	As-extruded	250	0.037

These data were supplied courtesy of Dr J. L. Nelson, INCO Research and Development Center, Sterling Forest, New York, USA.

communications. In particular, no seat-track data on Alcoa's alloys and no fatigue data on any alloys were available. Table VII compares the data obtained at present. The Alcoa data are from earlier, small commercial-scale products [121]. The Kaiser data are taken from work on ~7 kg pilot-scale extrusions of the seat track geometry.

Alcoa has achieved excellent tensile properties from MA67 alloy: 669 MPa tensile strength and 11% elongation. However, the SCC threshold at this strength is low, ~170 MPa, but can be raised to ~240 MPa by sacrificing 50 MPa in strength. MA87 alloy has a SCC threshold of 310 MPa, but the tensile strength is lower at 565 MPa. MR61 alloy seat tracks at 621 to 669 MPa tensile strength and 9–10% elongation show excellent strength and ductility. These tensile properties for MR61 are quite similar to those of MA67. IN 9051 alloy has been extruded in the seat-track configuration and produced material of excellent surface finish, but of lower strength than desired. This occurred because of the aforementioned work-softening phenomenon. Novamet has produced commercial material of attractive properties (586 MPa UTS, 545 MPa YS, 5% elongation and no SCC up to YS) and is now attempting to increase the strength of commercial IN 9051 alloy extrusions.

Narayanan, of Boeing, has performed exfoliation corrosion tests on MA67, MR61, and IN 9051 alloys and has generated SCC data on MA67 and MR61 alloys [126]. IN 9051 has by far the best exfoliation corrosion resistance of the three alloys [126]. MA67 and MR61 have similar SCC and exfoliation corrosion resistance with MA67 perhaps marginally the superior in each property [127].

In summary, the melt-atomized alloys made by Alcoa and Kaiser have the finest strength–ductility

combinations commercially available; however, they may not have sufficient corrosion resistance and SCC resistance for low maintenance-cost applications in the highest strength tempers. The melt-atomized approach appears to lose some of its advantage over 7xxx IM alloys in thick sections where quench rates are limited. IN 9051 alloy is clearly the most corrosion and SCC resistant of the high-strength alloys. Commercial-scale strength properties in IN 9051 alloy have been marginal, perhaps due to excessive powder annealing during de-gassing and, to a lesser extent, work-softening. These problems can probably be controlled sufficiently on a commercial scale to produce high-strength material with IN 9051 alloy still maintaining its inherent corrosion and stress corrosion resistance advantage.

Boeing's comparative study of these recently commercialized alloys is important to demonstrate the commercial viability of Al-PM alloys. Success in the seat-track application will probably increase interest in one or more of these alloys and foster other applications.

### 6.3. Work in the experimental stage

Numerous investigators [34, 105, 121, 128–130] have reported unusually strong room-temperature tensile properties of experimental alloys (see Table IX). Tensile strengths of greater than 827 MPa demonstrate the potential for substituting Al PM alloys for other more expensive (e.g., titanium) and denser (e.g., titanium, steel) high-strength metals. For instance, Roberts [34] of Kaiser produced a melt-atomized, 10.36 wt% Zn–3.08 wt% Mg–2.03 wt% Cu–1.74 wt% Mn–0.2 wt% Cr alloy having a tensile strength of 820 MPa. This over-alloyed material did not reach the production stage because of its propensity to SCC [34].

Grant and co-workers at MIT have experimented with numerous splat-cooled Al-alloys [64, 69]. The best properties reported by Grant are UTS of 717 MPa and elongation of 9% [119], obtained by splat-cooling an alloy of composition similar to 7049 but with added Ni and Fe. The ductility at this strength level is outstanding and indicates a potentially bright future for the alloy. Grant is presently working with Lockheed on splat-cooled alloy development.

In addition, early Alcoa work by Haarr [129, 130] produced material having 879 MPa tensile strength and 855 MPa yield strength. This phenomenal strength was achieved by consolidating melt-

TABLE IX Best properties obtained on high-strength experimental PM alloys\*

Company of manufacture	Name of alloy	Process of powder manufacture	Basic composition (wt %)	Product form	Yield Stress, YS (MPa)	Ultimate tensile strength, UTS (MPa)	Elongation (%)	Reduction in area (%)
Kaiser [34]		Atomized	$\left\{ \begin{array}{l} 10.36 \text{ Zn} \\ 3.08 \text{ Mg} \\ 2.03 \text{ Cu} \\ 1.74 \text{ Mn} \\ 0.2 \text{ Cr} \end{array} \right.$	Extrusion	810	820	4	
Kaiser [34]		Atomized	$\left\{ \begin{array}{l} 12.32 \text{ Zn} \\ 1.8 \text{ Mg} \\ 1.95 \text{ Cu} \\ 0.2 \text{ Cr} \end{array} \right.$	Extrusion	743	750	8	
MIT [105]	7049	Splat-cooled	$\left\{ \begin{array}{l} + \text{ Fe} \\ + \text{ Ni} \\ + \text{ ODS} \end{array} \right.$	Extrusion	634	717	9	20
Alcoa [129, 130]		Atomized	$\left\{ \begin{array}{l} 9.87 \text{ Zn} \\ 4.06 \text{ Mg} \\ 0.85 \text{ Cu} \\ 1.25 \text{ Mn} \\ 1.06 \text{ Fe} \\ 1.39 \text{ Ni} \end{array} \right.$		855	879	1.2	
Alcoa [121]	MA67	Atomized	$\left\{ \begin{array}{l} 8 \text{ Zn} \\ 2.5 \text{ Mg} \\ 1.0 \text{ Cu} \\ 1.5 \text{ Co} \end{array} \right.$	Extrusion	641	669	11	
Alcoa [121]	MA87	Atomized	$\left\{ \begin{array}{l} 6 \text{ Zn} \\ 2.5 \text{ Mg} \\ 1.5 \text{ Cu} \\ 0.4 \text{ Co} \end{array} \right.$	Extrusion	586	614	12	
Alcoa [121]	Modified 7xxx	Atomized			641	683	5	
Silag [132]†	2024		+ 25 vol % SiC	Extrusion		641	1	
Pratt and Whitney [14]		Splat-cooled	$\left\{ \begin{array}{l} 9.8 \text{ Zn} \\ 7 \text{ Zn} \\ 2.5 \text{ Mg} \\ 1 \text{ Cu} \\ 0.8 \text{ Co} \end{array} \right.$		665	720	8	

\*None of the data in this table, other than that for MA67 and MA87, should be construed as representing commercial properties.

†This alloy has exceptional Young's modulus of  $1.25 - 1.72 \times 10^5$  MPa (roughly twice that of conventional aluminium alloys).

atomized Al–9.87 wt % Zn–4.06 wt % Mg–0.85 wt % Cu–1.25 wt % Mn–1.06 wt % Fe–1.39 wt % Ni powder. Similar properties were obtained with material containing negligible Fe and Mn, but containing 1.44 wt % Co. As Haarr’s work progressed, his goal changed from developing an Al-base alloy having a yield strength of 862 MPa to developing an alloy having: (a) a SCC resistance that is equivalent to commercial alloys, (b) a 10 % increase in UTS over conventional alloys, and (c) practical ductilities. The success of his work paved the way for future Alcoa alloy development.

Cox [12–15], of the Pratt and Whitney Aircraft Division of United Technologies, has made experimental Al PM alloys by centrifugal atomization. Cooling rates of  $10^5$  to  $10^6$  K s<sup>-1</sup> were achieved. Cox evaluated 7xxx alloys containing cobalt and with increased zinc content. He was able to increase the 0.2 % yield strength of a modified 7075 alloy (0.8 wt % Co and 9.8 wt % Zn) to 727 MPa [14] and attributes this great strength to the increased Zn-content. Some of Cox’s data are included in Table IX.

Alloy development is continuing at INCO on mechanically alloyed aluminium with substantial progress in the Al–Li [131], Al–Mg [117], and Al–Cu–Mg systems, but the work has not yet reached a suitable stage for publication.

Finally, Silag, an Exxon subsidiary, has developed SiC-whisker-reinforced alloys which use 2024, 6061, or 7075 for the PM matrix [132]. The alloy has high strength (620 MPa) but low ductility. However, its most interesting property is its exceptional Young’s modulus value of 1.25 to  $1.72 \times 10^5$  MPa (roughly twice that of conventional aluminium alloys). If the ductility of the alloy could be enhanced and if it could be welded without loss in strength, the alloy could be utilized in stiffness-limited applications. Silag believes this may be possible [133].

#### 6.4. Experimental Al–Li PM alloys

Many aircraft parts are stiffness-limited. This fact, coupled with the desire to reduce weight, has generated interest in alloys having high specific modulus values. Al–Li IM alloys are known to possess high specific modulus values [4, 5, 134–136]. For example, Alcoa has developed the IM alloy x2020 [135, 137, 138] which has a high specific modulus as well as excellent elevated temperature properties [139]. Alloy x2020 was withdrawn from commercial production because

segregation effects lowered toughness and ductility [140] and because lithium’s high reactivity caused problems during melting. Recently, Sanders [141] undertook the development of an Al–Mg–Li alloy made by IM. He, too, found that the alloys developed were ductility limited, and his work includes a fine discussion of the metallurgical explanations for the limited ductility.

PM offers the possibility of eliminating some of the problems associated with Al–Li alloys. For example, the rapid solidification effected by atomization or splat-cooling can greatly reduce segregation effects. Sankaran [69] splat-cooled alloys based on the 2024 composition with both 1 and 3 wt % Li. The refined microstructure, of the alloys with a grain size of 2–2.5  $\mu$ m and 1–2  $\mu$ m Al<sub>3</sub>Li particle distribution, improved *S–N* fatigue properties with respect to 2024 T4 alloy.

Grant [119], Wold [142], and Lewis [143] are presently experimenting with rapidly solidified Al–Li alloys made by mechanical alloying. Unfortunately, much of the data acquired by these investigators have not yet been published.

### 7. Experimental aluminium alloys for service at elevated temperatures

Irmann [70, 71] invented SAP and demonstrated its superior high-temperature strength and stability (room-temperature strength after elevated-temperature exposure). This was the first Al PM alloy to have excellent properties at elevated temperatures. Bufferd and Grant [77] have improved the elevated-temperature properties of SAP; however, SAP is often limited in use by its poor elevated-temperature ductility which results from a somewhat coarse, non-uniform oxide dispersion. By mechanical alloying, Benjamin and Bomford [86] developed alloys with elevated-temperature strength and ductility superior to SAP. Subsequently, numerous investigators have made experimental Al-alloys for elevated-temperature service by atomization [16, 17] and splat-cooling [33, 62, 64].

Considerable development of aluminium alloys for use at elevated temperatures is underway. For example, the AFML is funding the development of an aluminium PM alloy for service at 230–340 °C in two parallel efforts: by atomization at Alcoa [17] and mechanical alloying at INCO [11]. Many alloy systems have been examined by each contractor. Al–Fe–Co is Alcoa’s most promising alloy and Al–4 wt % Ti [144] Al–Fe, Al–Ni, and Al–Cr



TABLE X Elevated-temperature properties of experimental aluminium PM alloys

Alloy composition (wt %)	PM technique	Ultimate tensile strength (MPa)			Reference
		Room temperature	232° C	343° C	
Al-8.2 Fe-1.8 Co	Atomization (Alcoa)	503	339	183	[17]
Al-8.0 Fe-3.4 Ce	Atomization (ALCOA)	550	395	176	[17]
Al-4 Ti	Mechanical alloying (INCO)	379	252	186	[144]
Al-8 Fe	Splat-cooled	372	290*	172*	[33]
Al-8 Fe-1 Zr	Splat-cooled	303	421*	228*	[33]
Al-8 Fe	Splat-cooled	303	183	130	[146]

\* Estimated from graph.

[145] are INCO's leaders. In addition, splat-cooled Al-8 wt % Fe alloys made with, and without, additional alloying elements have been investigated by numerous European research groups [33, 62, 146]. Al-8 wt % Fe-1 wt % Zr and Al-8 wt % Fe-3 wt % Mn appear to have the best elevated temperature properties attained by splat-cooling [33].

Table X compares the elevated-temperature tensile properties of experimental alloys. The splat-cooled, Al-8 wt % Fe-1 wt % Zr alloy developed by Thursfield and Stowell [33] appears to have the best 230-340° C strength, uncovered in the present review. It is believed that the elevated-temperature properties of the mechanically-alloyed materials are not as good as are ultimately possible because of the ultra-fine grain size produced by mechanical alloying [11]. Towner [81] has observed that the tensile strength of SAP in the temperature range 315-427° C improves after the alloy undergoes secondary re-crystallization. It is possible that the inducement of secondary re-crystallization could also improve the properties of INCO's experimental alloys, which are strengthened by similar mechanisms.

Lebo and Grant [64] have examined 2024 alloy made by splat-cooling (see Table I). Room-temperature strength was improved by about 16% over IM 2024 alloy and, although stress rupture properties at 150° C were enhanced, the stress rupture advantage diminished almost completely at 204° C. This result suggests that precipitates coarsened during elevated-temperature exposure. Sankaran [69], while in Grant's group at MIT, reported a decrease in room-temperature strength upon exposing a splat-cooled 2024 + 3 wt % Li alloy to elevated-temperatures. In addition, Co<sub>2</sub>Al<sub>3</sub> precipitates have been observed to coarsen upon elevated-temperature exposure [17]. These observations suggest that the stability of precipitation-strengthened, splat-cooled alloys is questionable. Table XI includes the available stability data. Unfortunately, the exposure times differ, thereby preventing a conclusive comparison. The data do show that the mechanically alloyed materials have excellent stability [11], in that no discernable softening occurs for up to 100 h exposure at 343° C. After long exposure, the stability of the splat-cooled alloy remains

TABLE XI Stability data of high-temperature aluminium PM alloys

Alloy	PM Method	Room-temperature ultimate tensile strength after exposure at higher temperature (MPa)			Exposure time (h)	Reference number
		Exposure temperature 20° C	Exposure temperature 232° C	Exposure temperature 343° C		
Al (ODS)	Mechanical alloying	418	410	419	100	[11]
Al-1.8 wt % Ti	Mechanical alloying	361	361	355	100	[11]
Al-8.2 wt % Fe-1.8 wt % Co	Melt-atomized	577	427	183	1000	[17]
Al-8 wt % Fe	Splat-cooled	600	600	621*	1	[33]

\* 327° C exposure.

unknown. However, the tensile properties obtained for the alloy developed by Thursfield and Stowell are superior to those of other splat-cooled alloys and, as mentioned earlier, are the best uncovered in the present review.

It is interesting to consider mechanical alloying of splat-cooled powder. The strengthening effect of a fine dispersion of oxide could be superimposed on the metastable, coherent, iron-aluminium clusters produced by the splat cooling of Al-Fe alloys [33, 38, 62]. Whether or not the heavy working induced by mechanical alloying disturbs the strengthening microstructure (i.e., Zone A) [38, 65] of the rapidly solidified alloy is unknown, but the concept is worth investigating.

## 8. Concluding remarks

PM can be used to produce Al-base alloys having mechanical and corrosion properties superior to those of IM alloys. This is possible because PM refines strengthening features and enables manufacture of alloys having compositions not practical by IM. High-strength PM alloys are being produced commercially and may in the near future replace conventional 7xxx alloys for some applications. PM alloys for elevated-temperature use are under development and will almost certainly replace 2xxx alloys in certain aerospace applications. The possibility also exists that alloys may be developed which can replace titanium in some aerospace applications. The biggest barriers to Al PM commercialization are the problems associated with the de-gassing and consolidation of the powder. In addition, PM will face the usual acceptance problems of any new technology that threatens to replace one that is well-established.

The following list highlights the technical conclusions reached, based on the present review.

(a) Several new PM alloys, manufactured on both the experimental- and pilot production-scale (7 to 80 kg billet) have mechanical and corrosion properties which are superior to those properties for IM alloys.

(b) The non-heat-treatable alloy, IN 9051, manufactured by Novamet (an INCO subsidiary) has the best corrosion and SCC resistance of any high-strength Al alloy. Its experimental strength properties are excellent; however, at present, its commercial-scale strength is marginal for high-strength aerospace applications. Fatigue data are limited.

(c) Experimental PM alloys which are manu-

factured by using a rapid solidification rate (atomization and/or splat-cooling) have the best high temperature properties. A splat-cooled Al-8 wt% Fe-1 wt% Zr alloy made in Europe has the highest elevated-temperature strength uncovered in this review. This is a result of its very high rapid solidification rate (RSR) value, higher than that realized during gas-atomization.

(d) The rapid solidification approach does not eliminate the need for costly heat treatments. This has caused Alcoa's "plant-scale" mill forms (from 1545 kg billet) of the melt-atomized alloys MA67 and MA87 (also called CT90 and CT91, respectively) to have properties inferior to those obtained from the same alloys produced on a smaller scale.

(e) Recent fatigue data on MA87 alloy are less promising than earlier data which showed MA87 to have a fatigue resistance unequivocally superior to that of IM alloys. Comparison with IM 7050 alloy shows that MA87 has a higher fatigue-crack growth rate at low  $\Delta K$  which some workers [148] attribute to an excessively-fine grain size. Alcoa is now generating fatigue data for a large number of MA87 specimens to determine the reason for this discrepancy.

(f) 2xxx and 7xxx alloys of conventional composition made by PM have superior corrosion resistance, smooth and notched fatigue resistance, and re-crystallization resistance to their IM counterparts.

(g) 3xxx and 5xxx alloy extrusions of conventional composition made by PM have tensile properties superior to their IM counterparts.

(h) In order to fully exploit the benefits of PM techniques, alloy compositions should be modified from those of the currently successful IM alloys.

(i) The most difficult, and hence costly, problems associated with PM technology involve de-gassing and consolidation of the product, and the resulting safety hazards. Several consolidation methods have been used successfully, but no one method demonstrates a clear superiority over the others.

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## References

1. K. H. ROLL, in "Modern Developments in PM" Vol. 3, edited by H. H. Hausner (Plenum Press, New York, 1965) p. 261.
2. H. FISCHMEISTER, *PMI* 10 (1978) 119.
3. R. W. CAHN, *Nature* 276 (1978) 209.
4. C. COVAULT, *Aviation Week and Space Tech.* 109 (1978) 14.
5. C. T. POST, *Iron Age* 221 (1978) 41.
6. W. M. GRIFFITH, *Azuza* 9 (1977) 15.
7. Proceedings of the Review of Government Sponsored Work on PM Aluminium, Stouffers Dayton Plaza, Ohio (Air Force Materials Laboratories (1980).
8. J. P. LYLE and W. S. CEBULAK, in "Proceedings of the 18th Sagamore Army Materials Research Conference on PM for High Performance" edited by J. J. Burke and V. Weiss (Syracuse University Press, Syracuse, 1972) p. 231.
9. R. E. LEWIS, Lockheed Interim Report LUSC-D674504, Palo Alto, March 1979.
10. R. E. LEWIS, D. WEBSTER and I. G. PALMER, Air Force Materials Lab. Final Report TR78-102, 1 June 1977 to 31 May 1978.
11. J. R. PICKENS and R. D. SCHELLENG, Air Force Materials Lab. WPAFB, Ohio, Contract Interim Report F33615-76-65227, 1979.
12. A. R. COX, Air Force Materials Lab. Report FR 10754, August, 1978.
13. *Idem*, Air Force Materials Lab., USA, Report FR 11102, December, 1978.
14. *Idem*, Air Force Materials Lab., USA, Report FR 2127, June, 1979.
15. *Idem*, Air Force Materials Lab., USA, Report FR 11690, March, 1979.
16. R. R. SAWTELL, W. L. OTTO, Jr. and D. L. LEGE, Air Force Materials Lab., USA, Contract No. F33615-77-C-5086 Report, March, 1978.
17. R. E. SANDERS, Jr, G. J. HILDEMAN and D. L. LEGE, Air Force Materials Lab., USA, Contract No. F33615-77-C-5086 Report March, 1979.
18. W. S. CEBULAK, US Army Armament Command, Rock Island, Illinois Contract No. DAAA 25-72-C-0593 Report April, 1977.
19. E. A. STARKE, *Mat. Sci. Eng.* 29 (1977) 99.
20. B. H. LeCERF and A. M. GREENE, *Iron Age* 221 (1978) 53.
21. M. V. HYATT, *Aluminio* 46 (1977) 81.
22. M. V. HYATT, W. E. QUIST and J. T. QUINLIVAN, *Met. Prog.* 111 (1977) 56.
23. E. H. SPUHLER and T. I. McCLINTOCK, Symposium on Aluminium Alloys in the Aircraft Industry, Turin, Italy, October 1976 (Technicopy Limited, Stonehouse, England, 1978) p. 1.
24. *Chemical Week* 122 (1978) 12.
25. R. J. REGAN, *Iron Age* 223 (1980) 52.
26. R. E. HARVEY, *ibid.* 222 (1979) 32.
27. A. H. COTTRELL, "Dislocations and Plastic Flow in Crystals" (Clarendon Press, Oxford, 1965).
28. C. R. BARRETT, W. D. NIX and A. S. TETELMAN, "The Principles of Engineering Materials," (Prentice Hall, Englewood Cliffs, New Jersey, 1973) Chap 7 and 8.
29. B. R. LAWN and T. R. WILSHAW, "Fracture of Brittle Solids" (Cambridge University Press, Cambridge, 1975).
30. C. J. PEEL and P. POOLE, Royal Aircraft Establishment, Farnborough, UK, Report 78034, April, 1978, p. 10.
31. D. O. SPROWLS and R. H. BROWN, Proceedings of the Conference on the Fundamental Aspects of Stress Corrosion Cracking, Ohio State University, September, 1967, edited by R. W. Staehle, A. J. Forty and D. Van Rooyen (National Association of Corrosion Engineers, Houston, 1969).
32. A. J. JACOBS, *Trans. ASM* 58 (1965) 579.
33. G. THURSFIELD and M. J. STOWELL, *J. Mater. Sci.* 9 (1974) 1644.
34. S. G. ROBERTS, Contract Report DA-04-200-507-ORD-886, US Army Department of Defense, p. 799.
35. *Idem*, US Patent number 3,462,248.
36. S. G. ROBERTS and T. R. PRITCHETT, *Aluminium* 52 (1976) 129.
37. P. FURRER and H. WARLIMONT, *Math. Sci. Eng.* 28 (1977) 127.
38. A. FONTAINE, in "Rapidly Quenched Metals, 2nd International Conference" Section I, (1975).
39. E. A. BLOCH, *Metall. Rev.* 6 (1961) 22.
40. G. JANGG and F. KUTNER, *PMI* 9 (1977) 24.
41. R. J. H. WANHILL and G. F. J. A. Van GESTEL, *Aluminium* 54 (1978) 7.
42. J. T. STALEY, *Met. Eng. Quart.* 16 (1976) 52.
43. R. J. H. WANHILL, *Aluminium* 54 (1978) 455.
44. M. A. REYNOLDS and J. G. HARRIS, *ibid.* 50 (1974) 592.
45. E. di RUSSO and M. BURATTI, Symposium on Aluminium Alloys in the Aircraft Industry, Turin, Italy, October, 1976 (Technicopy Limited, Stonehouse, England, October 1978) p. 125.
46. J. T. STALEY, Properties Related to Fracture Toughness, ASTM STP605 (1976) p. 71.
47. D. S. THOMPSON, *Met. Trans. A* 6A (1975) 671.
48. I. KIRMAN, *Met. Trans. A* 2 (1971) 1761.
49. J. T. STALEY, R. H. BROWN and H. HUNSICKER, US Patent number 3,881,966.
50. E. W. JOHNSON, Alcoa Technical Center, unpublished work, 1976.
51. M. V. HYATT, Air Force Materials Lab, USA, Report Number TR-73-224, September, 1973.
52. M. V. HYATT and W. E. QUIST, Presentation at AIME Spring Meeting, Las Vegas, Nevada, February, 1980.
53. S. J. DONACHIE, Novamet, Wykoff, New Jersey private communication, 1978.

54. L. BARKER, Kaiser Aluminum, Private communication, September, 1979.
55. R. J. WANHILL and G. F. Van GESTEL, NTS File N79-16967, June, 1978.
56. R. S. ALWITT, in "Oxides and Oxide Films" edited by J. W. Diggle and A. K. Vigh (Marcel Dekker, New York, 1976) p. 169.
57. G. M. SCAMANS and A. S. REHAL, *J. Mater. Sci.* **14** (1979) 2459.
58. N. J. GRANT, in "Proceedings of the International Conference on the Rapid Solidification Process" (Claitor's Publishing Division, Baton Rouge, Louisiana) p. 230.
59. *Idem*, "Powder Metallurgy for High-Performance Applications" (Army Materials and Mechanics Research Center, Watertown, Maine, 1972) p. 85.
60. J. J. DUNKLEY, *PMI* **10** (1978) 38.
61. C. E. MOBLEY, A. H. CLAUER and B. A. WILCOX, *J. Inst. Met.* **100** (1972) 142.
62. G. FANINGER, D. MERZ and H. WINTER, in "Rapidly Quenched Metals, 2nd International Conference" Section I, (1975).
63. J. P. H. A. DURAND, R. M. PELLOUX and N. J. GRANT, *Mat. Sci. Eng.* **23** (1976) 247.
64. M. LEBO and N. J. GRANT, *Met. Trans.* **5** (1974) 1547.
65. M. H. JACOBS, A. G. DOGGETT and M. J. STOWELL, *J. Mater. Sci.* **9** (1974) 1631.
66. V. FRANETOVIĆ, M. STUBIČAR and A. BONEFAČIĆ, *J. Mater. Sci.* **15** (1980) 353.
67. N. J. GRANT, *Z. Fizika, Suppl.* **2** (1970) 16.1.
68. O. A. LEBEDER, O. N. DRONYAEYA, B. F. YUDIN and V. G. GOPIYERKU, *Tr. VAMI* **98** (1977) 57.
69. K. K. SANKARAN, Ph.D. Thesis, MIT, 1978.
70. *Metal Industry* **22** August (1975) p. 143.
71. R. IRMANN, *Metallurgia* **46** (1952) 125.
72. A. von ZEERLEDER, "Modern Metals" Vols 8, 12 and 40 (1953).
73. D. GUCELANDI and P. JEBERSON "Modern Development in PM: Development of Future Prospects" Vol. 3, edited by H. H. Hausner (1965) p. 36.
74. G. S. ANSELL, *Met. Trans.* **215** (1959) 294.
75. C. G. GOETZEL, *J. Met.* **11** (1959) 189.
76. *Idem, ibid.* **11** (1959) 276.
77. A. S. BUFFERD and N. J. GRANT, *Trans. ASM* **60** (1967) 305.
78. G. H. REYNOLDS, F. V. LENEL and G. S. ANSELL, *Met. Trans.* **2** (1971) 3027.
79. S. C. PARK and W. K. PARK, *Int. J. Powder Metall. and Powder Tech.* **14** (1978) 305.
80. S. CEVESARA and P. FIORINI, *Powder Metall.* **1** (1979) 1.
81. R. J. TOWNER, *Trans. AIME* **230** (1964) 505.
82. J. H. SWARTZWELDER, *Int. J. Powder Metall.* **3** (1967) 53.
83. N. HANSEN, *Met. Trans.* **245** (1969) 2061.
84. T. M. NILSSON, *Int. J. Powder Metall.* **5** (1969) 43.
85. J. S. BENJAMIN, *Sci. Amer.* **234** (1976) 40.
86. J. S. BENJAMIN and M. J. BOMFORD, *Met. Trans. A* **8A** (1977) 1301.
87. A. W. THOMPSON, *Met. Trans. A* **8A** (1977) 833.
88. R. J. McELROY and Z. C. SZKOPIAK, *Int. Met. Rev.* **17** (1972) Rev. 167.
89. Y. W. KIM, Presentation at AIME Spring Meeting, Las Vegas, Nevada, February 1980.
90. A. F. BECK and P. R. SPERRY, in "Proceedings of Fundamental Aspects of SCC" edited by R. W. Staehl, A. J. Forty and D. Van Rooyen (Ohio State University Press, Ohio 1969) p. 513.
91. A. J. SEDRIKS, J. A. S. GREEN and D. L. NOVAK, Proceedings of the U. R. Evans International Conference on Localized Corrosion, Williamsburg, Pennsylvania, December 1971.
92. *Idem. Met. Trans.* **4** (1973) 1992.
93. J. R. PICKENS, R. D. SCHELLENG, S. J. DONACHIE and T. NICHOL, Patent Application, assigned to the International Nickel Corporation, Inc.
94. S. G. ROBERTS, AMMRC CTR 73-33, October, 1973.
95. S. G. ROBERTS, US Patent number 4,104,061.
96. L. A. ARBUZOVA, V. A. DANILKIN and L. L. KUNIN, *Poroschkovaya Metallurgiya* (1974) 1, or "Theory, Production, Technology and Properties of Powder and Fibers," translation IIDC 543.27; 621.672. 669.71, (Plenum Press, New York, (1976).
97. V. A. DANILKIN, V. M. FEDOROV, L. A. ARBUZOVA, R. V. TYUL'PAKORA and A. S. SOKOLOV, UDC-699.71, 069.84, No. 8 (1978) 97.
98. G. NAESER, in "Modern Developments in PM" Vol. 3, edited by Hausner (1965).
99. L. P. CLARK, AGARD-R-627, March, 1975.
100. B. AVITZUR and P. BLUM, "Forging and Extrusion of PM Preforms" (American Powder Metallurgy Institute, Princeton, New Jersey) p. 73.
101. K. E. BUCHOVECKY and M. R. REARICK, *Met. Prog.* **101** (1972) 74.
102. E. S. HODGE, in "Diversity—Technology Explosion" (SAMPE, Azusa, California, 1977).
103. A. I. ZENTSOV and V. D. REVTOV, *Poroschkovaya Metallurgiya* **5** (1979) 83.
104. H. A. JOHNSON, *Prog. Powder Metall.* **31** (1975) 223.
105. N. J. GRANT, Presentation at AIME meeting, Milwaukee, Wisconsin, September, 1979.
106. S. J. DONACHIE, ASM Materials Conference, Paper 64, (American Society for Metals, Metals Park, Ohio, 1977).
107. S. G. ROBERTS, US Patent number 3,954,458.
108. W. S. CEBULAK and D. J. TRUAX, US Army Contract DAAA-25-70-C0358, March, 1971).
109. W. S. CEBULAK, US Army Contract DAAA-25-70-C0358, August, 1970).
110. D. A. Van CLEAVE, *Iron Age* **219** (1977) 39.
111. A. LAWLEY, in "Rapid Solidification Principles and Technologies" (Citation Publishers, Reston, Virginia, 1978) 306.
112. S. STORCHHEIM, *Light Metal Age* **36** (1978) 5.
113. M. A. H. HOWES, Commercialization of Hot Pressing, Proposal number 79-508M, IIT Research Institute, Chicago (1979).
114. J. P. LYLE, Jr and W. S. CEBULAK, *Met. Eng. Quart.* **1** (1974) 52.
115. D. P. VOSS, Air Force Office Scientific Research

- 77-3440, Report number 2, December, 1978.
116. *Idem*, AFOSR 77-3440, October, 1979.
  117. J. R. PICKENS, INCO, Sterling Forest, Suffern, New York, unpublished work.
  118. D. R. HOLLOWAY, M.Sc. Thesis, Air Force Institute of Technology, Ohio, September, 1977.
  119. N. J. GRANT, Presentation at the First International Conference on Al-Li Alloys, Georgia Technical University, May, 1980.
  120. J. P. LYLE, W. S. CEBULAK and K. E. BUCHOVECKY, in "Progress in PM" Vol. 28, edited by A. S. Bufferd (Metal Powder Industries Federation, New York, 1972) 93,
  121. W. S. CEBULAK, E. W. JOHNSON and H. MARKUS, *Int. J. Powder Metall. and Powder Tech.* **12** (1976) 299.
  122. W. S. CEBULAK, US Army, Frankford Arsenal Contract DAAA25-70-C0358, December, 1970.
  123. W. S. CEBULAK and D. J. TRUAX, US Army Contract DAAA25-70-C0358, January, 1971.
  124. W. L. OTTO, Jr, Air Force Materials Laboratory Final Report TR 76-60, May, 1976.
  125. J. L. NELSON, INCO, Inc., private communication, August, 1979.
  126. H. NARAYANAN, Boeing Aerospace, private communication, August, 1979.
  127. *Idem*, Boeing Aerospace, private communication, January, 1980.
  128. J. A. NOCK, *Aluminium*, **1** (1967).
  129. A. P. HAARR, US Army, Frankford Arsenal Report 13-64-AP59S, October, 1964.
  130. *Idem*, US Army, Frankford Arsenal Report 13-65-AP59-S, December, 1965.
  131. J. R. PICKENS, "Design of a High-Strength, High Specific Modulus, Corrosion Resistant Al-Li Alloy by Mechanical Alloying" Patent Application, assigned to the International Nickel Corporation, Inc.
  132. Silag, Inc., Data Sheet on 2024 Al alloy with 25 wt% Silag M-8, Silag, Incorporated, Green, South Carolina, (1979).
  133. J. O. PICKINS, Silag Incorporated, Green, South Carolina, private communication, 1979.
  134. T. H. SANDERS and E. S. BALMUTH, *Met. Prog.* **113** (1978) 32.
  135. E. H. SPUHLER, A. H. KNOLL and J. G. KAUFMAN, *ibid.* **77** (1960) 80.
  136. A. Z. ZHNUDSKIY, P. A. MAKSIMYUK, V. D. MIKHALKO and V. A. GLEY, *Fiz. Metal Metall.* **27** (1969) 373.
  137. M. HOLT and J. A. NOCK, *Prod. Eng.* **31** (1960) 38.
  138. I. M. LeBARON, US Patent number 2,381,219.
  139. Aircraft and Missile Manufacturing, "Hotter Aluminum," (November 1958) 42.
  140. H. K. HARDY, *J. Inst. Met.*, **84** (1955) 429.
  141. T. H. SANDERS, Jr, NAVAIR Report NADC-76397-30, June, 1976.
  142. G. WOLD, AIME Conference, Milwaukee, Wisconsin, September, 1979.
  143. R. E. LEWIS, Lockheed Missiles Space Corporation-D68922, Defense Advanced Research Projects Administration, December, 1979.
  144. D. L. ERICH, INCO, private communication, August, 1979.
  145. R. D. SCHELLENG, INCO Research and Development Center, Sterling Forest, Suffern, New York, private communication, April, 1980.
  146. H. AHLBORN and D. MERZ, *Aluminium* **50** (1974) 583.
  147. Novamet Data Sheet on IN 9051, Novamet, Wyckoff, New Jersey, 1979.
  148. E. A. STARKE, Georgia Technical University, private communication, 1979.

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