Microstructural Study of Centrifugally Atomized Powders of Al-Li and Al-Li-Fe Alloys

By J. Hinojosa-Torres*, D. Ríos-Jara* and G. Champier**

Powders of the Al-Li and Al-Li-Fe alloys were produced by a centrifugal atomizing method, and the main structural characteristics of the powder particles were studied. We present a detailed description of the atomizing method, which was found to produce an appropriated distribution in size of the powder particles, for further consolidation and manufacturing processes. Also, a semi-empirical calculation based on simple dynamic equilibrium considerations is presented, which was found to predict fairly well the measured values of the mean diameter of the powder particles.

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I. Introduction

A high value of the specific modulus E/ρ , where E is the Young modulus and ρ is the density, is one of the required characteristics of materials for modern structural applications like in Aircraft Industry⁽¹⁾. The Al-Li alloys obtained by direct casting have a high specific modulus (32.5 MN.m/kg for the Al-3 mass% Li alloy), which makes them good candidates for those applications. However, the cast alloys are very brittle and their utilization is limited. This brittle behavior is due to a coarse equiaxed dendritic structure (170–1800 μm in size), with large $\delta(\text{AlLi})$ coherent precipitates (0.01–0.2 μm in diameter) inside the grains, which reduces the ductility of the alloys⁽¹⁾.

When cast aluminum-lithium alloys are solution heat treated, quenched in cold water, and artificially aged for different periods of time, their poor ductility and low fracture toughness still remain. It has been observed that, during those treatments, precipitates of an ordered metastable $\delta'(\text{Al}_3\text{Li})$ phase appear and grow obeying the Ostwald ripening kinetics⁽²⁾. These $\delta'(\text{Al}_3\text{Li})$ precipitates are easily sheared by dislocations and promote localization of slip along preferential crystallographic planes. It has been suggested that such slip planarity is a major cause of the poor ductility of aluminum-lithium alloys^{(3)–(6)}. Furthermore, during those heat treatments precipitate free zones (PFZ) appear close to the grain boundaries, which have also been associated with the poor mechanical characteristics of the alloys⁽⁵⁾.

In order to correct for the detrimental effects of slip planarity and PFZ's, the grain refinement resulting from the rapid solidification rates, associated with the centrifugal atomizing process, and the introduction of fine

dispersoids homogeneously distributed in the matrix have been used by several workers. This technique appears as a good attempt to avoid those problems, and improve the mechanical properties, through the control of the solute elements distribution. With this technique, powders are obtained by rapidly cooling extremely small quantities of the alloy (1.3×10^{-12} – 1.6×10^{-9} kg), at typical 10^5 K s^{-1} cooling rates⁽⁷⁾⁽⁸⁾. These rates are several orders in magnitude higher than those obtained in conventional casting.

A variety of atomizing techniques, using rapid solidification, are actually being developed. In this work the centrifugal atomizing method has been chosen, because of its good adequacy to metals which shows high and moderate reaction capability. Also, high rotation speeds (455 s^{-1}) were used, and found to produce powder particles with a mean diameter of about 50 μm (standard deviation of 30 μm).

We describe in Part I of this work the main experimental steps followed for the production of powders of Al-Li and Al-Li-Fe alloys by this technique, together with the more important morphological and microstructural features of the powder particles. In Part II of this work we discuss the method developed for the sintering of the powders, and present some mechanical properties measured in solution heat treated, quenched in cold water, and artificially aged powders of Al-Li and Al-Li-Fe alloys.

II. Experimental

Powders were prepared from Al-2.4 mass% Li and Al-2.4 mass% Li-1 mass% Fe alloys by using the centrifugal atomizing process. The effect of the addition of iron to the alloy will be discussed in Part II of this work.

Figure 1 is a schematic design of the experimental device. The whole system is placed into an isolated chamber where the atmosphere (nitrogen) can be controlled. The heating is made by using magnetic induction. The graphite crucible is covered with a protective coat of boron-nitride to prevent chemical reactions of the alloys

* Instituto de Investigaciones en Materiales, UNAM, Apdo. Postal 70-360, 04510 México, D. F., Mexico.

** Laboratoire de Physique du Solide, Ecole Nationale Supérieure de la Metallurgie et de l'Industrie des Mines de Nancy-54042 Nancy Cedex, France.

Fig. 1 Schematic of the centrifugal atomizer showing the arrangement used for the atomizing process. C: steel chamber, D: copper screen, K: turnplate, T_1 and T_2 : thermocouples, T: turbine, F: induction coil, L: crucible, P: gas inlet.

with the carbon atoms. The alloy in liquid state at 1023 K is forced to flow through the hole practiced at the bottom of the cylindrical crucible of graphite, by applying a pressure difference (ΔP) with nitrogen gas. The more relevant parameters of the system are listed in Table 1.

The liquid metal is poured as a fine jet onto the center of a flat turnplate, which rotates at an approximated rate of 455 s^{-1} . The turnplate is covered with a thin refractory material and maintained at a temperature approximately 100 K higher than the melting point of the Al-2.4 mass% Li or Al-2.4 mass% Li-1 mass% Fe alloys. A small step was machined at the edge of the turnplate in order to break the liquid surface tension and produce the droplets. In these conditions the liquid metal glides over the turnplate and, on leaving this surface, very small metallic droplets are formed and projected into the powder stocking chamber. Enough space for the cooling trajectory of the particles (0.45 m from the turnplate center) was provided. By measuring the distance from the turnplate at which the liquid droplets solidified, the cooling rate was estimated to be between 10^4 – 10^6 K/s .

No compensation for the decrease in temperature of the turnplate, during its rotation, caused a distribution in size and shape of the particles, which goes from 10 to $200 \mu\text{m}$ in size and from spherical to extended ones. In general, the small particles are spherical and the large

Fig. 2 Experimental distribution of Cumulative Mass Per cent (CMP) as a function of the powder size (D_d) for Al, Al-2.4 mass% Li, Al-2.4 mass% Li-1 mass% Fe powders.

ones are extended. Figure 2 shows the measured cumulative mass percent (C.M.P.) distribution as a function of the size of the particles of Al, Al-2.4 mass% Li, and Al-2.4 mass% Li-1 mass% Fe powders. Each curve represents the mean value of a series of ten measurements.

It was found that the control of the heat losses from the turnplate and the optimization of all the mentioned parameters result in an increase in the number of the spherical or quasi-spherical small particles (20 – $80 \mu\text{m}$). The mean size of the particles, obtained by considering all of the optimized solidification experiences in this work, was about $50 \mu\text{m}$. This is in good agreement with the value estimated by using the principle of matter conservation and dynamic equilibrium considerations, as discussed in the Appendix.

The morphology and microstructure of the hypercooled powders were studied by using optical and electron microscopies (scanning (SEM) and transmission (TEM)).

The polishing of the surfaces of the powder particles, for optical and SEM observations, was made by using the Keller's reagent. To provide suitable thickness during TEM observations, the loose powders were slightly crushed using a silica tube. The particles were either placed on grids coated with very thin layers of collodion, or embedded on perforated ribbons and thinned by electropolishing with a 20% perchloric acid – 80% ethyl alcohol solution while applying 15 V.

III. Identification of Microstructures

A distribution of spherical and elongated particles, with sizes between 10 and $200 \mu\text{m}$ was obtained, as shown in the cumulative-mass-percent distribution of Fig. 2. Examples of powder particles with spherical and elongated shapes are shown in the SEM micrograph of Fig. 3. SEM observations of polished surfaces showed that the smaller particles ($20 \mu\text{m}$) consist mostly in a dendritic structure; coarse particles ($100 \mu\text{m}$ or more) exhibit a mixed dendritic and equiaxed grains microstructure.

Table 1 Parameters of the centrifugal atomizing process.

Initial Pouring Temperature K	Plate Speed m/s	Melt Atomization Rate kg/s	Crucible-chamber Pressure difference Pa	Pressure of Nitrogen in the chamber Pa
1023	62.89	4.25×10^{-3}	0.3×10^5	1×10^5

Fig. 3 SEM Micrograph showing typical spherical and elongated shapes of Al-2.4 mass% Li atomized powder particles.

Fig. 4 SEM micrograph showing mixed dendritic (D) and equiaxed (E) microstructure observed in a 80 μm Al-2.4 mass% Li powder particle.

This becomes evident in Fig. 4, showing a SEM micrograph of the cross section of a powder particle of Al-Li with mean diameter of about 80 μm . These observations are in agreement with the general behavior of Co and Ni based alloys, as reported by Duflos and Stohr⁽⁹⁾, where a dendritic fraction varying from 6% for 350 μm to 85% for 20–40 μm particles was observed.

A linear relationship between the secondary dendrite arm spacing (SDAS) and the diameter of the powder particles was obtained, as shown in Fig. 5. From the dependence of the SDAS on the cooling rate in Al alloys, as reported by Matyja *et al.*⁽¹⁰⁾, cooling rates ranging from 10^4 to 10^6 K s^{-1} were deduced. Although a similar relationship between the SDAS and the diameter of the grains was found by Webster *et al.* in Al-2.7 mass% Li extruded powders⁽¹¹⁾, their values are almost three times larger than those in Fig. 5. This difference can be explained by considering the difference in cooling rates. In the present work, the cooling rates are higher than those used by Webster *et al.*, and this produces a refinement of the dendrite secondary arms with an associated decrease in the SDAS.

When observed in TEM, the quenched powders show

Fig. 5 Variation of the secondary dendrite arm spacing (SDAS) as a function of the powder particles diameter (D_d).

different microdendritic orientations inside the grains. Figure 6(a) shows elongated microdendrites which grew either perpendicular to the plane of the figure (region A) or parallel to it (region B). At higher magnifications, fine particles were observed and identified as δ' (Al_3Li) precipitates by means of dark field electron diffraction techniques. Figure 6(b) is a diffraction pattern of a small region in Fig. 6(a) showing a ring pattern superposed to the spots pattern of the matrix, and evidencing the random orientation of the δ' precipitates. Figure 6(c) is a centered dark field micrograph formed with δ' reflections, where a high density of these δ' precipitates is observed. The mean diameter of these precipitates is about 8 nm, which approximately represents the 15% of the total volume of the sample.

Powders of the Al-2.4 mass% Li-1 mass% Fe alloy presented the same dendritic structure observed in Al-Li powders. Figure 7 is an optical micrograph of a crushed and polished Al-Li-Fe powder particle; here, the clear zones correspond to the supersaturated solid solution of aluminum and the dark zones are rich in alloying elements. At higher magnifications, it became clear the existence of a micro-dendritic structure at the interior of the coarse dendrites. These micro-dendrites grew radially from the central region of the large dendrites. Precipitates within the coarse dendrites were not homogeneously distributed; instead, a core with large Al_6Fe precipitates at the central region of each coarse dendritic arm was observed, as shown in the transmission electron micrograph of Fig. 8(a) and in the enlarged region in Fig. 8(b). Between this central region and the border of each coarse dendrite, Al_3Li and Al_3Fe precipitates were observed to form in the interdendritic zones of the radial micro-dendrites. The size of these precipitates was found to be between 2–4 nm, with the Al_3Li showing a globular shape and the Al_3Fe an elongated one, as shown in Fig. 8(c) (which also correspond to an enlarged zone of Fig. 8(a)). The radially

Fig. 6 Transmission electron micrograph on a thin foil of an Al-2.4 mass% Li atomized powder particle. (a) dendritic structure inside the grain with growth direction perpendicular to the plane of the figure (area A) or parallel to it (area B); (b) selected area diffraction pattern from a region in Fig. 6(a) evidencing the random orientation of the δ' (Al₃Li) precipitates; (c) centered dark field image obtained with δ' superlattice reflection.

Fig. 7 Optical micrograph showing a dendritic structure in an Al-2.4 mass% Li-1 mass% Fe atomized and polished powder particle.

grown micro-dendrites are clearly seen in Fig. 8(d). The same microstructure was observed in the case of equiaxed grains.

Another characteristic of the powders is the appearance of cracks along the dendrite boundaries, due to severe collisions (Fig. 9). Similar observations were reported by Kear *et al.* in IN-100 powders⁽¹²⁾, where a columnar dendritic structure seemed to be particularly prone to such cracking. Moreover the same kind of defects was observed in powder particles crushed for obser-

vation in TEM even after long solution heat treatments, indicating that fracture along grain boundaries is another failure mechanisms.

In some cases, powder particles were observed to be enveloped by a shield, which evidently belonged to a second drop of alloy, deformed during a collision with the first one. Figure 10 shows an optical micrograph of a polished powder particle where this morphology can be clearly seen. This kind of arrangements can be explained by considering local differences in the solidification rates during the atomizing process. Similar observations have been reported by B. H. Kear *et al.*⁽¹²⁾

IV. Discussion

The centrifugal atomizing method, described in this work, appears as a good alternative for the production of powders of aluminum—lithium alloys. The method fulfills most of the required characteristics for hypercooling processes, while remaining sufficiently low cost. A good control of the parameters in the process results in a small mean diameter of the powder particles, with an adequate distribution in size and shape. In particular, the temperature of the turnplate, during the pouring of the liquid metal, was found to be a critical parameter in the production process. Changes in this parameter, in a controlled way, could allow the obtaining of a different distribution of diameters of the particles, which will be

Fig. 8 Transmission electron micrographs on a thin foil of an Al-2.4 mass% Li-1 mass% Fe atomized powder particle showing a coarse dendritic structure inside the subgrains. (a) core (c) with large Al_6Fe precipitates at the central region of a coarse dendrite arm. Note the radially grown fine dendrites going from the central region to the border of the coarse dendrite arm; (b) enlarged image of the core microstructure in Fig. 8(a); (c) enlarged region in Fig. 8(a) showing Al_3Li (globular) and Al_3Fe (elongated) precipitates; (d) enlarged region in Fig. 8(a) showing radially grown micro-dendrites.

Fig. 9 Evidence for collisions between solid particles involving grain boundary cracking (arrowed).

Fig. 10 Optical micrograph of Al-2.4 mass% Li atomized and polished powder particles with evidence for sticking collisions between a solid particle (A) and a semisolid "mushy" particle (B).

useful for particular applications. Also, the mean diameter of the particles can be controlled by the appropriated combination of values of the frequency of rotation and the diameter of the turnplate, as shown in the Appendix (Fig. 13). Concerning the microstructure of the powder particles, as compared with that of the cast

alloys, a reduction in grain size of the dendritic structure was observed and an associated decrease in the SDAS was measured.

In Al-Li alloys, small precipitates of the Al_3Li phase were observed to form and distribute homogeneously within the dendritic and interdendritic regions. The small

Fig. 11 Photograph under stroboscopic illumination showing atomization of milk with the turnplate in rotary state. Note the well defined filaments of fluid leaving the turnplate.

Fig. 12. Variation of the number of filaments (n_j) as a function of the frequency of rotation of the turnplate.

size of these precipitates represents a highly convenient starting parameter for further controlled growing during heat treatments; then allowing for the optimization of the mechanical behavior of the alloys, as will be discussed in Part II of this work.

In Al-Li-Fe alloys, precipitates of the Al_3Li and Al_3Fe phases were observed to form in the inter-microdendritic regions, close to the border of each arm of the coarse dendrites. In the central regions of each arm only Al_6Fe precipitates were detected. Such a selective distribution

Fig. 13 Variation of the diameters (D_d) of spherical droplets as a function of the frequency of rotation of the turnplate.

must be related with a competitive nucleation process between high aluminum-rich precipitates like Al_6Fe and precipitates like Al_3Fe and Al_3Li ; lower solute (Fe) concentrations are needed in the former case. Therefore, Al_6Fe precipitates are more easily formed in the Al-rich regions at the center of each coarse dendritic arm, while non equilibrium concentrations of the addition elements (Li and remaining Fe) are rejected towards the borders of the dendrites, where lower aluminum concentrations exists. The same argument can be used to explain the formation of these precipitates at the interdendritic regions of the microdendrites. On the other hand, it is not surprising that the same microstructure was observed in the case of equiaxed grains, since they result from the nucleation on fragments of predendrites, formed during the cooling process⁽⁹⁾.

V. Conclusions

(1) Powder particles with sizes between 10 and 200 μm and a mean diameter of 50 μm (30 μm of standard deviation) were produced by a centrifugal atomizing method. This size was in agreement with a semi empirical calculation based on simple dynamical equilibrium considerations.

(2) The dendritic fraction was observed to decrease with the powders particle diameter; a mixed dendritic and equiaxed grains microstructure was observed for the larger particles, while only dendrites appeared in the smaller ones.

(3) Microdendrites were observed to grow inside the coarse dendritic microstructure in both Al-Li and Al-Li-Fe alloys.

(4) Randomly oriented δ' (Al₃Li) precipitates were observed to form, with mean diameters ranging from 8 nm for Al-Li to 2–4 nm for Al-Li-Fe alloys. Also, Al₆Fe and Al₃Fe precipitates are formed in the latter.

(5) Due to the inhomogeneous distribution of addition elements in Al-Li-Fe alloys, the Al₆Fe precipitates grow in the central region of each coarse dendritic arm, while Al₃Fe and Al₃Li were observed in the intermicrodendritic regions close to the border of each arm of the coarse dendrites.

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APPENDIX

Simulation of the pulverization process and calculation of the mean diameter of the powder particles

In order to determine the appropriated parameters for the pulverization process, a simulation of it was carried out, prior to our experiences with the aluminum alloys. The different steps of the pulverization were followed by a photographic method, using stroboscopic illumination and a liquid (milk) with a high reflectivity and a dynamical viscosity (at room temperature) similar to that of aluminum alloys at 1023 K. Also, different diameters of the turnplate were tested.

By using the principle of mass conservation and a fluid mechanics analysis, Hinze *et al.*⁽¹³⁾ found an expression for the mean velocity, v_m , of the liquidus at the edge of a flat plate as,

$$v_m = \left(\frac{\rho \omega^2 Q^2}{6\pi^2 \mu D_t} \right)^{1/3} \quad (1)$$

with ρ =density of the liquidus, ω =angular velocity, Q =flow rate of the liquid poured into the turnplate, μ =dynamical viscosity of the liquidus and D_t =diameter of the turnplate.

In our case, when the liquidus reaches the outer edge of the turnplate it is split into many long filaments, which

are ejected out of the plate. Since there is no accumulation of liquidus, mass conservation means that the flow rate of the primary jet can be written as:

$$Q = n_j \frac{\pi D_f^2}{4} v_f \quad (2)$$

where n_j =number of filaments of liquidus leaving the turnplate at the same time, D_f =mean diameter of the filaments and v_f =radial velocity of the filaments.

On the other hand, when the liquidus is broken into filaments, the surface tension must be equal to the centrifugal force, then

$$\pi D_f \tau = \left(\frac{\pi D_f^2 L_f}{4} \right) \rho \omega^2 \frac{D_t}{2} \quad (3)$$

where τ =surface tension of the liquidus and L_f =length of the filaments. Once the filaments leave the turnplate, they become spherical and their volume is preserved; that is,

$$\pi \frac{D_f^2 L_f}{4} = \pi \frac{D_d^3}{6} \quad (4)$$

with D_d =diameter of the spherical droplets.

By taking the radial velocity of the filaments as proportional to the mean velocity of the liquidus, $v_f = \beta v_m$, and combining expressions 1 to 4, we came to an expression for the diameter of the droplets as:

$$D_d = \frac{3}{\beta^{1/6}} \left(\frac{\tau^6 \mu}{\rho^7} \right)^{1/18} \left(\frac{Q}{\omega^{14} D_t^5} \right)^{1/18} \frac{1}{n_j^{1/6}} \quad (5)$$

A value of $\beta = 14$ was deduced from expressions 1 and 2 for both milk and liquid aluminum. The number of filaments n_j was obtained by counting them in photographs like the one shown in Fig. 11. Figure 12 shows typical variations of n_j with the frequency of rotation of the turnplate ($\omega/2\pi$), for two different diameters of the turnplate (0.03 and 0.044 m) and for a constant primary flow rate of $1.83 \times 10^{-6} \text{ m}^3/\text{s}$. Typical variations of the diameter of the spherical droplets with the frequency of rotation of the turnplate, for milk and aluminum and for two different diameters of the turnplate, are shown in Fig. 13.

As an example, for aluminum at 1023 K, with $Q = 1.83 \times 10^{-6} \text{ m}^3/\text{s}$, $\omega = 2\pi\nu$, $\nu = 500 \text{ s}^{-1}$, $D_t = 0.044 \text{ m}$, $n_j = 812$, $\tau = 884 \times 10^{-3} \text{ N/m}$, $\mu = 0.098 \text{ Pa}\cdot\text{s}$, $\rho = 2.33 \times 10^3 \text{ kg/m}^3$ and $\beta = 14$, the diameter of the spherical droplets can be calculated as $D_d = 57 \mu\text{m}$. Comparing this value with the measured values of the mean diameters and their standard deviation of the powder particles for Al-Li and Al-Li-Fe alloys, as deduced from Fig. 2,

$$\text{Al-2.4 mass\% Li} \quad \bar{D}_d = 51 \mu\text{m}, \sigma = 29 \mu\text{m}$$

and

$$\text{Al-2.4 mass\% Li-1 mass\% Fe} \quad \bar{D}_d = 50 \mu\text{m}, \sigma = 31 \mu\text{m},$$

a good agreement can be deduced between calculated values and measured ones.